COMPUTING TRANSPORT PROPERTIES OF MOLECULAR AND IONIC
FLUIDS USING ATOMISTIC SIMULATIONS

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by

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Abstract

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The journey of thousand miles begins with one step.

.. Lao Tsze

[in ‘The Simple Way’]

We report the results of first atomistic simulation study to compute the thermal conductivity of ionic liquid as well as the effect of water content on the transport properties (such as viscosity and thermal conductivity) of these liquids. Atomistic simulations are conducted to examine the dependence of the transport properties of ionic liquids (1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide and 1-ethyl-3-methylimidazolium ethylsulfate) on temperature and water content. A nonequilibrium molecular dynamics procedure is utilized along with an established fixed charge force field. It is found that the simulations quantitatively capture the temperature dependence of the viscosity. They also qualitatively capture the drop in viscosity that occurs with increasing water content. Using mixture viscosity models, it is shown that the relative drop in viscosity with water content is actually less than that which would be predicted for an ideal system. This finding is at odds with the popular notion that small amounts of water cause an
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unusually large drop in the viscosity of ionic liquids. The simulations suggest that due to preferential association of water with anions and the formation of water clusters, the excess molar volume is negative. This means that dissolved water is actually less effective at lowering the viscosity of these mixtures when compared to a solute obeying ideal mixing behavior. The experimental results for thermal conductivity of 1-ethyl-3-methylimidazolium ethylsulfate were not yet available but the simulation results were in good agreement with the experimental results of other ionic liquids.

Classical atomistic simulations are also used to compute the enthalpy of vaporization of a series of ionic liquids comprised of the 1-alkyl-3-methylimidazolium cations paired with the bis(trifluoromethylsulfonyl)imide anion. The calculations show that the enthalpy of vaporization is the lowest for neutral ion pairs. Non-neutral clusters have much higher vaporization enthalpies than their neutral counterparts, and thus are not expected to make up a significant fraction of volatile species. The enthalpy of vaporization increases slightly as the cation alkyl chain length increases and as temperature decreases.
DEDICATION

To my mom, Mrs. Sheetal Kelkar, dad, Dr. Sushil Kelkar, younger brother Mohit and wife Anu.
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Gratitude is not only the greatest virtue, but the parent of all others.

.. Cicero
[in 'Proplancio' (106 BC – 43 BC)]

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CHAPTER 1

INTRODUCTION

Before you start some work, always ask yourself three questions: Why am I doing it? What the results might be? and will I be successful? Only when you think deeply and find satisfactory answers to these questions, go ahead.

.. Chanakya

[Indian politician, strategist and writer (350 BC – 275 BC)]

A few thousand years B.C., man invented the wheel, and the wheel of invention and innovation was set rolling. Over the next few centuries man added to his knowledge of the world and improved his standard of living. A man in the eighteenth and nineteenth centuries saw the industrial and chemical revolutions with machinery simplifying work load while chemists like Lavoisier working diligently to change the fate of Chemistry to what we know now. The industrial revolution needed the supply of certain chemicals to sustain this growth and hence the emergence of the chemical industry was inevitable. As the chemical industry grew, a new breed of engineers came into existence who were familiar with both chemistry as well as traditional engineering and the field of chemical engineering was born. Since then the scope of chemical engineering has increased enormously. It encompasses commodity chemicals like ethylene oxide and sulfuric acid to polymeric
lithographic supports for electronic industry and genetically modified biochemical agents [127]. Even our day-to-day life, from the moment we wake up to the time we go back to bed, has been simplified and aided by the chemical industry. The world as we know today would cease to exist without the existence of these chemical processes.

As time passed, however, by the layman, the term chemistry was perceived to be a lab with colored, boiling and fuming liquids being mixed by crazy scientists and the chemical industry was associated with Erin Brockowich and The Insider. As the society became aware of the environmental concerns, industries have had to spend billions of dollars [5] every year to manage wastes and emissions. With the emission standards becoming more and more stringent, chemical industries will have to spend even more on waste disposal. It is, therefore, incumbent upon us as chemical engineers and chemists to redeem our image and revolutionize chemical industry and the concept of green engineering leads the way.

Green engineering, as defined by the United States Environmental Protection Agency (US EPA) [204], is the design, commercialization, and use of processes and products, which are feasible and economical while minimizing generation of pollution at the source and risk to human health and the environment [204]. Mathematically, Risk can be defined as:

\[
Risk = f(Hazard, Exposure) \tag{1.1}
\]

where, Hazard is the quantitative or qualitative measure of adverse effect of a particular chemical on human health or environment and Exposure is the measure of the extent of contact of that chemical to human body or environment. Traditionally, chemical industries try to reduce the later, the Exposure, by implementing
end-of-pipe pollution reduction schemes. The concept of green engineering, however, would concentrate on the former, the Hazard and try to eliminate it from the process. Ideally, a chemical process would be simple, safe, energy efficient, give high yield and selectivity and use renewable or recyclable reagents or raw materials. In reality, however, it is really hard, if not impossible, to achieve all this simultaneously. The principles of green chemistry suggest a set of alternatives that an engineer or chemist can consider. These could be listed as [5]: alternative feedstock or raw materials, environmentally friendly or greener solvents, alternate synthesis pathways for inherently safer chemistry. Considering that an estimated 20 million tons of volatile organic compounds (VOCs) [5, 23] are discharged annually in the atmosphere on account of industrial processes, the idea of alternative solvents seems very attractive. It is in this area of alternative solvents that we would like to direct our attention.

There are four potential ways of avoiding the VOCs in the industrial processes [173] and these can be listed as: (1) Solventless processes, which are widely used in the least polluting chemical sector, the petrochemical industry; (2) Using water as a solvent is also environmentally friendly. However, not a lot of organic compounds dissolve easily in water; (3) Supercritical fluids, which exhibit both gas and liquid like properties, are very versatile and could be used instead of VOCs; (4) Ionic liquids (ILs). In the last decade or so, this new class of solvents have garnered a lot of interest. Simply put, as the name suggests, they are salts in the liquid state and are composed entirely of ions. The term “ionic liquid” was selected to avoid the inaccurate image that term “molten salts” [176] portrays. In contrast to a molten salt which is a liquid at very high temperature, ILs can be found in the liquid state at as low as -96°C. In the recent literature, as a result, the term “ionic
Figure 1.1. Representative cations and anions for some common ionic liquids. $X^-$ represents a choice of an anion. As denoted in the box on the right side, we can choose from many available anions including the ones studied as a part of this dissertation: bis(trifluoromethanesulfonyl)imide $[(CF_3SO_2)_2N]^{1-}$ (referenced as $[Tf_2N]^{1-}$ in the following text) and ethylsulfate $[CH_3CH_2SO_4]^{1-}$ (referenced as $[EtSO_4]^{1-}$ in the following text).

Room temperature ionic liquids are then the salts, that in their pure state, are in a liquid state at or near ambient temperature and pressure. In general, these salts are comprised of a bulky organic cation paired with an inorganic anion. A typical example of such cations and anions is shown in Fig. 1.1.

1.1 Ionic Liquids

Owing to their purely ionic nature, ILs have many characteristics of a good solvent. They have vanishingly low, if not zero, vapor pressure. ILs have a large liquidus range as opposed to the conventional solvents. Apart from these main advantages, many ILs exhibit low flammability, high thermal stability, high conductivity, large electrochemical window, controlled miscibility with organic compounds or favorable solvation behavior. The most interesting property of all, however, is their “tunable” nature. It is believed [169, 173] that, in theory, more
than a trillion different ILs can be synthesized, out of which millions could be stable. Which means, depending upon the choice of cation, anion and substituents on either of them, any property could be, in principle, tailored to the need.

Merited by these properties, ILs find many potential uses in the chemical industry. The low vapor pressure of ILs would reduce the risk of fugitive emissions if substituted for traditional molecular solvents. The ability of ILs to dissolve both polar and non-polar molecules makes them a good candidate as a solvent for hydrogenation, hydroformylations, Diels-Alder reactions and alkylation reactions to name a few. As the solubilities of different gases and liquids can be tailored in the ILs, they can potentially be used in gas or liquid separations or even as a cleansing agent. Properties like wide electrochemical window, high conductivity, large operating temperature range and a lower dielectric constant make them attractive for the fuel cell or battery applications. The wetting characteristics of ILs in addition to their hight thermal stability, low flammability, low vapor pressure, and good temperature-viscosity behavior makes them a good candidate for lubricants in high temperature applications.

In spite of all these benefits and potential applications, there are only a few examples of ILs being used commercially. The problem could be that there are still many question marks surrounding the field. The cost of ILs is a major concern. About 5 years ago the estimated price for an IL could range from $4000–$5000 per pound. This was mostly a laboratory preparation. As the interest in ILs is growing and they are being prepared on a larger scale, these prices have dropped to around $1–$2.5 per pound and this price range is comparable to those of traditional molecular solvents. There is still a lack of physico-chemical property data and a fundamental understanding of the structure and interactions withing ILs [218].
As alluded earlier, the “tunable” nature of ionic liquids leads to a combinatorial explosion. Determination of the physico-chemical properties by doing experiments on every single IL is thus improbable, if not impossible. However, understanding of the structure-property relationship and interaction within ILs is important to facilitate their use in commercial processes. Although, many experimental efforts are being directed toward achieving this objective, one can as well study these systems using computational methods including atomistic simulations. Atomistic simulations not only provide a fundamental understanding of processes, but also allow one to explore extreme conditions in temperature and pressure which might not be accessible experimentally. With the help of these methods, one can also explore new systems which haven’t yet been synthesized.

By this time, I would like to say that I have convinced myself and hopefully the reader, that the question posed in this dissertation is worth pursuing and the results that I would get will add to the current knowledge of the field and promote the commercialization of ILs. This would in turn help the field of chemical engineering to migrate toward “greener” and environmentally friendly processes. The only question remains to be answered, as suggested by the great Indian philosopher, would then be “will I be successful?”. I have convinced myself and hope to convince the reader by Chapter 3 that there is a high probability of success and the following chapters would show that indeed I have succeeded in solving the problem.

1.2 Objective of the Dissertation

As pointed out earlier [218], one of the obstacles for ILs to break into the industry is the lack of their physico-chemical property data. Knowledge of their
transport properties is part of that. Transport coefficients are very important as they determine the mass and heat transfer in the process. They also determine the reaction kinetics of a synthetic process or the transport of ions in electrochemical devices [43]. They influence the design of the heat exchangers and the chemical reactors in the process or dictate the power consumption through the piping and pumping in the chemical process. In this dissertation, we will focus on these essential properties.

The goal of this thesis is to evaluate the applicability of atomistic simulations to predict the transport properties of ionic liquid systems at several state points and also study the effect of water on these properties. To achieve this goal, we will implement, modify and develop different methods and algorithms. We will also test the applicability of these methods and algorithms on other systems like a set of polyhydric alcohols and benchmark our results (and hence the computer codes used in this study) against the available literature results. In addition, we would also like to study the vaporization process of an ionic liquid system.

1.3 Outline of the Dissertation

Chapter 2 will review the state of the field in terms of experimental and computational efforts in measuring or estimating transport properties of ILs.

Chapter 3 will outline different computational methods that are used in this particular study. Chapter 4 will summarize the simulation algorithms that will be used in the subsequent chapters (such as MIR [10] and RNEMD [140]) as well as the algorithms that are used in the literature (such as SLLOD and periodic perturbation method).

Chapter 5 deals with the application of one of such algorithms described in
Chapter 4, called Momentum Impulse Relaxation (MIR) [10]. This previously
developed method was modified and applied to different systems including \( n \)-alkanes and a bead spring model for polymers. The results are in agreement with
the previous simulations studies. The algorithm is general and could be extended
to other systems including ILs.

Chapter 6 deals with the validation of reverse nonequilibrium molecular dy-
namics (RNEMD) algorithm [140] as well as the application of that algorithm to
five different polyhydric alcohols. This chapter also discusses the benchmarking
results of this algorithm for simpler test systems. This study was conducted as a
part of an entry to the Industrial Fluid Properties Collective (IFPSC) challenge
[78]. The dependence of shear viscosity on pressure was studied at 373 K for five
polyhydric alcohols. The results are in good agreement with the experiments.

Chapter 7 discusses an application of RNEMD algorithm to an ionic liquid sys-
tem, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([\textit{emim}]^+\ [Tf_2N]^−). The temperature and water content dependence of the shear viscosity
was studied. The results were compared to different experimental results and
are in fairly good agreement. The molecular level study sheds some light on the
dependence of viscosity on water content.

Chapter 8 discusses yet another application of RNEMD algorithm to a dif-
ferrnet ionic liquid, 1-ethyl-3-methylimidazolium ethylsulfate ([\textit{emim}][\text{EtSO}_4]^−).
The forcefield for the ethylsulfate anion was developed and the pure component
equilibrium properties were studied. Simulations predicted the pure component
properties within 10–15% of the experimental values. The effect of water con-
tent on shear viscosity and thermal conductivity was also studied. This chapter
notes, according to the best of my knowledge, the first simulation study of thermal
conductivity for IL systems.

Chapter 9 digresses from the theme so far of this thesis. The vaporization process of an 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (\([R_n mim]^+[Tf_2 N]^-\)) based ionic liquids was studied. The enthalpies of vaporization of neutral and charged species were calculated. The study shows that a single ion pair is the most dominant species in the vaporization of the \([emim]^+[Tf_2 N]^-\). The contributions of van der Waals, Coulombic and intramolecular bonded energies were also calculated for the same system.

Chapter 10 summarizes the conclusions from this study and outlines the direction for future research in the area of molecular simulations of ILs.
CHAPTER 2

STATE OF THE FIELD

The history of ionic liquids may be viewed as a relatively recent one, or one extending back to 19th century. Which history you choose depends on your definition of ‘ionic liquid’ and how deeply you look for progenitors of the present materials receiving so much interest for green chemistry applications.

.. John S. Wilkes
[U.S. Air Force Academy]

As aptly pointed out by Wilkes [217], almost every discovery has its roots in the previous work. Like is the case for ILs, some times the references could be dated back a century. The so-called “red oil” formed in the Friedel-Crafts reaction and ethylammonium nitrate (melting point 12°C), ILs according to present working definition, were first reported in the mid 19th and early 20th century respectively. We can trace back the origins of these ILs in molten salt chemistry. ILs could be thought off as fluids with most of the advantages of traditional molten salts but without the high working temperatures. The interest in these “neoteric” solvents has grown exponentially over the past decade. This is apparent by the number of publications in the scientific literature which has risen from about one in four days to about four in one day (about 80 in 1997 to about 1400 in 2006). Granted these are approximate numbers, but still to keep track of this burgeoning field has
become a mammoth task and the review of this magnitude is beyond the scope of this dissertation. One can always refer to good reviews on ILs that are already present in the literature [23, 34, 40, 61, 67, 149, 177, 212, 217].

In general, researchers have taken two different pathways for studying ILs. In one case, a great deal of new ILs were synthesized and their properties were measured as a function of temperature, pressure, impurities and co-solvent content. The other approach was to study them on a more fundamental level, trying to understand the interactions within ILs and their effect on the properties. We will consider a few of these studies and review their findings from the point of view of this dissertation, i.e., in terms of their transport coefficients (self-diffusivities, shear viscosities, and thermal conductivities).

2.1 Self-Diffusivity

Self-diffusivity ($D_s$) is a measure of the mobility of a single particle in a system of identical particles. One of the popular methods to measure this quantity experimentally takes advantage of a well-known spectroscopic technique, Nuclear Magnetic Resonance (NMR). It is known as Pulsed Field Gradient NMR (PFG NMR). For a simple spin-echo pulse sequence ($\pi/2 - \tau - \pi - \tau$), the attenuation of the signal ($E$) is related to the experimental parameters through the expression

$$\ln(E) = \ln\left(\frac{S}{S_{g=0}}\right) = -\gamma^2 g^2 D_s \delta^2 (\Delta - \delta/3)$$

(2.1)

where $S$ is spin-echo signal intensity, $\gamma$ is gyromagnetic ratio, $g$ is the magnitude of the gradient field, $\delta$ is the duration of the field gradient, and $\Delta$ is the interval between the two gradient pulses. Care is generally taken to allow full relaxation by sufficient recycle delay. One can as well use stimulated-echo ($\pi/2 - \tau_1 - \pi/2$
\( \tau_2 - \pi/2 - \tau_1 \) pulse sequence. As will be discussed later, this pulse sequence has been shown to be more accurate and reliable than the spin-echo pulse sequence. The details of the method can be found in a review by Price [160, 161] and in a book by Kärger and Ruthven [85]. This method has gained popularity because of its noninvasive nature and its ability to measure self-diffusivities of the anions (\( D_- \)) and cations (\( D_+ \)) separately.

Noda et al. [146] measured the self-diffusivities of four different ILs at different temperatures. Data was fit to the Arrhenius equation

\[
D_s = A \exp \left[ \frac{E_{a,D}}{RT} \right]
\]

where \( A \) is a pre-exponential factor or a constant, \( R \) is the universal gas constant, \( T \) is the temperature and \( E_{a,D} \) is the activation energy for a diffusion process. They observed that the plots were not linear as expected by Arrhenius equation. They then fitted the data with Vogel-Fulcher-Tamman (VFT) [51, 52, 209] equation

\[
D_s = D_0 \exp \left[ \frac{-B}{T - T_0} \right]
\]

where \( D_0, B \) and \( T_0 \) are constants. \( B \) gives a measure of the activation energy while \( T_0 \) indicates the ideal glass transition temperature or the temperature at which the configurational entropy becomes zero. The data showed that even though the sizes of the cations were significantly larger than the corresponding anions, the diffusion coefficients of cations were comparable or higher than those of the anions. Data was analyzed using Stokes-Einstein (Eq. 2.4) and Nernst-Einstein (Eq. 2.5) equations.

\[
D_s = \frac{k_B T}{c \pi r_h \eta}
\]
where $k_B$ is Boltzmann constant, $T$ is the absolute temperature, $c$ is a constant between 4 and 6, $r_h$ is the effective hydrodynamic radius, and $\eta$ is the shear viscosity, and
\[
\Lambda = \frac{N_A e^2}{k_B T} (D_+ + D_-) \tag{2.5}
\]
where $\Lambda$ is the molar conductivity, $N_A$ is the Avagadro’s number, and $e$ is the electronic charge.

The hydrodynamic radii of cations and anions were calculated using Eq. 2.4 by substituting the self-diffusivity of corresponding ion and the viscosity of the IL. Even though the relation was derived for a spherical particle, the plot of $D_-$ or $D_+$ vs. $T/\eta$ is surprisingly linear. The hydrodynamic radii obtained from this relation, however, seem to be very low. Also, the computed hydrodynamic radius of a cation is lower than that of anion (owing to the fact that $D_+ > D_-$) which is not intuitive. Additionally, the idea of computing radii from a property like viscosity, which is the property of anion and cation put together, i.e. a mixture, is a suspect.

When the computed molar conductivities were compared against the measured values, the measured conductivities were very low. The ratio of measured to computed conductivities ranged from 0.3 to 0.8. This was attributed to the fact that ions could associate and form clusters. NMR does not distinguish between a nucleus in a free ion or in the cluster. However, neutral ion clusters, even though counted in NMR, do not contribute to the conductivities. Thus, the conductivity measured is always lower than that computed from the Nernst-Einstein equation (Eq. 2.5).

Huang et al. [74] also did a similar analysis for [emim]$^+$ tetrafluoroborate ([BF$_4$]$^-$). The hydrodynamic radius was computed for a range of temperature.
At around 330 K, the hydrodynamic radius showed a marked difference going from around 2.79 Å to 1.9 Å. This was attributed to the dissociation of an ion pair above 330 K. They have also found evidence of hydrogen bonding between $F^-$ of $[BF_4^-]$ and $H$ attached to the C2 carbon of the imidazolium ring. This was also supported by a study undertaken by Antony et al. [8].

In 2004, Hayamizu et al. [66] carried out the study of binary system of $[emim]^+[BF_4^-]$ and $[Li]^+[BF_4^-]$. This study also confirmed that $[emim]^+$ diffuses faster than significantly smaller $[BF_4^-]^-$. The diffusion coefficients for pure $[emim]^+[BF_4^-]$ were consistent with the previous results. A similar analysis was carried out with the help of Stokes-Einstein (Eq. 2.4) and Nernst-Einstein (Eq. 2.5) relationships. They also found that the computed value of conductivity was higher than that measured. It was then inferred that interactions between $[emim]^+^-[BF_4]^{-}$ could be weaker than those between $[Li]^+^-[BF_4]^-$.

As a result, $[BF_4]^{-}$ does not diffuse as a single ion but moves as a cluster.

Every et al. [43] studied the diffusion process using two different NMR methods. The aforementioned PFG NMR method was used to track cations or the hydrogen nuclei with a stimulated-echo pulse sequence while a fringe field gradient NMR (FFG NMR) method was used to track the anions or the fluorine nuclei with a spin-echo pulse sequence. For the later case, the attenuation can be given by

$$\ln(E) = \ln \left( \frac{S_{2\tau}}{S_0} \right) = -\frac{2}{3} \gamma^2 g^2 \Delta g \tau^3$$

where the symbols have same meaning as in Eq. 2.1.

They observed relatively high solid state conductivities with lower activation energies. The same observation was not noted for the diffusion coefficients. Curvature was observed in an Arrhenius plot leading to a VFT fit for cations, however,
in the case of anions, an Arrhenius relationship was followed. Analyzing data using a VFT fit, it was inferred that there exists a strong relationship between the diffusion coefficients and the free volume in the system. As the length of the alkyl side chain increased, the diffusion coefficient decreased as expected.

From the configurational entropy theory of Adam and Gibbs [3] the VFT equation for the diffusion coefficient can also be written in a slightly different form

$$D_s = AT^{1/2} \exp \left[ \frac{-k}{T - T_0} \right]$$  \hspace{1cm} (2.7)

where $k$ is pseudo activation energy, $T$ is the temperature, $T_0$ is the ideal glass transition temperature and the pre-factor $A$ is a constant proportional to radius ($r_D$) and mass ($M$) of the diffusing particle. The proportionality can be given as

$$A \propto \frac{r_D}{M^{1/2}}$$  \hspace{1cm} (2.8)

Thus, by plotting $AM^{1/2}$ against the alkyl chain length one can get an idea about the size of the diffusing particle. This plot shows that the radius of the diffusing particle increases from methyl to butyl side chain and then drops slightly before reaching a plateau. With the help of other NMR and infrared spectroscopy results, Every et al. [43] speculate that this effect could be a sign of longer alkyl side chains folding back toward the imidazolium ring. It would be interesting to see that if ionic association for the smaller cations has any significant effect on the reduction of the cationic radii. One additional thing to note from this study is that they cite an analysis of the crystal structure of [emim]$^+\ hexafluorophosphates ([PF_6]^-) which does not observe a strong interaction between cation and anion or an evidence of hydrogen bonding [53].
Umecky et al. [202] studied three \([R_n \text{mim}]^+\) hexafluorophosphates (\([PF_6]^-\)) (with \(R_n\) being butyl, hexyl and octyl) at 323 K. They observed that diffusivities for the cation were at least comparable, if not higher, than the anion. This is very interesting given that \([PF_6]^-\) has considerably smaller size compared to \([bmim]^+\) or \([hmim]^+\). As the length of alkyl side chain increases, the diffusion coefficient decreases. It looks like the size finally catches up with \([omim]^+\) and the diffusivities of anion are slightly higher than cation. Again, the similar analysis as described earlier was carried out. The computed hydrodynamic volumes were an order of magnitude lower than the computed van der Waals (VDW) volumes. Hydrodynamic radii for cation and anion were computed separately and the hydrodynamic volumes were calculated. The difference was attributed to ineffective friction. Despite the fact that Stokes-Einstein relationship was derived for a spherical particles, if we assume that the diffusivities are additive in their reciprocals, \(i.e.\)

\[
\frac{1}{D_t} = \frac{1}{D_+} + \frac{1}{D_-}
\]

where \(D_t\) is the diffusion coefficient of the IL molecule as a whole, the calculated hydrodynamic volumes are in much better agreement with molecular VDW volumes.

One more thing to be noted here is that even if the anion in all three systems is same, the diffusion coefficient of the anion drops as the cation moves slower and slower. Umecky et al. [203] also carried out another study to look at the effect of impurities on the diffusion coefficients. They showed that 3% impurities in the IL sample could change the diffusion coefficients by as much as 30%.

Starting in 2004 Tokuda et al. [195–197] carried out numerous experiments to study the effect of anion structure, cation structure and the length of alkyl side
chain on the physico-chemical properties of ILs. Even though PFG NMR method was used with spin-echo pulse sequence to measure the diffusion coefficients, the signal attenuation was given by

\[
\ln(E) = \ln\left(\frac{S}{S_{g=0}}\right) = -\gamma^2 g^2 D_s \delta^2 \left[\frac{4\Delta - \delta}{\pi^2}\right]
\]  

(2.10)

where the symbols have the same meaning. They studied a number of fluorinated anions paired with [bmim]\(^+\) cation to understand the effect of anion structure on the properties of ILs. As was the case in other studies, they also observed the curvature in the Arrhenius plots which led to fitting of the data with the VFT equation (Eq. 2.3). Other than for [bmim]\(^+[BF_4]^-\), the diffusivities for the cations were higher than those for the anions and the diffusivities for [bmim]\(^+\) change as the anion changes, another common observation in these studies. They see that, when the cationic and anionic diffusivities were added, they fall in the order [bmim]\(^+[Tf_2N]^-\) > [bmim]\(^+[BF_4]^-\) > [bmim]\(^+[PF_6]^-\) at 30\(^\circ\)C and the diffusivities were maximum with the bulkiest anion, i.e. for [bmim]\(^+[Tf_2N]^-\). They attributed this order to the Coulombic forces. Furthermore, the ratio of the observed or measured electric conductivities to the computed electric conductivities (from Nernst-Einstein (Eq. 2.5)) was less than 1, indicating association of ions to form neutral clusters.

When different cations were studied with a [Tf\(_2\)N\(^-\) anion, they noticed that the diffusion coefficients of an imidazolium based cation were higher than those of pyridinium or alkyl ammonium based cations. The effect of the length of alkyl side chain was studied by considering five different [R\(_n\)mim]\(^+\) cations paired with [Tf\(_2\)N\(^-\) anion. As expected, the diffusivities dropped as the length of the alkyl side chain increased, however, the diffusivity of the IL increased from
$[\text{dmim}]^{+}$ to $[\text{emim}]^{+}$. This trend was also in concert with the trend in the melting temperatures. The particular drop was attributed to the larger entropy gain during melting transition for $[\text{emim}]^{+}$ than that associated with $[\text{dmim}]^{+}$-$[\text{Tf}_{2}\text{N}]^{-}$. They also point out that the existence of ionic association or clusters could be observed in the FAB-MS measurements.

Recently, Annat et al. [7] pointed out, however, that one needs to be more careful while selecting the pulse sequence for PFG NMR. They showed that spin-echo pulsed sequence could lead to up to 20% error in diffusion coefficient measurements and that a few of the peaks in the NMR spectrum are not resolved by this method, especially for mixtures. A stimulated-echo method, on the other hand, was found to be more reliable and accurate in this regard. But we also need to note that these errors are amplified for the larger viscosity ILs. The ILs considered in this dissertation are relatively low viscosity liquids and this problem is not a major cause of concern. Hence, the simulations results of this study can directly be compared with the available experimental results.

To summarize the experimental findings, we can say that even though cations have larger sizes, generally they diffuse faster than the anions. The diffusivities of both species are affected by each other, i.e., diffusivities of the same cation are different when paired with different anions and same is true for the anions when paired with different cations. As the size of the alkyl side chain increases, the diffusivity of cation decreases. In general, these compounds do not follow an Arrhenius type of relationship and instead are fitted better with a VFT equation. These results are generally analyzed with the help of Stokes-Einstein and Nernst-Einstein equations, as described above. The estimates for hydrodynamic volumes for the cations obtained from these theories are lower than that of the
anions and both of these volumes are an order of magnitude lower than the VDW volumes. The idea of computing the hydrodynamic radius of a single ion from the viscosity of the mixture of ions in a suspet. In general, one needs to invoke the idea of ineffective friction or pairing or clustering of ions or folding of alkyl side chain toward the ring to describe the results obtained from the application of these theories. There is no direct experimental evidence, however, to support this hypothesis. These results indicate that, these equations, which are derived for simpler spherical particles do not work well for these systems and are insufficient to model ILs.

Using atomistic simulation techniques, on the other hand, we can get a useful molecular level insight in these systems. Such insight could prove important in order to get better understanding of the system and in designing new ILs for specific applications. We will visit the concept of molecular simulations in Chapter 3.

Effort to understand these new materials on a more fundamental or molecular scale began with the first study carried out by Hanke et al. [64] in 2001. They developed a new forcefield and studied a system of \([\text{dmim}]^+[\text{Cl}^-]\) by molecular dynamics (MD) simulations. Both an \textit{united atom} model and an \textit{all atom} model were studied. They observed that an united atom representation was inaccurate and large differences were seen as compared to the results of an all atom model. One thing we need to note here that the type of forcefield that this study employed is different than what is generally used nowadays. Also, a study done by Shah \textit{et al.} [181] using Monte Carlo (MC) techniques in our research group at Notre Dame around the same time showed that one can optimize the parameters for united atom model to get a better representation of the system. Having said that, an all
atom representation does give more physical picture of a molecule. Nonetheless, in both cases Hanke et al. found that $D_+$ was greater than $D_-$ even though the size of cation was significantly larger than that of anion. The diffusion coefficients predicted by the united atom model were about a factor of 4–5 smaller than those predicted by an all atom model. They also observed that, as expected, the diffusion coefficient increases as the temperature is raised. Many of the molecular simulation studies that followed this work were about developing a new type of forcefield or modifying an existing forcefield to best match the available experimental data. In addition, diffusion coefficient being a transport or a dynamics property, most of these studies are carried out using molecular dynamics (MD). Besides, as will be discussed later (Chapter 4), diffusion coefficients are one of the easiest properties to estimate using molecular simulations and one can check the validity of a new forcefield by comparing the diffusivity of the system to the experimental value relatively easily.

In 2002, de Andrade et al. [35] studied a system of $[\text{emim}]^+[\text{AlCl}_4]^-$. They developed a forcefield by drawing similarities from a histidine molecule in AMBER forcefield [27, 28, 157] for cation. The anion model was borrowed from the literature. They found a good agreement with the experimental diffusivity and also found that $D_+$ was greater than $D_-$. Later they developed another forcefield based on AMBER [27, 28, 157] and DREIDING [124]. This forcefield is expected to be extendable as the alkyl chain length increases. They see that as alkyl chain length increases, the value of the diffusion coefficient decreases. Even though the diffusion coefficient for $[\text{emim}]^+$ dropped about 30% from their previous study, it still agrees very well with the experimental value. One thing to note about this study is that their calculation show that heat of vaporization decreased going
from $[\text{emim}]^+$ to $[\text{bmim}]^+$ for both anions considered. They observe that even though the van der Waals contribution goes up a little bit, the Coulombic contribution decreased by a significant amount leading to a drop in the overall value.

However, other studies and measurements show that, at least for other anions, heat of vaporization increases as the alkyl chain length increases.

Morrow and Maginn [136] in our research group at Notre Dame developed a different forcefield based on CHARMM [113]. They studied the system of $[\text{bmim}]^+-[\text{PF}_6]^-$ at three temperature and also considered the effect of charge transfer and polarization. They computed the diffusion coefficients and the rotational relaxation times of the molecules. They, as others in the literature, found that the rotational relaxation times of an anion is smaller than that of cation and yet $\mathcal{D}_+$ is larger than $\mathcal{D}_-$. Based on the anisotropy that they observed in diffusion coefficients and the cage correlation analysis, they pointed out that very long simulations might be needed to be able to predict the diffusion coefficient for these slow-moving liquids. They also estimated the diffusion coefficient from an activated hopping process. It was in fairly good agreement, even though the estimates were about three times larger than the simulation results and about ten times larger than the results obtained from Stokes-Einstein relationship (Eq. 2.4).

Margulis et al. [118] developed another forcefield based on OPLS all atom model [82] for imidazolium cations while borrowing the parameters for a $[\text{PF}_6]^-$ from the literature. In the mean-squared displacement plots they see three different regions. First one, on very short time scales, which was thought to be more than just ballistic motion as usually is the case. A second, nonlinear region, which was assumed to be a region in which basin hopping dominates while the last one
was the linear region. The diffusion coefficients can be calculated from the slope of the curve in this last region. The calculated diffusion coefficients were in good agreement with the previous data [136]. Margulis [117] then extended this study by considering the effect of alkyl chain length on the system. He found that, even when the alkyl chain length was 10 (decyl chain) the diffusion coefficients of cations and anion were comparable and for dodecyl chain they were slightly lower than the corresponding anion diffusion coefficients. He observed that as the alkyl chain length increased, the pair radial distribution functions ($g(r)$s) indicated that the liquid became more and more structured.

Liu et al. [106] modified an AMBER forcefield [27, 28, 157] and studied five different ILs at three different temperatures. The computed diffusion coefficients for $[\text{bmim}]^{+}[\text{PF}_6]^{-}$ agreed well with the previous simulation results [118, 136]. However, when a system of $[\text{dmim}]^{+}[\text{Cl}]^{-}$ was considered, the estimated diffusion coefficients were about a factor of ten smaller than those reported by Hanke et al. [64].

In 2005, Lee et al. [101] developed another forcefield based on CHARMM [113]. The parameters for cation were taken from the similar atomic groups in histidine molecule. They studied five different ILs in which $[\text{bmim}]^{+}$ cation was paired with five different fluorinated anions. They observed that other than for $[\text{bmim}]^{+}$ trifluoroacetate ([CF$_3$COO]$^-$), the diffusion coefficients for cation were higher than those for anions. The diffusion coefficients estimated for $[\text{bmim}]^{+}$-$[\text{PF}_6]^{-}$, however, were about a factor of ten smaller than those estimated in the previous studies [106, 118, 136].

Del Pópolo and Voth [36] studied IL $[\text{emim}]^{+}$ nitrate ([NO$_3$]$^-$) at 400 K. The forcefield parameters for cation were borrowed from AMBER while those for
were taken from the work of Baaden [11]. The data was analyzed using \textit{linearity} parameter ($\beta$) and a \textit{non-Gaussian} parameter ($\alpha_2$). These parameters will be discussed later in the dissertation (in Chapter 7), but for now, it is sufficient to know that for a system to be in purely diffusive regime, $\beta$ should approach \textit{one} while $\alpha_2$ should approach \textit{zero}. If value of $\beta$ is \textit{less} than one, it means that the system is in sub-diffusive regime and the value of a diffusion coefficient obtained from the mean-squared displacement plot is only an \textit{apparent} diffusivity. As found in the previous studies, three regions were apparent in the plot of mean-squared displacement against time. The first region corresponded to a ballistic motion while the third was the diffusive region. In the second region, which was found to be about 400 ps, value of $\beta$ was less than one and the system showed sub-diffusive dynamics, a signature of glassy behavior. As alluded to by Morrow and Maginn [136], long simulations times are required for estimations of \textit{true} diffusion coefficients. Also, an evidence of short lived cation-anion pairs as well as dynamical heterogeneity was observed.

In a follow up study, the same system of $[\text{emim}]^+[\text{NO}_3]^{-}$ was studied by Yan \textit{et al.} [223] with the help of a polarizable forcefield. The effect of electronic polarization was seen to be more like increasing temperature. The molecules become more \textit{mobile}. As a result, the diffusion coefficients were estimated to be about three times \textit{larger} than those of a non-polarizable forcefield described earlier. It is interesting to note that, the effect of polarization makes molecules more \textit{mobile} which is same effect as increasing temperature, while application of shear is expected to have a similar effect on the system. We will analyze this case in more detail in Chapter 7 and 8.

Bhargava and Balasubramanian [15] studied a system of $[\text{dmim}]^+[\text{Cl}]^{-}$ at 425
K using a forcefield developed by Lopes et al. [108, 109]. The density was within 5% of the experimental value. The diffusion coefficient was estimated to be about 2 – 3 times smaller than that estimated by Hanke et al. [64] and about three times larger than that predicted by Liu et al. [106]. They concluded that the forcefield underestimates the diffusion coefficient.

Micaelo et al. [133] developed a new forcefield based on GROMOS [175] histidine molecule for the cation and borrowed the parameters for the anions from the literature. They studied [bmim]$^+$[PF$_6$]$^-$ and [bmim]$^+$[NO$_3$]$^-$ at eight different temperatures with this forcefield. They observed that diffusion coefficient for the cation was higher than that of the anion in [bmim]$^+$[PF$_6$]$^-$ but they were comparable in case of [bmim]$^+$[NO$_3$]$^-$. The diffusion coefficients computed for [bmim]$^+$[PF$_6$]$^-$ were about a factor of two lower than those observed in previous studies [106, 118, 136], however, they were in good agreement with the experiments. The diffusion coefficients for [bmim]$^+$[NO$_3$]$^-$ were found to be in good agreement with the previous results for [emim]$^+$[NO$_3$]$^-$ using polarizable forcefield [223] even though this study did not employ a polarizable forcefield.

One thing to note about this study is that they find a small peak corresponding to cation-cation interaction in the radial distribution function at lower distances than the first cation-anion peak. Even if the magnitude of this peak (in both cases) is small the ordering in the fluid is clear. A study of [emim]$^+$[NO$_3$]$^-$ using polarizable forcefield [223] has found a shoulder in cation-cation $g(r)$ about the same location as the first peak in cation-anion $g(r)$ but of very small magnitude and was attributed to a possibility of the orientational correlation in cation-cation spatial arrangement. Previous studies on [bmim]$^+$[PF$_6$]$^-$, however, do not show such shoulder or peak at a distance lower than the first cation-anion peak. A
shoulder or peak in a $g(r)$ means that there is a preferential orientation or ordering in the fluid. It indicates the probability of observing the other species at a given separation distance with respect to a random orientation. Thus, a shoulder in this case would indicate that there is a probability (even if lower than in random configuration) to observe a cation closer to another cation than the anion.

Rey-Castro and Vega [170, 171] studied a system of $[\text{emim}]^+ [\text{Cl}]^-$ using a previously developed forcefield at four different temperatures. They calculated the diffusion coefficient using a Green-Kubo formula, which will be discussed in Chapter 4. The integral in the formula needs to be computed until time $(t) \rightarrow \infty$. To extend to an infinite time limit, the authors fit an empirical function of the form

$$ D(t) = D + a \exp \left[ -bt \right] \quad (2.11) $$

to the asymptotic portion of the running integral of the diffusion coefficient. They also found that $D_+$ is greater than $D_-$. The diffusion coefficients followed the Arrhenius relationship. The analysis of the activation energies of cations and anions showed that anions have higher activation energy for diffusion than cations. This could be pictured as if the anions are in deeper energy wells than cations and the hindrance for cation movement along the plane is less.

Recently, Cadena et al. [26] in our research group at Notre Dame studied the systems of ILs based on pyridinium cations (1-$n$-hexyl-3-methylpyridinium [hmppy]$^+$, 1-$n$-octyl-3-methylpyridinium [omppy]$^+$, and 1-$n$-hexyl-3,5-dimethylpyridinium [hdmpy]$^+$) and $[Tf_2N]$ anions with a forcefield developed in the lines of CHARMM [113]. The forcefield for anions were taken from work of Lopes and Pádua [110]. The collision diameters for the Lennard-Jones atoms on the ring were scaled by 15% to match experimental densities of the system. They also measured
diffusion coefficients using PFG NMR method, discussed above. Experimentally, they found that for hexyl side chain cation diffused faster than the anion but for other two cases cation moved slower. In simulations, when the mean squared displacement plots were analysed using $\alpha_2$ and $\beta$ parameters discussed above, there was an evidence of the sub-diffusive dynamics. Even after 5 ns runs, especially at lower temperatures, the diffusive region was not reached. Consistent with the previous simulations results, this indicates that even longer simulations need to be run to reach the diffusive regime. As a result, the diffusion coefficients obtained from the simulations were only apparent diffusion coefficients and could not be directly compared to the experiments. As the temperature was raised, however, the dynamics seemed to be indicative of the diffusive regime. Cadena and Maginn [25] then extended this study to triazolium based cations paired with $[NO_3]^{-}$ and perchlorate ($[ClO_4]^{-}$) anions, also known as the energetic ILs. They found that for those systems, the diffusion coefficients for the cations were smaller than those of the anions. One thing that can be noted here is they observed that for the case of $[NO_3]^{-}$ anions, the first peak in the anion-anion $g(r)$ was at smaller distances than the first peak in the cation-anion $g(r)$. Again, the magnitude of this peak is not high but the the order in the fluid can be noticed.

2.2 Shear Viscosity

Shear viscosity ($\eta$) is a measure of momentum transport in a mass undergoing viscous flow under a shear gradient. It can be given by Newton’s law:

$$\mathcal{I}_{\text{momentum}} = \tau_{\alpha\beta} = -\eta \left[ \frac{\partial}{\partial \beta} v_\alpha \right] = -\eta \dot{\gamma} \tag{2.12}$$
where $\mathcal{J}_{\text{momentum}}$ is the momentum flux, $\tau$ is the shear stress, $\alpha$ and $\beta$ are the $x$, $y$ or $z$ directions, $v_\alpha$ is the component of the velocity in the $\alpha$ direction, and $\dot{\gamma}$ is the shear rate.

Among all the viscometers used to measure the viscosity for ILs, *cone-plate* viscometer and *capillary* viscometer seem more popular than others. In the case of *cone-plate* viscometer, fluid of interest (in this case IL of interest) is placed between a flat plate and a cone, while the cone is rotated. The fluid placed in between resists the motion of the cone owing to its viscosity. As a result a torque is required to keep the cone in constant circular motion. Analysis becomes easier if we have fluid at constant shear rate in the apparatus. As the radius increases, or as we move away from the center, the linear velocity of the fluid and with it the shear rate increases. With cone in place, the gap between the two surfaces also increases. This helps to keep the shear rate constant throughout. The angle of the cone with flat plate is kept very small. With all other variables and constants (such as torque, maximum radius of the cone, angular velocity, angle of the cone (with the flat surface)) known, one can easily calculate the viscosity of the fluid.

In the other case, *i.e.* a *capillary* viscometer, one measures the time required for the fluid to pass through a capillary. The flow time is directly proportional to the kinematic viscosity of that fluid

$$\nu = \frac{\eta}{\rho} = Ct$$

where $C$ is the proportionality constant determined by calibration of the equipment.

Bonhôte et al. [17] in 1996 measured many physico-chemical properties, including viscosity, of several hydrophobic ILs based on dialkylimidazolium cation.
They also considered a few hydrophilic ILs as well. They found that ILs with $[CF_3COO]^- \text{ and } [Tf_2N]^- \text{ anions gave rise to lower (relatively speaking) viscosities. They argue that this is because the former combines a minimal molecular weight with moderate basicity, while the later combines moderate molecular weight with minimal basicity. They also found that viscosity was minimum for } [emim]^+ \text{ cation. They suggest this is because } [emim]^+ \text{ combines a sufficient side chain mobility with low molecular weight. They also observe that methylation at the C2 position on the imadazolium ring increases viscosity significantly, while methylation at C4 position does not have nearly the same effect. As hydrogen bonding ability of cation decreases with C2 methylation, the viscosity was expected to be lower. Molecular simulation study carried out by Hunt [77] suggests that methylation at C2 position eliminates a few of the conformations which are stable otherwise while also increasing the barrier for the dihedral motion. She indicates that the loss of entropy overcompensates for the hydrogen bonding.}

McEwen et al. [129] studied many different ILs from the electrochemical capacitors perspective. They found that most of the ILs follow Arrhenius type of relationship

$$\eta = A \exp \left( \frac{E_{a,\eta}}{RT} \right)$$

(2.14)

where $A$ is a pre-exponential factor or a constant, $R$ is the universal gas constant, $T$ is the temperature and $E_{a,\eta}$ is the activation energy for a viscous process. At lower temperatures, however, they do observe a curvature in the Arrhenius relationship plots. They also suggest that viscosity is largely affected by ion volume and the larger ion controls the viscosity of the fluid.

As mentioned above, Noda et al. [146] studied four different ILs. They found that the viscosity followed a VFT type of relationship rather than an Arrhenius
\[ \eta = \eta_0 \exp \left[ \frac{-B}{T - T_0} \right] \]  

(2.15)

where \( \eta_0 \), \( B \) and \( T_0 \) are constants. Their results are in good agreement with the previous studies [17].

As alluded to earlier, Tokuda et al. [195–197] carried out a systematic study of the effect of anion and cation structure on ILs using a cone-plate viscometer. They observed that all the viscosity data followed VFT equation (Eq. 2.15) better than the Arrhenius (Eq. 2.14) one. When only an anion was changed in an IL [195], they found that the viscosity of \([PF_6]^-\) was higher than that of \([BF_4]^-\) which was higher than \([CF_3COO]^-\), and \([Tf_2N]^-\) had lowest viscosity. This trend compared very well with their trend in diffusion coefficient, which showed the opposite trend. By varying cation type [197], they observed that the imidazolium cation had lowest viscosity and the viscosity increased from imidazolium to pyridinium to alkyl ammonium cations. This trend also agreed well with the trend in diffusion coefficients. When the alkyl side chain length was increased [196], they found that viscosity decreased from \([dmim]^+\) to \([emim]^+\) and then increased again as the length was increased further. As mentioned earlier, they attribute this behavior to the larger entropy gain during melting in case of \([emim]^+\) than in the case of \([dmim]^+\). Once again, this trend agreed well with their trend in diffusivities. They also point out that this behavior suggests that the microscopic properties like diffusion reflects the macroscopic properties like viscosity. One interesting thing to note about the trend in the viscosities is that, if we plot the viscosity of \([dmim]^+\)-\([Tf_2N]^-\) and \([emim]^+[Tf_2N]^-\) as a function of temperature, the viscosity for \([emim]^+\) starts out lower but as the temperature increases, at around 390 K, \([emim]^+\) and \([dmim]^+\) swap the trend in the viscosities and \([dmim]^+\) now
becomes a lower viscosity compound.

In 2005, Harris et al. [65] studied the effect of temperature and pressure on the viscosity of $[\text{bmim}]^+ [\text{PF}_6]^-$. Using a falling body viscometer. The governing equation can be given as

$$\eta(T, p) = \frac{t(1 - \frac{\rho}{\rho_s})}{A[1 + 2\alpha(T - T_{ref})] \left[1 - \frac{2\beta(p - p_{ref})}{3}\right]}$$

where $t$ is the falling time, $\rho$ is the density of the fluid, $\rho_s$ is the density of the sinker, $\alpha$ is the coefficient of thermal expansion, $\beta$ is the bulk compressibility of sinker, and $A$ is the calibration constant. The measured viscosity ranged from 25 to 2700 cP. They found that a simple Litovitz equation [104, 105] can capture the temperature dependence.

$$\eta = A \exp \left[ \frac{B}{RT^3} \right]$$

where $A$ and $B$ are constants. They also tried to fit the data with VFT equation (Eq. 2.15) and found that it fits the data better than Litovitz equation (Eq. 2.17). They point out that for normal molecular liquids, $\sqrt{T}/\eta$ curves could be collapsed on each other by shifting them on molar volume ($V_m$) axis, however, this was not the case for ILs. They observed that isotherms were best fit by $f(\exp(p))$ rather than $f(\exp(V_m))$, as is the case for molecular fluids. As the pressure increased, $A$ or the pre-factor value decreased while the value of $B/T_0$ increased. The value of $T_0$ was not affected by the pressure, which suggests the pseudo activation energy value increased. When they studied a modified version of both of these equations, they observed that the strength parameter (equivalent to $B/T_0$) increased as the pressure increased, indicating that as the pressure was raised the ILs became more like normal molecular liquids.
The impurities play a huge role in determining the physico-chemical properties of ILs. Even a small fraction of impurities can alter the properties by a large amount, which is even more pertinent to the viscosities. In 2000 Seddon et al. [177] studied the influence of impurities like chloride ion ([Cl]$^-$), water and organic solvents on the viscosities of ILs. As the concentration of [Cl]$^-$ goes up so does the viscosity. They suggest that this effect is mostly due to stronger hydrogen bonding of [Cl]$^-$ with the cation. A study carried out by Hayamizu et al. [66] also found the similar effect with increasing [Li$^+$] concentration in [emim]$^+$[BF$_4$]$^-$.

Seddon et al. [177] observe that choice of anion has a primary effect on the solubility, while the choice of cation has a secondary effect. The solubility goes down as the alkyl side chain length increases and it increases as the dielectric constant of the solute increases. They also observe a relationship like

$$\eta_{mix} = \eta_{IL} \exp \left( \frac{-x_{cs}}{a} \right)$$

(2.18)

where $\eta_{IL}$ is the viscosity of pure IL, $x_{cs}$ is the mole fraction of the co-solvent and $a$ is a IL dependent constant, is generally followed. They tested a number of different IL – co-solvent mixtures and all seem to follow this general trend. The nature of exponential relationship is interesting. Just as a test, if we plot (not shown here) the viscosity of the solution using the mixture viscosity models (as in Chapter 7, Eq. 7.10, 7.11 and 7.12) we see that Eq. 7.11 predicts almost the same drop in viscosity as does the equation (Eq. 2.18) considered here (with parameters for [bmim]$^+$[BF$_4$]$^-$). Note that the Eq. 7.11 also has the exponential dependence in it. This suggests that the effect of added solvent may be mostly colligative. We will revisit this observation again in Chapter 7. The authors also draw similarities between this and a previous study [155], which indicates that
the effect was pronounced for the high dielectric constant liquids. They suggest that this observed effect of water as a co-solvent could be as a result of water decreasing the electrostatic attraction between the ions.

A more rigorous study of water content and its effect on viscosity was carried out by Widengren et al. [216]. They studied the viscosity of three ILs as a function of water content using a capillary viscometer. To accurately determine the water content, Karl Fischer titration were conducted before and after each pass through the capillary. They observed a large drop in viscosity as water content increased. We will revisit this study again in Chapter 7 and will try to analyze the effect of water as briefly alluded to above. They anticipate that this could be the main reason of disagreement between various studies, however, they also point out other possible reasons for this disagreement such as: $[Cl]^{-}$ or other ion impurities in ILs, decomposition of ILs at working temperature, inappropriate working or improper calibration of viscometer, and inconsistent experimental technique.

Rodriguez and Brennecke [172] at Notre Dame studied the effect of water content on three different ILs. They measured the viscosity of the solution using a cone-plate viscometer. They found that the viscosity of the solution decreased as the temperature or water content increased. They also observed that the temperature dependence of viscosity could be approximated by a second order polynomial function or a modified version of VFT equation.

$$\eta = A T^{1/2} \exp \left[ \frac{-k}{T - T_0} \right]$$ (2.19)

where $A$, $k$ and $T_0$ are constants. $k$ and $T_0$ could be compared to the pseudo activation energy and the glass transition temperature as in Eq. 2.7, respectively. As the water content changed, a large difference in the fitted value of $T_0$ was
observed. In the excess molar volume ($v^E$) plots they see a sign change around the mole fraction of water of 0.8. Note that this composition is lower than the composition where water would dominate the system in terms of occupied molar volume or mass. An excess viscosity was calculated along the same lines as the molar volume ($\eta^E = \eta_{mix} - \sum x_{W,i} \eta_i$). One could analyze this excess component better with other mixture viscosity models such as mentioned above or considered by Wang et al. [210].

In summary, we can say, in general, that imidazolium based cations have lower viscosity than those containing most other cations examined to date. As the alkyl side chain length increases so does the viscosity, except for going from $[\text{dmim}]^+$ to $[\text{emim}]^+$, when it drops for the reasons noted above. Branching of these chains also leads to the increase in the viscosity. Methylation of cation at C2 position has a large effect in terms of increasing the viscosity but methylation at C4 (or C5) position does not affect the property as much. Anions have dramatic effects on the viscosity of ILs. Generally, $[\text{Tf}_2\text{N}]^-$ has the lowest viscosities followed by $[\text{CF}_3\text{COO}]^-$. It has been noted before that the van der Waals forces govern the viscosity of ILs rather than Coulombic forces. Charge delocalization and chain flexibility affect the viscosity. Of course, adding a functional group can change the viscosity significantly. It is observed that adding a hydroxyl group on the cation increases the viscosity while adding an ether group to the cation reduces the viscosity. Fluorination on the cation increases the viscosity, however, fluorination on the anion decreases the viscosity. It has been pointed out that adding fluorine to a compound increases the van der Waals attraction energy. It is also interesting to note that fluorine is the most electronegative element in the entire periodic table. Thus, one can see that when added to a cation, it pulls
electron density from the ring or a positive center, in turn making it even more electron deficient and increasing its strength as a cation. When it is added to an anion, however, pulling electron density from a negative center makes the charge delocalized, decreasing its charge density and in turn decreasing its strength as an anion. Impurities can alter the properties of ILs by a significant amounts. Since impurities have such a dramatic effect on the properties of ILs, care must be taken when measuring, reporting or referring to such properties.

All this amount of work and progress in synthesizing ILs and measuring their viscosities is greatly contrasted by the amount of theoretical or molecular level studies in this area. Until very recently, when Yan et al. [223] computed the viscosity of $[\text{emim}]^+[\text{NO}_3]^{-}$ in August of 2004, there was no study in this direction. This is in part because viscosity is a harder quantity to compute in a simulation than its transport friend self-diffusivity. As will be discussed in Chapter 4, viscosity is a property of the entire system, as opposed to a property of every molecule as is the case for diffusivity. But then again, the efforts in the area of molecular simulations for ILs did not start until year 2001.

As described earlier, Yan et al. [223] compared a polarizable forcefield with a non-polarizable forcefield. They implemented a modified dipole tensor method previously described by Thole [194] using a smeared dipole-dipole interaction. They computed the viscosity using a transverse current correlation function method, which was generalized using a memory function model. We will discuss this method briefly in Chapter 4. As noted earlier, the effect of polarization is analogous to increasing temperature. At 400 K, the viscosity of $[\text{emim}]^+[\text{NO}_3]^{-}$ was reduced by about a third when a polarizable forcefield was used. The polarization is expected to make the fluid more mobile and there by reducing the cage
effects. The agreement between the simulation results and the experiments was greatly improved using a polarizable forcefield. As suggested earlier, the effect of imposing shear on the system is also to increase mobility of the system, and we will consider this approach in Chapter 7.

Bhargava and Balasubramanian [15] computed the viscosity of \([\text{dmim}]^+[\text{Cl}]^-\) using an equilibrium Green-Kubo method implementing a fixed charge or non-polarizable forcefield from Lopes et al. [108, 109]. More on this method will be discussed in Chapter 4. They observed that the method converges very slowly and long simulations are required to get a reliable estimate. Considering that the viscosity of \([\text{emim}]^+[\text{Tf}_2\text{N}]^-\) is higher than \([\text{dmim}]^+[\text{Tf}_2\text{N}]^-\) at 425 K and assuming the same trend holds true for \([\text{emim}]^+\) and \([\text{dmim}]^+\) \([\text{Cl}]^-\), the estimated value of viscosity is about a factor of three higher than the estimated or expected experimental value for \([\text{dmim}]^+[\text{Cl}]^-\).

Rey-Castro and Vega [170, 171] used a different non-polarizable forcefield from the literature [183] to compute the viscosity of \([\text{emim}]^+[\text{Cl}]^-\). They also used the above mentioned Green-Kubo formula to estimate the viscosity. As in the previous study, they also found that the method has poor convergence and is inaccurate at longer times. They employed a double-decay exponential function of the form

\[
\eta(t) = A\alpha\tau_1 [1 - \exp(-t/\tau_1)] + A(1 - \alpha)\tau_2 [1 - \exp(-t/\tau_2)] 
\]

fit to the running integral to improve the estimate. Here, \(A\) and \(\alpha\) are fitting parameters (with \(0 < \alpha < 1\)) and \(\tau_1\) and \(\tau_2\) are characteristic decay times. The computed value of viscosity is about an order of magnitude different than experimental results from Seddon [178], however, the qualitative temperature dependence is captured fairly well, with good agreement in activation energies.
As mentioned earlier, Micaelo et al. [133] developed a new fixed charge based force field for GROMOS. They computed shear viscosity using the *periodic perturbation* method. This method will also be discussed briefly in Chapter 4. They observe that the computed shear viscosity is *underestimated* at lower temperatures but as the temperature is raised, agreement with the experiments improved.

Borodin and Smith [19] calculated the viscosity of \( \text{N–methyl–N–propylpyrrolidinium (}[mppy]^+ [Tf_2N]^- \) at temperatures ranging from 303 K to 393 K using equilibrium molecular dynamic method (discussed in Chapter 4) and a polarizable model. Instead of a Green-Kubo integral, these authors used an Einstein relation to compute the viscosity (see Chapter 4) [6]. Their estimated viscosity at 298 K was about 25% *lower* than the experimental value.

Recently, Hu and Margulis [73] carried out a simulation on the largest system size ever reported for ILs (\([hmim]^+ [Cl^-] \)). The goals of their study were to see the effect of different perturbations on the system, to compute the shear viscosity of this liquid and to check the validity of linear response theory for this system. They studied the system using *spontaneous fluctuation, periodic perturbations* and *initial pulse perturbation* or *transverse current correlation function* methods. A brief introduction to these methods will be given in Chapter 4, but one can always refer to a good review by Hess [68]. They observed that even for their largest system size the hydrodynamic limit was not reached and only a periodic perturbation method could give a reliable estimate of the shear viscosity. They also note that a short time response of the systems seems to match well with the linear response theory prediction, however, the long time response deviates as the strength of the perturbation is increased.

Abbott *et al.* [2] measured the physical properties of different glycols with
choline chloride and the data was fitted to *hole theory*. They observed that at higher salt concentrations (greater than 0.2 mole fraction), the dominant mode of charge transfer is through motions of holes and the systems have properties like ILs.

To summarize, atomistic simulations have been used to compute viscosities for a small sample of pure ionic liquids. Agreement with experiments varies considerably, from near perfect quantitative agreement to differences of a factor of ten or more. Inclusion of realistic electronic polarizability almost certainly *lowers* the viscosity relative to that obtained with a simpler fixed charge model, although this does not necessarily guarantee *more accurate* viscosities. Fixed charge force-fields have been shown to faithfully reproduce both thermodynamic and transport properties of a number of other fluids [138, 139, 221] and it is reasonable to expect that the same is true of ILs. It is well established that the viscosity that one obtains from an atomistic simulation depends on a number of factors, including the intramolecular [54] and intermolecular van der Waals terms in the forcefield (as will be discussed in Chapter 3). As shown by Micaelo *et al.* [133], it is possible to obtain very accurate IL viscosities using a fixed charge model without sacrificing the accuracy of thermodynamic properties. This is encouraging, because, as mentioned earlier, fixed charge models are more computationally efficient than their polarizable counterparts. All things being equal, one of course would like to use models that treat the physics of the system in the most realistic manner possible. The recent simulation results for ILs suggests, however, that the added realism of a polarizable forcefield may not be essential for obtaining accurate thermodynamic and transport properties.

In addition to the studies presented here, one can refer to an excellent review by
Hunt [76] on the simulation efforts on ILs. It needs to be noted that even though in recent years there has been more work in the area of computing viscosity using molecular simulations, the time line of it overlaps with the work presented in this dissertation. Also, to the best of my knowledge, the effect of water content on the viscosity of ILs has not yet been studied using molecular simulation approach. I hope to convince you by the end of this document that this work was done independently of other studies and it adds value to the already existing literature on computing transport properties of ILs using molecular simulations.

2.3 Thermal Conductivity

Thermal conductivity \( (\lambda_T) \) is the measure of heat transport under a temperature gradient in a system. It can be given by Fourier’s law:

\[
\mathcal{J}_{\text{heat}} = q = -\lambda_T \left[ \frac{\partial}{\partial r} T \right]
\]  

(2.21)

where \( \mathcal{J}_{\text{heat}} \) (and \( q \)) is the heat flux.

There has not been a significant work done in the area of thermal conductivity as a whole for ILs. Not many references with the measured values of the thermal conductivity of ILs are available in open literature. In 2005, however, Van Valkenburg et al. [206] measured the thermal conductivity of three ILs in order to compare their physico-chemical properties to the conventional heat transfer fluids. They were interested in the heat transfer fluid for the large-scale solar energy collectors for electric power generation. They used a transient hot wire method to measure the thermal conductivity of ILs. This method is one of the absolute methods, \( i.e. \), it gives the absolute value for the thermal conductivity, which for reference fluids, can directly be compared with the literature data. The method
involves heating a wire with constant current and measuring the temperature of
the wire as it is being heated. One can determine the value of thermal conductivity
from the following equation:

\[
\Delta T = \left[ \frac{q}{4\pi \lambda_T} \right] \ln(t) + \left[ \frac{q}{4\pi \lambda_T} \right] \ln \left[ \frac{4\kappa}{a^2 C} \right]
\]

where \(\kappa\) is the thermal diffusivity, \(q\) is the heat generation per unit length (given
by \(i^2 R/l\); \(l\) being length of the wire, \(i\) and \(R\) are the current and the resistance
of wire respectively), \(a\) is the radius of wire, \(t\) is the time elapsed, \(C = \exp(\gamma)\)
and \(\gamma\) is Euler’s constant (thus, \(C = 1.781\)). Thermal conductivity is determined
from the slope of the plot of \(\Delta T\) versus \(\ln(t)\). The authors point out that when
compared with toluene and water, the behavior of IL is more close to toluene than
water. The effect of water on these systems was also studied and it was observed
that water does affect the thermal conductivity significantly. They observed that
adding 25 wt.% water to IL changes thermal conductivity by about 30%. The
effect is more pronounced for \([\text{bmim}^+][\text{BF}_4^-]\) than for \([\text{emim}^+][\text{BF}_4^-]\).

To the best of my knowledge, there has not been any simulation study of ILs to
compute thermal conductivity. This will be the first attempt to study this property
and we will also see the effect of water content on the thermal conductivity of ILs
in Chapter 8.

As pointed out earlier, there have been significant advances in synthesizing new
ILs and measuring their physico-chemical properties. In recent years, however, the
theoretical and computational part is catching up. This dissertation is directed
toward adding more information to the data base and toward adding a molecular
level insight into the transport properties of ILs.
A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.

- Albert Einstein

In 1965, Gordon Moore, a co-founder of Intel, made an observation that the number of transistors on a chip doubles about every two years [79]. The observation is now commonly known as the Moore’s law. Even today, forty years after the fact, the statement seems to hold true. The law indicates the performance of modern computers and estimates that the speed of the processors would increase by an order of magnitude every five years or so. With this ever-increasing power of todays computers, (approaching a speed of petaflop/s) they have impacted almost all the fields. One of the fields that has significantly benefited from it is the field of computer simulations. This field of computer simulations is rather young, dating back only a few decades. One of the very first computer simulation was carried out in early 1950s, when computers were made available for non-military use after
World War II. In the beginning, the field had its fair share of doubters, and it still does. As the complexity of systems under consideration grew, however, the space on the back of the proverbial envelope seemed to be insufficient, and the use of computers for performing such calculations was imminent. A typical computer simulation in the field of chemistry involves mimicking the behavior of atoms and molecules in a system, these are also known as atomistic or molecular simulations. As pointed out by Leach [100], an idealistic and a mathematical representation, i.e. a model, is used to mimic such intermolecular or intramolecular behavior and fittingly the field is also known as molecular modeling.

Atomistic simulations are most commonly used to predict the properties of materials. Measuring these properties experimentally, however, seems much easier than estimating them using computer programs. The advantage of using the simulations becomes more apparent away from ambient conditions. While measuring a property experimentally at very high temperatures and pressures poses problems in terms of the experimental set up and cost, the computer does not care! It makes only a small difference estimating a property at elevated pressures using simulations, and they actually perform better at higher temperatures. One can as well estimate properties of materials which have not yet been synthesized. When screening for a particular property, the absolute number may not be as important as the relative order between a few candidates and their trends with respect to temperature and pressure or concentration. In this case these atomistic simulations are very useful. Even though the simulations might never replace experiments, the atomistic level details that these simulations provide can be successfully used to complement the experiments or to provide directions for future research.
One can also use simulations as a bridge between experiments and theory. As simulations can give an exact solution to the model, one can test the validity of model by comparing it with experimental results. On the other hand, one can as well get an exact solution from a simulation and compare it with the results of a theory. If our model predictions do not agree with experiments, we can consider improving the model. Similarly, if the theory does not agree with the simulations, we can think about improving the theory.

Finally, as aptly pointed out by Cummings [31, 32], performing experiments have high capital costs associated with them and they also tend to be labor intensive. Theory has a low capital cost but is even more labor intensive than experiments. The simulations, however, are not as labor intensive. The more important thing is: computers are becoming faster by an order of magnitude every a few years and their costs are decreasing as well, a feat that can not be matched by experimental equipment or people power!

Having motivated the reader about the usefulness or the importance of atomistic simulations, we will now go a step ahead and look at the underlying details more closely. Fig. 3.1 shows a rudimentary algorithm for carrying out an atomistic simulation. We will skim through each of these steps one-by-one from the point of view of this dissertation, but one can refer to the literature cited within those sections for a more detailed explanation.

3.1 Molecular Representation

Generating a molecular representation is the first step in simulating any material. In this step you tell the program or the algorithm what substance you want to mimic, i.e., give the program a mathematical and simplified model of
Figure 3.1. Concept of *atomistic simulations*. This figure is based on the figure due to Maginn [114].
the material of interest. There are two basic ways of providing the molecular geometry to your simulation package: (1) One can give the Cartesian coordinates of each of the atoms or representative particles and then give the connectivity information within them separately. This would be analogous to the lab coordinates of the system. (2) One can also give the same information in terms of internal coordinates, in which a z-matrix is generated which can completely describe the entity. A more detailed discussion could be found elsewhere [6, 49, 100]. Often the systems being studied using these simulations are molecular in nature and often each of the atoms involved in a molecule is represented individually. However, it is a common practice to represent a group of atoms together and thereby coarse grain the model in order to save computational time. Both types of models will be encountered in this dissertation. Going from a detailed model (an all-atom representation in the context of this dissertation) to a coarse grained model (an united-atom representation in the context of this dissertation) one loses details of the physical picture of the system but gains significantly on the time of execution. It is up to the researcher to weigh these factors and choose one over the other based on the desired outcome.

3.2 Quantum Mechanics

The aim of this exercise is to be able to calculate the total energy ($\mathcal{T}$) of a particular system. The total energy can be broken down into two parts: kinetic energy ($\mathcal{K}$) and potential energy ($\mathcal{U}$). Kinetic energy contributions to the total energy can be easily calculated from $\sum (m_i/2)v_i^2$, where $m_i$ is the mass of an atom and $v_i$ is the velocity. As an atomistic simulation can keep track of positions and velocities of all the atoms, calculating kinetic energy is not a difficult task.
Calculating potential energy, on the other hand, can become quite difficult. In this chapter we will consider several of methods that help us compute the potential energy of the system, viz quantum mechanics and empirical forcefields.

Once one has an all-atom representation of a molecular system where the different atoms comprising a molecule or a system are known, one can go ahead and analyze this configuration using quantum mechanics principles. It is interesting to note that many of these quantum mechanical theories predate the computer era. Electrons are generally explicitly represented in these methods and thus are expected to provide the properties that are based on electronic distribution.

At the heart of any quantum mechanics discussion is the time-dependent Schrödinger equation [100]:

\[
\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V \right\} \Psi(r, t) = i\hbar \left[ \frac{\partial}{\partial t} \Psi(r, t) \right]
\]  
(3.1)

where \(\hbar = h/2\pi\), \(h\) is the Plank’s constant, \(m\) is a mass of single particle, \(V\) is the applied external field, \(r\) is the position vector, \(t\) is time, \(\Psi\) is the wave function and

\[
\nabla^2 = \frac{\partial^2}{\partial r^2} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}
\]  
(3.2)

When the external field is independent of time, the above equation (Eq. 3.1) can be simplified:

\[
\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V \right\} \Psi(r) = E\Psi(r)
\]  
(3.3)

Now, recognizing that the left hand side of this equation (Eq. 3.3) is nothing but the Hamiltonian operator \(\mathcal{H}\), we can re-write this equation as:

\[
\mathcal{H}\Psi = E\Psi
\]  
(3.4)
This is the commonly known eigen value problem form of the Schrödinger equation. The equation seems simple on paper, however, it can be solved exactly only for a few simple cases. Even for the system size of three, this equation (Eq. 3.3) cannot be solved exactly. Thus most molecular systems cannot be treated with this equation exactly. The Born-Oppenheimer approximation simplifies the situation significantly. It says: on account of the huge difference in mass of an electron and the nucleus \(m_{\text{nucleus}} = 1836\ m_{\text{electron}}\), the motion of electron and nucleus may be considered as decoupled. With this, one can solve the Schrödinger equation (Eq. 3.4) for the simplest molecular species like \(H_2^+\). In general for the systems of practical importance, however, this equation is not exactly soluble and one has to use approximate methods. Two of such approximate methods that are used in this dissertation are: molecular orbital (MO) and density functional theory (DFT) methods. The former can be thought of as an exact solution to an approximate equation while the later can be looked at as an approximate solution to an exact equation.

Many times in an electronic structure calculation, one is concerned about calculating molecular orbitals. The variation theorem helps us going about doing it. The theorem says that the true energy (i.e. energy calculated from the true ground state wave function) is always lower than or is equal to the energy calculated from the approximation wave function. That means the quality of the wave function improves as the energy predicted goes down. This lead to the development of the Hartree-Fock (HF) method. In the HF approach, every electron is assumed to be moving in a mean field of all other electrons in the system. Electron correlations are neglected in this method which might be critical in some situations, such as bond breaking and forming. There are several methods which try to recover this
neglected contribution. In this dissertation we use second-order Möller-Plesset perturbation theory, also known as MP2, the simplest post-HF treatment of electron correlation[134, 158]. There are two main classes of MO methods: \textit{ab-initio} and \textit{semi-empirical} methods. As the name suggests, in \textit{ab-initio} methods, calculations are performed from the first principles and only the physical constants are required as inputs. On the other hand, the \textit{semi-empirical} methods use parameters instead of some integrals and also neglect a few terms from the true Hamiltonian to simplify the calculations.

The other important approach is DFT. The electron correlations are inherently included in the DFT method [70, 94, 153]. The DFT method is based on a theorem that there is a correlation between total energy and the electronic density. It aims at calculating the total energy and the electronic density distribution. HF method can be systematically improved by including electron correlation at different levels, while there is no formal way of systematically improving on the DFT method. One can then think of adding a fraction of the exact exchange energy computed from the HF method to the energy calculated from the DFT method. These methods are called \textit{hybrid} methods. One of the more popular such functional is B3LYP and is used extensively in this dissertation.

Generally, in \textit{ab-initio} calculations, Gaussian functions of the form

\[ x^a y^b z^c \exp \left( -\alpha r^2 \right) \]  \hspace{1cm} (3.5)

are used to approximate Slater functions, which are typically difficult to implement efficiently, in the basis sets. As the number of such Gaussian functions used increases the quality of the approximation improves. A detailed discussion on the nomenclature of such methods can be found elsewhere [100]. In the context of this
dissertation we make use of one of such basis sets: 6-311++G. It indicates that we use a single zeta core ("6" Gaussians are used to describe the core orbitals) and triple zeta valence ("3" Gaussians with linked coefficients for each inner valence basis function with "1" uncontracted primitive for 2nd layer of valence and "1" uncontracted primitive for outer layer of valence) representations. "++" implies that the diffuse functions are set only for heavy atoms, while "+++" implies that diffuse functions are set for all atoms including hydrogen. One can add "*" or "**" after "G" indicating the addition of polarization functions on all heavy atoms and on hydrogen atoms as well respectively.

With this type of quantum mechanical analysis, one can arrive at the optimized gas-phase geometry of the molecule or the system. One can as well get the energy associated with that structure and compare it with energies of other structure to get an idea about the relative stability of a particular structure. One can get an estimate of polarization of a molecule by computing the charge distribution on the atoms. Now the atomic charges are not quantum mechanical "observables" and there are many different approaches for going about doing it. One can use an algorithm like CHELPG [21] to compute the atom-centered point charges which will reproduce the total electrostatic potential. This procedure is extensively used in the forcefield development part of the dissertation.

3.3 Forcefields

As discussed earlier, quantum mechanical methods account for all electronic properties. The number becomes too large very quickly as the system size increases. In addition, the methods, many times, do not scale well with the number of electrons considered. For instance, MP2 calculations mentioned above, scale as
$n^5$ where $n$ is the number of electrons. For a moderate sized molecule or a system of atoms, these calculations become prohibitively expensive even on today’s fast computers. The use of forcefields help us get around this problem when handling $\mathcal{O} 10^2–10^6$ atoms.

A forcefield for atomistic simulations attempts to reproduce the energy ($\mathcal{W}$) of the system. It considers two types of energy contributions from bonded and non-bonded interactions. One can split these contributions further into bond stretching, angle bending, torsion angle rotation and improper angle bending for bonded interactions, while non-bonded interactions can be further divided into van der Waals or repulsion-dispersion and Coulombic interactions. Atoms separated by 1, 2, or 3 bonds are considered under bonded interactions while atoms separated by more than 3 bonds as well as atoms on different molecules are considered under non-bonded interactions. One can group all bonded interactions and the non-bonded interactions within same molecule into one category known as intramolecular interactions and the remaining non-bonded interaction can be grouped under intermolecular interactions. We will consider each of these contributions and give a brief description of them as they are considered in this dissertation. However, the detailed discussion of all these contribution may be found in various literature sources [6, 49, 100].

3.3.1 Bond Stretching

The interaction between atoms or sites directly bonded to one another is treated by a bond potential. Typically, it is described using Hooke’s law or a
harmonic bond stretching potential

\[ U_{\text{bond}} = \sum_{\text{bonds}} k_r (r - r_0)^2 \]  \hspace{1cm} (3.6)

where \( k_r, r, \) and \( r_0 \) are the bond stretching constant, bond length, and nominal bond length respectively. The harmonic bond potential can be easily derived from performing a Taylor expansion of energy about the equilibrium bond length, then neglecting higher order terms from the expansion, and imposing the condition that energy is at a minimum (the first derivative of energy is zero) at the equilibrium distance. This is one of the reasons that sometimes \( k_r \) is also represented as \( k_r' / 2 \) as in the Taylor expansion notation. This potential form is widely used to model the bond energy term. However, this is not the most accurate representation of bond stretching. The energy profile for a bond stretch can be modeled more accurately by Morse-type potential

\[ U_{\text{bond}} = \sum_{\text{bonds}} D_e \left\{ 1 - \exp \left[ -a(r - r_0) \right] \right\}^2 \]  \hspace{1cm} (3.7)

where \( D_e \) is the well depth, and \( a \) is given by \( \omega \sqrt{\mu / 2 D_e} \) where \( \mu \) is the reduced mass and \( \omega \) is the frequency of bond vibration. This potential allows a bond to dissociate at large distances. Even though this potential form gives a closer or more accurate representation of the actual bond stretching potential, it is computationally expensive and requires three parameters to be defined. Therefore, this type of bond potential is not widely used in the simulation community. In addition, in common simulations, the bond distance does not significantly deviate from its equilibrium value. In these cases, a harmonic potential effectively captures the actual energy profile of a bond vibration. We will, therefore, use only
the harmonic representation for bond stretching in this dissertation.

To model the polymer chains, however, another type of bond interaction is introduced, known as the *finitely extensible nonlinear elastic (FENE)* spring [211] potential. This is

$$U_{\text{bond}} = \begin{cases} \infty & \text{if } r_{ij} \geq R_0 \\ -\left(\frac{1}{2}\right) \left(k_r R_0^2\right) \ln \left[1 - \left(\frac{r_{ij}}{R_0}\right)^2\right] & \text{if } r_{ij} < R_0 \end{cases} \quad (3.8)$$

where $R_0$ is the maximum stretch permitted.

### 3.3.2 Angle Bending

Interaction between atoms or sites connected by two consecutive bonds, through one common atom, is modeled using an angle potential. A harmonic potential representation can be used to model this interaction, as in the case of bonds

$$U_{\text{angle}} = \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 \quad (3.9)$$

where $k_\theta$, $\theta$, and $\theta_0$ are the bending constant, bending angle, and nominal bending angle, respectively. Again, $k_\theta$ can as well be represented as $k_\theta'/2$ as in the term in the Taylor expansion.

In some cases, one can add a “spring” between the two end atoms (*i.e.* harmonic potential) and introduce an additional energy contribution like the bond potential (Eq. 3.6). These type of interactions are known as Urey-Bradley potentials.
3.3.3 Torsion Angle Rotation

The interaction between atoms or sites separated by three consecutive bonds is modeled as a torsional or dihedral interaction. In the literature, it is modeled using a cosine series in one of two ways: an OPLS form [81–84] and an AMBER or CHARMM form [27, 28, 113, 157]. The OPLS form is given as

\[ U_{\text{torsion}} = \sum_{\text{dihedrals}} c_0 + c_1[1 + \cos(\phi)] + c_2[1 - \cos(2\phi)] + c_3[1 + \cos(3\phi)] \]  

(3.10)

where \( \phi \) is the dihedral angle and \( c_n (n = 0, 1, 2, 3, \ldots) \) are constants. These constants \( (c_n) \) are sometimes represented as \( c_n'/2 \). In the newer versions of this potential form the zeroth term \((c_0)\) is dropped and only last three terms are considered in modeling a torsion or a dihedral angle potential.

The AMBER or CHARMM form, may be represented as

\[ U_{\text{torsion}} = \sum_{\text{dihedrals}} \sum_n k_\phi [1 + \cos(n\phi - \delta)] \]  

(3.11)

where \( k_\phi \) is the constant, \( n \) is the multiplicity, and \( \delta \) is the phase shift. In general, if possible, only one term is used (either with \( n = 1 \) or \( 2 \) or \( 3 \)) to maintain simplicity, however one can use as many terms as needed to accurately represent or reproduce a torsional potential. In this dissertation, we have made use of one term and three term potentials to model dihedral energies. In general, it is easy to convert from OPLS form to three term CHARMM form using mathematical manipulations, or by fitting to quantum mechanical data, without loss of accuracy.
3.3.4 Improper Angle Bending

Interactions between three atoms bonded to a common atom are modeled using an improper angle bending potential. It describes the energy penalty for out of plane bending. For example, a hydrogen atom attached to a benzene ring oscillating out of the ring plane would be modeled with an improper angle bending potential. This energy can be given as a harmonic potential

\[ \mathcal{U}_{\text{improper}} = \sum_{\text{impropers}} k_\psi (\psi - \psi_0)^2 \]  

(3.12)

where \( k_\psi \) is the force constant and \( \psi_0 \) is the reference angle, which in most cases is set to zero as the angle for atom residing in the plane is defined to be zero. It is not very common to include this term in the potential form. Even the magnitude of energy associated with such bend is very small. However, in the study conducted for ILs in this dissertation, we have included this contribution to the total energy.

3.3.5 van der Waals or Repulsion-Dispersion Interactions

Interactions between atoms or sites separated by more than three bonds or atoms on two different molecules are treated with non-bonded interactions. Only two atoms are considered to be interacting at a time and the total energy is assumed to be pairwise additive. The non-bonded interactions, as mentioned earlier, are modeled using two components: van der Waals (or repulsion-dispersion) interactions and Coulombic (or electrostatic or charge-charge) interactions.

The deviations from ideal behavior that can not be accounted for by electrostatic interactions were first analyzed by van der Waals and thus, such kinds of interactions are known as van der Waals (or simply VDW) interactions. At large
separation distances atoms do not feel each other and there are no interactions between them. At moderate distances, however, they do interact through dispersive or attractive forces. These forces are known to have a $r^{-6}$ dependence, where $r$ is the separation distance. As the atoms come too close, the repulsive force dominates. These forces vary exponentially with the separation distance. The Lennard-Jones (LJ) potential function combines these interactions to give

$$U_{LJ}(r_{ij}) = \sum_{i=1}^{N-1} \sum_{j>i}^{N} 4 \epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$

(3.13)

where $r_{ij}$, $\epsilon_{ij}$, $\sigma_{ij}$ are the separation between atoms $i$ and $j$, LJ well depth or energy parameter, and LJ diameter or collision diameter, respectively. This is a particular form ($12-6$ form) of the Lennard-Jones potential. The $r^{-6}$ term accounts for the dispersion interactions while for computational convenience, the steep exponential repulsion part is approximated using $r^{-12}$ term. One can use any power instead of 12 in order to approximate the repulsive or the exponential part of the curve. In addition to this $12-6$ form, one can use a 9-6 or 12-10 forms.

3.3.6 Coulombic Interactions

The other part of non-bonded interactions are the Coulombic or the electrostatic interactions. One can easily model them using Coulomb’s law

$$U_{qq}(r_{ij}) = \sum_{i=1}^{N-1} \sum_{j>i}^{N} \frac{q_i q_j}{4\pi \epsilon_0 r_{ij}}$$

(3.14)

where $q_i$, and $q_j$ are the partial charges for a pair of atoms $i$ and $j$. $\epsilon_0$ is the permittivity of the vacuum. Although this expression looks simple, practically these interactions prove to be the bottle neck of the computation. The energy
varies as \( r^{-1} \), which means energy decays very slowly, at least as compared to repulsion-dispersion interactions and one has to consider the interactions at longer distances. Researchers have developed many algorithms to tackle this problem, including the *Ewald sum, reaction field,* and *Wolf* methods to name a few. One can find a detailed discussion on these methods in many good books and articles in the literature [6, 49, 100] and the references therein. One can think of VDW interactions as arising from induced dipole interactions while Coulombic interaction can be thought of as arising from permanent charge and dipole. One can use either a fixed charge model or a polarizable (fluctuating charge) model to account for electrostatic interactions. Even though the fluctuating charge model is superior to the fixed charge model in term of representing actual physics, it comes with a significant computational cost. It is for that reason, in this particular dissertation, we use the fixed partial charges on each of the atom centers to account for electrostatic interactions.

Including all the previously described interactions, the total form of the internal energy looks like:

\[
U_{\text{total}} = U_{\text{bond}} + U_{\text{angle}} + U_{\text{torsion}} + U_{\text{improper}} + U_{\text{LJ}} + U_{\text{qq}}
\]

\[
U_{\text{total}} = \sum_{\text{bonds}} k_r (r - r_0)^2 + \sum_{\text{angles}} k_{\theta} (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} k_{\phi} [1 + \cos(n \phi - \delta)] + \sum_{\text{impropers}} k_{\psi} (\psi - \psi_0)^2 + \sum_{i=1}^{N-1} \sum_{j=1}^{N} \left\{ 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\epsilon_0 r_{ij}} \right\}
\] (3.16)

Sometimes the non-bonded interactions are computed for atoms separated by
three bonds, i.e., the atoms or sites generally considered for torsional interactions. The energies from these interactions, however, are generally scaled by 50%. To save computation time, the distance over which the interactions is computed is truncated. This distance is known as the cut-off distance. This distance is generally long enough such that the VDW interactions are very small beyond that distance and people use the correction term to account for that small difference. The VDW function, however, does not go to exactly zero at this distance and to avoid discontinuity, switching functions ($S$) are used. The use of these functions eliminate the need for the correction term and make sure that forces and energies are not discontinuous at the cut-off. One such switching function used in this study has the form,

$$S(|\vec{r}_{ij}|) = \begin{cases} 
1 & \text{if } |\vec{r}_{ij}| \leq r_s \\
\frac{(r_c^2 - |\vec{r}_{ij}|^2)^2(r_c^2 + 2|\vec{r}_{ij}|^2 - 3r_s^2)}{(r_c^2 - r_s^2)^3} & \text{if } r_s < |\vec{r}_{ij}| < r_c \\
0 & \text{if } r_c \leq |\vec{r}_{ij}| 
\end{cases}$$  \hspace{1cm} (3.17)

where $r_c$ is the cut-off distance and $r_s$ is the onset distance for the switching function.

There are a few features of these forcefields that should be noted. In general, atoms are distinguished by their respective atom types. A particular atom type attempts to capture or signify the unique environment of the atom. Each atom type is characterized by the LJ $\sigma$ and $\epsilon$ as well as the atomic partial charge. For instance, the atom type for an oxygen atom in water would be different than that in alcohol which would again be different than that in a carboxylic acid. When two interacting atoms have the same atom types we can use the above
non-bonded potential equations to model those interactions. However, when the interacting atom types differ, one needs to use combining rules. There are different combining rules available in the literature, for instance, the Geometric or Lorentz-Berthelot combining rules. The combining rules are an integral part of a forcefield. Strictly speaking, changing a combining rule would lead to a different forcefield even though all other parameters are the same. In this dissertation we use the Lorentz-Berthelot combining rules \([14, 111]\), \(i.e., \sqrt{\sigma_i \sigma_j} \) and \(\frac{1}{2}(\sigma_i + \sigma_j)\).

Ideally, one would like to derive all the fixed parameters in Eq. 3.16 from the quantum mechanical calculations, \(i.e., \) from the first principles, but this is a non-trivial exercise. Even though one can reliably estimate the values of the bond and angle force constants and the partial charges on atom centers (for the forcefield) from quantum mechanical calculations, it is not easy to determine the terms in a torsional potential or the \(\sigma\) and \(\epsilon\) terms in a LJ potential. In most cases, the forcefields are empirical. One tries to find a set of parameters that works well for a system in terms of reproducing some experimentally observable quantities. For example, the Transferable Potential for Phase Equilibria (TraPPE) forcefield \([29, 120, 121, 190]\) is optimized based on the vapor-liquid equilibria of various systems. Even though they are physically important, there is not much science involved in coming up with the numerical values of \(\sigma\) and \(\epsilon\) terms in a LJ potential and are often fit to better reproduce the experimental data. Consequently, one can use additional terms than those used in Eq. 3.16, to better represent the interactions present in a particular system. Unless one derives all the parameters from first principles, one would not like to invest time to come up with the optimum parameters for each and every system. This is where the transferability of the parameters proves to be important. Generally, while developing new forcefields,
people try to assign the numerical values to these parameters such that they could be used in chemical systems where the environment for a particular atom is similar or conserved. For instance, in the TraPPE forcefield, the authors designate LJ parameters for a $CH_2$ group. These parameters can be used for a $CH_2$ group when modeling $n$-butane, $n$-hexane, or in $n$-dodecane where the environment is similar.

In most of these forcefields we assume energy to be pairwise additive and neglect the three-body interactions. Even though their contribution to the total energy is not large, they still are important. However, when one tries to optimize the parameters of a forcefield by fitting the computed properties to the actual experimental properties, the contribution from the three-body interactions is considered implicitly.

Finally, the accuracy of any computed thermophysical property depends on the quality of the forcefield used and would be same irrespective of the algorithm or method used to compute it. The algorithms or methods, however, can change the efficiency of the computation significantly.

3.4 Statistical Mechanics

Even though, in Fig. 3.1 Propagators or Generators come before of statistical mechanics, we will jump ahead to statistical mechanics part of the algorithm as the propagators borrow some of the concepts from this field.

About 125 years ago, van der Waals pointed out that matter is consisted of constantly moving particles or molecules and these molecules can interact through both attractive and repulsive forces [114]. This conceptual breakthrough implied that there is a connection between the way molecules move or interact microscopi-
cally and the macroscopic properties portrayed by the material. However, tracking $\mathcal{O}10^{23}$ particles and their interactions in order to get the macroscopic properties is impossible. On the other hand, as there are so many particles, just like in the surveys, we can select a few representative particles to study the statistical behavior of the system, and hence the macroscopic properties. It is this particular link that is provided by statistical mechanics. Of course, as in the field of statistics, as the sample size or the number of representative particles increases, the quality of the statistical analysis also improves. The key concept here then is that of the 

*ensemble*. We need to come up with many such representatives in order to appropriately describe the macroscopic behavior. This approach is based on two key postulates: (1) The Ergodic hypothesis, which states that given an infinite time, a system will visit all the microstates consistent with the constraints. (2) Equal *apriori* probabilities, which states that all the microstates with same energy are equally probable. Given these postulates, one can study different ensembles in statistical mechanics formulations.

The simplest or the easiest of all the ensembles is the *microcanonical* ensemble. In this ensemble, the total number of atoms ($N$), volume ($V$) and energy ($E$) are kept constant and hence is also represented as $NVE$. The partition function, or sum over all states, for this ensemble ($Q_{NVE}$) is

$$Q_{NVE} = \frac{1}{h^{3N}N!} \int \delta(\mathcal{H}(r,p) - E) dr dp$$

(3.18)

where $r$ and $p$ indicate the position and momentum of particles and $\int dr dp$ indicates the integral over $6N$ phase space coordinates [6]. $h$ is Planck’s constant, $\mathcal{H}$ is the Hamiltonian, and $\delta$ is Kronecker delta for the discrete states and is Dirac delta function for the continuous states. The link to classical thermodynamics
comes from the relationship

\[ S = k_B \ln [Q_{NVE}] \]  

(3.19)

where \( S \) is the entropy and \( k_B \) is the Boltzmann constant, named after Ludwig Boltzmann who originally proposed this relationship. Even though Boltzmann died before people accepted his theory, this famous equation will forever be inscribed on his tombstone.

If instead of keeping energy (\( E \)) constant, we keep the temperature (\( T \)) constant, we get another ensemble called the canonical (\( NVT \)) ensemble. The partition function for this ensemble (\( Q_{NVT} \)) is

\[ Q_{NVT} = \frac{1}{h^{3N}N!} \int \exp \left[ -\frac{\mathcal{H}(\mathbf{r}, \mathbf{p})}{k_B T} \right] d\mathbf{r} d\mathbf{p} \]  

(3.20)

Most of the work in this dissertation is performed in this particular ensemble. The appropriate link to classical thermodynamics in this case comes from

\[ A = -k_B T \ln [Q_{NVT}] \]  

(3.21)

where \( A \) is the Helmholtz free energy.

If instead of keeping volume (\( V \)) constant, if we keep the pressure (\( P \)) constant, we get an isothermal-isobaric ensemble, commonly denoted as \( NPT \). Generally, experiments are carried out under these conditions. The partition function for this ensemble (\( Q_{NPT} \)) is

\[ Q_{NPT} = \frac{1}{V_0 h^{3N}N!} \int dV \int \exp \left[ -\frac{\mathcal{H}(\mathbf{r}, \mathbf{p}) + PV}{k_B T} \right] d\mathbf{r} d\mathbf{p} \]  

(3.22)
and the link to classical thermodynamics comes from

\[ G = -k_B T \ln [Q_{NPT}] \] (3.23)

where \( G \) is the Gibbs free energy. There are other ensembles available and a detailed review of these can be found in a classic book on statistical mechanics by McQuarrie [130].

The definitions of these partition functions require the computation of at least \( 6N \) integrals. Only for a few simple systems can these integrals be solved analytically. However, this becomes a non-trivial exercise for even a moderately-sized system. This is where atomistic simulations can play an important role. One can sample the configurations from the probability distribution consistent with the partition function using the Propagators or Generators, described in the next section.

One thing needs to be noted that all these ensembles are, in fact, artificial constructs and in thermodynamic limit would produce the same average properties [6]. It is also possible to transform from one ensemble to another. A more formal procedure for ensemble transformation is detailed by Hill [69] and Münster [144], while a good summary is also given by Allen and Tildesley [6]. The averages in an ensemble can be related to the basic thermodynamic properties. One can calculate the temperature and pressure of the systems, including the model-dependent, non-ideal contribution, using the virial theorem. Equilibrium properties like the constant-volume (or constant-pressure) heat capacity \( (C_V \text{ (or } C_P)) \), the isothermal compressibility \( (\beta_T) \), and the thermal expansion coefficient \( (\alpha_p) \) can be computed using the RMS fluctuations in the basic observable quantities like energy and temperature. One can not only use the statistical mechanical formulations to
compute the structural properties like pair radial distribution functions ($g(r)$), but one can also compute dynamic or transport properties of the system using time correlation functions. As the focus of this dissertation is to compute the transport properties, we will briefly consider this approach in the next chapter (Chapter 4). One can also formally derive the expressions for the corrections due to a cut-off distance approach, known as long range corrections (as mentioned in section 3.3), using statistical mechanics.

3.5 Propagators or Generators

Once we have the description of the system in terms of the molecular representation and the parameters to account for all the energetic interactions, we can watch the system evolve and reach equilibrium using the Propagators or the Generators. As mentioned above, we need to generate many configurations representing an ensemble and this can be achieved in one of two ways: (1) Deterministically: molecular dynamics simulation methods or (2) Stochastically: Monte Carlo simulation methods. A detailed review of these individual methods can be found elsewhere [6, 49, 100]. Here we will briefly point out a few main features of these methods.

3.5.1 Molecular Dynamics

Molecular dynamics (MD) methods deal with solving the classical equations of motion for a given system. These equations can be written in different forms [6, 58] but one of the very fundamental approaches is that of Lagrangian. The
Lagrangian equation of motion is

$$\frac{d}{dt} \left[ \frac{\partial}{\partial \dot{r}} \mathcal{L} \right] - \left[ \frac{\partial}{\partial r} \mathcal{L} \right] = 0 \quad (3.24)$$

where $\mathcal{L}$ is known as the Lagrangian, which is given as

$$\mathcal{L} = \mathcal{H} - \mathcal{U} \quad (3.25)$$

here $\mathcal{H}$ and $\mathcal{U}$ are the kinetic and potential energies of the system respectively and are defined in terms of the generalized coordinates, $r$, their time derivatives, $\dot{r}$, and time, $t$, such that $\mathcal{L} = \mathcal{L}(r, \dot{r}, t)$. The generalized momenta $p$ can be given as

$$p = \left[ \frac{\partial}{\partial \dot{r}} \mathcal{L}(r, \dot{r}, t) \right] \quad (3.26)$$

Now, we can apply Legendre transforms and write these equations in terms of the Hamiltonian ($\mathcal{H}$):

$$\mathcal{H}(r, p, t) = \sum \dot{r}p - \mathcal{L}(r, \dot{r}, t) \quad (3.27)$$

Even though both Lagrangian and Hamiltonian equations are one and the same, in the literature, Hamiltonian equations are preferred as they are simpler to work with. The Hamiltonian equations of motion can be given as:

$$\dot{r} = \left[ \frac{\partial}{\partial p} \mathcal{H} \right] \quad (3.28)$$

$$\dot{p} = -\left[ \frac{\partial}{\partial r} \mathcal{H} \right] \quad (3.29)$$

Assuming that the kinetic energy is a function of only momenta ($\mathcal{H} = \mathcal{H}(p)$), while the potential energy is a function of only positions ($\mathcal{U} = \mathcal{U}(r)$), these
equations can be modified to

\[ \dot{\mathbf{r}} = \frac{\mathbf{p}}{m} \quad (3.30) \]
\[ \dot{\mathbf{p}} = -\left[ \frac{\partial}{\partial \mathbf{r}} \mathcal{H} \right] = \mathbf{F} \quad (3.31) \]

These equations are also known as Newton’s equations of motion. We can now solve the \( 6N \) first-order differential equations to get the trajectories of \( N \) particles. It can be noted that these equations of motion are time reversible. Thus, given the positions and momenta of particles at any point in time, we can deterministically follow the trajectory of a particle forward or backward in time. These equations also conserve the total energy of the system, meaning these equations of motion sample from the \( NVE \) ensemble. We can use any of the available integrators, \textit{i.e.}, \textit{Gear Predictor-Corrector}, \textit{Verlet}, or \textit{Leap-Frog}, to integrate these equations of motion. In practice, as the Verlet algorithm lends itself easily for time reversibility, it is used in this dissertation to integrate the equations of motion. One can also use the \textit{Liouville operator} formalism using Trotter factorization to derive the equations of motion. Following this formalism one can easily reach at the time reversible form of the integrator. This makes it easy to understand and program the integrator algorithm. It is also a common practice to split the forces into rapidly changing intramolecular contributions and slowly changing intermolecular contributions. These contributions are integrated on different time scales to tackle the problem of the \textit{stiffness} of these equations of motion. The method is called the \textit{multiple time step algorithm}. This \textit{Liouville operator} formalism also helps one to split the integrator in these two parts. One such algorithm that makes use of multiple time stepping and is reversible in time is known as r-RESPA algorithm.
One can also derive equations of motion that sample the $NVT$ ensemble. Here, thermostats are used to keep the temperature constant. There are different thermostatting algorithms available in the literature, including the Gaussian thermostat and the Berendsen thermostat. One of the more commonly used thermostats is the Nosé-Hoover thermostat. This is an example of an extended system method. One can arrive at these equations of motion by deriving these from the extended system Hamiltonian. These equations of motion can be given as:

\[
\begin{align*}
\dot{\mathbf{r}} &= \frac{\mathbf{p}}{m} \\
\dot{\mathbf{p}} &= \mathbf{F} - \mathbf{p}v_\zeta \\
\dot{v}_\zeta &= v_\zeta \\
\dot{\zeta} &= G_\zeta(\mathbf{p})
\end{align*}
\] (3.32)

where $v_\zeta$, $\zeta$, and $G_\zeta$ are Nosé-Hoover [72, 147] thermostat variables. This thermostat samples from the $NVT$ ensemble, however, the performance of this integrator can be improved by using a Nosé-Hoover chain thermostat [122].

One can as well write the equations of motion which sample from the $NPT$ ensemble. Even if one can not derive the extended system Hamiltonian for this ensemble, the proposed Hamiltonian is sufficient. In addition to a thermostat, in this case, we also need to use a barostat. A detailed discussion of these extended system equations of motion and the resulting algorithm can be found in an excellent publication by Martyna et al. [123].

The MD algorithm tracks the true dynamical behavior of the system. However, sometimes, for systems with very slow dynamics, such as ILs, this method suffers
from poor sampling efficiency. In such cases simulating systems using a Monte Carlo algorithm offers a possible advantage. However, the dynamical information is lost. As MD gives us information about the dynamics in the system, we can compute the accompanying dynamic or transport properties using this technique. We will use MD techniques extensively in this dissertation for elucidating transport properties.

3.5.2 Monte Carlo

Even though the work in this dissertation is concerned with only MD techniques, we include a short description of Monte Carlo technique for its historic and scientific significance. As mentioned earlier, in early 1950s the super computer MANIAC became available for non-military use. In 1953, the first simulations of a dense liquid phase were run by Metropolis et al. [131] using a stochastic algorithm. Metropolis and Ulam [132] named the algorithm Monte Carlo as it made extensive use of random numbers to generate different configurations sampling from a particular ensemble. The evolution of the system from one state to other is achieved by establishing a Markov chain. It is important to note that the outcome of one move only depends on the move immediately preceding it. Importance sampling algorithm, as described by Metropolis [131], is used to determine the transition probability from one state \( o \) to another \( n \). The transition probability is established such that once the system reaches equilibrium, it remains in that state. This is met by making sure that the number of accepted moves for going from \( o \) to \( n \) is equal to the number of accepted moves for going from \( n \) to \( o \) at equilibrium. This is also known as the microscopic reversibility condition. A Monte Carlo algorithms, in general, contain 2 steps [180]: (1) A system is displaced from \( o \) to
n with certain probability. (2) The move is probabilistically accepted or rejected. More often than not, this acceptance criterion is based on the change in energy of the system. If the move in step 1 results in a lower energy configuration, that move is always accepted. However, if the energy increases in going from \( o \) to \( n \), it is *not* always rejected.

One can devise smart, yet sometimes unphysical, moves in this context and increases the sampling efficiency of the algorithm. One needs to be careful, however, that if a bias is introduced in the sampling, it needs to be accounted for through the acceptance rules and it must be assured that the microscopic reversibility condition is satisfied. A drawback of this method is that it does not keep track of time. Even though there are some *dynamic Monte Carlo* methods available that attempt to account for time, they are not commonly used. As a result, the algorithm loses the dynamical information about the system and dynamic or transport properties can not be computed using Monte Carlo methods. Sometimes combining these two algorithms can accelerate the equilibration of the system under consideration.
All programmers are optimists. Perhaps this modern sorcery especially attracts those who believe in happy endings and fairy godmothers. Perhaps the hundreds of nitty frustrations drive away all but those who habitually focus on the end goal. Perhaps it is merely that computers are young and, programmers are younger, and the young are always optimists. But however the selection process works, the result is indisputable: “This time it will surely run” or “I just found the last bug.”

.. Frederick Brooks, Jr.

[The Mythical Man Month]

Having laid the ground work, even if briefly, we can now go ahead and look at the algorithms that are generally used to compute the transport properties of a system. As described earlier, transport coefficients are the measure of the response of a system toward a perturbation that forces the system away from equilibrium. The inherent or spontaneous fluctuations in the system, which die as time progresses, can be described by the autocorrelation function. And with the help of statistical mechanical formulations, we can relate this function to the transport property of the system. These relations are described as the Green-Kubo
relations for the transport coefficients. It is generally defined as an infinite time integral of the autocorrelation function

\[ \gamma = \int_0^\infty \left\langle \dot{\mathcal{A}}(t)\dot{\mathcal{A}}(0) \right\rangle dt \quad (4.1) \]

where \( \gamma \) is the transport coefficient, \( \langle \ldots \rangle \) is the ensemble average and \( \mathcal{A} \) is the variable appearing in the perturbation expression of the Hamiltonian. One can as well represent this equation in terms of the so-called Einstein relation, which is

\[ \gamma = \lim_{t \to \infty} \frac{1}{2t} \left\langle (\mathcal{A}(t) - \mathcal{A}(0))^2 \right\rangle \quad (4.2) \]

This equation is generally valid when time \( (t) \) is large compared to the correlation time.

4.1 Self-Diffusivity

**Self-diffusivity** \( \mathcal{D}_s \), as mentioned earlier, is a measure of the mobility of a single particle in a system of identical particles. The Green-Kubo relation for self-diffusivity is

\[ \mathcal{D}_s = \frac{1}{3} \int_0^\infty \left\langle \mathbf{v}(t)\mathbf{v}(0) \right\rangle dt \quad (4.3) \]

where \( \mathbf{v} \) is the velocity of center-of-mass of a single molecule. The Einstein equivalent for this relation is

\[ \mathcal{D}_s = \lim_{t \to \infty} \frac{1}{6t} \left\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \right\rangle \quad (4.4) \]

In an atomistic simulation, the trajectory of every molecule (i.e. center-of-mass) in terms of the position and velocity is followed. As diffusivity is a property of
individual molecules, one can compute the above quantities separately for each molecule and then average it to improve the statistical accuracy. It is for this reason, self-diffusivity is the simplest transport quantity to be computed using atomistic simulations.

Usually, this quantity can be calculated by running a long equilibrium molecular dynamic simulation and plotting the mean-squared displacement versus time. At longer times one can fit a straight line through the data and compute the self-diffusion coefficient from the slope of that line. When the dynamics become sluggish, however, computation of self-diffusivity becomes a little tricky. Generally, two regions are apparent in a log-log plot of mean-squared displacement versus time. At very short time the curve has a slope of two and this part is associated with the ballistic motion. At longer time, the curve has a slope of one, which means that system is in diffusive regime, as mentioned earlier. When the system exhibits sluggish or glass-like dynamics, like for instance ILs, one can observe a third region between the ballistic motion regime and the diffusive regime. The slope of the curve in this regime is lower than one, and the system is said to be in sub-diffusive regime. In this case before reporting a value, one needs to make sure that the system is in diffusive regime. As described earlier, we can make use of the linearity parameter and the non-Gaussian parameter to determine the state of the system. We will discuss this in Chapter 7 and 8.

4.2 Shear Viscosity

Shear viscosity ($\eta$) is a measure of momentum transport in a mass undergoing viscous flow under a shear gradient. Unlike self-diffusivity, shear viscosity is the property of entire system and averaging over the number of molecules is no
longer possible. It is for this reason computing viscosity in an atomistic simulation becomes much harder than computing self-diffusivity. As mentioned earlier, viscosity is of considerable importance to chemical engineering and several methods have been developed to compute this quantity. These methods can broadly be classified into two categories: (1) Equilibrium methods and (2) Nonequilibrium methods. We will discuss both of them and review those methods that have been developed to compute these quantities. For more detailed explanation of each of these methods the reader is encouraged to look at the references therein.

4.2.1 Equilibrium Methods

Estimation of viscosity by equilibrium methods involves computation of time correlation function of pressure fluctuations. The Green-Kubo formula [6] calculates a time correlation function of the off-diagonal elements of the pressure tensor $P$. For shear viscosity ($\eta$), this formula is

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{\alpha\beta}(0) P_{\alpha\beta}(t) \rangle \, dt$$

(4.5)

where $P_{\alpha\beta}$ is the off-diagonal element of the pressure tensor. The equivalent Einstein formula is

$$\eta = \lim_{t \to \infty} \frac{V}{2k_B T t} \langle (\varphi_{\alpha\beta}(t) - \varphi_{\alpha\beta}(0))^2 \rangle$$

(4.6)

where

$$\varphi_{\alpha\beta} = \frac{1}{V} \sum r_{\alpha} P_{\beta}$$

(4.7)

The statistical accuracy can be improved by averaging over additional components of the stress tensor [33]. While this approach has been successfully used for many
systems, there are several well-documented drawbacks. Both of these methods are known to converge slowly as the pressure is one of the harder quantities to measure and fluctuates wildly in a simulation. As these methods rely on natural fluctuations in the system, they suffer from weak signal-to-noise ratio. The autocorrelation function for pressure decays with a long time-tail, which makes it even harder to estimate the viscosity accurately. Besides, these methods suffer from non-monotonic system size dependence.

4.2.2 Nonequilibrium Methods

Nonequilibrium methods involve measurement of a steady state response of the system to an externally imposed perturbation. One can select the magnitude of such fluctuations (within some limits) such that they can be distinguished from the natural fluctuations in the system. As a result, these methods have a slightly better statistical performance in that they have better signal-to-noise ratio.

4.2.2.1 SLLOD Method

One of the more successful nonequilibrium algorithms for calculating shear viscosity, called SLLOD [42, 98], imposes the Couette flow on the system. The equations of motion are modified in such a way that a steady linear velocity profile is developed in the system over time. The modified equations of motion are

\[
\dot{\mathbf{r}} = \frac{\dot{\mathbf{p}}}{m} + \dot{\gamma}\mathbf{y}\mathbf{e}_x \quad (4.8)
\]

\[
\dot{\mathbf{p}} = \mathbf{F} - \dot{\gamma}\mathbf{p}_y\mathbf{e}_x \quad (4.9)
\]

where \(\dot{\gamma}\) is the applied shear rate. These equation are non-Hamiltonian equations of motion. They are proposed by swapping a term in the Dolls tensor algorithm,
hence the name SLLOD. Pressure fluctuations are then used to compute the viscosity.

\[ \eta = \frac{\langle P_{\alpha\beta} \rangle}{\dot{\gamma}} \quad (4.10) \]

This method imposes the linear velocity profile (i.e. shear rate, \( \dot{\gamma} \)) and measures the shear stress (i.e. computes the pressure tensor). In an actual experiment it is done the other way around. Even though this method gives the same results for simpler molecules, it may fail to give the correct results for complicated molecules like ILs [68]. In addition, this method induces a rotational motion in the system. One also needs to use the sliding brick or deforming cell boundary conditions to handle the fact that molecules in different layers move with different velocities. This algorithm becomes non-trivial for the systems involving charged particles [213]. As the imposed shear rate becomes smaller and smaller, we lose the advantage of using a nonequilibrium method over an equilibrium method.

In the equilibrium and nonequilibrium methods described above, the stress is computed in response to a natural and an imposed shear rate, respectively. That is, the “cause” is the imposed velocity gradient and the “effect” is the measured momentum flux. Unfortunately, at low strain rates, (i.e. in the near Newtonian regime) the stress tends to vary wildly in a simulation, and therefore convergence can take a long time. As an alternative, one can impose the quantity that is difficult to compute in a simulation (the momentum flux) and compute the easy to determine quantity (the shear rate or velocity profile). This is the idea behind the methods described below.
4.2.2.2 Periodic Perturbation Method

The transient motion of a Newtonian fluid is governed by Navier-Stokes equation. Neglecting the effects of viscous heating, in Cartesian coordinate system this equation is

\[
\rho \left[ \frac{\partial}{\partial t} + u \cdot \nabla \right] u = -\nabla P + \eta \nabla^2 u + \rho a \quad (4.11)
\]

where \( \rho \) is density, \( a \) is external force per unit mass of the fluid and \( u \) is the velocity field generated by that force. If we choose \( a \) such that it results in an unidirectional flow in “x” direction and if \( a_x \) is a function of “y” alone, at steady state, this equation reduces to

\[
\nu \frac{\partial^2}{\partial y^2} u_x(y) + a_x(y) = 0 \quad (4.12)
\]

where \( \nu \) is the kinematic viscosity, which is related to the shear viscosity \( \eta \) by \( \nu = \eta/\rho \). Now, if we consider forcing function to be a cosine function such that \( a_x(y) = u_0 \cos(ky) \), equation 4.12 can be solved to give

\[
u \frac{\partial^2}{\partial y^2} u_x(y) = \mathcal{C} \left[ 1 - \exp \left( \frac{t}{\tau_r} \right) \right] \cos(ky) \quad (4.13)
\]

where \( \mathcal{C} = \frac{\rho u_0}{\eta k^2} \) and \( \tau_r = \frac{\rho}{\eta k^2} \). In practice, a known acceleration can be added to each atom every timestep and the steady state velocity profile is measured. Then the viscosity can be calculated as

\[
\eta = \frac{\rho u_0}{\mathcal{C} k^2} \quad (4.14)
\]

This method was first applied by Gosling et al. in 1973 [60].
4.2.2.3 Transverse-Current Correlation Function Method

If starting from the same Navier-Stokes equation (Eq. 4.11), in addition to neglecting the effects of viscous heating, we assume that the external field is absent, we can further simplify the equation to

$$\frac{\partial}{\partial t} u_x(y, t) = \nu \frac{\partial^2}{\partial y^2} u_x(y, t) \quad (4.15)$$

Now, if we impose a one directional plane wave velocity field

$$u = u_0 \cos(ky) \mathbf{e}_x \quad (4.16)$$

at time $t = 0$, the solution to this equation (Eq. 4.15) is

$$u_x(y, t) = u_0 \left[ \exp \left( \frac{t}{\tau_r} \right) \right] \cos(ky) \quad (4.17)$$

where $\tau_r = \frac{\rho}{\eta k}$. It can be noted that the plane wave decays exponentially with time and the rate of decay is inversely proportional to the viscosity. The viscosity, now, can be computed from the autocorrelation of the amplitude of the plane waves, which is also known as transverse-current correlation function. This function contains the long-time and large-distance behavior of the system, and at short time the correlation function is not pure exponential. This can be tackled by using a memory function as in the viscoelastic theory [223]. A detailed discussion on this is given by Hess [68] and Yan et al. [223].
4.2.2.4 Momentum Impulse Relaxation Method

Instead of using an unidirectional plane wave velocity profile, let us consider a Gaussian flow profile such as that shown in Fig. 4.1 in which a velocity \( u(x, t) \) expressed as \([u_x(y, t), 0, 0]\) is imposed on the system at time \( t = 0 \), and let \( u_x(y, t) \) be given by a Gaussian of the form

\[
u_x(y, 0) = a_0 \exp \left[-b_0 y^2\right] \quad (4.18)
\]

where \( a_0 \) is the amplitude and \( b_0 \) is the inverse of the variance of the Gaussian profile. Under a set of reasonable assumptions \([10]\), this velocity profile will decay as

\[
u_x(y, t) = \left[\frac{a_0^2}{1 + \frac{t}{t_0}}\right]^{1/2} \exp \left[-\frac{b_0 y^2}{\left(1 + \frac{t}{t_0}\right)}\right] \quad (4.19)
\]

where \( t_0 = 1/4\nu b_0 \). Note that, the solution of this equation indicates that the profile will be Gaussian at all times.

In the original implementation of this method, a system of equilibrated molecules was subjected to the velocity profile shown in Fig. 4.1 \( i.e. \) Gaussian velocity profile. The response of the system to this imposed profile was tracked through the maximum or “peak” velocity \( u_p(t) \) of the Gaussian. The decay of the profile was then fit to the equation of the form

\[
u_p(t) = \nu_p(0) \left(1 + \frac{t}{t_0}\right)^{-1/2} \quad (4.20)
\]

from which the shear viscosity was easily obtained as, \( \eta = \rho/4t_0b_0 \).

This new method was first developed by Arya \( et al. \) \([10]\), and is called \textit{Momentum Impulse Relaxation} (MIR). Among other things, this method avoids running
Figure 4.1. Three dimensional Gaussian profile which is imposed on the system in the MIR method. The profile is imposed in the “y”-direction. $a_0$ is the peak height while $b_0$ is the inverse of the variance of the Gaussian profile.

longer simulations. A detailed discussion of this method can be found in the original reference [10]. We will use this method and look at a possibility of improving it in Chapter 5.

4.2.2.5 Reverse Nonequilibrium Molecular Dynamics Method

The methods described so far either used pressure fluctuations or momentum fluctuations to determine the viscosity. Another method, called reverse nonequilibrium molecular dynamics (RNEMD) developed by Müller-Plathe and co-workers [18, 140, 141], uses an unphysically imposed stress to compute the viscosity.

Again, the details of this method can be found in the original publication by Müller-Plathe [140]. Here we briefly summarize the method and try to point out
some key features of this method. The simulation box is divided into $N$ small bins or slabs in the “$y$” direction, as shown in Fig. 4.2. A stress or momentum flux in the “$y$” direction is imposed on the system by exchanging the momentum between an atom with the most negative “$x$” momentum in bin $n = 1$ with another atom in bin $n = n_c = (N/2) + 1$ that has the largest momentum in the positive “$x$” direction. If both atoms have the same mass, the total linear momentum and the kinetic energy is conserved. The momenta swaps are carried out periodically, so that the total exchanged momentum is

$$p_{\text{total}} = \sum (p_{x,n_c} - p_{x,n_1})$$

(4.21)

Note that the frequency of the swaps determines the total imposed flux on the
system. After any time $t$, the imposed momentum flux is

$$ j_y(p_x) = \frac{P_{\text{total}}}{2tL_xL_z} $$

(4.22)

where $L_x$ and $L_z$ are the lengths of the simulation box in “x” and “z” directions, respectively. The system responds to the unphysical imposed momentum flux by establishing a real momentum flow in the opposite direction. This sets up a linear velocity profile in the upper and lower halves of the simulation box. From the slopes of the velocity profiles (which are easy to measure in a simulation) and the imposed momentum flux, the shear viscosity may be determined from Eq. 2.12. We have chosen to utilize this method extensively in the work undertaken in this dissertation. And the validation and applications of this algorithm will be discussed in Chapter 6 - 8.

In all the nonequilibrium methods described above, one gets a shear viscosity as a function of either shear rate or the wavelength. As the shear rate decreases, or the wavelength increases, the statistical performance starts to degrade with decrease in the signal-to-noise ratio. In either case, however, one need to extrapolate to the Newtonian regime (zero shear or infinite wavelength). There is no generally accepted way of extrapolating this data to Newtonian regime. In this particular study we make use of three different extrapolating methods and we will discuss this in the following chapters.

4.3 Thermal Conductivity

Thermal conductivity ($\lambda_T$) is the measure of heat transport under a temperature gradient in a system. Like shear viscosity, thermal conductivity is also the property of the entire system (or collective property) and averaging over the
number of molecules is not possible. Similar to viscosity, one can compute this quantity using an equilibrium or a nonequilibrium method.

4.3.1 Equilibrium Methods

In the Green-Kubo formulation, the thermal conductivity is

$$\lambda_T = \frac{V}{k_B T^2} \int_0^\infty \langle j_\alpha^H(t) j_\alpha^H(0) \rangle \, dt$$  \hspace{1cm} (4.23)

where $j_\alpha^H$ is the energy current along axis “$\alpha$” and is

$$j_\alpha^H = \frac{d}{dt} [\delta \mathcal{H}_\alpha]$$  \hspace{1cm} (4.24)

and

$$\delta \mathcal{H}_\alpha = \left[ \frac{1}{V} \sum r_\alpha (\mathcal{H} - \langle \mathcal{H} \rangle) \right]$$  \hspace{1cm} (4.25)

The equivalent Einstein relationship is

$$\lambda_T = \lim_{t \to \infty} \frac{V}{2k_B T^2} \frac{1}{t} \langle (\delta \mathcal{H}_\alpha(t) - \delta \mathcal{H}_\alpha(0))^2 \rangle$$  \hspace{1cm} (4.26)

4.3.2 Nonequilibrium Methods

The RNEMD method described above, was first developed for computing thermal conductivity [140] and then extended to its shear viscosity version. The method works almost exactly same, the only difference being, instead of atoms with maximum positive or negative “x” directional momenta, we select atoms with maximum and minimum kinetic energies respectively. We then swap all three components of the velocity instead of just “x” component as in the case of viscosity calculation. This unphysical swap of kinetic energy, sets up a temper-
ature gradient in the system and the profile is linear. We can then measure the slope of the profile, just as we did for shear viscosity, and compute the thermal conductivity value using the known imposed heat flux and Eq. 2.21. We have used this particular method to compute the thermal conductivity of IL 1-ethyl-3-methylimidazolium ethylsulfate and its mixtures with water.
CHAPTER 5

RAPID SHEAR VISCOSITY CALCULATION BY MOMENTUM IMPULSE RELAXATION MOLECULAR DYNAMICS

*Computing is not about computers anymore. It is about living.*

.. Nicholas Negroponte

5.1 Introduction

As alluded to in the previous chapter, collective transport properties, such as the shear viscosity, are among the most challenging properties to compute with molecular simulation methods. They are traditionally calculated using two main methods, as mentioned before: equilibrium methods and nonequilibrium methods (NEMD). Equilibrium methods usually require the calculation of the Green-Kubo integral of the off-diagonal elements of a pressure tensor [6]. While rigorous, this technique requires extraordinarily long simulations to obtain reliable results, and the computational burden increases dramatically as viscosity increases. Nonequilibrium methods such as the SLLOD algorithm [42, 98] can offer computational advantages over equilibrium methods [214, 215], but still require long simulations, particularly for large molecules.

Arya et al. [10] proposed the use of a transient simulation technique which we termed “momentum impulse relaxation” or MIR for rapid determination of
fluid viscosity. The origin of this type of transient simulation approach for computing transport properties can be traced to earlier work on diffusion [115]. The basic idea behind the MIR method, as explained briefly earlier, is to establish a flow profile (in this case, a Gaussian velocity profile) through imposition of an external driving force. By matching the rate with which the flow profile decays to the corresponding solution of the Navier-Stokes equation, a Newtonian shear viscosity can be determined directly. The advantage of the MIR procedure is that the time it takes for the profile to decay and yield an accurate shear viscosity is significantly shorter than the time required to perform either equilibrium or conventional nonequilibrium simulations (like SLLOD) for the same system. Like the Gosling method (explained as periodic perturbation method in previous chapter, section 4.2.2.2), only velocities must be computed, not the stress tensor. Unlike the Gosling method, the imposed profile has a pseudo-infinite wavelength, and so a single simulation can, in principle, yield the Newtonian viscosity. In the original study [10], the viscosities of liquid argon and n-butane were computed in 10 ps, whereas the conventional methods required simulations that were roughly 100 times as long. The MIR method does require larger system sizes, however, thus resulting in an estimated net computational savings of 20–30 times over the conventional methods.

In this chapter, we revisit the use of the MIR method, and address several technical aspects of its implementation that were not considered in the original publication [10]. In particular, we consider the effect of different velocity boundary conditions on the computed viscosity and develop a more robust method of matching the velocity decay to the corresponding decay predicted by solution of the Navier-Stokes equation. We also implement a new set of equations of mo-
tion that automatically generate the desired initial Gaussian velocity profile, and show that failure to properly equilibrate the system with this method leads to inaccurate viscosity estimates for large molecules with slow relaxation dynamics. We apply these enhancements in the calculation of the shear viscosity for united atom models of $n$-butane and $n$-hexane as well as a 10 unit bead-spring model of a polymer. We demonstrate that the MIR method can be used to determine the viscosity of these and similar molecular systems in a fraction of the time required for conventional methods. This work was originally reported in the ref. [86].

5.2 Simulation Details

To test the new implementation details described here, we performed simulations of $n$-butane and $n$-hexane as well as a bead-spring model of a polymer. The alkanes were modeled using parameters listed in Table 5.1. The intramolecular terms were taken from the work of Mundy and co-workers [142], while the non-bonded parameters are those reported by Martin and Siepmann [119]. The state point was $T = 298 \, K$ and $\rho = 0.655 \, g/cm^3$ for $n$-hexane and $T = 291.5 \, K$ and $\rho = 0.583 \, g/cm^3$ for $n$-butane. A bead-spring model [95, 96, 179] was used with ten beads connected via finitely extensible nonlinear elastic (FENE) (Eq. 3.8) springs [211]. Potential parameters are given in Table 5.1. In keeping with convention, reduced units (designated with an asterisk) are used for all the bead-spring model simulations. The state point was $T^* = 1.0$ and $\rho^*_n = 0.84$, where $T^*$ and $\rho^*_n$ are reduced temperature and number density, respectively. These systems were chosen because they represent widely used model types and their viscosities have either already been determined or they can be computed accurately using conventional simulation techniques. They thus provide a rigorous test of the MIR
A cut-off radius of 10.0 Å with long range corrections was used for the alkanes. A reduced cut-off radius of $2^{1/6}$ was used for the bead-spring model, in keeping with the cut-off used in previous studies of this system. A multiple time step algorithm r-RESPA [201] was employed with inner time step of 1 fs and outer step of 4 fs.

In addition to the imposed MIR velocity profile, each molecule has its own thermal fluctuation velocity, with a mean of zero and a standard deviation which goes as $kT/m$. For the MIR method, these thermal fluctuations can be viewed as a departure from the expected value of the imposed velocity. As the number of observations (molecules) increases, the statistical average of these fluctuations tends to zero and thus the uncertainty in the decaying profile decreases. This means that the greater the number of molecules simulated, the smaller the statistical error in the computed viscosity. The desired number of molecules can be achieved by either running many simulations with a relatively small system size or running a small number of simulations with larger system sizes. There is a limit, however, on how small the system may be. As discussed in the original publication [10], the Gaussian profile should be mostly contained inside the simulation box (large $b_0$) to reduce the magnitude of the imposed velocities at the box boundaries. This minimizes the role played by the artificial velocity boundary condition (discussed below). The initial peak velocity $a_0$ should also be large so that the decaying velocity distribution can be resolved easily against the thermal fluctuations. The distribution cannot be too sharply peaked, however, as this leads to large local shear rates and the possibility of shear thinning behavior. Thus the values of $a_0$ and $b_0$ must be optimized to obtain accurate results in a computationally effi-
TABLE 5.1

Potential energy functions and potential energy parameters for united atom models of \(n\)-butane and \(n\)-hexane [119, 142], and the bead-spring model [95, 96, 179].

<table>
<thead>
<tr>
<th></th>
<th>Potential energy parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)-alkanes</td>
<td></td>
</tr>
<tr>
<td>Non-bonded</td>
<td>(\sigma_{CH_3} = 3.77 \text{ Å}, \epsilon_{CH_3}/k_B = 98.1 K)</td>
</tr>
<tr>
<td></td>
<td>(\sigma_{CH_2} = 3.93 \text{ Å}, \epsilon_{CH_2}/k_B = 47.0 K)</td>
</tr>
<tr>
<td>Bond stretching</td>
<td>(k_b/k_B = 452900 K \text{Å}^{-2})</td>
</tr>
<tr>
<td></td>
<td>(r_0 = 1.54 \text{ Å})</td>
</tr>
<tr>
<td>Bond-angle bending</td>
<td>(k_\theta/k_B = 62500 K \text{rad}^{-2})</td>
</tr>
<tr>
<td></td>
<td>(\theta_0 = 114^\circ)</td>
</tr>
<tr>
<td>Torsion</td>
<td>(c_0/k_B = 0.0 K)</td>
</tr>
<tr>
<td></td>
<td>(c_1/k_B = 355.03 K)</td>
</tr>
<tr>
<td></td>
<td>(c_2/k_B = -68.19 K)</td>
</tr>
<tr>
<td></td>
<td>(c_3/k_B = 791.32 K)</td>
</tr>
<tr>
<td>bead-spring model</td>
<td>(reduced units, (\epsilon = \sigma = m = 1))</td>
</tr>
<tr>
<td>Bond stretching</td>
<td>(R_0^* = 1.5)</td>
</tr>
<tr>
<td>(FENE potential)</td>
<td>(k_b^* = 30)</td>
</tr>
</tbody>
</table>

86
cient manner. An extensive discussion of the bounds on $a_0$ and $b_0$, and how these bounds relate to the various parameters of the system, may be found elsewhere [10]. Further optimization may be achieved by using a non-cubic simulation box elongated in the “y” direction, which enables a relatively large peak velocity to be used while maintaining a small local shear rate ($du/dy$) and a small imposed velocity at the box boundary. In this chapter, all the simulation boxes had equal dimensions in the “x” and “z” directions, but were elongated in the “y” direction such that the aspect ratios varied from 4 for $n$-butane to 8 for $n$-hexane to 320 for the bead-spring model. This large aspect ratio was required for the latter system due to its shear thinning tendency. A total of 15 independent simulations were carried out for $n$-butane and $n$-hexane with 1000 molecules, while for the 10-unit bead-spring model, 19 independent simulations with 600 molecules were executed.

5.3 Implementation Enhancements and Discussion

5.3.1 Boundary Conditions

Conventional nonequilibrium methods for computing shear viscosity typically require some type of modified boundary condition. For example, most implementations of the SLLOD algorithm utilize *sliding-brick* boundary conditions [102]. To mimic a pseudo-infinite velocity wavelength and thus obtain the Newtonian shear viscosity in a single simulation, a Gaussian perturbation is used in the MIR method. The use of an pseudo-infinite Gaussian velocity profile within a finite simulation box, however, requires that standard periodic boundary conditions be modified. A system with a decaying velocity profile such as that shown in Fig. 4.1 will conserve momentum in the “y” and “z” directions, but will constantly lose its “x”-component of momentum along the “y”-direction. In the previous MIR
implementation [10], this was modeled by using normal periodic boundary conditions for molecule positions as well as for velocities in the “y” and “z” directions. The “x”-components of atomic velocities were modified to allow momentum to leak out of the system in the following manner.

Let the position and velocity of an atom at time step \( n \) be \( r_n = (x_n, y_n, z_n) \) and \( v_n = (\ddot{x}_n, \ddot{y}_n, \ddot{z}_n) \) respectively. The equations of motion are integrated for a single time step, and the new tentative positions and velocities (denoted with a prime) are given by \( r'_{n+1} = (x'_{n+1}, y'_{n+1}, z'_{n+1}) \) and \( v'_{n+1} = (\ddot{x}'_{n+1}, \ddot{y}'_{n+1}, \ddot{z}'_{n+1}) \), respectively (Note that \( u \) is the imposed velocity profile, while \( v \) is the actual velocity which includes the thermal fluctuation velocity). Under normal periodic boundary conditions, the actual position of an atom at step \( n + 1 \) is modified if one of the Cartesian components exceeds the edge length of the simulation box, while the velocities remain unchanged. As shown in Fig. 5.1, the actual position of the atom that leaves the central simulation box in the “y” direction becomes

\[
x_{n+1} = x'_{n+1} ; \quad y_{n+1} = y'_{n+1} + L_y ; \quad z_{n+1} = z'_{n+1}.
\]  

(5.1)

Here we have assumed that an atom leaves the central simulation box from the negative “y”-direction and hence the image of this atom enters the simulation cell from the positive “y”-direction (i.e. \( y_{n+1} = y'_{n+1} + L_y \)). As with regular periodic boundary conditions, the “y” and “z” directional velocities are replaced by their tentative values. To simulate a leak in momentum, however, the “x”-component of the velocity must be modified. There are several choices one can make for this modified velocity. In the original work [10], the following boundary condition was
Figure 5.1. Two dimensional representation of the modified periodic boundary condition. The particle leaves the central simulation box from the bottom face (negative “y”-direction) and its image enters the central simulation box from the top face (positive “y”-direction).

used for the case described above

\[ \hat{x}_{n+1} = u_G(y_n + L_y) \]  

(5.2)

where \( u_G(y_n + L_y) \) is the *extrapolated* Gaussian velocity of the image atom at time \( t_n \) (see Fig. 5.1). The procedure for determining the appropriate Gaussian profile is discussed below. The boundary condition given by Eq. 5.2 will be designated as boundary condition 1 (BC1). This boundary condition fixes the velocity of an image atom to the prevailing Gaussian profile at the position of that image atom, regardless of its actual velocity. Given the direct relationship between the momentum loss at the boundary and the computed viscosity, the use of the proper boundary condition that most closely mimics the idealized infinite system
is important. For this reason, an additional boundary condition was investigated to see what role the velocity boundary conditions play on the accuracy of the method.

Boundary condition 2 (BC2) modifies the velocity of an image atom based upon its tentative velocity and the difference between the Gaussian velocities at the positions of the original atom and its image at the previous time step. This boundary condition is given by

$$
\dot{x}_{n+1} = \dot{x}'_{n+1} - \left[u_G(y_n) - u_G(y_n + L_y)\right]
$$

Note that $u_G(y_n + L_y)$ corresponds to an extrapolated velocity which will be less than $u_G(y_n)$ at all times for cases such as that shown in Fig. 5.1. This means the quantity in brackets in Eq. 5.3 will always be positive, and will thus always reduce the “x”-component of momentum for any atom leaving the box through the “x-z” plane relative to the case in which regular periodic boundary conditions are used. We expect BC2 to yield better results than BC1 since it utilizes information about the predicted velocity $\dot{x}'_{n+1}$.

To test the importance of the boundary conditions on the computed viscosity, simulations were run on all three systems using BC1 and BC2. The results are shown in Table 5.2.

There are small differences between the viscosities computed with equilibrium and nonequilibrium methods, but the results mostly agree within the uncertainties reported. It appears that BC1 yields viscosities that are somewhat lower than that obtained with BC2, and that BC2 gives values that agree well with the reported values. For this reason, BC2 is the preferred boundary condition. Note that the MIR results in Table 5.2 were obtained from using the Gaussian pre-equilibration
TABLE 5.2

Comparison of shear viscosities obtained from MIR (using both BC1 and BC2 along with Gaussian pre-equilibration) with those from equilibrium and SLLOD methods. The values reported for MIR are the estimates obtained after pre-equilibrating the Gaussian profile and neglecting the rotational relaxation times for the respective systems. Uncertainties are determined from the 95% confidence interval for the fit. (*) indicates the SLLOD method results of Kioupis et al. [92], which were fit to Eq. (5.19). Subscripts indicate the statistical uncertainties in the final digit.

<table>
<thead>
<tr>
<th>System</th>
<th>(η, cP) equilibrium</th>
<th>(η, cP) nonequilibrium</th>
<th>MIR (η, cP) BC1</th>
<th>MIR (η, cP) BC2</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butane</td>
<td>0.1357 [10]</td>
<td>0.1306 [10]</td>
<td>0.1241</td>
<td>0.1271</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1441</td>
<td></td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.202 [92]</td>
<td>0.2148*</td>
<td>0.1872</td>
<td>0.2243</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2236</td>
<td></td>
</tr>
<tr>
<td>BSM</td>
<td>N/A</td>
<td>0.5357 [96]</td>
<td>0.5117</td>
<td>0.5508</td>
</tr>
</tbody>
</table>
procedure as well as by neglecting initial short time rotational relaxation. Both of these factors are discussed in detail later.

5.3.2 Fitting the Velocity Profile and Estimating the Viscosity

The boundary conditions described above require that the Gaussian distribution consistent with the atomic velocities be known at each timestep. Since the Gaussian velocity profile must decay in a self-similar manner, this means two parameters must be determined: the velocity at the center or peak of the distribution, \( u_p(t) \), and the variance of the distribution \( \sigma^2(t) \) [10]. This is achieved by uniformly dividing the box along the “y”-axis into bins. The number of bins is set so that each bin will contain roughly 100 atoms. The velocities of the atoms in each bin are averaged, thereby giving discrete spatially varying velocities along the “y”-axis. On average, only the “x”-component velocities will be non-zero, and this profile is fit to a Gaussian at each time step using a least-squares method to obtain \( u_p(t) \) and \( \sigma^2(t) \). Other procedures, such as three point averaging or moving range averaging, could be used to further increase the fidelity of the profile. The best-fit Gaussian velocity profile is updated each time step and used in the velocity boundary condition procedure described in the previous section.

The main result of each simulation is a set of velocities whose “x”-component will vary with time and position along the “y”-direction. This set of velocities for a given simulation \( i \) will be represented as \( v_x^i(y,t) \). By fitting this set of velocities to Eq. 4.19, one can in principle solve for the unknown parameter \( \eta \) and thus determine the shear viscosity. In practice, the results of any one simulation of a reasonable size system will have large fluctuations in \( v_x(y,t) \), so some degree of averaging is required to obtain a reliable viscosity. The most straightforward
procedure is to simply average the viscosities obtained from multiple independent simulations. Let viscosity be a known function $f$ of the velocity profile, such that

$$\eta_i = f(v^i_x(y, t)).$$

(5.4)

The average viscosity and uncertainty of the estimate from $N_{\text{runs}}$ simulations can be determined as

$$\langle \eta \rangle = \frac{1}{N_{\text{runs}}} \sum_{i=1}^{N_{\text{runs}}} \eta_i$$

(5.5)

$$\sigma_\eta = \left[ \frac{1}{N_{\text{runs}} - 1} \sum_{i=1}^{N_{\text{runs}}} (\eta_i - \langle \eta \rangle)^2 \right]^{1/2}$$

(5.6)

Unfortunately, this averaging procedure turns out to be inaccurate, since each estimate in Eq. 5.4 is subject to large uncertainty due to the fluctuations in velocities from individual simulations. More reliable results can be obtained if velocity averaging is performed prior to application of the fitting function $f$.

Two procedures were used in this work. In the first, which we denote profile averaging, velocity profiles from independent simulations at discrete points in time $t$ are averaged to obtain an average velocity distribution for that particular time

$$\langle v_x(y, t) \rangle = \frac{1}{N_{\text{runs}}} \sum_{i=1}^{N_{\text{runs}}} v^i_x(y, t).$$

(5.7)

These averaged velocity profiles for all times are then fit to a Gaussian velocity distribution $u_G(y, t)$

$$u_G(y, t) = f_G(\langle v_x(y, t) \rangle)$$

(5.8)

where $f_G$ is the Gaussian function given by Eq. 4.19. The average velocity at the
peak of the Gaussian distribution, \( \langle v_p(t) \rangle \), is thus found as

\[
\langle v_p(t) \rangle = u_p = u_G(0, t)
\]  

(5.9)

The viscosity may be obtained from \( \langle v_p(t) \rangle \) using the procedure described below.

For the second method, which we denote peak averaging, Gaussian profiles are fit to every simulation at each point in time to obtain individual Gaussian profiles for each simulation \( i \)

\[
v^i_G(y, t) = f_G(v^i_x(y, t))
\]  

(5.10)

and then individual peak velocities at each time are determined as

\[
v^i_p(t) = v^i_G(0, t).
\]  

(5.11)

The average peak velocity as a function of time is found from

\[
\langle v_p(t) \rangle = \frac{1}{N_{\text{runs}}} \sum_{i=1}^{N_{\text{runs}}} v^i_p(t).
\]  

(5.12)

In both averaging procedures, the viscosity is determined by relating \( \langle v_p(t) \rangle \) to \( \eta \). In the original work [10], the peak averaging procedure was used to obtain an estimate of \( \langle v_p(t) \rangle \), which was then used in the following expression to solve for the unknown fitting parameter \( \nu = \eta/\rho \)

\[
\langle v_p(t) \rangle = \left[ \frac{a_0^2}{(1 + 4 \nu b_0 t)} \right]^{1/2}
\]  

(5.13)

This procedure turns out to be sensitive to the long time decay profile and thus can lead to inaccurate results. A more robust procedure is obtained by linearizing
Eq. 5.13

\[
\left( \frac{a_0}{\langle v_p(t) \rangle} \right)^2 = 1 + 4 \nu b_0 t
\]  

(5.14)

From Eq. 5.14 the viscosity can be obtained by plotting \((a_0/\langle v_p(t) \rangle)^2\) versus \(t\). The result will be a straight line with the slope \(4\nu b_0\) and an intercept of unity. The shear viscosity is simply found from the slope of this line. In all cases, the reported viscosity was obtained by forcing the \(t = 0\) intercept of the data fit to Eq. 5.14 to pass through unity. If this constraint is relaxed, the difference in estimated viscosity changes by less than the uncertainty of the estimate. This method of obtaining estimates of the viscosity is more reliable than fitting \(\langle v_p(t) \rangle\) to Eq. 5.13 and thus was used in all subsequent calculations. Due to this pre-averaging procedure, uncertainty in the viscosity cannot be estimated in a straightforward manner as in Eq. 5.6. Instead, we estimated uncertainties from the error in the linear fit using the Levenberg-Marquardt approach. In addition, it turns out that the differences in the estimated viscosity obtained from profile averaging and peak averaging are smaller than the statistical accuracy of the estimates. Therefore, we only report the results obtained using the profile averaging technique.

Using BC2, the profile averaging result for \(n\)-butane is shown in Fig. 5.2 (a). Without using the pre-equilibration method described below, and fitting to Eq. 5.14 from \(t = 0\) to \(t = 10\) ps, the estimated viscosity for \(n\)-butane is 0.126 cP which agrees with the accepted values obtained using conventional methods. Previous equilibrium method (EMD) studies [10] determined the shear viscosity at this state point to be \(0.135 \pm 0.007\) cP, while SLLOD method (NEMD) results [10] give the shear viscosity as \(0.130 \pm 0.006\) cP and SLLOD method simulations conducted as part of the present study yield a shear viscosity of \(0.144 \pm 0.001\) cP.

Tables 5.3 and 5.4 and Fig. 5.3 summarize the SLLOD method results for
Figure 5.2. (a) MIR result for $n$-butane over 10 ps without Gaussian pre-equilibration. The line is a least squares fit of Eq. 5.14 to the data. (b) MIR result for $n$-butane over 20 ps without Gaussian pre-equilibration. Three different relaxation regions are apparent.
Figure 5.3. Shear viscosities ($\eta$) of $n$-butane and $n$-hexane estimated using SLLOD method as a function of shear rate ($\dot{\gamma}$). The dashed lines are the Carreau fits (Eq. 5.19) to the data. The error bars are standard deviation from five independent simulations.

$n$-butane and $n$-hexane from the present study. These results can then be used to validate the results obtained from the implementation of MIR method.

Note that the current simulations used a box aspect ratio (AR) of 4, with results nearly identical to previous MIR calculations for $n$-butane with an AR of 2. Interestingly, the data in Fig. 5.2 (a) are not perfectly linear; the simulation results appear to show more than one linear regime. This can be seen more clearly in Fig. 5.2 (b), where we plot MIR results over 20 ps and fit straight lines to the data from 0–2 ps, 2–10 ps, 10–20 ps. Three different slopes are obtained. As discussed below, the relaxation event from 2–10 ps should be used when estimating the viscosity. These multiple relaxation events become more apparent when examining larger molecules.
TABLE 5.3
Shear viscosities of \textit{n}-butane and \textit{n}-hexane obtained from SLLOD method simulations. Subscripts indicate the statistical uncertainties in the final digit(s).

<table>
<thead>
<tr>
<th>Shear Rate ($1/ps$)</th>
<th>Shear Viscosity $\eta$ (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{n}-butane</td>
<td>\textit{n}-hexane</td>
</tr>
<tr>
<td>0.01</td>
<td>0.154$<em>{27}$ 0.227$</em>{27}$</td>
</tr>
<tr>
<td>0.031623</td>
<td>0.144$_4$ 0.226$_6$</td>
</tr>
<tr>
<td>0.056234</td>
<td>0.145$_3$ 0.219$_7$</td>
</tr>
<tr>
<td>0.1</td>
<td>0.144$_1$ 0.210$_4$</td>
</tr>
<tr>
<td>0.17783</td>
<td>0.142$_1$ 0.197$_2$</td>
</tr>
<tr>
<td>0.31623</td>
<td>0.138$_6$ 0.178$_2$</td>
</tr>
<tr>
<td>0.56234</td>
<td>0.1316$_2$ 0.157$_1$</td>
</tr>
<tr>
<td>1.0</td>
<td>0.1193$_6$ 0.135$_1$</td>
</tr>
<tr>
<td>1.2023</td>
<td>0.1138$_3$</td>
</tr>
<tr>
<td>1.4125</td>
<td>0.1093$_4$</td>
</tr>
<tr>
<td>1.5849</td>
<td>0.1057$_3$</td>
</tr>
<tr>
<td>1.7783</td>
<td>0.1027$_6$</td>
</tr>
</tbody>
</table>
TABLE 5.4

Fit parameters for the Carreau model (Eq. 5.19). The significance of the parameters is discussed in the text. The error bars represent 95 % confidence limits for the model fit. Subscripts indicate the statistical uncertainties in the final digit(s).

<table>
<thead>
<tr>
<th>System</th>
<th>$\eta_0$</th>
<th>$\lambda$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cP)</td>
<td>(ps)</td>
<td></td>
</tr>
<tr>
<td>$n$-butane</td>
<td>0.144$_1$</td>
<td>1.5$_1$</td>
<td>0.16$_1$</td>
</tr>
<tr>
<td>$n$-hexane</td>
<td>0.223$_6$</td>
<td>7.0$_{1.5}$</td>
<td>0.13$_1$</td>
</tr>
</tbody>
</table>

Fig. 5.4 (a) shows the MIR result for $n$-hexane molecules for the first 9 ps of the simulation. Again, the Gaussian pre-equilibration technique discussed below was not used. This results in an estimated viscosity of 0.176 cP, which is significantly smaller than the accepted SLLOD method value of 0.22 cP and the equilibrium method value of 0.20 cP. As with $n$-butane, there appears to be more than one relaxation process, which can be seen clearly in Fig. 5.4 (b), where we plot MIR results over 32 ps. Three relaxation events are observed: a short time ($< 7$ ps), intermediate time ($7$–$20$ ps), and long time ($> 20$ ps). As argued below, the intermediate relaxation event is the appropriate process to use when determining the viscosity. Indeed, when the data between 7 and 20 ps are fit to Eq. 5.14 a shear viscosity of 0.210 cP is obtained which is in accordance with both of the accepted results.
Figure 5.4. (a) MIR result for $n$-hexane over 9 ps without Gaussian pre-equilibration. The line is a least squares fit to Eq. 5.14. (b) MIR result for $n$-hexane over 32 ps without Gaussian pre-equilibration. As with $n$-butane, three relaxation processes are evident.
The non-linearity of the velocity profile decay for longer molecules suggests that there are other relaxation processes occurring in addition to viscous dissipation. The short time behavior is a convolution of viscous dissipation and intramolecular relaxation processes in which the molecule responds to the sudden imposition of the Gaussian velocity profile. Including these other relaxation processes in the MIR response leads to erroneous estimates of the viscosity. Since small molecules can respond almost instantly to such an imposed velocity profile, the effect is small for molecules such as argon and $n$-butane. For this reason, the MIR results for $n$-butane are relatively insensitive to the time over which the fit is performed. This is also why the first relaxation process occurs only over the first 2 ps, but this initial relaxation event persists over 7 ps for $n$-hexane. This means that the more degrees of freedom a molecule has, the more pronounced are the other relaxation events on the MIR decay profile. To account for this, one could simply fit the long time relaxation behavior of a given system, but this has many drawbacks. First, it is not always clear at what point the system exhibits pure viscous relaxation, which leads to ambiguity in how to fit the profile. Second, the magnitude of the peak velocity relative to thermal velocity fluctuations shrinks as the simulation progresses, leading to a reduction in the signal-to-noise ratio at long times. Also, as discussed in the original publication [10], at longer times localized acoustic fluctuations can corrupt the profile. This means there is greater error involved in fitting the long time portion of the velocity profile as opposed to the short time region. Lastly, the whole point of the MIR method is that the viscosity can be estimated rapidly. As larger molecules are simulated, the initial relaxation processes will take longer and longer to dissipate before the final viscous dissipation behavior could be monitored. However, as viscosity increases, the time it takes
for an imposed velocity profile to relax decreases, posing an obvious problem for
the operational window of the method.

5.3.3 Time Constants and Rotational Relaxation Time

The origin of the initial relaxation process stems from the response of the
system to the imposition of the Gaussian velocity profile. At $t = 0$, the system
consists of molecules pre-equilibrated at the prevailing equilibrium state point
which are then subjected to a sudden spatially varying momentum impulse. We
expect that the dominant relaxation event at short times will be re-orientational
relaxation, as the molecules adapt to this spatial variation in velocity. The time
associated with rotational relaxation can be estimated by computing the end-to-end
vector rotational relaxation time from a short equilibrium molecular dynamics
simulation. This is found by computing the following correlation function,

$$
C(t) = \langle e_1(0) \cdot e_1(t) \rangle
$$

(5.15)

where $e_1$ is the end-to-end unit vector. The rotational relaxation time, $\tau$, can
be obtained in one of two ways. For $n$-butane and $n$-hexane, $C(t)$ was found to
exhibit a single exponential decay such that $\tau$ was found from

$$
C(t) = \exp\left[\frac{-t}{\tau}\right]
$$

(5.16)

The bead spring model did not exhibit a single exponential decay, so $\tau$ was
found using the following expression

$$
\tau = \int_0^\infty C(t) \, dt \approx \left[ \frac{\int_0^{t_0} C(t) \, dt}{1 - C(t_0)} \right]
$$

(5.17)
where the end-to-end vector is assumed to decay with a single exponential beyond time \( t = t_0 \). For the bead-spring model \( t_0 \) is 50 ps.

Using this approach, the computed rotational relaxation time for \( n \)-butane is 1.7 ps, while for \( n \)-hexane it is 7.5 ps. These times agree well with the initial slope change in the MIR results shown in Fig. 5.2 and 5.4. For the bead-spring model \( \tau = 65.9 \) ps, suggesting that a long rotational relaxation time must be accounted for before tracking momentum decay.

Fig. 5.5 (a) shows how the right hand side of Eq. 5.14 varies with time for \( n \)-butane when the first 1.6 ps of the MIR profile have been neglected and the intercept forced through unity.

Fig. 5.5 (b) is the equivalent plot for \( n \)-hexane with the first 7.6 ps neglected. By fitting the butane data out to 10 ps and the hexane data to 20 ps, the estimated viscosities are 0.131 cP and 0.231 cP, respectively. The result for butane is essentially the same as that obtained by fitting the data from 0–10 ps, as it should be, given the very short rotational relaxation time. The \( n \)-hexane results, however, are significantly improved when the initial relaxation process is neglected. This same approach can be applied to the bead-spring model. Fig. 5.6 shows a plot of the right hand side of Eq. 5.14 for the bead-spring model relaxation neglecting the first 66 ps.

The estimated viscosity from the fit is 0.462 cP, which is still 14 % lower than the accepted value [96]. Clearly, for the longer chain system there are additional relaxation processes that are interfering with the pure viscous dissipation mechanism required for the MIR method.
Figure 5.5. (a) The same MIR result for \( n \)-butane as in Fig. 5.2, but with the initial 1.6 ps rotational relaxation time neglected. (b) The same MIR result for \( n \)-hexane as in Fig. 5.4, but with the initial 7.6 ps rotational relaxation time neglected. For both figures: The data are normalized based on the value of the peak velocity after rotational relaxation time. The solid line is the fit to the data, which is forced to have a “y”-intercept of 1.0.
Figure 5.6. MIR result for a 10 unit bead-spring model without Gaussian pre-equilibration. The response of the system prior to the rotational relaxation time is neglected and the data are normalized based on the value of the peak velocity after 66 ps. The solid line is the fit to the data, forced to have a “y”-intercept of 1.0.
5.3.4 Imposition of Gaussian Velocity Profile

In the original implementation of the method [10] and in the work described so far, the Gaussian “x”-component velocity profile given by Eq. 4.18 was instantaneously superimposed over the thermal components of the velocities of an equilibrated system of molecules. This instant was taken as time \( t = 0 \), and the decay of the velocity profile was then tracked to obtain the viscosity. While this approach worked well for the simple test systems examined (argon, \( n \)-butane, and even \( n \)-hexane if the initial rotational relaxation time is neglected), the bead-spring results demonstrate that the method fails for molecules with many intramolecular degrees of freedom.

To solve this problem, we do not impose a Gaussian velocity profile instantaneously, but rather pre-equilibrate the system with the desired Gaussian profile to allow all intramolecular relaxation processes associated with the profile to occur before tracking the MIR decay. Once the molecules adapt to the flow field, the force that generates this profile can be removed and the decay of the velocity profile monitored. With this approach, the dominant process responsible for the decay of the flow profile will be viscous dissipation, and the normal MIR method can be utilized to obtain the viscosity from the first few ps of a simulation. The initial rotational relaxation time will still have to be neglected in the MIR fitting procedure, but we expect that other relaxation processes will be minimized with this approach.

To generate the proper steady-state Gaussian velocity profile, a new set of equations of motion are required. A set of equations of motion consistent with
where \( v_\zeta, \dot{\zeta} \) and \( G_\zeta \) are Nosé-Hoover thermostat variables and \( e_x \) is the “x”-component of the unit vector. Eq. 5.18 was derived using a Lagrangian approach; complete details are presented in Appendix section 5.6.

The form of Eq. 5.18 means that the linear momentum is non-zero in the “x”-direction. Two methods can be used to impose this condition on the system prior to the start of a simulation. In the first approach, the proper fraction of the total “x”-component of momentum consistent with the desired Gaussian velocity profile is added to the thermal velocity of each atom in the system. That is, the velocities of each atom are initially chosen from an appropriate distribution (e.g. Maxwell-Boltzmann) and the linear momentum zeroed in all directions. Then, the appropriate additional momentum is added to the “x”-component of the velocity of each atom. After this, the system is equilibrated using Eq. 5.18. When this procedure is followed, the desired Gaussian velocity profile naturally evolves, as shown in Fig. 5.7(a) and 5.7(b), in which the full velocity profile and peak velocity for \( n \)-hexane are shown as a function of equilibration time, respectively. The set-point peak velocity (in this case, 0.225 nm/ps) is reached in roughly 150 ps, after which the velocity profile is stable.

The second way in which the proper momentum can be added to the system is
Figure 5.7. (a) The evolution of the Gaussian velocity profile using the modified equations of motion (Eq. 5.18). The symbols are the values of average bin velocities at different instances in time while the dashed curves are the Gaussian fits to the data. The open circles denote the final timestep in the equilibration procedure and the solid curve denotes the Gaussian fit (Eq. 4.18) to these data points. (b) The average velocity of the central bin as the velocity profile evolves.
to instantaneously impose the desired Gaussian velocity profile on the system at the beginning of the simulation, before a normal equilibrium velocity distribution is generated. The profile is then stabilized by equilibration using Eq. 5.18. The desired steady-state profile is still maintained, but it is obtained in a shorter time than when the additional “x”-momentum is added uniformly. Both methods yield the same viscosities, but the latter method achieves a stable velocity distribution faster than the former approach, and so it is the preferred way of equilibrating the system.

To apply this new Gaussian pre-equilibration method, the desired steady-state Gaussian velocity distribution is generated using Eq. 5.18 and then at \( t = 0 \) the normal canonical ensemble equations of motion are switched on, allowing the velocity distribution to relax. After discarding the initial rotational relaxation time, the decay profile is fit to Eq. 5.14 and the viscosity obtained from the slope. Using this approach the computed viscosities for \( n \)-butane and \( n \)-hexane were 0.127 cP and 0.224 cP, respectively. The pre-equilibrated relaxation profiles are compared with those obtained without pre-equilibration in Fig. 5.8.

These values are equivalent to those obtained with conventional methods, and similar to those computed from MIR with no Gaussian pre-equilibration. On the other hand, the Gaussian pre-equilibration procedure provides a dramatic improvement in the results of the bead-spring model. Fig. 5.9 compares the MIR results with and without Gaussian pre-equilibration for the bead-spring model.

Using the Gaussian pre-equilibration method, a viscosity of 0.550 cP was obtained, which is consistent with the nonequilibrium method study carried out by Kröger et al. [96]. Without the Gaussian pre-equilibration, however, the computed viscosity is 0.462 cP. Clearly, proper equilibration of the Gaussian velocity
Figure 5.8. (a) MIR results for $n$-butane. (b) MIR results for $n$-hexane. For both figures: The filled diamonds are the results without Gaussian pre-equilibration and the open circles are the results with Gaussian pre-equilibration (Eq. 5.18). The response of the system prior to the rotational relaxation time is neglected and the data are normalized based on the value of the peak velocity after this time. The lines are best fits based on Eq. 5.14.
Figure 5.9. MIR results for the bead-spring model. The filled diamonds are results without Gaussian pre-equilibration and the open circles are the results with Gaussian pre-equilibration (Eq. 5.18). The response of the system prior to the rotational relaxation time (66 ps) is neglected and the data are normalized based on the value of the peak after that time. The lines are the best fits based on Eq. 5.14.
profile is essential for obtaining accurate viscosities of long chain molecules.

From Fig. 5.9, there are indications that the response of the system begins to deviate from the straight line behavior beyond 180 ps. This may be due to noise or feedback from the boundary conditions. It may also be evidence of a *recoil effect* which is observed in polymeric liquids, when a steady Couette flow is stopped suddenly [16]. For this reason we fit the data points only up to 180 ps and not beyond that.

As the tendency of the molecules to shear thin increases, the size of the simulation box required in MIR must also increase to maintain the local shear rate below the critical value. As the viscosity of the system increases, however, the time it takes for the Gaussian velocity profile to decay *decreases*. This means that while viscous systems will require many molecules, not much more than 30 ps of simulation production time will be required to obtain an estimate of the viscosity once the initial rotational relaxation process is overcome. This suggests that the MIR method is well-suited for parallelization strategies such as domain decomposition.

5.4 Computational Performance

As demonstrated above, the MIR method can be used to compute the shear viscosity of multi-atom molecular liquids. The advantage of this method over conventional techniques is that much shorter simulation times are required. We have shown that accurate viscosities can be obtained in as little as 10 ps, while 1–2 orders of magnitude longer simulations are required to obtain Newtonian shear viscosities with the conventional methods. Meaningful timing comparisons with equilibrium and nonequilibrium techniques are difficult to obtain, given differences
in system size, equilibration requirements, the number of simulations needed and, more importantly, uncertainty in how to properly relate statistical accuracy to the length of a simulation. Total CPU time is not necessarily the best measure of algorithmic performance. For perfectly parallel methods such as MIR and SLLOD, ready access to large computer clusters makes the execution time of the slowest simulation the most relevant metric for the comparison of the efficiency of an algorithm. Since equilibrium method enables the calculation of the Newtonian shear viscosity from a single simulation, this execution time is the appropriate measure to use. SLLOD techniques, on the other hand, require a series of simulations at decreasing shear rate in order to extrapolate to the Newtonian limit (see Fig. 5.3). The simulations at the lowest shear rate require the most time, and are typically shorter than (but of the same order of magnitude) a comparable equilibrium simulation. For this reason, we have chosen to benchmark the MIR method against the SLLOD technique to obtain a sense of the relative computational efficiency of the method. In these comparisons, the same base code was used for the integrator and force calculations, thereby allowing an unbiased test of the performance of the two methods.

To obtain a reliable shear viscosity for \( n \)-hexane using SLLOD, between 1000–1500 ps of production run time with 200 molecules was required. The simulations were run at eight different shear rates, with five simulations at each shear rate used to obtain an estimate of the uncertainty of each point. Note that simple block averaging of a single simulation tends to severely underestimate the true uncertainty of the low shear rate results. The results of the SLLOD calculations are summarized in Table 5.3 and plotted in Fig. 5.3. The data were fit to the
3-parameter Carreau model of the form

\[ \eta(\dot{\gamma}) = \frac{\eta_0}{1 + (\lambda \dot{\gamma})^2} \]  

(5.19)

where the parameters have the following meaning. \( \eta_0 \) is the limiting Newtonian viscosity as the shear rate \( \dot{\gamma} \to 0 \) and \( \lambda \) is a characteristic time constant, which has been found to be roughly equal to the rotational relaxation time for many systems. At high shear rates, a power law behavior is approached with \( \eta \propto \dot{\gamma}^{-2p} \).

The simulation data were fit to the model with equal weighting as well as by weighting the data to the inverse square of the error bars. The results using the weighting procedure are summarized in Table 5.4. The simulations at the lowest shear rate (0.01 ps\(^{-1}\)) were run for 2000 ps. For 200 molecules this took 16 hours of wall clock time on a Sun V60x running Linux with a 3.06 GHz Xeon processor. The error associated with the lowest shear rate is 10%, although by fitting the results to the model, the ultimate error in the Newtonian viscosity is less than this. We therefore estimate that sufficient accuracy could be obtained for the lowest shear rate point with a simulation of 1000 ps, thus requiring approximately 8 wallclock hours. Note that five simulations at each of the other shear rates must also be run, but these will take less than 8 hours apiece to obtain sufficient accuracy. For the MIR method, a larger system is required to resolve an accurate velocity profile. Using 1000 \( n \)-hexane molecules, several 20 ps production runs are required to obtain a reliable Newtonian shear viscosity. This corresponds to approximately 0.8 hours of real time. Both the SLLOD and MIR method require that the systems be equilibrated prior to data collection, the time of which is roughly comparable for the same size systems. In some cases, the MIR method requires larger system sizes, in which case the equilibration times must also be
considered. Thus for \( n \)-hexane, the MIR method results in approximately a factor of ten savings in production time. When equilibration time is factored in for this particular case however, the advantage of the MIR method is reduced somewhat due to the larger system size requirements. Importantly, this comparison is only for the single processor case. If parallelization is considered, the MIR method has distinct advantage over NEMD, since domain decomposition strategies can be used to minimize system size dependence but not simulation time.

For the bead-spring model an accurate viscosity was obtained in 22 hours using MIR. We did not perform a full SLLOD method simulation of this system, so direct timings are not available. However, Kröger et al. [96] report that 200,000 timesteps are required for the 10 bead system at the highest shear rate. This corresponds to a simulation of approximately 90 hours on a single processor using our code. Since it is at the highest shear rate, this is the minimum amount of time required to obtain a reliable Newtonian viscosity. Thus the MIR method is at least a factor of 4 faster than nonequilibrium method of the same system size. It may be possible to use a smaller system with nonequilibrium method and thus reduce the equilibration time. Nevertheless the computational savings for the production phase of the MIR method are still significant. We note that the overhead associated with fitting the Gaussian profile each time step is minimal. A summary of the timing comparisons is given in the Table 5.5.

5.5 Summary

We have shown that the MIR method can be used to reliably estimate the shear viscosity of multi-atom molecular liquids. Total production simulation times of only 10 ps for \( n \)-butane, 20 ps for \( n \)-hexane, and 180 ps for a 10 bead polymer
TABLE 5.5

Production run timing comparison between MIR and nonequilibrium (SLLOD) method. The nonequilibrium method values for \( n \)-butane and \( n \)-hexane are obtained from this work, while that for BSM is estimated from the study carried out by Kröger et al. [96].

<table>
<thead>
<tr>
<th>System</th>
<th>NEMD</th>
<th>MIR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(SLLOD)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(hr:min)</td>
<td>(hr:min)</td>
</tr>
<tr>
<td>( n )-butane</td>
<td>10 : 20</td>
<td>00 : 15</td>
</tr>
<tr>
<td>( n )-hexane</td>
<td>15 : 54</td>
<td>00 : 50</td>
</tr>
<tr>
<td>BSM</td>
<td>&gt; 90 : 00</td>
<td>22 : 00</td>
</tr>
</tbody>
</table>
model are required. This represents roughly one order of magnitude savings in simulation times as compared to conventional equilibrium and nonequilibrium methods.

The present work has demonstrated several refinements to the original MIR method. We showed how a simple linear fitting procedure can be used to more accurately extract the shear viscosity from time-dependent velocity profiles and proposed a more accurate velocity boundary condition. We derived a new set of nonequilibrium equations of motion that automatically generate the desired Gaussian velocity profile and show that proper pre-equilibration of the system with this profile is necessary to obtain an accurate viscosity for long chain molecules. We also showed that the MIR fit should be made after the time for rotational relaxation of the system, which can be significant for large molecular species.

5.6 Appendix: Derivation for the Modified Equations of Motion

In this section we provide the derivation of Eq. 5.18 used to equilibrate the imposed Gaussian velocity profile.

We start with the Lagrangian \( \mathcal{L} \) for the system, defined as

\[
\mathcal{L} = \mathcal{K} - \mathcal{U}
\]  

(5.20)

where \( \mathcal{K} \) is the kinetic energy of a system of \( N \) atoms and is given by

\[
\mathcal{K} = \sum_{i}^{N} \frac{1}{2} m_{i} [(\dot{\mathbf{r}}'_{i})^{2}] = \sum_{i}^{N} \frac{1}{2} m_{i} [((\dot{\mathbf{r}}_{i} - \mathbf{u}_{i}))^{2}]
\]  

(5.21)

Primed quantities denote peculiar quantities (where the imposed velocity profile is excluded) while unprimed quantities represent overall values. Thus, \( \dot{\mathbf{r}}'_{i} \) is the
thermal or *peculiar* velocity of atom \( i \), \( \mathbf{\dot{r}}_i \) is the total velocity of \( i \), and \( \mathbf{u}_i \) is the desired Gaussian velocity profile. Formally,

\[
\mathbf{\dot{r}}' = \begin{bmatrix}
\dot{r}'_x \\
\dot{r}'_y \\
\dot{r}'_z
\end{bmatrix}, \quad \mathbf{\dot{r}} = \begin{bmatrix}
\dot{r}_x \\
\dot{r}_y \\
\dot{r}_z
\end{bmatrix}, \quad \text{and} \quad \mathbf{u} = \begin{bmatrix}
u_x \\
u_y \\
u_z
\end{bmatrix} = \begin{bmatrix}
a_0 e^{-b_0 (r_y)^2} \\
0 \\
0
\end{bmatrix}
\]

The potential energy of the system, \( \mathcal{U} \), is given by

\[
\mathcal{U} = \frac{1}{2} \sum_{i,j} \phi(r_{ij})
\] (5.22)

where \( \phi_{ij} \) is the pair potential between atoms \( i \) and \( j \). Dropping the subscripts, the Lagrangian is thus

\[
\mathcal{L} = \frac{1}{2} m \left[ (\dot{\mathbf{r}}')^2 \right] - \phi(\mathbf{r})
\] (5.23)

The peculiar momenta are defined as

\[
\mathbf{p}' = \frac{\partial \mathcal{L}}{\partial \mathbf{\dot{r}}'} = m \mathbf{\dot{r}}'
\] (5.24)

The total momenta \( \mathbf{p} \) is defined as,

\[
\mathbf{p} = m \mathbf{\dot{r}}
\] (5.25)

so that

\[
\mathbf{p}' = \mathbf{p} - m \mathbf{u}
\] (5.26)
Note that $\mathbf{r}' = \mathbf{r}$. The Hamiltonian ($\mathcal{H}$) of the system can be obtained by Legendre transformation, as discussed in the previous chapter

$$
\mathcal{H}(\mathbf{p}', \mathbf{r}', t) = (\mathbf{p}' \dot{\mathbf{r}}') - \mathcal{L}(\dot{\mathbf{r}}', \mathbf{r}', t) = \frac{1}{2m} [(\mathbf{p}')^2] + \phi(\mathbf{r})
$$

The equations of motion for the peculiar variables can be derived from the Hamiltonian as,

$$
\dot{\mathbf{r}}' = \frac{\partial}{\partial \mathbf{p}'} \mathcal{H} \quad (5.28)
$$

and

$$
\dot{\mathbf{p}}' = -\frac{1}{m} \frac{\partial}{\partial \mathbf{r}'} \mathcal{H} \quad (5.29)
$$

From Eq. 5.27, we can write

$$
\dot{\mathbf{r}}' = \left[ \begin{array}{c} \mathbf{p}' \\ m \end{array} \right] \quad (5.30)
$$

and using Eq. 5.25 one obtains

$$
\dot{\mathbf{r}}' = \left[ \begin{array}{c} \frac{\mathbf{p}}{m} - \mathbf{u} \end{array} \right] = \frac{\mathbf{p}}{m} - a_0 e^{-b_0 (r_y)^2} \mathbf{e}_x \quad (5.31)
$$

where $\mathbf{e}_x$ is the “x”-component of the unit vector.

Starting again from 5.27, one obtains

$$
\dot{\mathbf{p}}' = -\frac{1}{m} \frac{\partial}{\partial \mathbf{r}'} [\phi(\mathbf{r})] = \mathbf{F} \quad (5.32)
$$

119
Since we wish to keep track of the total momenta $\mathbf{p}$, we can re-write the above equation using Eq. 5.26 as,

$$\dot{\mathbf{p}}' = \dot{\mathbf{p}} - m \dot{\mathbf{u}} = F \quad (5.33)$$

so that

$$\dot{\mathbf{p}} = F + m \dot{\mathbf{u}}$$

$$= F - 2 a_0 b_0 r_y p_y \exp[-b_0 (r_y)^2] \mathbf{e}_x \quad (5.34)$$

To maintain temperature control, we utilize a Nosé-Hoover thermostat. The final equations of motion that generate a steady-state velocity profile consistent with Eq. 4.18 are thus

$$\dot{\mathbf{r}}' = \frac{\mathbf{p}}{m} - a_0 \exp[-b_0 (r_y)^2] \mathbf{e}_x$$

$$\dot{\mathbf{p}} = F - 2 a_0 b_0 r_y p_y \exp[-b_0 (r_y)^2] \mathbf{e}_x$$

$$- (\mathbf{p} - m a_0 \exp[-b_0 (r_y)^2] \mathbf{e}_x) \nu_\zeta$$

$$\dot{\nu}_\zeta = \nu_\zeta$$

$$\nu_\zeta = G_\zeta \left( \mathbf{p} - m a_0 \exp[-b_0 (r_y)^2] \mathbf{e}_x \right) \quad (5.35)$$

where only the peculiar momenta are thermostatted.
CHAPTER 6

PREDICTION OF VISCOSITIES FOR FIVE POLYHYDRIC ALCOHOLS

\[ I \text{ do not fear computers. I fear the lack of them.} \]

.. Isaac Asimov

[1920–1992]

6.1 Introduction

As emphasized earlier, knowledge of the physical properties of a given molecular fluid is of great importance in a wide variety of industrial settings. In many instances attaining these properties experimentally is prohibitive, for example, due to a compound’s instability, safety concerns or, economic factors. For this reason, the calculation of fluid properties by molecular simulation is becoming an increasingly popular and useful tool. In addition, simulation allows for microscopic insight that is often not attainable experimentally. This insight can be extremely useful in better understanding processes at the molecular-level.

In this chapter, we test the accuracy of the united atom version of the transferable potentials for phase equilibria (TraPPE-UA) forcefield (mentioned earlier) for the prediction of the Newtonian viscosities and vapor-liquid equilibria of five polyhydric alcohols, namely 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, and 1,2,4-butanetriol. Compounds of this type are widely used
as lubricants and heat transfer liquids in heating and cooling systems. Therefore, accurate knowledge of their physical properties over a wide range of state points is of great value in the design of equipment for these and other applications. In addition to the physical property predictions, our collaborators on this study (Jake L. Rafferty and Prof. J. Ilja Siepmann from University of Minnesota) have used the trajectories from the simulations for a microscopic-level hydrogen bond analysis. This analysis was done to help rationalize the relative orders of viscosities, boiling points, enthalpies of vaporization, and critical properties.

Part of the work presented here is in response to the *Molecule Transferability* Problem of the 2006 Industrial Fluid Properties Simulation Challenge [78](http://fluidproperties.org/challenge/third/challenge.html). The task of this Simulation Challenge was to predict the Newtonian viscosities of the five polyhydric alcohols at two pressures, 1 MPa and 250 MPa, and a temperature of 373 K. The rest of the work presented here, i.e. computing viscosities at additional state points and predicting vapor-liquid equilibria (which was again done by the collaborators), was done to further demonstrate the transferability of the TraPPE forcefield to predict multiple properties at a wide range of state points.

Results from this study show that the TraPPE forcefield achieves very good agreement with experiment. For example, where experimental values were available, the collaborators were able to reproduce the correct order of boiling points, critical temperatures and critical densities of the polyhydric alcohols. Quantitative agreement was also very good in most cases. Values of critical and boiling temperatures computed from Gibbs ensemble simulations on average deviate by only 1 and 2% from experiment, respectively. For the majority of the compounds studied, the computed viscosities also compare well to experimental data. The TraPPE
forcefield yields viscosities for 1,2-butanediol and 1,2,4-butanediol within an average of 10% from experiment while 1,4-butanediol and 2-methyl-1,3-propanediol are within 15%. However, the viscosity of 1,3-butanediol is substantially overestimated by an average of 34%.

It should be stressed that although the non-bonded parameters of the TraPPE forcefield were obtained by fitting to vapor-liquid equilibria of selected test molecules, none of the polyhydric alcohols investigated in the present work were used in the fitting process. In fact, all non-bonded and bonded parameters needed for these simulating polyhydric alcohols have previously been published [29, 120, 121, 190]. Furthermore, the TraPPE forcefield has never been parameterized to reproduce transport properties, such as viscosities. Thus, the results presented herein are pure predictions and further validate the transferability of the TraPPE forcefield and its ability to reproduce a variety of properties at a wide range of state points. The complete discussion on this study can be found in the publication [89].

6.2 Simulation Method

MIR method, described in the previous chapter, is very efficient in computing the shear viscosities of molecular fluids. However, for highly viscous systems with relatively larger relaxation times it poses the problem of operational window. Also, the modification of periodic boundary condition to accommodate the diffusing or decaying Gaussian velocity profile, poses additional problems when incorporating charged systems through modification of Ewald algorithm, which is non-trivial. Recently, a different nonequilibrium method was proposed by Müller-Plathe called reverse nonequilibrium molecular dynamics (RNEMD) method [140]. The idea behind this method is described in Chapter 4. This method eliminates
the requirement of modified periodic boundary condition as the velocity profile imposed by this method is periodic in space.

6.3 Validation of the RNEMD Method

Before we applied the RNEMD method to the Challenge systems, mentioned above, we validated the method and our codes by computing the viscosity of several test systems for which literature data are available. These include argon, n-hexane, water and molten sodium chloride (NaCl). These systems were chosen because they represent widely used model types and their viscosities have either already been determined or they can be computed accurately using conventional simulation techniques. They thus provide a rigorous test of the RNEMD method.

All the simulations were carried out in the canonical ensemble with a Nŏse-Hoover chain thermostat [122]. A multiple time step algorithm, r-RESPA [201] was used, with the inner timestep ranging from 0.5 fs for water to 1 fs for n-hexane to 2 fs for NaCl to 4 fs for argon. The outer timesteps range from 1.5 fs for water to 2.0 fs for NaCl to 4.0 fs for both n-hexane and argon. The aspect ratio (AR) of all the simulation boxes used for validation of this method was 3.0, i.e. $L_y/L_x = L_y/L_z = 3.0$, except for water where the aspect ratio was set to 1.0. The box was divided into 20 bins to determine the velocity profile. A cutoff radius of 10.0 Å was used for Lennard-Jones interactions for all the systems other than for argon, where a cutoff radius of 10.215 Å was used. Long range corrections were applied. The electrostatic interactions were handled using a particle mesh Ewald approach with a real space cutoff of 10 Å. We used a locally developed software package (our group software APSS) for all the viscosity simulations.

In the argon simulations, 2592 atoms at a density $\rho = 1.427 \ g/cm^3$ and a
temperature $T = 86.5 \, K$ were simulated. The Lennard-Jones parameters were identical to those used by Müller-Plathe [140]. For $n$-hexane, 2000 molecules were simulated with intramolecular terms taken from the work of Siepmann and co-workers [187]. Non-bonded parameters were the same as those reported by Martin and Siepmann [119]. The state point was $T = 298 \, K$ and $\rho = 0.655 \, g/cm^3$, which is the same as studied by Kioupis et al. [92]. For water, a flexible SPC/E model was used. The potential parameters, force constants for bond stretching and the angle bending were taken from the work of Fuller and Rowley [54]. 500 water molecules were simulated at $T = 300 \, K$ and $\rho = 1.004 \, g/cm^3$, as also considered by Fuller and Rowley [54]. For NaCl, 512 ion pairs (512 $[Na]^+$ and 512 $[Cl]^-\,$) were simulated using the well known Born-Huggins-Mayer potential with the parameters set by Tosi and Fumi [9, 55, 198]. The simulations were carried out at the state point studied by Delhommelle et al. [37], i.e. $T = 1500 \, K$ and $\rho = 1.5 \, g/cm^3$.

A range of swap rates was used for all the systems considered. The Newtonian viscosities were determined for all systems except water by fitting the shear rate dependent viscosities to a Carreau model (Eq. 5.19). To enable comparison with the results by Fuller and Rowley [54], the shear-dependent viscosities were fit to a mode coupling model (Eq. 7.1). The results of the validation runs for all these systems are summarized in Table 6.1. We also show the literature or the accepted values for the shear viscosity of these systems. As can be seen, our calculations yield estimates of the shear viscosity that are in good agreement with the literature values.
TABLE 6.1

Shear viscosities of the systems used to validate the method. Subscripts indicate the statistical uncertainties in the final digit.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Temperature (T, K)</th>
<th>Density (ρ, gm/cm³)</th>
<th>Shear Viscosity (η, cP)</th>
<th>Literature</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>argon</td>
<td>86.5</td>
<td>1.427</td>
<td>0.290 [18]</td>
<td>0.305</td>
<td></td>
</tr>
<tr>
<td>n-hexane</td>
<td>298.0</td>
<td>0.655</td>
<td>0.223 [86]</td>
<td>0.227₂</td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>300.0</td>
<td>1.005</td>
<td>0.680 [54]</td>
<td>0.66₁</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>1500.0</td>
<td>1.500</td>
<td>0.790 [37]</td>
<td>0.815₂</td>
<td></td>
</tr>
</tbody>
</table>
6.4 Simulation Details

6.4.1 Force Field

All of the polyhydric alcohols in this study were represented by the united atom version of the transferable potentials for phase equilibria (TraPPE-UA) forcefield [29, 120, 121, 190]. In this united atom forcefield CH\textsubscript{x} groups are modeled as pseudo atoms with sites located on the carbon atoms while atoms in all other functional groups are modeled explicitly. Non-bonded interactions in the TraPPE-UA forcefield are described by a combination of pairwise additive Lennard-Jones (LJ \textit{i.e.} VDW interactions) (Eq. 3.13) and Coulombic (Eq. 3.14) terms. For unlike interactions we use the Lorentz-Berthelot combining rules [14, 111]. A spherical potential truncation for bead-bead interactions beyond 14 Å together with analytic tail corrections (long range corrections) are used for the LJ portion of the potential, while the electrostatic interactions were evaluated using the Ewald summation technique with $\kappa = 0.2$ and tin foil boundary conditions [6].

Non-bonded interactions are considered for all sites belonging to different molecules and for sites on the same molecule when they are separated by four or more bonds. Coulombic interactions are also included for sites separated by three bonds but scaled by a factor of 0.5. In addition, there is a special short range repulsive intramolecular term for hydroxyl groups on neighboring carbon atoms [190] to prevent an overestimation of 1–5 intramolecular hydrogen bonds. The following simple potential [190] is used between hydroxyl hydrogens and oxygens separated by four bonds

$$U_{\text{repulsive}}(r_{ij}) = \frac{a}{r_{ij}^{12}}$$

where $a/k_B = 7.5 \times 10^7 K Å^{12}$. A full list of the non-bonded interaction parameters
used in this study are given in Table 6.2.

Torsional interactions for sites separated by three bonds are modeled by a cosine series [81] in Eq. 3.10. Due to the relative complexity of the molecules in this study, a few of the torsional potentials were not present in the original TraPPE-UA forcefield nor available in the literature for \( \text{CH}_x \) pseudo atoms. In these cases, we assume that two torsional potentials, \( \text{A–B–C–D} \) and \( \text{W–X–Y–Z} \) are equivalent under two conditions: (1) both atoms \( \text{B} \) and \( \text{X} \), and atoms \( \text{C} \) and \( \text{Y} \) are the same and have the same hybridization, (2) both atoms \( \text{A} \) and \( \text{W} \), and atoms \( \text{D} \) and \( \text{Z} \) are in the same row of the periodic table. For example, the 1,2-diol torsion \( \text{O–CH–CH}_2–\text{O} \) was not available so we have used the \( \text{CH}_x–\text{CH–CH}_2–\text{CH}_y \) torsional potential in its place. The \( c_n \) coefficients used in this study are listed in Table 6.3.

A harmonic potential is used to model the interaction of sites separated by two bonds (Eq. 3.9). Table 6.3 contains a list of the values for \( k_\theta \) and \( \theta_0 \) used here.

Finally, the interaction of atoms directly bonded together was treated in two different ways depending on the type of simulation. In all of the Monte Carlo simulations, done by our collaborators, they use fixed bond lengths while in our molecular dynamics simulations we use a harmonic bond stretching potential like in Eq. 3.6. This choice was made since using fixed bond lengths somewhat increases the efficiency of configurational-biased Monte Carlo (CBMC) simulations and it has been previously shown that replacing fixed bond lengths with harmonic stretching potentials has no significant effect on liquid densities or vapor-liquid phase equilibria [143]. In contrast, harmonic stretching potentials are more convenient for molecular dynamics simulations and the use of fixed bond lengths has
TABLE 6.2
NONBONDED PARAMETERS FOR THE TRAPPE-UA FORCFIELD. \(^a\) INDICATES CH\(_x\) GROUPS NOT DIRECTLY BONDED TO A HYDROXYL OXYGEN ATOM, WHILE \(^b\) INDICATES CH\(_x\) GROUPS DIRECTLY BONDED TO A HYDROXYL OXYGEN ATOM.

<table>
<thead>
<tr>
<th>site</th>
<th>source</th>
<th>(\sigma) ((\text{\AA}))</th>
<th>(\epsilon/k_B) (K)</th>
<th>(q) (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3^a)</td>
<td>[120]</td>
<td>3.75</td>
<td>98.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CH(_2^a)</td>
<td>[120]</td>
<td>3.95</td>
<td>46.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CH(^a)</td>
<td>[121]</td>
<td>4.68</td>
<td>10.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CH(_2^b)</td>
<td>[29]</td>
<td>3.95</td>
<td>46.0</td>
<td>+0.265</td>
</tr>
<tr>
<td>CH(^b)</td>
<td>[29]</td>
<td>4.33</td>
<td>10.0</td>
<td>+0.265</td>
</tr>
<tr>
<td>O</td>
<td>[29]</td>
<td>3.02</td>
<td>93.0</td>
<td>−0.700</td>
</tr>
<tr>
<td>H</td>
<td>[29]</td>
<td>0</td>
<td>0</td>
<td>+0.435</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>special 1–5 interaction</th>
<th>source</th>
<th>(a/k_B) (K (\text{\AA}^1)^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–O–CH(_x)–CH(_x)–O–H</td>
<td>[190]</td>
<td>(7.5 \times 10^7)</td>
</tr>
</tbody>
</table>
TABLE 6.3
Torsional, bond bending parameters for the TraPPE-UA forcefield.

<table>
<thead>
<tr>
<th>torsion type</th>
<th>source</th>
<th>$c_\alpha/k_B$</th>
<th>$c_1/k_B$</th>
<th>$c_2/k_B$</th>
<th>$c_3/k_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CH_x-CH_2-CH_2-CH_y$</td>
<td>[81]</td>
<td>0</td>
<td>355.03</td>
<td>-68.19</td>
<td>791.32</td>
</tr>
<tr>
<td>$CH_x-CH-CH_2-CH_y$</td>
<td>[187]</td>
<td>-251.06</td>
<td>428.73</td>
<td>-111.85</td>
<td>441.27</td>
</tr>
<tr>
<td>$CH_x-CH_2-CH_2-O$</td>
<td>[80]</td>
<td>0</td>
<td>176.62</td>
<td>-53.34</td>
<td>769.93</td>
</tr>
<tr>
<td>$CH_x-CH_2-CH-O$</td>
<td>[187]</td>
<td>-251.06</td>
<td>428.73</td>
<td>-111.85</td>
<td>441.27</td>
</tr>
<tr>
<td>$CH_x-CH-CH_2-O$</td>
<td>[187]</td>
<td>-251.06</td>
<td>428.73</td>
<td>-111.85</td>
<td>441.27</td>
</tr>
<tr>
<td>$CH_x-CH_2-O-H$</td>
<td>[80]</td>
<td>0</td>
<td>209.82</td>
<td>-29.17</td>
<td>187.93</td>
</tr>
<tr>
<td>$CH_x-CH-O-H$</td>
<td>[80]</td>
<td>215.89</td>
<td>197.33</td>
<td>31.46</td>
<td>-173.92</td>
</tr>
<tr>
<td>O–CH$_2$–CH–O</td>
<td>[187]</td>
<td>-251.06</td>
<td>428.73</td>
<td>-111.85</td>
<td>441.27</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>bend type</th>
<th>$\theta_0$</th>
<th>source</th>
<th>$k_\theta/2k_B$</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CH_x-CH_2-CH_y$</td>
<td>114.0</td>
<td>[186]</td>
<td>31,250</td>
<td>[205]</td>
</tr>
<tr>
<td>$CH_x-CH-CH_y$</td>
<td>112.0</td>
<td>[187]</td>
<td>31,250</td>
<td>[205]</td>
</tr>
</tbody>
</table>
TABLE 6.4
Bond length parameters for the TraPPE-UA forcefield and bond stretching parameters from the AMBER forcefield.

<table>
<thead>
<tr>
<th>bond type</th>
<th>$r_0$ (Å)</th>
<th>source</th>
<th>$k_r/2k_B$ (K/Å(^2))</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_x)–CH(_y)</td>
<td>1.54</td>
<td>[186]</td>
<td>1.35\times10^5</td>
<td>[30]</td>
</tr>
<tr>
<td>CH(_x)–O</td>
<td>1.43</td>
<td>[30]</td>
<td>1.61\times10^5</td>
<td>[30]</td>
</tr>
<tr>
<td>O–H</td>
<td>0.945</td>
<td>[30]</td>
<td>2.78\times10^5</td>
<td>[30]</td>
</tr>
</tbody>
</table>

been shown to lead to an under prediction of viscosities [54]. Since the TraPPE-UA forcefield does not contain bond stretching constants, we have taken these from the AMBER forcefield [30] without further modification. These stretching constants and equilibrium distances (which are also the fixed distances in the MC simulations) are given in Table 6.4.

6.4.2 Viscosity Calculations

The first step in predicting the viscosities of the five polyhydric alcohols was to compute their liquid densities at the four state points of interest ($T = 373 \text{ K}$; $P = 0.1, 25, 100 \text{ and } 250 \text{ MPa}$). These density calculations were done by our collaborators. For this purpose, they used coupled-decoupled configurational-bias Monte Carlo (CBMC) simulations [121, 185, 208] in the $NPT$ ensemble [128]. The details of application of this method to these polyhydric alcohols can be found in
the publication [89].

Using these computed densities, molecular dynamics simulations in the \(NVT\) ensemble were carried out to compute the viscosities of each compound at the four state points. A system size of 400 molecules and orthogonal boxes with an aspect ratio (AR) of 2.0 were used in these calculations. As with the validation runs, the reversible multiple time stepping algorithm r-RESPA [201] was used with an inner time step of 0.5 fs and an outer time step of 2 fs. A three chain No\-se-Hoover thermostat [122] was used to control the temperature. The box was divided into 14 bins to determine the velocity profile. The system was equilibrated without momentum swaps for 250 ps. Following this, production runs using momentum swaps were conducted for the time required for the viscosity to reach a plateau. An example of this convergence behavior is shown in Fig. 6.1.

6.4.3 Gibbs Ensemble Simulations of Vapor-Liquid Equilibria

To determine the vapor-liquid coexistence curves, our collaborators used coupled-decoupled CBMC simulations [121, 135, 185, 208] in the \(NVT\) Gibbs ensemble [99, 151, 152] were performed. Again, the details of these calculations can be found in the publication [89].

6.4.4 Data Analysis

A typical result of a RNEMD run is a velocity profile and an estimate of the shear viscosity as a function of time. Fig. 6.1 shows the velocity profile for 1,4-butanediol at \(P = 25 \text{ MPa}\) and \(T = 373 \text{ K}\). The slope of each half combined with the known frequency of momentum swaps gives an estimate of the viscosity via Eqs. 2.12 and 4.22. The time averaging of the data is done on the fly by
Figure 6.1. RNEMD shear viscosity evolution over time for 1,4-butanediol at 25 MPa and 373 K. (a) The “x”-directional velocity profile in “y”-direction. (b) Evolution of viscosity as function of time. Four different swap rates are included; black, red, green, and blue lines represent rates resulting from one swap every 20, 40, 50, and 80 outer timesteps, respectively.
averaging the data after every 10 timesteps. A least squares fit of the data is then used to determine the shear viscosity and the error. As an example of the typical convergence behavior, the shear viscosity as a function of time for 1,4-butanediol at the same state point is shown in Fig. 6.1. In general, the stress obtained from the imposed swap rate was independent of pressure. At 250 MPa, the stress was very slow to reach steady state, while at lower pressures the stress converged quickly. As a result for all but one system at 250 MPa, the stress at 100 MPa was used in Eq. 2.12.

Error bars were calculated in two different ways. For argon and n-hexane, each velocity profile was linear and enabled a straightforward determination of the viscosity at each shear rate. Five independent simulations were run for each shear rate, from which an average viscosity and error estimate (from the standard deviation) were obtained. A Carreau fit to the data was then used to estimate the zero shear viscosity. For all other systems, we ran only one simulation at each of the shear rates and state points. It was observed that for some systems at the lowest shear rates, the profiles were not completely linear, but exhibited a small discontinuity near the boundary where momentum swaps occur. This can clearly be seen in Fig. 6.1. Our work on ILs, which will be discussed in the next chapter [88], has shown that this is indicative of sluggish dynamics, in which the time scale of the momentum transfer becomes commensurate with the underlying dynamical time scale of the liquid. A line connecting the velocities in the boundary bins \((n = 1 \text{ and } n = n_c)\) will tend to underestimate the viscosity, while a fit to only the linear middle region \((n = 2 \text{ through } n = n_c - 1)\) will tend to overestimate the viscosity. As a practical compromise, we estimated the viscosity and error in the following manner. A least squares regression was performed on three parts...
of the velocity profile: (1) the two end bin velocities \( n = 1 \) and \( n = N_c \); (2) the middle section of the profile \( n = 2 \) through \( n = n_c - 1 \); and (3) the entire velocity profile \( n = 1 \) through \( n = n_c \) \[1\]. Each fit results in a slightly different viscosity estimate and shear rate. The average and standard deviation of these three viscosities at the average shear rate was then used to obtain the zero shear rate viscosity for the alcohols by fitting these data points to a Carreau model (Eq. 5.19). The standard error on \( \eta_0 \) is then taken as the estimate of the error bar on the zero shear viscosity. As stated earlier, a mode coupling theory fit was used for water in order to compare the results with literature values (we will discuss about the mode coupling fit in the next chapter (Chapter 7, Eq. 7.1)).

For the case of 1,4-butanediol at 250 MPa, the estimates of the viscosity showed an increasing trend with lowering of shear rate. We did not have enough data in the Newtonian regime to fit a Carreau model (Eq. 5.19) through the data. It is for this reason we fit a mode coupling model (Eq. 7.1) through these data points in order to estimate the zero shear viscosity. However, for the cases of 1,2,4-butanetriol at 0.1, 25 and 250 MPa pressures and for 1,2-butanediol and 1,3-butanediol at 250 MPa pressure (Fig. 6.2), all the simulations were in the Newtonian regime. For these cases, a horizontal line was fit through the data set to get an estimate of the zero shear viscosity. In all the cases the data were weighted by the magnitude of the error bars. The standard deviation on the fitting parameter is noted as the estimate of the standard error on the viscosity.

The consistency of the estimates of individual shear rates is cross-checked using the so-called time-temperature superposition method \[16\], a method often used with polymers to obtain the shear dependent viscosity. This method has subsequently been applied to linear and branched alkanes \[12, 126\]. The method is
Figure 6.2. The shear viscosities as a function of shear rate for all five systems. Circles, triangles, diamonds, and squares are used to represent 0.1, 25, 100, and 250 MPa, respectively.
normally applied to scale the viscosities at different temperatures to one temperature. As the effect of changing temperature or changing pressure is mostly on the change of density of the system, we can apply the method to scale the viscosity at different pressures to one pressure, here scaling data at 0.1, 25 and 250 MPa to 100 MPa (Fig. 6.4). A master curve is obtained at any desired pressure in two steps [16]: (1) the curve at pressure $P$ is shifted vertically by $\log[\eta_0(P_0)/\eta_0(P)]$; and (2) the resulting curve is then shifted horizontally such that the two curves superpose. As shown later, the data sets at both pressures fall right on top of each other, giving us an indication that both sets are consistent.

6.5 Results and Discussion

6.5.1 Viscosity Prediction

Densities at different state points computed from the $NPT$ MC simulations are given in Table 6.5. Where comparison to experiment was available, the simulations were able to reproduce the relative order of the densities and the experimental values within 2% or better. It is these computed values that were used to run our constant density ($NVT$) molecular dynamics simulations.

The results for all five systems at four different state points along with comparison to experimental values [59] are summarized in Table 6.6 and also in Fig. 6.2. The fitted parameters for Eq. 5.19 are also summarized in Table 6.7. Since the goal of this study was to estimate the zero-shear viscosities, simulations were mainly run in the Newtonian regime. As a result, there were insufficient data in the non-Newtonian regime for aforementioned systems to use a Carreau fit. For the other systems, however, a Carreau fit was performed on the data.

Compared to the experimental data for the Newtonian viscosities at low pres-
TABLE 6.5

Liquid densities (g/mL) for the TraPPE-UA forcefield computed from NPT MC simulations at 373 K. Subscripts indicate the statistical uncertainties in the final digit. For comparison, the experimental values at 373 K and 0.1 MPa for 1,2-butanediol, 1,3-butanediol, and 1,4-butanediol are 0.942, 0.949, and 0.967 g/mL, respectively [191].

<table>
<thead>
<tr>
<th>molecule</th>
<th>0.1 MPa</th>
<th>25 MPa</th>
<th>100 MPa</th>
<th>250 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-butanediol</td>
<td>0.926₁</td>
<td>0.949₂</td>
<td>0.995₁</td>
<td>1.052₁</td>
</tr>
<tr>
<td>1,3-butanediol</td>
<td>0.961₁</td>
<td>0.974₂</td>
<td>1.007₃</td>
<td>1.059₂</td>
</tr>
<tr>
<td>1,4-butanediol</td>
<td>0.963₃</td>
<td>0.976₂</td>
<td>1.010₂</td>
<td>1.057₃</td>
</tr>
<tr>
<td>2-methyl-1,3-propanediol</td>
<td>0.961₁</td>
<td>0.975₁</td>
<td>1.011₁</td>
<td>1.056₁</td>
</tr>
<tr>
<td>1,2,4-butanetriol</td>
<td>1.127₁</td>
<td>1.142₂</td>
<td>1.176₂</td>
<td>1.204₃</td>
</tr>
</tbody>
</table>
TABLE 6.6
Viscosities (cP) for the TraPPE-UA forcefield computed from molecular dynamics simulations at 373 K and comparison to available experimental data [59]. Subscripts indicate the statistical uncertainties in the final digit(s).
“μ/μs” are the mean unsigned and mean signed percent errors in viscosity, respectively.

<table>
<thead>
<tr>
<th>molecule</th>
<th>0.1 MPa</th>
<th>25 MPa</th>
<th>100 MPa</th>
<th>250 MPa</th>
<th>$\alpha P(\times 10^3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-butanediol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sim</td>
<td>2.327</td>
<td>3.2211</td>
<td>5.3215</td>
<td>9.5354</td>
<td>5.77</td>
</tr>
<tr>
<td>expt</td>
<td>2.437</td>
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<td>4.7</td>
<td>10.43</td>
<td>5.60</td>
</tr>
<tr>
<td>μ/μs $^b$</td>
<td>9/3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-butanediol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sim</td>
<td>5.4133</td>
<td>6.8618</td>
<td>9.0041</td>
<td>15.111</td>
<td>3.78</td>
</tr>
<tr>
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<td>6.8</td>
<td>14.64</td>
<td>5.29</td>
</tr>
<tr>
<td>μ/μs</td>
<td>34/34</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,4-butanediol</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>4.2911</td>
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</tr>
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</tr>
<tr>
<td>μ/μs $^c$</td>
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<td></td>
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<tr>
<td>2-methyl-1,3 propanediol</td>
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<td>10.0714</td>
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<td>5.33</td>
</tr>
<tr>
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<td>21.87</td>
<td>5.67</td>
</tr>
<tr>
<td>μ/μs</td>
<td>16/4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,4-butanetriol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sim</td>
<td>18.6668</td>
<td>17.613</td>
<td>26.3565</td>
<td>51.617</td>
<td>4.25</td>
</tr>
<tr>
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<td>17.15</td>
<td>19.4</td>
<td>27.7</td>
<td>52.816</td>
<td>4.44</td>
</tr>
<tr>
<td>μ/μs</td>
<td>6/−2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>molecule</td>
<td>$\eta_0$ (cP)</td>
<td>0.1 MPa</td>
<td>25 MPa</td>
<td>100 MPa</td>
<td>250 MPa</td>
</tr>
<tr>
<td>------------------------------</td>
<td>---------------</td>
<td>---------</td>
<td>--------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>1,2-butanediol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\eta_0$ (cP)</td>
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<td>3.22</td>
<td>5.32</td>
<td>9.53</td>
<td></td>
</tr>
<tr>
<td>$\lambda$ (ps)</td>
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<td>146.73</td>
<td>141.90</td>
<td>N/A$^a$</td>
<td></td>
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ure (0.1 MPa) reported by Gordon et al. [59] for these five polyhydric alcohols, the TraPPE forcefield underpredicts the viscosities of 1,2- and 1,4-butanediol by 5 and 14%, respectively, overestimates those of 2-methyl-1,3-propanediol and 1,2,4-butaneetriol by 15 and 9%, respectively, and substantially overestimates that of 1,3-butanediol by 43%. As a consequence of the overprediction of the viscosity for 1,3-butanediol, the simulated viscosities for the three butanediol isomers increase from 1,2-butanediol to 1,4-butanediol to 1,3-butanediol. In contrast, the experimental viscosities at 373 K and 0.1 MPa order as follows: 1,2-, 1,3-, and 1,4-butanediol. However, it should be noted that the experimental measurements by Sun et al. [191] show that for temperatures lower than about 320 K, 1,3-butanediol does have a higher viscosity than 1,4-butanediol. As temperature increases, the viscosity of 1,3-butanediol falls below that of 1,4-butanediol.

Compared to the experimental data for the Newtonian viscosities at high pressure (250 MPa) reported by Gordon et al. [59] for these five polyhydric alcohols, the TraPPE-UA forcefield underpredicts the viscosities of 1,2-butanediol and 1,2,4-butaneetriol by 8 and 2%, respectively, overestimates those of 1,3-butanediol and 1,4-butanediol by 4 and 10%, respectively, and substantially underestimates that of 2-methyl-1,3-propanediol by 23%. However, as the predicted viscosity increase with pressure is underestimated for 1,3-butanediol and overestimated for 1,4-butanediol, the order of the predicted viscosities for five polyhydric alcohols at 250 MPa agrees with the experimental data.

Compared to the experimental data at all four pressures (0.1, 25, 100, and 250 MPa), the TraPPE forcefield yields mean unsigned and mean signed percent errors (averaged over the five polyhydric alcohols) of 16 and 6%, respectively.

Fig. 6.3 shows the viscosity as a function of pressure obtained from the simula-
Figure 6.3. Comparison of experimental (open symbols and lines) and simulated (filled symbols) viscosities as a function of pressure at 373 K. Black, red, green, blue, and orange are used to represent 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, and 1,2,4-butanetriol, respectively.

tions and experiments. From this plot, it is apparent that the simulations capture the viscosity trends quantitatively. The pressure dependence of the viscosity is often modeled with the Barus equations [62, 188], given by

$$\eta(P) = \eta_0 \exp \alpha_P P$$  \hspace{1cm} (6.2)

where $\alpha_P$ is the Barus coefficient. The results follow this equation very well. Table 6.6 shows a comparison of the Barus coefficient obtained from experiments and simulations, weighted by the standard error. Although the predicted $\alpha_P$ for 1,2-butanediol, 2-methyl-1,3-propanediol, and 1,2,4-butanetriol agree very well with
the experimental data of Gordon et al. [59] (the percent errors are +3, −6, and −4%, respectively), $\alpha_P$ for 1,3-butanediol is underestimated by 28% and that for 1,4-butanediol is overestimated by 35%. Nevertheless, the overall agreement is comparable or better than previous simulation data for linear and branched alkanes [93, 125, 142].

The four sets of viscosities at four different pressures were then scaled to $P = 100$ MPa using a method very similar to time-temperature superpositioning, described earlier. The results of this scaling are summarized in Fig. 6.4. As can be seen from the plot the scaling confirms that all four sets of viscosities are consistent to each other. We also fit the scaled data sets to a Carreau fit as described before. This fit can be used as the universal curve for those particular diols and triols. These scaled viscosities are in good agreement with the viscosities estimated using individual sets.

6.5.2 Molecular-level Analysis of Relative Viscosities

To help explain the relative orders of viscosities molecular moments of inertia and the hydrogen bond structure of the liquids at $T = 373$ K and $P = 0.1$ and 250 MPa were analyzed by our collaborators. Intermolecular oxygen-oxygen and oxygen-hydroxyl hydrogen radial distribution functions (RDFs) from this analysis and their corresponding number integrals were also analyzed. And the figures and tables concerning this can be found in the publication [89]. Here we will summarize their findings. Some of the general features of the RDFs are shared between all of the polyhydric alcohols studied. The oxygen-oxygen RDFs show their first maximum at 2.7 Å and first minimum at 3.6 Å while the oxygen-hydrogen RDFs show a maximum and minimum at 1.8 and 2.6 Å, respectively. The position
Figure 6.4. Superposition of the data sets at 0.1, 25, and 250 MPa onto the data set at 100 MPa. The Carreau fit (Eq. 5.19) is given by the dashed lines for respective sets. Colors as in Fig. 6.3.
and shape of the second and further peaks in each of the RDFs vary much more but this is most directly a consequence of the each alcohol having at least two hydroxyl groups but at different positions along the backbone of the molecule, i.e. the second and/or third nearest neighbor peaks may correspond to the same molecule as the first.

The effect of increasing pressure on liquid structure is also of interest. The plots indicate that there are no substantial changes in liquid structure upon increasing pressure. There is a slight decrease in the height of the first peak of all the RDFs at 250 MPa, but this is a consequence of the normalization to a uniform distribution and not to a decrease in hydrogen bonding [165]. For 1,2-butandiol and 1,2,4-butanetriol large peaks are observed in the RDFs centered at 2.9 Å for the oxygen-oxygen pairs and 2.6 Å for the oxygen-hydrogen pairs which is an indication of intramolecular hydrogen bonding. The other alcohols showed only small peaks corresponding to intramolecular hydrogen bonding.

The distributions of hydrogen bond energies showed that 1,4-butanediol and 2-methyl-1,3-propanediol have slightly stronger hydrogen bonds than the rest of the alcohols while 1,2-butandiol appeared to have the weakest. This suggests that hydroxyl groups on the chain ends can form stronger hydrogen bonds because there is less steric hindrance. In all cases, the minimum in these distributions appeared to be at about $-10 \text{ kJ/mol}$. A substantial change in the energy distribution upon change in pressure was not observed.

Based on the RDFs, the following simple criteria for a hydrogen bond was chosen: An oxygen-oxygen distance less than 3.6 Å and oxygen-hydrogen distance less than 2.6 Å. Since each hydrogen may only participate in one hydrogen bond, when there were two possible acceptor oxygens that satisfy the above criteria only
the one closest to the donor hydrogen was counted. The average number of hydrogen bonds per molecule was calculated from NPT MC simulations using the above criteria. Of the four diols, 1,4-butanediol formed the most intermolecular hydrogen bonds while 1,2-butanediol formed the least. It was also observed that intramolecular hydrogen bonding was more important for 1,2-butanediol and 1,2,4-butanetriol than for the other alcohols. However, even for these two alcohols, intramolecular hydrogen bonds accounted for no more than 3% of the total hydrogen bonds in a molecule.

The size distribution of hydrogen bonded clusters could also have an impact on the viscosity of the alcohols. These distributions at the lowest and highest were pressures examined. From these it was observed that at 0.1 MPa 1,2-butanediol had the sharpest distribution of clusters with the smallest cluster size (5) at its maximum. 1,3-butanediol, 1,4-butanediol, and 2-methyl-1,3-butanediol had a much broader distributions with maxima around 25. However, these diols still have a significant probability of smaller cluster sizes. 1,2,4-butanetriol had the widest distribution, a maximum at around 50, and the lowest probability of smaller clusters. Upon increasing pressure, the position of the maximum shifted to larger cluster sizes in all systems. Additionally, the shape of the distribution changed. The probability of smaller clusters decreased while the probability of larger clusters increased.

To better understand the shapes of molecules and how this relates to viscosity, the distribution of the principal moments of inertia and their average ratios were computed. The ratios of moments of inertia indicated that all molecules have cylindrical like shapes. However, 1,4-butanediol was the most elongated followed by 1,3-butanediol. 1,2-butanediol was the least elongated. The distribution of
the moments of inertia was the broadest for 1,4-butanediol and 1,2,4-butanetriol and the narrowest for 1,3-butanediol. The narrow distribution for 1,3-butanediol indicated that one conformer was predominantly present in its liquid phase. The principle moments of inertia for all five polyhydric alcohols showed little dependence on pressure. Thus, the conformational distributions were affected little by pressure.

Having presented some aspects of liquid structure, we now discuss possible explanations for the relative order of the viscosities that were computed. At all pressures, 1,2-butanediol has the lowest viscosity. This correlates well with the density, the number of hydrogen bonds this molecule forms, and the position of the maximum in the aggregate size distribution, which are all also the lowest among the five molecules. On the other side, 1,2,4-butanetriol has the highest viscosity, the most hydrogen bonds, the largest aggregate sizes and the highest density.

In the middle, the trends are not as clear. For example, 1,4-butanediol has more hydrogen bonds per molecule than both 1,3-butanediol and 2-methyl-1,3-propanediol, yet a lower viscosity. These three molecules have very similar densities and aggregate size distributions so these cannot be used to explain the differences. The ratios of the moments of inertia clearly indicated that 1,4-butanediol was the most linear of the three molecules. Additionally, the distributions of the moments of inertia for 1,4-butanediol were much broader than both 1,3-butanediol and 2-methyl-1,3-propanediol. Together the more elongated shape and higher flexibility of 1,4-butanediol should reduce the barrier for diffusive processes, and indeed it has a lower viscosity than the other two isomers at all pressures.

With that said, perhaps the reason for the overestimation of the viscosity of 1,3-butanediol compared to experiment is a torsional potential with unrealistically
high barrier heights. It is worthy to note that these barrier heights should not affect the vapor-liquid equilibria, however, the position and height of the minima in the torsional potential have a much greater influence on the viscosity of the system. Since the vapor-liquid equilibria of 1,3-butanediol was predicted quantitatively, this suggests that the intermolecular interactions and conformational distributions are well modeled and that the source for error in the viscosity calculation is not the non-bonded terms in the forcefield, but possibly the barrier heights in one or more of the torsional potentials that were unique to this molecule.

6.5.3 Vapor-Liquid Phase Equilibria

The normal boiling points and critical properties were obtained for the TraPPE-UA model. A good agreement with the experiments was observed. As the simulations described in this section were undertaken by our collaborators we will just provide the findings of these simulations. However, one can refer to the detailed explanation in our publication [89]. Normal boiling points were reproduced within 2%, critical temperatures within 1%, critical densities within 5%, and critical pressures within 20%. Despite that the values were closely spaced between the different alcohols, the relative order of all of them except for the critical pressure, was faithfully reproduced. In general, it was found that the forcefield tends to slightly underestimate boiling and critical temperatures and overestimate critical densities and pressures.

Vapor-liquid coexistence curves, Clausius-Clapeyron plots, and heats of vaporization for TraPPE-UA forcefield were also analyzed. The Clausius-Clapeyron plots and heats of vaporization showed excellent qualitative agreement with experiment in that the relative experimental orders of \( \ln p \) and \( \Delta H_{\text{vap}} \) were reproduced.
over a wide temperature range. However, a small tendency of the TraPPE model to overestimate the pressure and underestimate the enthalpy was observed.

Using the hydrogen bond criteria outlined above, for consistency, the number of hydrogen bonds per molecule in the liquid phase at each of temperatures simulated were computed. From this a good correlation between the number of hydrogen bonds and the liquid to vapor thermodynamics for the isomeric butanediols was seen. For a given system the number of hydrogen bonds in the liquid phase decreased with increasing temperature as did the enthalpies of vaporization. At a given temperature the liquid with the largest number of hydrogen bonds had the highest enthalpy and entropy of vaporization. And, finally, for two compounds with similar heats of vaporization at different temperatures the one with the higher entropy of vaporization had more hydrogen bonds.

6.6 Conclusions

Nonequilibrium molecular dynamics and equilibrium Monte Carlo simulations were employed to predict the Newtonian viscosities and vapor-liquid coexistence curves for five polyhydric butanediol isomers. All forcefield parameters were taken from the literature and none of these parameters had been fit to experimental data on viscosity or on the compounds in this study. For pressures ranging from 0.1 to 250 MPa, the mean unsigned error of the predicted viscosities was 9% for 1,2-butanediol, 34% for 1,3-butanediol, 14% for 1,4-butanediol, 16% for 2-methyl-1,3-propanediol, and 6% for 1,2,4-butanetriol. Thus, the predictions for all polyhydric alcohols but 1,3-butanediol are rather satisfactory. Both qualitative and quantitative agreement with experiment was observed for the predicted vapor-liquid equilibria. The correct trends were obtained for vapor-liquid coexistence
curve but not for the viscosities. This could be explained from the previous studies [145] which suggest that the torsional potential affects the viscosity more than it affects vapor-liquid coexistence curve. The predicted orders of both boiling points and critical temperature agreed with experiment and their values were within 2 and 1%, respectively. Furthermore, a structural analysis allows one to rationalize the relative order of the viscosities and vapor-liquid coexistence curves. The results demonstrate the predictive power of the methods used in this study, the transferability of the TraPPE forcefield to both multiple properties and state points, and the usefulness of simulation for explaining bulk properties with molecular-level observations.

As mentioned earlier, this study was our entry to the 3rd Industrial Fluid Properties Collective challenge. We were in good agreement with the experimental data at lower pressure but the agreement with the experiments was not good when our 25 MPa results were compared to 250 MPa experimental results. Hence, we did not win the competition, instead we finished as Runner-up award winners, but the silver lining was that the molecular level analysis that we had carried out, won us the Best in Show award.
CHAPTER 7

EFFECT OF TEMPERATURE AND WATER CONTENT ON THE SHEAR VISCOSITY OF THE IONIC LIQUID 1-ETHYL-3-METHYLIMIDAZOLIUM BIS(TRIFLUOROMETHANESULFONYL)IMIDE

When there is a hard problem, one has to work a long time and has to be persistent. In order to be persistent, you have got to be convinced that it’s worthwhile working so hard, that you’re going to get somewhere. And that takes a certain kind of fooling yourself.

.. Richard P. Feynman

7.1 Introduction

As for other industrial solvents and processes, viscosity is a key physical property of ILs. When used as a solvent, a low viscosity is generally desired to minimize pumping costs and increase mass transfer rates. For other applications such as lubrication or use in membranes, higher viscosities may be favorable. As alluded to earlier in Chapter 2, it is known that the viscosity of ILs varies widely depending on the type of cation and anion. While typical organic solvents may exhibit viscosities ranging from 0.2 to 10 cP, ILs can have variations in room temperature viscosities that span several orders of magnitude [184]. Like conventional liquids,
the viscosity of ionic liquids is a strong function of temperature, although deviations from classical Arrhenius behavior consistent with glass forming materials is typically observed [17, 222], as discussed in Chapter 2. It is also known that small amounts of impurities such as water and halides can dramatically change the viscosity of ILs [177, 216]. In fact, much of the discrepancies in experimental viscosity measurements are thought to be due to varying amounts of impurities among the different samples. To develop ILs that are optimized for a given application, it is therefore important to know how the viscosity depends on the type of ion, water content and thermodynamic state point.

Atomistic simulations have proven useful in helping develop an understanding of the link between the physical properties of a fluid and its structure and composition [6]. As discussed in Chapter 2, this is no different in the case of ILs, where state-of-the-art simulations have been carried out concurrently with experimental measurements to determine several thermodynamic and transport properties. Up to this point, there have only been a handful of simulation studies conducted in which the viscosity of an IL has been computed (see Chapter 2).

In addition to variations in computed viscosities due to differences in the force-field, as mentioned in Chapter 2, it may also be that the accuracy of a viscosity calculation depends on how the calculation is carried out. Even though, all methods in principle, should give us the same value for the viscosity, the efficiency and accuracy of them vary based on the quantities they need to compute. Aside from the work of Micaelo et al. [133] and Yan et al. [223], all previous IL viscosity calculations have relied on equilibrium methods. Of these calculations, the ones that tended to overestimate the viscosity the most were the ones that relied on the integration of autocorrelation functions in either momentum or stress. While
these methods are formally correct for computing the viscosity, from a practical standpoint the integrals involved are notoriously difficult to compute numerically. The initial decay of the stress-stress time correlation function is rapid but then it decays very slowly, oscillating about zero for a long time. These long time fluctuations are often of the same size as the random noise in the stress tensor. However, since the dynamic behavior of ILs is so sluggish, this long time behavior must be accurately integrated to get a reliable viscosity. For example, in the work of Bhargava and Balasubramanian [15], the relevant correlation function exhibited strong short-time oscillations and decayed to nearly zero after only 3 ps. However, Bhargava and Balasubramanian had to integrate the stress-stress time correlation function out to 500 ps to obtain a converged estimate of the viscosity. Similar problems arise when integrating momentum correlation functions. This calls into question whether it is possible to get the true global viscosity from simulations in which the equilibrium fluctuations in stress or momentum are used to compute the viscosity. These equilibrium fluctuations decay on time scales orders of magnitude faster than the long rotational and translational relaxation times that are responsible for momentum transfer, and thus they may be probing only local viscosities. On the other hand, nonequilibrium simulations such as those used by Micaelo et al. probe the long time steady state response of the system to an external perturbation. This response can be averaged over for time scales longer than any other dynamical time scale in the system, and thus may provide a better means for calculating the viscosity of the ILs. We note that the Einstein approach used by Borodin and Smith [19] also enables long-time behavior to be tracked. Indeed, in our previous work with alkanes [91–93], we found that nonequilibrium techniques provided a more robust and reliable means for computing viscosities.
than did equilibrium Green-Kubo methods. As will be shown later, the use of nonequilibrium simulations enables diffusive behavior to be observed on simulation time scales, while equilibrium simulations for greater than 2 ns are still in the sub-diffusive regime for the IL investigated in this work. Also, as was seen from previous chapter, the recently developed RNEMD method [140] can be used to compute the viscosity of a system accurately and efficiently. It is for this reason, we have chosen to use a nonequilibrium molecular dynamics method, RNEMD, to compute the viscosity in the work explained in this chapter.

In this chapter we report the results of a series of equilibrium and nonequilibrium MD simulations of $[\text{emim}]^+[Tf_2N]^−$. We compute the viscosity and volumetric properties of this IL as a function of temperature and the water composition. The complete study has been published in reference [88]. This IL was chosen because the interest in ILs based on imidazolium cations and bistriptylamide anions. They have high thermal stability and are easy to synthesize. Bonhôte [47] finds them one of the most interesting ILs as it has high electrochemical window (greater than 4V) and is stable in air at temperatures in excess of 400°C, which makes it a promising candidate for applications like photovoltaic cells and electrochromic devices. It also has potential applications in the lithium ion batteries reducing the safety risks posed by the conventional solvents [48]. Moreover, this IL is one of the smallest or simplest $[Tf_2N]^−$ based ILs and has a relatively low viscosity. Also a significant amount of experimental data exists against which the simulation results can be compared. In addition, forcefields have been developed for both the cation and anion that accurately reproduce thermodynamic properties. Details of the calculation procedure are provided in the next section, followed by a discussion of the results and a brief summary.
7.2 Simulation Method and Details

As described in the previous chapter, RNEMD is an efficient and accurate method to compute the viscosity. And we also have validated the RNEMD method and our code by computing the viscosity of several test systems for which literature data are available [89]. These include argon, n-hexane, water, molten sodium chloride and five polyhydric alcohols. These systems were chosen because they represent widely used model types and their viscosities have either already been determined or they can be computed accurately using conventional simulation techniques. They thus provide a rigorous test of the RNEMD method. The details of this method are given in Chapter 4 and the benchmarks or validation simulations are discussed in the previous chapter (i.e. Chapter 6).

An extensive body of prior work [64, 108, 109, 117, 136, 137, 220] has shown that ILs can be modeled accurately with a forcefield having the a functional form given by Eq. 3.16 in Chapter 4. The forcefield parameters for the [emim]+ cation were taken from the work of Cadena and Maginn [24, 26] while those for the [Tf2N]− anion were taken from the work of Lopes and Pádua [110]. The forcefield parameters for water correspond to the modified TIP3P model given in CHARMM forcefield, and were taken directly from the work of Price and Brooks [159]. Intramolecular non-bonded energies were neglected for atoms separated by fewer than three bonds and were scaled by 50% for atoms separated by exactly three bonds. For all other cases, full interactions were used. Note that this is the convention used by Lopes and Pádua for the [Tf2N]− anion, but a slightly different exclusion scaling was used by Cadena and Maginn for the cation. Using energy minimization, we verified that the exclusion rule used in the present work had a negligible effect on cation structures, and so decided to use the same
exclusion rule for both cation and anion. Lorentz-Berthelot combining rules were used to compute the cross interactions. A complete list of forcefield parameters are summarized in the Tables 7.1, 7.2, 7.3, 7.4, and 7.5. They can also be found in the Supporting Information of our publication [88].

### TABLE 7.1
LJ parameters (σ and ε) and the charges for [emim]+, [Tf2N]− and Water.

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**Water \([H_2O]\)**

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**TABLE 7.2**

**Equilibrium bond distances** \((r_0)\) **and bond force constants** \((k_b)\) **for** \([\text{emim}]^+\), \([\text{Tf}_2\text{N}]^-\) **and** \(\text{Water}\).

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<th>(r_0) ((\text{Å}))</th>
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### TABLE 7.2

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### TABLE 7.3

**Equilibrium angle values ($\theta_0$) and angle force constants ($k_\theta$)**


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TABLE 7.3

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### TABLE 7.3

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TABLE 7.4

Dihedral parameters in the CHARMm form for $[\text{emim}]^+$, $[\text{Tf}_2\text{N}]^-$ and Water.

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Water [H2O]

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Anion $[Tf_2N]^{-}$

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<tbody>
<tr>
<td>FTF2 - CTF2 - STF2 - OTF2</td>
<td>0.1734</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>STF2 - NTF2 - STF2 - OTF2</td>
<td>-0.0018</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>FTF2 - CTF2 - STF2 - NTF2</td>
<td>0.1580</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>STF2 - NTF2 - STF2 - CTF2</td>
<td>7.8329</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>STF2 - NTF2 - STF2 - CTF2</td>
<td>-2.4904</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>STF2 - NTF2 - STF2 - CTF2</td>
<td>-0.7636</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>
TABLE 7.5

EQUILIBRIUM IMPROPER ANGLE ($\psi_0$) AND IMPROPER ANGLE FORCE CONSTANTS ($k_\psi$) FOR [emim]$^+$, [Tf$_2$N] $^-$ AND Water.

<table>
<thead>
<tr>
<th>At Type - At Type - At Type - At Type</th>
<th>$k_\psi$ (kcal/mol $-\text{rad}^2$)</th>
<th>$\psi_0$ (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation [emim]$^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CPH2 - NR1 - NR1 - HR1</td>
<td>0.50</td>
<td>0.00</td>
</tr>
<tr>
<td>NR1 - CPH1 - CPH2 - CN7B</td>
<td>0.60</td>
<td>0.00</td>
</tr>
<tr>
<td>CPH1 - CPH1 - NR1 - HR3</td>
<td>0.50</td>
<td>0.00</td>
</tr>
<tr>
<td>Water [H2O]</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>Anion [Tf$_2$N]$^-$</td>
<td></td>
<td>N/A</td>
</tr>
</tbody>
</table>

A switching function of the form of Eq. 3.17 is used to truncate the Lennard-Jones interactions and force them to be exactly zero at the cut-off for the equilibration calculations. In this study, a cut-off distance ($r_c$) of 14 Å and an onset distance ($r_s$) of 12.5 Å were used. Electrostatic interactions were computed with the particle-mesh Ewald algorithm [41] with real space cut-off distance of 14 Å. For production runs, instead of a switching function, the potential was cut-off at 14 Å and long range corrections were used.
7.2.1 State Points and System Size

For the pure ionic liquid calculations, a system of 200 ion pairs of \( [\text{emim}]^+ -[Tf_2N]^− \) was studied at five different temperatures: \( T = 293, 313, 343, 400, 500 \) K. The effect of water content on the viscosity of this IL was explored by carrying out simulations at three different water concentrations at \( T = 293 \) K. Water contents of 460.4 ppm (by mass), 4604 ppm and 13811 ppm were considered. This translates into 2, 20 and 60 water molecules in the system containing 200 pairs of \( [\text{emim}]^+ [Tf_2N]^− \), respectively. Note that the highest water concentration is at the experimental saturation limit.

The simulation boxes for all runs were orthogonal with an aspect ratio (AR) of 3.0, i.e. \( L_y/L_x = L_y/L_z = 3.0 \). For the RNEMD calculations, the box was divided into 14 bins along its long axis and the average velocity within each bin was used to determine the velocity profile. A reversible multiple timestepping algorithm, r-RESPA [201] was used with inner timestep \( (\delta) \) of 0.5 fs and an outer timestep \( (\tau) \) of 2.0 fs. A four chain Nosé-Hoover thermostat [122] was used to control the temperature.

The first step in predicting the viscosities of the IL as a function of temperature and water composition was to compute liquid densities at the state point under consideration. For this purpose, molecular dynamics simulation runs of 2 ns were carried out in the isothermal-isobaric (NPT) ensemble using the program NAMD [156]. The average densities from these simulations are compared with experimental densities in Table 7.6.

Computed densities are systematically higher than the experimental values, but the agreement is within 2% at all temperatures. Using the computed densities, additional equilibration runs ranging from 1–4 ns were carried out in the canonical
**TABLE 7.6**

Computed liquid densities at different temperatures compared with experimental data [46].

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\rho_{exp}$ (g/cm$^3$)</th>
<th>$\rho_{sim}$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>1.5257</td>
<td>1.5536</td>
</tr>
<tr>
<td>313</td>
<td>1.5064</td>
<td>1.5177</td>
</tr>
<tr>
<td>343</td>
<td>1.4775</td>
<td>1.4868</td>
</tr>
<tr>
<td>400</td>
<td>1.4228</td>
<td>1.4422</td>
</tr>
<tr>
<td>450</td>
<td>1.3746</td>
<td>1.3905</td>
</tr>
<tr>
<td>500</td>
<td>1.3264</td>
<td>1.3418</td>
</tr>
</tbody>
</table>
(NVT) ensemble at all the state points. These equilibrated conformations were then used as initial configurations for the RNEMD simulations, which were run at constant density and temperature using a locally developed code.

7.2.2 Data Analysis

As mentioned in the previous chapter, a typical result of a RNEMD run is a velocity profile and an estimate of the shear viscosity as a function of time. Fig. 7.1 shows a typical result when the algorithm is applied to an IL system. The slope of the two velocity profiles combined with the known momentum exchange rate gives an estimate of the viscosity via Eqs. 2.12 and 4.22. Production runs using different momentum exchange frequencies were conducted until the viscosity estimate oscillated about a steady state value, as shown in Fig. 7.1(b). Note that the velocity of each bin along the profile was obtained by averaging over all atomic velocities in the bin every $10 \tau$, discarding the first 0.2 ns of the RNEMD run. The velocity profiles were then fit to the average bin velocities using a least squares procedure. The uncertainty of each shear viscosity was taken as the standard error of the fit.

In our previous use of the RNEMD method on simple fluids like alkanes, water and alcohols [89], velocity profiles were mostly linear, which enabled straightforward estimation on the shear-dependent viscosity at each shear rate. To obtain the Newtonian shear viscosity, the individual shear viscosities were fit to a Carreau model of the form given in Eq. 5.19. As the shear rate approaches zero, the shear viscosity plateaus to $\eta_0$, the Newtonian viscosity. This is the value that can be compared to experimental shear viscosities. At very high shear rates the viscosity decreases, showing a non-linear or shear-thinning response to the imposed
Figure 7.1. (a) Converged velocity profiles obtained from RNEMD simulations of $[\text{emim}]^+[T_{f2}N]^-$ at 293 K and momentum exchange rates of $(20\tau)^{-1}$ and $(22\tau)^{-1}$. (b) The time evolution of the viscosity for the simulations in (a). Note that the estimated shear viscosity differs for the two cases, because at these momentum exchange rates the system is in the non-Newtonian (shear thinning) regime.
shear rate. The apparent viscosity exhibits a power-law behavior where $\eta \propto \dot{\gamma}^{-2p}$.
The parameter $\lambda$ is a characteristic time constant, which has been found to be approximately equal to the inverse of the shear rate at which shear thinning behavior begins. Many previous studies have found that $\lambda$ roughly corresponds to the inverse of the rotational relaxation time $(\tau_{\text{rot}})^{-1}$ of the molecule. This makes physical sense, since at shear rates higher than $(\tau_{\text{rot}})^{-1}$ the molecules cannot orientationally relax in response to the flow field, thereby resulting in nonequilibrium conformations. When $\dot{\gamma} \ll (\tau_{\text{rot}})^{-1}$, the molecules are free to adopt equilibrium conformations and linear response behavior is expected.

The difficulty in applying Eq. 5.19 to ionic liquids is that, to obtain a reliable fit to the model, several simulations must be conducted at shear rates less than $(\tau_{\text{rot}})^{-1}$. Unfortunately, the rotational relaxation times for the ILs tend to be very long, especially at low temperatures. This translates to the need to use prohibitively small shear rates to access the Newtonian region of the ILs.

Mode coupling theory [57] is an alternative extrapolation procedure that has been used widely for simple fluids. In this approach, the shear viscosity is assumed to obey the following relation

$$\eta(\dot{\gamma}) = \eta_{\text{mc}}(0) - A\dot{\gamma}^\beta$$

where $\beta = 1/2$, $A$ is a constant and $\eta_{\text{mc}}(0)$ is the mode coupling estimate of the Newtonian viscosity. It has been found in several recent simulation studies [20, 199], however, that while the viscosity does obey mode coupling behavior at high shear rates, below a critical crossover shear rate the computed viscosity deviates from simple mode coupling theory. In fact, it was observed that at the lowest shear rates the viscosity flattens out and becomes independent of shear.
rate, as it must in the Newtonian regime. The lowest shear rate results could thus be fit with a short horizontal line [20] on a plot of shear viscosity versus $(\dot{\gamma})^{0.5}$, while at higher shear rates the viscosity could be adequately modeled using Eq 7.1. Therefore, the viscosity estimated using Eq. 7.1 will tend to overestimate the Newtonian viscosity.

In the spirit of these findings, the following approach was used to estimate the viscosities of the ILs. A series of simulations at relatively high shear rates were conducted. At these shear rates, the signal-to-noise ratio was good and the resulting shear-dependent viscosities were fit very accurately to Eq. 7.1. The crossover shear rate $\dot{\gamma}_c$ was estimated as the inverse of the rotational relaxation time of the cation (as cations tend to have slower dynamics), $(\tau_{\text{rot}})^{-1}$, which was obtained from equilibrium molecular dynamics simulations as described below. It was assumed that at shear rates below $\dot{\gamma}_c$ the system would be in the Newtonian regime, such that the the shear viscosity could be estimated as

$$\eta(0) = \eta_{mc}(0) - A\dot{\gamma}_c^{0.5}$$ (7.2)

We have verified that Eq. 7.2 gives quantitative agreement with the viscosity calculated for short $n$-alkanes using accepted equilibrium simulation techniques as well as Carreau model extrapolations of nonequilibrium simulations. Thus it is superior to standard mode coupling theory extrapolations and is expected to give a good estimate of the viscosities for the ILs.

Using the assumption that $\dot{\gamma}_c \approx (\tau_{\text{rot}})^{-1}$, the rotational relaxation time at each temperature and water content was determined by computing the end-to-end vector rotational relaxation time of the cation during an equilibrium molecular dynamics simulation. To do this, the correlation function in Eq. 5.15 was computed.
The time dependence of $C(t)$ was fit using two stretched exponentials of the form

$$C(t) = a \exp \left[ \left( \frac{-t}{\tau_0} \right)^\beta \right]$$

(7.3)

where $a$ and $\tau_0$ are fitting parameters. The relaxation behavior was accurately fit in this manner, as demonstrated by Fig. 7.2. The rotational relaxation time, $\tau_{\text{rot}}$, was then computed numerically from

$$\tau_{\text{rot}} = \int_0^\infty C(t) dt$$

(7.4)

Table 7.7 summarizes the rotational relaxation times computed in this manner. As can be observed, these relaxation times increase dramatically as the temperature decreases, approaching the total length of the simulations used here. It is for this reason that the integration of correlation functions over very short time scales are likely to result in erroneous estimates of the viscosity at low temperature.

The rotational dynamics of this system at low temperature indicate that these materials have very slow dynamics, especially in comparison to the time scales accessible by MD. This is consistent with previous simulations [26, 36] and experiments [222]. To accurately determine transport properties using simulations, the liquid must show diffusive behavior. Two metrics can be used to determine whether or not a simulation has reached the diffusive regime. First, a so-called non-Gaussian parameter $\alpha_2(t)$, can be computed via the following expression [164]

$$\alpha_2(t) = \frac{3 \langle |\Delta r(t)|^4 \rangle}{5 \langle |\Delta r(t)|^2 \rangle^2} - 1$$

(7.5)

where $\Delta r(t)$ is the displacement of an atom over time $t$. At short times $\alpha_2 > 0$,
Figure 7.2. Example of the fit obtained using two stretched exponentials of the form given in Eq. 7.3 to model the rotational relaxation time of the \([emim]^+\) cation at 293 K. The vertical dashed line shows the time where the first fit ends and the second fit begins.
TABLE 7.7

Rotational relaxation times for the $[\text{emim}]^+$ cation in $[\text{emim}]^+\text{[Tf}_2\text{N]}^-$ at different temperatures.

<table>
<thead>
<tr>
<th>Temperature $T$ (K)</th>
<th>Rotational Relaxation Time $\tau$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>2710</td>
</tr>
<tr>
<td>313</td>
<td>800</td>
</tr>
<tr>
<td>343</td>
<td>293</td>
</tr>
<tr>
<td>400</td>
<td>103</td>
</tr>
<tr>
<td>500</td>
<td>29</td>
</tr>
</tbody>
</table>
but as diffusive (i.e. random walk) behavior is approached, \( \alpha_2 \to 0 \). Del Pópolo and Voth [36] have shown that, even at relatively high temperatures, \([emim]^+[-NO_3]^-\) has values of \( \alpha_2 > 0 \) over hundreds of ps. The same observation has been made for other ILs [25, 26].

Another metric for assessing whether a system is in the diffusive regime or not is a linearity parameter, \( \beta(t) \), defined as

\[
\beta(t) = \frac{d \log (\Delta r^2(t))}{d \log(t)} \tag{7.6}
\]

By definition, a system is in the diffusive regime when \( \beta(t) = 1 \).

As expected, \( \alpha_2(t) \) was very slow to decay to zero, even at relatively high temperatures. Fig. 7.3 shows that during equilibrium MD simulations at 293 K and 343 K, \( \alpha_2(t) \) increases for \([emim]^+[Tf_2N]^-\) to a value greater than 0.3. After about 1 ns, \( \alpha_2(t) \) begins to drop, but the data are noisy at long times due to statistical error. This suggests that equilibrium simulations much longer than 1 ns are required to obtain transport properties. Interestingly, it was found that the imposition of the external forcing during the nonequilibrium simulations served to shorten the time required for \( \alpha_2(t) \) to begin to decay, as can be seen in Fig. 7.3.

The same type of behavior was observed with \( \beta(t) \). Fig. 7.4 (a) shows that during equilibrium MD simulations, \( \beta(t) \) very slowly approaches unity at 293 K, rising only to about 0.55 after 1 ns. This means that the system is still in the sub-diffusive regime, and that estimating a self-diffusivity by applying the Einstein relation would yield incorrect results. If one ignores this and applies the Einstein relation to the equilibrium MD results, an apparent self-diffusivity is obtained as a function of time, as shown by the dashed line in Fig. 7.4 (b). We stress that
Figure 7.3. Comparison of non-Gaussian parameter ($\alpha_2$) Eq. 7.5 at two temperatures under equilibrium conditions and under shear at $T = 293$ K. The presence of a shear causes the system to approach random walk dynamics faster than occurs during equilibrium simulations.
Figure 7.4. (a) Plot of $\beta$ as a function of time for both the system under shear as well as for the system without shear. The value of $\beta$ is calculated as an average value over all three directions for the equilibrium system, while for the system under shear, $\beta$ is the average over the “y” and “z”-directions. (b) The estimated self-diffusion coefficient versus time for the equilibrium and nonequilibrium simulations. Only the first 1 ns run is shown in the plot. The dotted line represents the experimental value of self-diffusion coefficient [146].
this apparent self-diffusivity is not a true diffusivity, because the mean squared displacement is not yet linear with respect to time. At times on the order of 10 ps, where the dynamics are strongly influenced by short time ballistic motion, the apparent self-diffusivity is actually quite close to the experimental value [146], which is given by the dotted line in Fig. 7.4 (b). As time increases, however, the apparent self-diffusivity drops well below the experimental self-diffusivity, reaching a value about an order of magnitude lower than experiment after 1 ns. This is not surprising, given that the liquid is still in the sub-diffusive regime after only 1 ns. From the trend in \( \beta(t) \), it appears that diffusive behavior will not be obtained until times much longer than 1 ns. Clearly, equilibrium MD is a very inefficient method for estimating transport properties when liquid dynamics are as slow as those observed here.

In the presence of shear, however, the dynamics are altered and the system approaches diffusive behavior much more rapidly. The solid line in Fig. 7.4 (a) shows the value of \( \beta(t) \) calculated for the directions orthogonal (“y” and “z”) to the direction of imposed shear (“x”). The self-diffusivity can only be computed for the “y” and “z”-directions because the imposed shear induces flow along the “x”-direction. After only 300 ps, \( \beta(t) \) reaches unity and fluctuates around this value for the duration of the simulation. The self-diffusivity can then be computed from

\[
\mathcal{D}_i = \frac{1}{2} (\mathcal{D}_{yy} + \mathcal{D}_{zz})
\]

where each component of the self-diffusivity tensor is given by

\[
\mathcal{D}_{ii} = \frac{1}{2} \lim_{t \to \infty} \frac{d}{dt} \langle (r_i(t) - r_i(0))^2 \rangle
\]
The computed self-diffusivity from the nonequilibrium simulations at 293 K is
\[ 1.1 \times 10^{-10} \pm 0.05 \times 10^{-10} \, \text{m}^2/\text{s} \], which is about a factor of two higher than the experimental value of \( 5.32 \times 10^{-11} \, \text{m}^2/\text{s} \). Self-diffusivities were not computed at other temperatures.

Taken together, these results suggest that the external perturbation caused by the momentum exchanges serves to break up the liquid and thereby overcome the inherent sluggish behavior that leads to sub-diffusive dynamics. At low temperatures and very small momentum exchange rates, even the nonequilibrium simulations exhibited evidence of sub-diffusive behavior over long times. In these cases, the velocity profiles along the long axis of the simulation box became non-linear. Fig. 7.5 shows the velocity profile for \([\text{emim}]^+[^2\text{F}_2\text{N}]^-\) at 293 K and a very low momentum exchange rate (compare the scale for the velocities with Fig. 7.1(a)). Near the slabs where momentum exchanges occur, there is a discontinuity in the velocity profile; the momentum changes more rapidly near the regions where exchanges are made, but does not propagate across the entire simulation box. It is likely that these velocity profiles would eventually flatten out, given sufficiently long simulations. As a practical matter, simulations which resulted in non-linear velocity profiles were not included in the viscosity calculations.

Thus, the calculation of the viscosity involves three steps. First, equilibrium molecular dynamics simulations are conducted to determine the rotational relaxation time of the cation, using Eq. 7.4. The crossover shear rate is taken as \( \dot{\gamma}_c = (\tau_{\text{rot}})^{-1} \). Next, a series of RNEMD simulations are run and the shear-dependent viscosity consistent with mode coupling theory is estimated by fitting the steady-state velocity profile to a straight line using a least squares procedure, followed by application of Eqs. 2.12 and 4.22. Finally, the Newtonian viscosity
Figure 7.5. A typical velocity profile at very low shear rates and low temperature. The discontinuity in the profile about the middle and the end bins is apparent.

is determined using Eq. 7.2. Due to the computationally intensive nature of the calculations, only one simulation was run at each shear rate for each state point. Therefore, the error associated with a given viscosity was assumed to have two components. One part arises from the uncertainty associated with the estimation of the rotational relaxation time, and the second comes from the uncertainty associated with fit to the mode coupling model. A detailed analysis of the pure [emim]⁺[Tf₂N]⁻ simulations at 293 K shows that the uncertainty in \( \tau_{rot} \) is approximately 33%. Although this can vary as a function of state point, it can be taken as the conservative estimate of the error at all the state points. The uncertainty associated with the fit to Eq. 7.1 was taken as the standard error in the estimate of the parameter \( A \), with each shear viscosity point weighted by the standard error obtained from the least squares fit to the velocity profile. To be
conservative, it was assumed that these errors were additive, such that

$$\Delta \eta = \sqrt{((\Delta \eta_r)^2 + (\Delta \eta_A)^2)}$$ (7.9)

where $\Delta \eta$ is the uncertainty in the estimate of viscosity, $\Delta \eta_r$ is the error in the viscosity due to error in the estimation of the rotational relaxation time, and $\Delta \eta_A$ is the error in viscosity due to error in the mode mode coupling theory fit.

7.3 Results and Discussion

The viscosity of pure $[\text{emim}]^+[\text{Tf}_2\text{N}]^-$ was computed at five temperatures using the RNEMD method outlined above. The results are given in Table 7.8 and are compared against a series of experimental data [17, 22, 38, 129, 146, 162, 168, 216] in Fig. 7.6. The dashed curve is a Vogel-Fulcher-Tammann (VFT) fit to the data of Noda et al. The simulations do a reasonable job matching the experimental viscosities over the entire temperature range, with a root mean squared deviation of 15%.

To study the effect of water content, the viscosity was computed at 293 K for the neat liquid as well as for mixtures with water contents of 460.4 ppm, 4604 ppm and 13811 ppm. Fig. 7.7 shows a comparison between the simulations and the experimental data of Widegren et al. [216]. The simulations capture the fact that the viscosity drops with increasing water concentration. At low water concentrations, the simulations agree very well with the experimental data. At the highest water concentrations, the experimental viscosities are somewhat lower than what is predicted by the simulations.

It has been well documented in the literature that water content has a large effect on the viscosity of ionic liquids. To see how large this effect is, the ex-
TABLE 7.8

Computed viscosities as a function of temperature for $[\text{emim}]^+[T_f_2 N]^-$.
Subscripts indicate the statistical uncertainties in the final digit.

<table>
<thead>
<tr>
<th>Temperature $T$ (K)</th>
<th>Viscosity $\eta$ (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>$42_2$</td>
</tr>
<tr>
<td>313</td>
<td>$30_4$</td>
</tr>
<tr>
<td>343</td>
<td>$13_1$</td>
</tr>
<tr>
<td>400</td>
<td>$5_2$</td>
</tr>
<tr>
<td>500</td>
<td>$1.7_4$</td>
</tr>
</tbody>
</table>
Figure 7.6. The effect of temperature on the viscosities of the pure IL system. The experimental shear viscosities [17, 22, 38, 129, 146, 162, 168, 216] are plotted with the simulation predictions to compare the accuracy of the predictions.

Experimental data can be compared against several different empirical models for mixture viscosities. One model, referred to here as Model (1), has the following form [4]

$$\eta_{\text{mix}}^{1/3} = x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3}$$  \hspace{1cm} (7.10)

where $x_1$ and $x_2$ are the mole fractions of species 1 and 2 in the mixture while $\eta_1$ and $\eta_2$ are the pure liquid viscosities. Another model, designated here as Model (2), weights the logarithm of the pure liquid viscosities by the mole fraction [92]

$$\ln \eta_{\text{mix}} = x_1 \ln \eta_1 + x_2 \ln \eta_2$$  \hspace{1cm} (7.11)

Both Model (1) and Model (2) are *ideal mixing* models, since they contain no cross interaction parameter. A third model, Model (3), extends Model (2) by adding
Figure 7.7. Comparison of the three mixture viscosity models with the experiments. Model (1) is given by Eq. 7.10, Model (2) is given by Eq. 7.11 and Model (3) is given by Eq. 7.12.

Models (1) and (2) can also be thought of as *pseudo-colligative* models, since they predict that the viscosity of a mixture depends only on the composition and pure component viscosities; they neglect any non-ideal chemical effects. In Model (3), the interaction parameter $G_{12}$ can be adjusted to better fit the data. A value of $G_{12} = 0$ recovers Eq. 7.11, while the degree to which this parameter deviates from zero indicates the extent of non-ideality in the system. Fig. 7.7 shows the comparison of the models and the experimental data. It is surprising that the actual viscosity of the water-containing IL *does not drop as much as the ideal models predict*. Contrary to the common sentiment, what is unusual about
the viscosity of IL-water mixtures is not that the viscosity drops so much with increasing water content. Rather, the viscosity drops less than would be expected for an ideal system. The absolute magnitude of the drop is large because the viscosity of water is so small and the amount of dissolved water is typically high for IL. Model (3) fits the data very well with a value of $G_{12} = 1.08$, as shown in Fig. 7.7. The fact that $G_{12} > 0$ confirms that the mixture viscosity is higher than might be expected. For hydrocarbon mixtures, it has been shown that $G_{12} \approx 0.5^{92}$.

The simulations provide clues as to why IL-water mixtures have a higher than expected viscosity. Fig. 7.8 shows the fraction of water associated with a particular species as a function of water content. Water was assumed to be associated with a species anytime the distance between the two molecules was less than the distance of the first minimum in the radial distribution function for these two species. Note that under this criterion it is possible for water to be simultaneously associated with more than one species. At all water concentrations, more than 90\% of the water molecules are associated with a $[Tf_2N]^-$ anion. This is similar to the behavior seen by Hanke and Lynden-Bell $^{63}$ with $[Cl^-]$ and $[PF_6^-]$ anions paired with the 1,3-dimethylimidazolium cation. In studies of water mixed with alkali halide salts $^{166}$ it has also been shown that water associates preferentially with anions, most likely due to steric reasons. For ILs, another contributing factor is the relatively high charge density present on the anions relative to the cations.

At the lowest water concentrations there is also a high probability that water is associated with a cation, but these water molecules are almost always also associated with an anion as well. The category labeled water-IL in Fig. 7.8
comprises those cases when water is close to both a cation and an anion simultaneously. The fact that these associations occur with roughly the same probability as water-cation associations, indicates that it is rare for water to interact solely with a cation. Instead, the anion interacting with water *draws* the water to the cation. As the water concentration increases, water-anion association probabilities remain high but water-cation associations drop while water-water associations increase. At the highest water concentrations, nearly half the water is associating with other water molecules, despite the fact that the mole fraction of water at this state point is less than 0.25. This indicates that water tends to cluster in ILs. Again, this same phenomenon was observed in previous simulations of ILs [63].

Fig. 7.9 shows the fraction of the water molecules in a particular cluster size. There are a number of ways a cluster can be defined; here we chose too define a water cluster as the collection of water molecules mutually associating with
Figure 7.9. Comparison of the cluster size of water at three different water contents.

each other. An association between two water molecules is assumed whenever the distance between two oxygen atoms is less than or equal to 0.3 nm. Most water molecules are isolated, even at the highest water concentrations. This is consistent with the findings of Hanke and Lynden-Bell [63]. There is evidence for the formation of dimers, trimers, tetramers and even larger clusters. The relative number of these clusters increases as water concentration increases.

The excess molar volume of the mixtures can also be computed from the simulations. Table 7.9 shows that the excess molar volume of this system is negative, meaning that the molar density is higher than what would be expected of a system having ideal mixing. Due to its ability to hydrogen bond with the anion and itself, water takes up less volume than it would otherwise be expected to. Hence, the gravimetric density of the system is insensitive to water content. This result, coupled with the finding that water forms clusters at higher water concentrations,
provides a physical explanation for why the viscosity of this system does not drop as much as ideal models would suggest. At low water loadings, the anions become hydrated and weaken the interaction energy between the cations and anions. The water is mostly dispersed uniformly in the system, and the excess molar volume is close to zero. Not surprisingly, the viscosity falls in a manner consistent with the ideal models. As the water concentration increases, however, water clusters begin to form and the excess molar volume becomes negative. Water clusters are an indication of non-ideal mixing, with the resulting density being higher than would otherwise occur under ideal mixing conditions. Viscosity is sensitive to molar volume, so the negative excess molar volumes result in viscosities being higher than what the ideal solution models predict. To test this hypothesis, we carried out preliminary viscosity simulations (not shown) using a water model that is identical to the modified TIP3P model used previously, except the charges were removed. As expected, the uncharged water did not form clusters as readily as the charged water model, and the computed viscosities were lower than what was obtained using the water model with charges. This suggests that, everything remaining same, at the same concentrations, non-polar solutes should actually lower the viscosity of this IL more than water. It cannot be said yet whether this is a universal phenomenon; we note that positive excess molar volumes have been observed for other ionic liquid-water systems [63].

7.4 Summary

Atomistic simulations have been carried out to understand the way in which the viscosity of the IL 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide ([emim]⁺[Tf₂N]⁻) depends on temperature and water concentration. A
steady-state nonequilibrium technique was used to compute viscosities, and agreement with experiment was generally good. It was shown that the nonequilibrium method was more efficient at obtaining transport properties like self-diffusivity and viscosity than equilibrium MD approaches. The simulations capture the non-Arrhenius dependence of the viscosity on temperature, as well as the large drop in viscosity observed when water is added to the system. By applying mixture viscosity models to the results, it was found that, while the viscosity of this mixture does indeed drop significantly with increasing water content, the reduction in viscosity is actually less than what would be expected for an ideal system. This finding is at odds with the popular notion that small amounts of dissolved water cause an unusual drop in the viscosity of ILs. On the contrary, at least for the system examined here, the viscosity does not drop as much as it should. The simulation results suggest that this is because water preferentially solvates the anions and then begins to form clusters at higher concentrations. This results in a negative

<table>
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<th>$V^e, cm^3/mol$</th>
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<td>1.548</td>
<td>197.148</td>
<td>-0.751</td>
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excess molar volume, meaning that the density of the mixture is higher than what would be obtained with an ideal mixing. As a result, the viscosity remains higher than expected. These results suggest that non-polar species dissolved in this IL at the same concentration will actually lower the viscosity more than water. It would be interesting if this prediction was tested experimentally.

Indeed, there are two studies that look at the effect of co-solvents on the viscosity of ILs. The first study was carried out by Wang et al. [210]. They studied the excess molar volume and excess viscosity for several ketones as co-solvents in ILs. To define the excess viscosity, they used a relationship very similar to that given by Eq. 7.11 or Eq. 7.12. The last term in the Eq. 7.12 was their estimate of excess viscosity. The only difference being, our definition limits us to estimate the excess quantity in a symmetric way about the mole fraction of 0.5 \( (x_{\text{co-solvent}} = 0.5) \), while if we consider just the whole term, the excess property can be skewed about \( x_{\text{co-solvent}} = 0.5 \). Wang et al. observe that the excess viscosity is skewed about mole fraction of 0.5 and has a maximum near \( x_{\text{co-solvent}} = 0.3 \). They also observe that as the dielectric constant of the co-solvent increases the deviation from the ideal behavior also increases. The excess viscosity measured in their study is positive which is similar to the positive value for \( G_{12} \). This would indicate that for a high dielectric constant co-solvent there would be a slower drop in the mixture viscosity as the co-solvent mole fraction increases as concluded in this chapter.

On the other hand, a study carried out by Li et al. [103] notes that the viscosity would drop slowly if the dielectric constant of the co-solvent is smaller and the drop would be faster for high dielectric constant co-solvents, contradicting the observations in this chapter. The results of Li et al. [103] seem to indicate that this
effect is system specific and varies as the IL under consideration is changed. For example, water, when added to $[\text{bmim}]^+[\text{PF}_6]^-$ or $[\text{bmim}]^+[\text{BF}_4]^-$ decreases viscosity faster than chloroform, but when added to $[\text{bmim}]^+[\text{CF}_3\text{COO}]^-$, decreases viscosity slower than chloroform. When analyzed in terms of volume fraction, instead of mole fraction, however, the decrease in the mixture viscosity seems to be faster with water and slower with chloroform for all the systems under consideration.
CHAPTER 8

EFFECT OF TEMPERATURE AND WATER CONTENT ON THE IONIC LIQUID 1-ETHYL-3-METHYLIMIDAZOLIUM ETHYLSULFATE

One of the difficulties of scientific research is that it is impossible to make progress without clear understanding, yet this understanding can come only from the work itself; every completed piece of research represents a victory over this contradiction.

.. A. B. Migdal

8.1 Introduction

In 1850, Edmond Carré engineered the first absorption-cooling unit with water and sulfuric acid [182]. His brother then extended this design for ammonia-water system and received the first United States patent for an absorption-refrigeration system. Although with the advent of vapor-compression cycle the use of absorption-refrigeration has reduced, it is still being used in industrial settings and is still an area of active research. Fig. 8.1 shows a schematic diagram for the absorption-refrigeration cycle. Over the years, in addition to ammonia-water, other mixtures including water-LiBr and fluoroalkanes-organic solvents have also been used in this process. With increasing cost of power and relatively inexpensive heat source these absorption-refrigeration systems are getting more popular and already have
a good market in India and Asia Pacific. In recent years, the possibility of ILs being used as an absorbent in these systems is being explored. An ionic liquid with moderately negative heat of mixing would be considered as a good choice of absorbent, such that water is completely miscible in the IL and it is not too difficult to get it back out. Also as water reduces the viscosity of IL significantly with small quantities, a water miscible IL can be thought off as a good low viscosity solvent replacing VOCs in the chemical processes [172].

One such IL being investigated is 1-ethyl-3-methylimidazolium ethylsulfate ([emim]^[EtSO_4]^-). It is easy to prepare from a common industrial agent diethyl sulfate [71]. It has low cost, it is water miscible and also is air stable. It is also expected to be less corrosive and was not found to be toxic in preliminary studies [48]. For any industrial application of this IL, however, its thermodynamic and transport properties need to be known. Experimental efforts in this regard are

Figure 8.1. A schematic representation of an absorption refrigeration cycle. The figure is based on a figure by Shiflett and Yokozeki [182].
underway, including at the University of Notre Dame [45, 172]. However, it is difficult to carry out experiments at elevated temperatures and pressures. The simulations, on the other hand, do not care! As mentioned earlier, they actually perform better at higher temperatures.

The goal of this chapter is then to complement the experimental efforts and provide a molecular level understanding of the system. We will study [emim]$^+\cdot[EtSO_4]^-\,$ ionic liquid at different temperatures and also study the IL-water system at different compositions. We will compute different equilibrium (e.g. densities, heats of mixing, heats of vaporization) and transport (e.g. viscosity, thermal conductivity) properties at 348 K and at different water compositions including. The objective is to assess the predictability of molecular simulations at known state points and then obtain the properties at state points which are difficult to access experimentally. We will also make some predictions regarding some properties which have not yet been measured experimentally, such as enthalpy of vaporization, including the first simulation study of thermal conductivity for ILs.

8.2 Simulation Method and Details

As mentioned in the previous chapter (section 7.2), RNEMD method offers distinct advantages over the conventional equilibrium and nonequilibrium methods. We also have implemented this method or algorithm in our group code APSS and have validated this method against the test cases [89]. Also, as mentioned in Chapter 2 (section 2.3), it takes only a small modification of the algorithm to compute the thermal conductivities of the fluid, which is one of the goals of this study. It is for this reason we have chosen to use this method to compute the viscosity and thermal conductivity of IL [emim]$^+\cdot[EtSO_4]^-\,$. We would also like
to study the effect of water content on these properties.

In the previous chapter we have shown that ILs can be modeled accurately with a forcefield having the a functional form given by Eq. 3.16 in Chapter 3. The forcefield parameters for the \([\text{emim}]^+\) cation were taken from the work of Cadena and Maginn [24], except in this case the equilibrium angles and distances and the charges were re-assigned. The structure of the cation was re-optimized by performing quantum mechanical geometry optimization on the isolated cation at the B3LYP 6-311++G** level of theory. The partial atomic charges were derived using CHELPG method [21]. The forcefield parameters for the \([\text{EtSO}_4]^–\) anion were initially taken from CHARMM forcefield [113] and the extension to those parameters provided by the work of Huige and Altona [75]. Again, the equilibrium distances and charges were re-assigned using the geometry optimization on an isolated anion at the same level of theory. A short molecular mechanics geometry optimization algorithm was run on an isolated anion to check the validity of the forcefield. The resulting structure was compared with the optimized structure from quantum mechanical methods. The agreement between the structure optimized by molecular mechanics using this forcefield and that obtained from quantum mechanical methods was not good. One of the dihedral angles seemed to be at odds. This disagreement was handled by re-fitting the forcefield parameters for that particular dihedral angle using the quantum mechanical methods.

The \([\text{EtSO}_4]^–\) anion can be visualized as given in the Fig. 8.2. The dihedral angle under consideration is \(C_1 – C_2 – O_3 – S_4\). This dihedral angle was scanned through 360°, in steps of 10°, using quantum mechanical methods in Gaussian 03 [50] to get an energy profile as a function of the dihedral angle. The energies at each of these dihedral angles are calculated both using a DFT method and MP2.
This energy profile is denoted as $E_{QM}(\phi)$. The same configurations at each of those dihedral angles were analyzed using the above forcefield in molecular mechanics. The only difference is that in this case the dihedral potential parameters for this $C_1 - C_2 - O_3 - S_4$ dihedral were set to zero, i.e., the energy contribution of this dihedral to the total energy of the configuration was zero. These molecular mechanics energies were denoted as $E_{MM}(\phi)$.

Both energy profiles were then referenced to a dihedral angle of $0^\circ$, i.e., $\phi = 0$. The difference in the energies at each $\phi$ was assumed to be due solely to the missing dihedral energy and was assigned to that particular dihedral ($U_{torsion}(\phi_{C_1-C_2-O_3-S_4}) = E_{QM}(\phi) - E_{MM}(\phi)$). Now, we have a dihedral potential energy profile as a function of $\phi$. This energy profile was then fit using three different potential models, viz OPLS potential with zero term, a 3 term CHARMM potential and a 1 term CHARMM potential. Which can be represented
Figure 8.3. Comparison of the three torsional potentials: Eq. 8.1 (blue curve), 8.3 (red curve) and 8.3 (dashed green curve). Black filled circles represent the simulation data.

as

\[
U_{\text{torsion}} = \sum_{\text{dihedrals}} c_0 + c_1 [1 + \cos(\phi)] + c_2 [1 - \cos(2\phi)] + c_3 [1 + \cos(3\phi)] \tag{8.1}
\]

\[
U_{\text{torsion}} = \sum_{\text{dihedrals}} k_{1,\phi} [1 + \cos(\phi - \delta_1)] + k_{2,\phi} [1 + \cos(2\phi - \delta_2)] + k_{3,\phi} [1 + \cos(3\phi - \delta_3)] \tag{8.2}
\]

\[
U_{\text{torsion}} = \sum_{\text{dihedrals}} k_{1,\phi} [1 + \cos(\phi - \delta_1)] \tag{8.3}
\]

respectively. The comparison of these fit is shown in Fig. 8.3.

As can be seen from the plot, 3 term CHARMM (8.3) and OPLS (8.1) forms of potential perform much better than 1 term CHARMM (8.3) model and hence
only the prior two forms are used in this study. The potential parameters for these fits can be found in the Table 8.1 or in the Supporting Information in the reference [90]. The energy contribution from these potentials is then added to the molecular mechanics forcefield. The comparison of this molecular mechanical energy and the energies computed using quantum mechanical methods is shown in Fig. 8.4.

It can be clearly noticed that 3 term CHARMM (Eq. 8.3) and OPLS (Eq. 8.1) potentials fit the energy profile really well and out perform the 1 term CHARMM potential (Eq. 8.3). When this new torsional potential is used, the quantum mechanically optimized geometry is reproduced using molecular mechanics forcefield. Also it can be noticed that the energy profiles are reproduced by OPLS potential
TABLE 8.1
Dihedral parameters for the three fits in Eqs. 8.1, 8.3 and 8.3.

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<th>c₁</th>
<th>c₂</th>
<th>c₃</th>
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<td>180</td>
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</table>
and 3 term CHARMM potential are almost identical and could be used interchangeably. In this study for the equilibration runs we use a 3 term CHARMM potential (Eq. 8.3) while for the production runs for viscosity and thermal conductivity we use an OPLS form of potential (Eq. 8.1).

The forcefield parameters for water correspond to the SPC model [13] with flexibility added through bonds and angles. In this study we have chosen a different forcefield to model water interactions from that in the previous chapter as one of the goals of this study is to model water solubility in this IL. The SPC water model has been shown to perform better in terms of the vapor-liquid equilibria than the other simple models available [163]. The study of water solubility in IL will be carried separately from the study reported in this chapter and the details of the study can be found in the ref. [90].

As in the previous study, intramolecular non-bonded energies were neglected for atoms separated by fewer than three bonds and were scaled by 50% for atoms separated by exactly three bonds. For all other cases, full interactions were used. Lorentz-Berthelot combining rules were used to compute the cross interactions. A complete list of forcefield parameters can be found in the Tables 8.2, 8.3, 8.4, 8.5, and 8.6. They can also be found in the Supporting Information of our publication [90].
**TABLE 8.2**

LJ parameters (σ and ε) and the charges for [emim]$^+$, [EtSO$_4$]$^-$ and Water.

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<th>LJ (σ)</th>
<th>LJ (ε)</th>
<th>Mass (amu)</th>
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TABLE 8.2

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**Water \([H2O]\)**

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**Anion \([EtSO_4^-]\)**

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TABLE 8.2

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<td>H11</td>
<td>HAL3</td>
<td>0.034634</td>
<td>2.388</td>
<td>0.0240</td>
<td>1.0080</td>
</tr>
<tr>
<td>12</td>
<td>H12</td>
<td>HAL3</td>
<td>0.034634</td>
<td>2.388</td>
<td>0.0240</td>
<td>1.0080</td>
</tr>
</tbody>
</table>

TABLE 8.3

Equilibrium bond distances \((r_0)\) and bond force constants \((k_b)\)


<table>
<thead>
<tr>
<th>At Type - At Type</th>
<th>(k_b) ((kcal/mol\cdotÅ^2))</th>
<th>(r_0) (Å))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPH1 - CPH1</td>
<td>410.0000</td>
<td>1.3597</td>
</tr>
<tr>
<td>CPH1 - NR1</td>
<td>400.0000</td>
<td>1.3797</td>
</tr>
<tr>
<td>CPH1 - HR3</td>
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<td>1.0747</td>
</tr>
<tr>
<td>CPH2 - NR1</td>
<td>400.0000</td>
<td>1.3350</td>
</tr>
<tr>
<td>CPH2 - HR1</td>
<td>340.0000</td>
<td>1.0755</td>
</tr>
<tr>
<td>CH2N - NR1</td>
<td>220.0000</td>
<td>1.4815</td>
</tr>
<tr>
<td>CH3N - NR1</td>
<td>220.0000</td>
<td>1.4686</td>
</tr>
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</table>

Continued on next page
TABLE 8.3

*continued from previous page*

<table>
<thead>
<tr>
<th>At Type - At Type</th>
<th>$k_b$</th>
<th>$r_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kcal/mol-A$^2$)</td>
<td>(Å)</td>
</tr>
<tr>
<td>CH3N - H3CN</td>
<td>309.0000</td>
<td>1.0866</td>
</tr>
<tr>
<td>CH2N - H2CN</td>
<td>309.0000</td>
<td>1.0884</td>
</tr>
<tr>
<td>CH2N - CT3</td>
<td>200.0000</td>
<td>1.5240</td>
</tr>
<tr>
<td>CT3 - H3C</td>
<td>322.0000</td>
<td>1.0893</td>
</tr>
</tbody>
</table>

Water [$H2O$]

| HSPC - OSPC         | 450.0000  | 1.0000 |

Anion [$EtSO_4]$$^-$

<p>| SL - O2L            | 525.0000  | 1.4574 |
| SL - OSL            | 230.0000  | 1.6863 |
| CTL2 - OSL          | 320.0000  | 1.4195 |
| CTL2 - CTL3         | 222.5000  | 1.5211 |
| CTL2 - HAL2         | 309.0000  | 1.0946 |
| CTL3 - HAL3         | 322.0000  | 1.0920 |</p>
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<thead>
<tr>
<th>At Type - At Type - At Type</th>
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<th>$\theta_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kcal/mol - rad$^2$)</td>
<td>(deg.)</td>
</tr>
<tr>
<td><strong>Cation [emim]$^+$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR1 - CPH1 - CPH1</td>
<td>130.00</td>
<td>107.15</td>
</tr>
<tr>
<td>HR3 - CPH1 - CPH1</td>
<td>25.00</td>
<td>130.65</td>
</tr>
<tr>
<td>NR1 - CPH1 - HR3</td>
<td>25.00</td>
<td>122.19</td>
</tr>
<tr>
<td>HR1 - CPH2 - NR1</td>
<td>25.00</td>
<td>125.50</td>
</tr>
<tr>
<td>NR1 - CPH2 - NR1</td>
<td>130.00</td>
<td>109.00</td>
</tr>
<tr>
<td>CPH1 - NR1 - CPH2</td>
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<td>108.35</td>
</tr>
<tr>
<td>CH2N - NR1 - CH1</td>
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<td>125.90</td>
</tr>
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<td>125.74</td>
</tr>
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<td>125.73</td>
</tr>
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<td>125.90</td>
</tr>
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<td>109.30</td>
</tr>
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<td>35.50</td>
<td>109.65</td>
</tr>
<tr>
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<td>106.73</td>
</tr>
<tr>
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<td>112.31</td>
</tr>
<tr>
<td>H2CN - CH2N - H2CN</td>
<td>35.50</td>
<td>107.58</td>
</tr>
<tr>
<td>H2CN - CH2N - CT3</td>
<td>33.40</td>
<td>111.58</td>
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*Continued on next page*
TABLE 8.4

*continued from previous page*

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<th>$\theta_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kcal/mol - rad$^2$)</td>
<td>((deg.))</td>
</tr>
<tr>
<td>H3C - CT3 - CH2N</td>
<td>33.40</td>
<td>110.64</td>
</tr>
<tr>
<td>H3C - CT3 - H3C</td>
<td>35.50</td>
<td>108.27</td>
</tr>
</tbody>
</table>

**Water [H2O]**

| HSPC - OSPC - HSPC         | 55.00     | 109.47     |

**Anion [EtSO$_4$]$^-$**

| O2L - SL - O2L            | 140.00    | 114.98     |
| O2L - SL - OSL            | 100.00    | 103.17     |
| CTL2 - OSL - SL           | 100.00    | 114.74     |
| OSL - CTL2 - CTL3         | 75.70     | 108.07     |
| HAL2 - CTL2 - OSL         | 60.00     | 109.67     |
| HAL2 - CTL2 - CTL3        | 34.60     | 110.75     |
| HAL2 - CTL2 - HAL2        | 35.50     | 107.94     |
| HAL3 - CTL3 - CTL2        | 34.60     | 110.57     |
| HAL3 - CTL3 - HAL3        | 35.50     | 108.35     |
TABLE 8.5
Dihedral parameters in the CHARMm form for [emim]$^+$, 

<table>
<thead>
<tr>
<th>At Type - At Type - At Type - At Type</th>
<th>$k_\phi$</th>
<th>n</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kcal/mol)</td>
<td>(deg.)</td>
<td></td>
</tr>
<tr>
<td>Cation [emim]$^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR1 - CPH1 - CPH1 - HR3</td>
<td>3.0000</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>NR1 - CPH1 - CPH1 - NR1</td>
<td>14.0000</td>
<td>2</td>
<td>180</td>
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<td>2</td>
<td>180</td>
</tr>
<tr>
<td>CPH1 - CPH1 - NR1 - CH2N</td>
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<td>1</td>
<td>0</td>
</tr>
<tr>
<td>CPH1 - CPH1 - NR1 - CH3N</td>
<td>0.0000</td>
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<tr>
<td>HR3 - CPH1 - CPH1 - HR3</td>
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<td>2</td>
<td>180</td>
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<td>2</td>
<td>180</td>
</tr>
<tr>
<td>HR3 - CPH1 - NR1 - CH3N</td>
<td>0.0000</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>HR1 - CPH2 - NR1 - CPH1</td>
<td>3.0000</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>HR1 - CPH2 - NR1 - CH2N</td>
<td>0.0000</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>HR1 - CPH2 - NR1 - CH3N</td>
<td>0.0000</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>NR1 - CPH2 - NR1 - CPH1</td>
<td>14.0000</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>NR1 - CPH2 - NR1 - CH2N</td>
<td>0.0000</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>NR1 - CPH2 - NR1 - CH3N</td>
<td>0.0000</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>CPH1 - NR1 - CH2N - H2CN</td>
<td>0.0000</td>
<td>3</td>
<td>0</td>
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</tbody>
</table>

Continued on next page
TABLE 8.5

*continued from previous page*

<table>
<thead>
<tr>
<th>At Type - At Type - At Type - At Type</th>
<th>$k_\phi$</th>
<th>n</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kcal/mol)</td>
<td>(deg.)</td>
<td></td>
</tr>
<tr>
<td>CPH1 - NR1 - CH3N - H3CN</td>
<td>0.0000</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>CPH1 - NR1 - CH2N - CT3</td>
<td>0.2000</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>CPH2 - NR1 - CH2N - H2CN</td>
<td>0.1950</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>CPH2 - NR1 - CH3N - H3CN</td>
<td>0.1950</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>CPH2 - NR1 - CH2N - CT3</td>
<td>0.1000</td>
<td>3</td>
<td>180</td>
</tr>
<tr>
<td>NR1 - CH2N - CT3 - H3C</td>
<td>0.0000</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>H2CN - CH2N - CT3 - H3C</td>
<td>0.1950</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>

Water [H2O]

N/A

Anion [EtSO4]−

<table>
<thead>
<tr>
<th>At Type - At Type - At Type - At Type</th>
<th>$k_\phi$</th>
<th>n</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kcal/mol)</td>
<td>(deg.)</td>
<td></td>
</tr>
<tr>
<td>HAL2 - CTL2 - OSL - SL</td>
<td>0.0000</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>CTL2 - OSL - SL - O2L</td>
<td>0.0000</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>OSL - CTL2 - CTL3 - HAL3</td>
<td>0.1600</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>HAL2 - CTL2 - CTL3 - HAL3</td>
<td>0.1600</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>CTL3 - CTL2 - OSL - SL</td>
<td>3.7870</td>
<td>1</td>
<td>180</td>
</tr>
<tr>
<td>CTL3 - CTL2 - OSL - SL</td>
<td>0.0275</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>CTL3 - CTL2 - OSL - SL</td>
<td>−0.4968</td>
<td>3</td>
<td>180</td>
</tr>
</tbody>
</table>
### Table 8.6

Equilibrium improper angle ($\psi_0$) and improper angle force constants ($k_\psi$) for $[\text{emim}]^+$, $[\text{EtSO}_4]^{-}$ and Water.

<table>
<thead>
<tr>
<th></th>
<th>$k_\psi$ (kcal/mol $\cdot$ rad$^2$)</th>
<th>$\psi_0$ (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation $[\text{emim}]^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CPH2 - NR1 - NR1 - HR1</td>
<td>0.50</td>
<td>0.00</td>
</tr>
<tr>
<td>NR1 - CPH1 - CPH2 - CH2N</td>
<td>0.60</td>
<td>0.00</td>
</tr>
<tr>
<td>NR1 - CPH1 - CPH2 - CH3N</td>
<td>0.60</td>
<td>0.00</td>
</tr>
<tr>
<td>CPH1 - CPH1 - NR1 - HR3</td>
<td>0.50</td>
<td>0.00</td>
</tr>
<tr>
<td>Water $[\text{H}_2\text{O}]$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR1 - CPH1 - CPH2 - CH3N</td>
<td>0.60</td>
<td>0.00</td>
</tr>
<tr>
<td>CPH1 - CPH1 - NR1 - HR3</td>
<td>0.50</td>
<td>0.00</td>
</tr>
</tbody>
</table>

A switching function of the form of Eq. 3.17 is used to truncate the Lennard-Jones interactions and force them to be exactly zero at the cut-off for the equilibration calculations. In the equilibration runs, a cut-off distance ($r_c$) of 12 Å and an onset distance ($r_s$) of 10.0 Å were used. Electrostatic interactions were computed with the particle-mesh Ewald algorithm [41] with real space cut-off distance of 12 Å. For production runs, instead of a switching function, the potential was cut-off at 12 Å and long range corrections were used.
8.2.1 State Points and System Size

For pure the IL calculations, a system of 200 ion pairs of $[\text{emim}]^+ [\text{EtSO}_4]^- $ was studied at four different temperatures, $T = 308, 328, 348$ and $368$ K. To study the effect of water content on transport properties, three different water loadings ($x_{\text{water}} = 0.26, 0.5$ and $0.75$; where $x_{\text{water}}$ is the mole fraction of water in the system) were studied at $348$ K. To study the effect of water content on the equilibrium properties such as density and heat of mixing, nine additional compositions ($x_{\text{water}}$ ranging from $0.8$ to $0.96$) were studied at the same temperature of $348$ K. To compare the change in the properties, a pure water simulation was also carried out with 2000 SPC water molecules at $348$ K.

The simulation boxes for all runs were orthogonal with an aspect ratio (AR) of 2.5. For the RNEMD calculations, the box was again divided into 14 bins along its long axis as in the previous chapter and the average velocity within each bin was used to determine the velocity profile. A reversible multiple timestepping algorithm, r-RESPA [201] was used with inner timestep ($\delta$) of $0.5$ fs and an outer timestep ($\tau$) of $2.0$ fs. A four chain Nosé-Hoover thermostat [122] was used to control the temperature.

8.3 Results and Discussion: Equilibrium Properties

8.3.1 Calculation of Error Bars

Error bars on the properties which can be directly measured from the simulations are computed as the standard deviation on those properties. In the case of the properties which are derived from the observable properties in a simulation we compute the error bars from the following error propagation formula. If we assume property $F$ to be a function of say $x, y$ and $z$ independent variables. And
if the error bars on each of these variables are denoted as $\delta x$, $\delta z$, $\delta z$, then the error propagation formula gives the error bar on $F(x, y, z)$ (i.e., $\delta F$) as

$$
\delta F = \sqrt{\left(\frac{\partial F}{\partial x} \delta x\right)^2 + \left(\frac{\partial F}{\partial y} \delta y\right)^2 + \left(\frac{\partial F}{\partial z} \delta z\right)^2}
$$

(8.4)

The error bars on the quantities are computed based on this formula. For the cases of excess quantities, the error bars on the pure components ($x_i = 0$ or 1) are set to zero by definition.

8.3.2 Densities as a Function of Temperature

As discussed in the previous chapter, the first step in predicting the transport properties of any system, is to compute liquid densities at the state point under consideration. For this purpose, molecular dynamics simulation runs of 2 ns were carried out in the isothermal-isobaric ($NPT$) ensemble using the program NAMD [156] at all the state points mentioned above. The average densities for pure IL from these simulations are compared with experimental densities in Table 8.7. Computed densities are systematically lower than the experimental values [172], but the agreement is within 1.5% at all temperatures. It has been noted in the previous simulation studies [26] that these systems tend to behave like glassy systems and the density computed from two different starting points may not agree. To check for such glassy behavior 2–3 independent simulation runs were carried out. The predicted density in all the cases did not show a systematic increase or decrease depending upon the starting configuration. The density predicted by all the replicated runs were in good agreement with the densities noted here.

Using the computed densities, additional equilibration runs of 5 ns were carried out in the canonical ($NVT$) ensemble at all the temperatures. These equi-
TABLE 8.7
Computed liquid densities at different temperatures compared with experimental data [172]. Note that the experimental density was not available at 368 K and is predicted by simulations. Subscripts indicate the statistical uncertainties in the final digit.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\rho_{exp}$ (g/cm$^3$)</th>
<th>$\rho_{sim}$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>308</td>
<td>1.2306</td>
<td>1.217$_5$</td>
</tr>
<tr>
<td>328</td>
<td>1.2172</td>
<td>1.203$_0$</td>
</tr>
<tr>
<td>348</td>
<td>1.2040</td>
<td>1.189$_0$</td>
</tr>
<tr>
<td>368</td>
<td>N/A</td>
<td>1.174$_6$</td>
</tr>
</tbody>
</table>
librated conformations were then used as initial configurations for the RNEMD simulations, which were run at constant density and temperature using a locally developed code APSS.

8.3.2.1 Volumetric Expansivity

From the volumes of the simulation boxes in the isothermal-isobaric ensemble and from the densities computed here, one can estimate the value of *volumetric expansivity* as

\[
\alpha_P = \frac{1}{\langle V \rangle} \left( \frac{\partial \langle V \rangle}{\partial T} \right)_P .
\]  \hspace{1cm} (8.5)

The experimental value for this quantity is $5.37 \times 10^4 \text{ K}^{-1}$ while the simulations estimate this value to be $6.26 \times 10^4 \text{ K}^{-1}$ which is about 16.5% higher than the experimental number.

8.3.3 Heat Capacities

The constant pressure heat capacity, $C_P$, was computed for $[\text{emim}]^+[\text{EtSO}_4]^-$ at 348 K by following the procedure described in a publication by Cadena et al. [26]. To summarize their procedure, the total potential energy $\mathcal{U}$ is split into intermolecular and intramolecular terms; i.e., $\mathcal{U} = \mathcal{U}^{\text{inter}} + \mathcal{U}^{\text{intra}}$, where $\mathcal{U}^{\text{inter}}$ includes all Lennard-Jones and Coulombic interactions (or non bonded interactions) while $\mathcal{U}^{\text{intra}}$ includes all the bonded terms (i.e., bond stretching, angle bending, dihedral angle rotation and improper angle bending terms). The total enthalpy can then be given as

\[
H = \mathcal{U}^{\text{inter}} + \mathcal{U}^{\text{intra}} + \mathcal{K} + PV \hspace{1cm} (8.6)
\]
where, $\mathcal{H}$ is the kinetic energy. If we consider the contribution from $U^{\text{intra}} + \mathcal{H} + Nk_B T$ to be ideal gas contribution, $H^{IG}$ and the contribution from the remaining terms ($U^{\text{inter}} + PV - Nk_B T$) to be residual contribution, we can now write the total enthalpy of the system as

$$H = H^{IG} + H^{res}$$

(8.7)

The constant pressure heat capacity ($C_P$) is given as

$$C_P(T, P) = \left( \frac{\partial}{\partial T} \langle H \rangle \right)_P$$

(8.8)

Thus we can split $C_P$ into two parts: $C_P^{IG}$ and $C_P^{res}$. Each of these terms are calculated as follows. Simulations were carried out in an isothermal-isobaric ensemble at same pressure but at different temperatures to compute residual part of $C_P$ from the Eq. 8.8. The ideal gas contribution to the heat capacity, however, was obtained from a frequency analysis of the optimized geometry structures of the individual ions using quantum calculations in Gaussian 03 [50]. The constant volume heat capacity of both the cation or the anion in an ideal gas state was obtained from the frequency analysis of the optimized structure of that particular ion using Gaussian 03. This value is computed at 298 K and at 1 bar pressure. This number was then scaled to the required temperature (348 K in this case) and pressure (1 bar) by using a module in Gaussian 03. A scaling factor also needs to be used to adjust for the quantum mechanical method and basis set. One can look up this number from the ref. [148]. In this case for the basis set used here, the scale factor turns out to be 0.97. When we adjust for the scale factor and the temperature and pressure of our simulation, we can get the ideal gas contribution
to $C_p$. Put together, the simulations estimate this value to be 454.3 J/mol-K which is about 12% higher than the experimental quantity reported by Ficke et al. [45].

8.3.4 Enthalpy of vaporization

The enthalpy of vaporization ($\Delta H_{vap}$) of a fluid is given as

$$\Delta H_{vap}(T,P) = \langle U_{gas}(T) \rangle - \langle U_{liq}(T,P) \rangle + RT - PV$$  \hspace{1cm} (8.9)

The contribution from the $PV$ term is generally very small as compared to the other terms and can be neglected. A relatively elaborate discussion of how to compute $\Delta H_{vap}$ can be found in the following chapter (Chapter 9). The contribution from the $U_{gas}$ can be computed by simulating an isolated ion pair in the gas phase (i.e. simulating an ideal gas composed of such ion pairs) while the $U_{liq}$ can be computed from the isobaric-isothermal ensemble runs using molecular mechanics forcefield discussed above. The computed enthalpy of vaporization for $[\text{emim}]^+[\text{EtSO}_4]^-\,$ is 178 kJ/mol. The experimental data for this property is not yet available but the number compares well with the heats of vaporization of other ILs as can be seen in the next chapter. As the temperature increases the enthalpy of vaporization decreases by about 2 kJ/mol per 20 K.

8.3.5 Densities as a Function of Water Content

The effect of water content on the system densities was also studied in a similar way. The comparison against the experiments is shown in Fig. 8.5. Given that no forcefield parameters were adjusted for water or for two ions ($[\text{emim}]^+$ or $[\text{EtSO}_4]^-$) to match the experimental data, the agreement is very good. The er-
Figure 8.5. Comparison of the experimental [172](open circles) and simulation (filled circles) densities as a function of water content ($x_{\text{water}}$) at 348 K. The dashed and the dotted lines are just guides to the eyes.

Error bars on the simulation data were calculated as the standard deviation in the density in the isothermal-isobaric ensemble simulation runs. One can as well compute it from running multiple independent simulation runs at each composition, however, this estimate seems more conservative.

8.3.5.1 Excess Molar Volume ($V_m^E$)

The excess molar volumes ($V_m^E$) can be obtained from the average molar volumes of the mixture as

$$V_m^E = V_{m,\text{actual}} - [x_{\text{IL}} V_{m,\text{IL}} - x_{\text{water}} V_{m,\text{water}}] \quad (8.10)$$

where $x_i$ is the mole fraction of component $i$ in the mixture and $V_{m,\text{IL}}$ and $V_{m,\text{water}}$ are the pure component molar volumes of the IL and water respectively. The
quantity in the square bracket is the molar volume of the ideal mixture. One can as well compute the same from the density information as

\[ V_{m}^E = \sum_i x_i M_i \left[ \frac{1}{\rho_{\text{actual}}} - \frac{1}{\rho_i} \right] \]  \hspace{1cm} (8.11)

where \( \rho_i \) is the density of the pure component and \( M_i \) is the molecular weight of the pure component. Both of these formulae give the same results. The excess molar volumes computed from the simulation results are compared with the experimental results of Rodriguez and Brennecke [172] in Fig. 8.6. As can be observed from the figure, the simulations overestimate the magnitude of excess molar volumes. The experimental data from these authors, however is in good agreement with another experimental study carried out by Lu et al. [112]. We can also see from the Fig. 8.6 that the error bars on the numbers at low water loadings are high. It can be noted, however, that the estimate of excess molar volume is extremely sensitive to the shape of density versus mole fraction curve (shown in Fig. 8.5). Even though the absolute estimates of the density as a function of mole fraction are within 1.5\% to that of experiments, a very small change in the curvature at any composition (i.e. slope of that curve at any composition) makes a huge difference in the predicted excess molar volumes.

8.3.6 Enthalpy of Mixing (\( \Delta h_{\text{mix}} \))

Similarly, one can compute the enthalpy of mixing (\( \Delta h_{\text{mix}} \)) as

\[ \Delta h_{\text{mix}} = h_{\text{actual}} - [x_{IL} h_{IL} + x_{\text{water}} h_{\text{water}}] \]  \hspace{1cm} (8.12)
Figure 8.6. Comparison of the experimental [172](open circles) and simulation (filled circles) excess molar volumes as a function of water content ($x_{\text{water}}$) at 348 K. The dashed and the dotted lines are just guides to the eyes.

where $h_{\text{actual}}$ indicates the molar enthalpy of the system based on the total number of moles in the mixture. Again, $h_{\text{IL}}$ and $h_{\text{water}}$ are the molar enthalpies of the pure IL and water respectively and the quantity in the square bracket denotes the enthalpy of mixing of the ideal mixture. The enthalpies of mixing computed from the simulations are compared with the experimental data of Ficke et al. [45] in Fig. 8.7. As can be seen from the plot that simulations overestimate the magnitude of the enthalpy of mixing. However, the difference between the measured and predicted values is about 5–6 kJ/mol, which is not significantly large on the absolute scale. We postulated that this discrepancy is due to a over attractive SPC water model, i.e., the attraction terms in the potential are larger than the actual value. To verify this we reduced the charges on the atoms of water by 15% and recalculated the enthalpy of mixing. We find that changing the
Figure 8.7. Comparison of the experimental [45](open circles) and simulation (filled circles) enthalpies of mixing as a function of water content ($x_{\text{water}}$) at 348 K. The dashed and the dotted lines are just a guide to the eye.

Partial charges on water atoms reduces the density of water at 348 K significantly to 0.797 gm/cc but does not significantly change the estimate of the enthalpy of mixing at $x_{\text{water}} = 0.26$, changing the value of the estimate to -4.3 kJ/mol from -4 kJ/mol. This means that the discrepancy associated with simulation results is not a direct result of higher charge-charge interactions between IL and water molecules.
Partial Molar Enthalpy ($\tilde{h}$)

Partial molar enthalpy of a species in a binary mixture can be given as

$$
\tilde{h}_{IL} = \Delta h_{mix} - x_{water} \frac{\partial \Delta h_{mix}}{\partial x_{water}} + h_{IL} \tag{8.13}
$$

$$
\tilde{h}_{water} = \Delta h_{mix} - x_{IL} \frac{\partial \Delta h_{mix}}{\partial x_{IL}} + h_{water} \tag{8.14}
$$

where $h_{IL}$ and $h_{water}$ are the pure component molar enthalpies of IL and water systems respectively. All the terms in the above equation are already known from the simulation, except the $\frac{\partial \Delta h_{mix}}{\partial x_i}$. To compute these partial derivatives we fit the $\Delta h_{mix}$ versus $x_i$ curve with a known functional form. Once the coefficients in that function are known, we can calculate the derivative of the function at each of the values of $x_i$. We select two such forms of functions: a 4th order polynomial of the form $A_4x^4 + A_3x^3 + A_2x^2 + A_1x$ and a van Laar function of the form $x(1-x)[A_1x + A_2(1-x)]$. The polynomial function fits the data very well, however, it does not give the value of the function to be exactly zero at one of the end points. One can add more constrains in the polynomial fitting procedure to force the value to zero at the end points. The van Laar function does not fit the data as well as the polynomial function but still does a reasonable job. Additionally, the value of the function at either end points is zero by definition. The comparison of two fits when $\Delta h_{mix}$ is plotted against $x_{water}$ is shown in the Fig. 8.8. With the coefficients of these curves, we can compute the partial molar enthalpies of each of the species. The computed partial molar enthalpies of water are shown in the Fig. 8.9. A similar analysis can be done to compute the partial molar enthalpies of IL (not shown). It can be noted from the plot that the partial molar enthalpy of water at infinite dilution limit is very sensitive to
Figure 8.8. Comparison of the two fitting methods for $\Delta h_{\text{mix}}$ at 348 K. The dashed line shows the van Laar fit while the dotted line indicates the polynomial fit.

even the method of fitting. It also needs to be noted that, by definition of partial molar quantities, $\sum_i x_i \tilde{h}_i = h_{\text{actual}}$. However, when the total molar enthalpy is computed from these fits it does not add up exactly to the actual or observed molar enthalpy of the system. The difference between the two quantities is about 5 kJ/mol, which is roughly the uncertainty of these calculations.

8.4 Results and Discussion: Dynamic Properties

8.4.1 Rotational Relaxation Times

As described in the previous chapter, the rotational relaxation time at each temperature and water content was determined by computing the end-to-end vector rotational relaxation time of the cation during an equilibrium molecular dynamics simulation. To do this, the correlation function in Eq. 5.15 was computed.

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Figure 8.9. Partial molar enthalpy of water computed at 348 K using two different fitting methods (i.e. van Laar fit and a polynomial fit). The dashed line with filled symbols indicate the partial molar enthalpy computed from van Laar fit while the dotted line with open symbols indicate the partial molar enthalpies computed from polynomial fit.
The time dependence of $C(t)$ was fit using two stretched exponentials of the form in Eq. 7.3. As demonstrated in the previous chapter, the relaxation behavior of pure ILs was accurately fit in this manner. The rotational relaxation time, $\tau_{\text{rot}}$, was then computed numerically from Eq. 7.4. One can as well compute the rotational relaxation time by integrating the area under the curve in $C(t)$ versus $t$. Both estimates of rotational relaxation times agree very well with each other. Table 8.8 summarizes the rotational relaxation times computed for pure ILs at different temperatures. As was observed previously, these relaxation times increase dramatically as the temperature decreases. And it is for this reason that the integration of correlation functions over very short time scales are likely to result in erroneous estimates of the viscosity at low temperature. Even though the rotational relaxation time for anion at 308 K was higher than the cation, as the temperature increases, the rotational relaxation times for anion become lower than that of the cation.

The rotational relaxation time at each water content ($x_{\text{water}}$=0, 0.26, 0.50, 0.75 and 1.0) was determined in the similar fashion as described above. Only in this case as the correlation function, $C(t)$ drops all the way to zero well before the simulation length, the direct estimate of relaxation times, i.e. by using the area under the curve rather than two exponential fits, seems to be more accurate method to determine the rotational relaxation time. Table 8.9 summarizes the rotational relaxation times computed for different water loadings at 348 K. It is interesting to note that the correlation function, $C(t)$ for the anion in $x_{\text{water}}$ = 0.5 decreases rapidly but does not go all the way to zero. The cumulative sum of the area under the curve shows increasing trend even after 5 ns and hence an accurate estimate of relaxation time is not possible (with either method) and the
TABLE 8.8

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\tau_{cation}$ (ps)</th>
<th>$\tau_{anion}$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>308</td>
<td>1777</td>
<td>2321</td>
</tr>
<tr>
<td>328</td>
<td>623</td>
<td>454</td>
</tr>
<tr>
<td>348</td>
<td>361</td>
<td>263</td>
</tr>
<tr>
<td>368</td>
<td>216</td>
<td>149</td>
</tr>
</tbody>
</table>
relaxation time is marked with an asterisk (*) in the Table 8.9. Even though the estimate at this water loading is hard to calculate, we can see that as the water content increases initially the rotational relaxation time for anion first increases and then goes back down, while the relaxation times for the cation and for water show decreasing trend as the water content increases. Also, it should be noted that the rotational relaxation time for pure water was determined to be around 1 ps. The trajectory which is analyzed to get this number is written at a frequency of 1 ps and hence this estimate may not be accurate or the actual relaxation time for SPC model water may be even smaller than this.

8.4.2 Self-Diffusion Coefficients

We can compute the self-diffusion coefficient for a fluid using the formula given in Chapter 4. In the simulations this is done by computing an auto correlation function (Eq. 4.3) or through an Einstein’s relationship (Eq. 4.4). In this study, we compute self-diffusivity for \([\text{emim}]^+ [\text{EtSO}_4]^-\) and IL-water systems using the Einstein relationship through the slope of the mean-squared displacement plots at longer times.

As pointed out in previous chapter, ILs can exhibit glass like behavior and one needs to confirm that we actually are in the diffusive regime before making any estimates about the self-diffusion coefficients. We can use the method outlined in Chapter 7 (section 7.2.2) and compute a linearity parameter (\(\beta\)) using Eq. 7.6. If this value of beta approaches unity, we can assume that we are in diffusive regime. In the case of \([\text{emim}]^+ [\text{EtSO}_4]^-\), with and without water, the value of \(\beta\) never reaches unity exactly. This may be, in part, due to the statistical uncertainty of the data at longer times. However, if we assume that a diffusive behavior is
**TABLE 8.9**

Rotational relaxation times for the \([\text{emim}]^+\) cation and \([\text{EtSO}_4]^–\) anion and water molecule as a function of water content. (*) indicates that the estimate of rotational relaxation is inaccurate and the actual number would be higher than the reported value.

<table>
<thead>
<tr>
<th>Water Content</th>
<th>Rotational Relaxation Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(x_{\text{water}})</td>
</tr>
<tr>
<td></td>
<td>(–)</td>
</tr>
<tr>
<td>0.00</td>
<td>361</td>
</tr>
<tr>
<td>0.26</td>
<td>352</td>
</tr>
<tr>
<td>0.50</td>
<td>252</td>
</tr>
<tr>
<td>0.75</td>
<td>152</td>
</tr>
<tr>
<td>1.00</td>
<td>–</td>
</tr>
</tbody>
</table>
exhibited when the value of $\beta$ is larger than 0.85, we can make some estimates about the diffusion coefficients and compare them to the experiments [207].

Table 8.10 shows the self-diffusivities for the pure IL([emim]$^+$[EtSO$_4$]$^-$) computed from simulations, while Fig. 8.10 compares the simulation results with the experimental results obtained using PFG NMR technique [207]. It can be clearly seen that, as observed in the previous simulations and experiments, the diffusion coefficients for the cations are higher than those of the anions. Table 8.10 shows that simulations predict the diffusivities about a factor of 2 lower than the experimental values. It should be noted that at 308 K the values of $\beta$ were around 0.66 for cation and 0.55 anion. Also at 348 K the value of $\beta$ for anion is 0.75. This indicates that the estimate is only an apparent self-diffusivity and not the actual self-diffusivity. The temperature dependent diffusivity can then be analyzed using Arrhenius relationship (Eq. 2.2) to get the activation energies for the diffusion process. The simulations predict the activation energies to be -31.23 kJ/mol for cations and -34.64 kJ/mol for the anions. These numbers compare well with the experimental values of -30.2 kJ/mol for the cations and -34.0 kJ/mol for the anions [207].

Table 8.11 gives the self-diffusivities of [emim]$^+$[EtSO$_4$]$^-$ at different water loadings. As can be seen, the self-diffusivity of individual species increases as the mole fraction of water increases. The SPC water model predicts the self-diffusivity to be $3.5 \times 10^{-9}$ m$^2$/s at 348 K. The experimentally determined value for water at 343 K is about $5.6 \times 10^{-9}$ m$^2$/s [97]. These results compare reasonably with the experimental self-diffusivity.
TABLE 8.10

Simulation results for Self-diffusivities for the [emim]$^+$ cation and [EtSO$_4$]$^-$ anion in [emim]$^+$[EtSO$_4$]$^-$ at different temperatures. (*) indicates the value of $\beta$ lower than 0.85

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Self-diffusivities ($m^2/s \times 10^{12}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>$D_+$</td>
</tr>
<tr>
<td></td>
<td>$D_-$</td>
</tr>
<tr>
<td>308</td>
<td>4.9*</td>
</tr>
<tr>
<td></td>
<td>1.9*</td>
</tr>
<tr>
<td>328</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
</tr>
<tr>
<td>348</td>
<td>21.4</td>
</tr>
<tr>
<td></td>
<td>9.5*</td>
</tr>
<tr>
<td>368</td>
<td>39.3</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
</tr>
</tbody>
</table>
Figure 8.10. Comparison of the self-diffusivities for the cations and anions with the experimental results [207]. Back filled circles denote simulations results for the cations while red filled circled show the results for anions. The open symbols have the similar meaning for the experimental results. Solid and dashed lines are just for visual aid.
TABLE 8.11

Simulation results for Self-diffusivities for the \([\text{emim}]^+\) cation and \([\text{EtSO}_4]^-\) anion in \([\text{emim}]^+\)[\text{EtSO}_4]^- at different temperatures. (*) indicates the value of \(\beta\) lower than 0.85.

<table>
<thead>
<tr>
<th>Mole fraction of water (x_{\text{water}})</th>
<th>Self-diffusivities (D) (\text{m}^2/\text{s}, \times 10^{12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x_{\text{water}})</td>
<td>(D_+) (D_-) (D_{\text{water}})</td>
</tr>
<tr>
<td>0.00</td>
<td>21.4 9.5(^*) --</td>
</tr>
<tr>
<td>0.26</td>
<td>24.7 13.8 45.8</td>
</tr>
<tr>
<td>0.50</td>
<td>28.0 19.6 80.6</td>
</tr>
<tr>
<td>0.75</td>
<td>63.3 44.7 203.6</td>
</tr>
<tr>
<td>1.00</td>
<td>-- -- 3500</td>
</tr>
</tbody>
</table>
8.4.3 Shear Viscosity

The effect of water content on the viscosity of $[\text{emim}]^+ [\text{EtSO}_4^-]$ was studied by carrying out simulation at 5 different water compositions, including pure water and pure IL ($x_{\text{water}} = 0.0, 0.26, 0.50, 0.75, 1.00$). The modified mode coupling method, described in the previous chapter (Eq. 7.2), is used to compute the viscosities of the mixtures. The simulation viscosities are summarized in Table 8.12. It can be noticed that as water content increases the viscosity of the mixture decreases. However, the viscosity of the mixture does not drop significantly for the first 0.25 mole fraction of water and then decreases rapidly to the viscosity of pure water over the next 0.75 mole fraction range. Fig. 8.11 compares the simulation viscosity to the experimentally observed viscosity from Rodriguez and Brennecke [172]. It can be seen from this figure that even though, simulations are able to predict the pure component viscosity of IL in very good agreement with the experiments, they fail to capture the rapid fall of viscosity as the composition of water increases in the system. The same figure also gives the ideal solution model (or pseudo colligative model) viscosities discussed in the last chapter (Eq. 7.10 and Eq. 7.11) and compares it with the simulation and the experimental results. As was the case of $[\text{emim}]^+ [\text{Tfn}_2^-]$ - water system, the ideal solution (pseudo colligative) models predict even faster drop of viscosity as the water content increases. The observation is in accordance with the hypothesis of the previous chapter that even if the polar water molecules associate preferentially with an anion and thereby reduce the cation-anion interaction, they still retain some of the rigidity of the fluid in account of their own electrostatic interactions with the ions in the solution and within themselves. This leads to a negative excess molar volume at low water contents and the drop in the viscosity is not as much. We think our SPC water
TABLE 8.12

Shear viscosity of $[\text{emim}]^+[\text{EtSO}_4]^{-}$ as a function of water composition. Subscripts indicate the statistical uncertainties in the final digit.

<table>
<thead>
<tr>
<th>Mole fraction of water $x_{\text{water}}$</th>
<th>Shear viscosity $(cP)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>19.1</td>
</tr>
<tr>
<td>0.26</td>
<td>18.1</td>
</tr>
<tr>
<td>0.50</td>
<td>15.2</td>
</tr>
<tr>
<td>0.75</td>
<td>7.723</td>
</tr>
<tr>
<td>1.00</td>
<td>0.3184</td>
</tr>
</tbody>
</table>

potential is *too attractive* in nature, i.e., the attraction between water molecules and the IL molecule is more than that in the real mixture. This contributes to the larger excess molar volumes observed in the simulations as compared to the experimental excess molar volumes (Fig. 8.6) and leads to smaller drop in viscosity than what is observed experimentally.

8.4.4 Thermal Conductivity

As described in Chapter 4, a different (the original) version of RNEMD algorithm is used to compute the thermal conductivity of IL-water systems. Instead of just the “x” component of velocity, all the components of velocity are exchanged and a temperature gradient is set up. A typical result of a RNEMD run to calcu-
Figure 8.11. Comparison of the shear viscosities for $[\text{emim}]^+ [\text{EtSO}_4]^- \text{ computed from simulations (filled circles) and the experimental viscosities (open circles) as function of water content. Dotted line are just a guide for the eye. The solid line shows the predicted mixture viscosity based on the Eq. 7.11 [denoted as model(1)], while the dashed line is the mixture viscosity based on Eq. 7.10[denoted as model(2)].}
TABLE 8.13

**Thermal conductivities of the systems used to validate the method. (∗) indicates the use of reduced units.**

<table>
<thead>
<tr>
<th>Systems</th>
<th>Temperature ($T$, K)</th>
<th>Density ($\rho$, gm/cm$^3$)</th>
<th>Thermal conductivity ($\lambda_T$, W/m$-K$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Literature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>argon</td>
<td>0.694*</td>
<td>0.849*</td>
<td>7.05* [140]</td>
</tr>
<tr>
<td>NaCl</td>
<td>1500.0</td>
<td>1.325</td>
<td>0.493 [56]</td>
</tr>
<tr>
<td>This work</td>
<td></td>
<td></td>
<td>6.92*</td>
</tr>
</tbody>
</table>

late the thermal conductivity is a temperature profile and an estimate of thermal conductivity as a function of time instead of a velocity profile and an estimate of the shear viscosity as a function of time. As in the case for the shear viscosity when the algorithm was first coded in the group software APSS, we used two test systems (Lennard-Jones Argon, and molten sodium chloride) to validate our code and the algorithm. The results of the validation runs compared against the literature values are summarized in the Table 8.13. As can be seen, the agreement between the literature values and the computed thermal conductivities is good. Thus, we can go ahead and compute the same for IL-water systems.

The same water loadings, as considered in the study of shear viscosity, are considered to compute the thermal conductivity of pure [emim]$^+$$[EtSO_4]^- \text{ as well as to study the effect of water loadings on the thermal conductivity of IL. Table 8.14 summarizes the results for IL-water systems ($x_{water} = 0.0, 0.26, 0.50, 0.75, 1.00$) at 348 K. As the thermal gradient increases, thermal conductivity also}
increases. Hence the thermal conductivity is calculated by averaging over the value which are in plateau region. The standard deviation of the average value is taken as the error bar on the number. As expected, the thermal conductivity of mixture increases as the water content increases. The thermal conductivity of pure water at 348 K was calculated to be 0.85±0.1 W/m-K while the experimental value at this temperature is about 0.66 W/m-K [167]. However, this value is in good agreement with the simulation results for SPC/E water model using the same RNEMD method [193, 225]. The data set for pure IL showed continuing decrease as the thermal gradient decreased and the value noted in this study is a rough estimate of the thermal conductivity at 348 K. The decrease in the thermal conductivity, however, was not significant and the actual value is not expected to be very different from the one reported here.

As noted in Chapter 2, to the best of my knowledge, this is the first simulation study to compute the thermal conductivity of any IL. Thus, there are no other simulation studies to compare our results. As far as I know, there is no literature data for the thermal conductivity of [emim]+[EtSO₄]− (both experimental or simulation) and therefore we can not compare these numbers to the experimental value. However, as mentioned in Chapter 2, the thermal conductivity of few other ILs has been measured as well as the effect of water content on the thermal conductivity [206]. Results presented in this chapter are in good agreement with the thermal conductivities measured in that study.

8.5 Summary

Forcefield was modified for [EtSO₄]− to reproduce the quantum mechanically optimized geometry. This modified forcefield for the anion along with forcefield
TABLE 8.14

Thermal conductivity of $[\text{emim}]^+[\text{EtSO}_4]^{-}$ as a function of water composition. Subscripts indicate the statistical uncertainties in the final digit.

<table>
<thead>
<tr>
<th>Mole fraction of water</th>
<th>Thermal conductivity $(\frac{W}{m-K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{\text{water}}$</td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>0.167$_2$</td>
</tr>
<tr>
<td>0.26</td>
<td>0.176$_3$</td>
</tr>
<tr>
<td>0.50</td>
<td>0.187$_3$</td>
</tr>
<tr>
<td>0.75</td>
<td>0.242$_5$</td>
</tr>
<tr>
<td>1.00</td>
<td>0.85$_1$</td>
</tr>
</tbody>
</table>
used in the previous chapter for the cation was then used to compute several equilibrium and dynamic properties of pure IL ([emim]$^+$[EtSO$_4$]$^-$) and IL-water systems. In that pure IL was simulated at four different temperatures. By studying these systems, we have computed liquid densities, volumetric expansivity, heat of vaporization and heat capacity for pure [emim]$^+$[EtSO$_4$]$^-$ at 348 K. We have also studied the effect of water content on this IL by computing equilibrium properties like excess molar volume, enthalpy of mixing and partial molar enthalpy for water and IL at 348 K. In general, a fair agreement was observed with the available experimental results. The computed value of partial molar enthalpy of water in the infinite dilution regime showed marked difference with two different fitting methods. The computed excess molar volumes also showed a very high sensitivity to the computed densities. The computed excess molar volumes do not show experimentally observed reversal of sign near $x_{\text{water}} = 0.9$ and the computed values for excess molar volumes and heats of mixing show a significant deviation in magnitude from the experimental results. We think that this is a result of the over attractive SPC water model. Further simulations need to be carried out to see the effect of water model used on these properties. However, a reduced charge SPC water model was studied to compute the heat of mixing at $x_{\text{water}} = 0.26$ and did not show significant deviation from the original SPC water model.

Additionally, the effect of water content on the transport properties was studied at 348 K by considering 3 different water loadings and the pure component properties ($x_{\text{water}} = 0.0, 0.26, 0.50, 0.75, 1.0$). As expected, as the water content increased, the self-diffusivity and thermal conductivity increased while the shear viscosity decreased. The simulations fail to reproduce experimental drop in viscosity from $x_{\text{water}} = 0.0$ to $x_{\text{water}} = 0.25$. However, the experiments also confirmed
that the viscosity does not drop as much as it would if the mixtures were ideal. We think, again, this might be in part due to the over attractive water model. More simulations, however, need to be run to explain this effect. The systems also needs to be analyzed, as in previous chapter, to see if significant clusters are being formed. Also an additional solubility study is being carried out in parallel to this effort to shed some more light on this IL-water system. As pointed out earlier, to the best of my knowledge, this is the first instance in which a thermal conductivity is studied using atomistic simulations for ILs. Even though experimental thermal conductivities were not available for $[\text{emim}]^+[\text{EtSO}_4]^-$, the simulation results are in good agreement with the experiments carried out on other ILs.
CHAPTER 9
CALCULATING THE ENTHALPY OF VAPORIZATION FOR IONIC LIQUID CLUSTERS

Probably the most important advantage is that they (ionic liquids) have no measurable vapor pressure. Unlike conventional solvents used in the industrial syntheses of organic chemicals, they are nonvolatile and therefore do no emit vapors.

.. Kenneth R. Seddon
[to C&E News in 1998]

9.1 Introduction

Contrary to many widely stated claims that ILs are non-volatile liquids, it has been appreciated for some time that they have a detectable (if very low) vapor pressure [154, 192, 224], just like other molten salts. Indeed, recent experimental studies [39] have shown that ILs can be distilled to some extent. This latter study has stimulated a strong interest in understanding the nature of the vapor phase of ILs. ILs can volatilize by two different mechanisms. In the first mechanism, neutral species are formed in the liquid either via thermal decomposition or proton transfer. These neutral species are sufficiently volatile that they can be detected in the vapor phase and give rise to a measurable vapor pressure. Upon condensation,
these species can reform into ILs. Such a vaporization mechanism was observed in early studies of mixtures containing alkylimidazolium chloride and aluminum chloride [150]. It is also possible for ion pairs, ion clusters, or non-neutral clusters to volatilize. This is the mechanism thought to occur in aprotic ILs and was the operative mechanism in the study by Earle et al. [39]. The nature of the vapor species formed could not be determined in that work.

Our research group at Notre Dame has used atomistic simulations over the past several years to compute the enthalpy of vaporization of a number of different ILs, including 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim]⁺-[PF₆]⁻) [136, 181], 1-n-butyl-3-methylimidazolium nitrate ([bmim]⁺[NO₃]⁻) [25], three different alkyl-pyridinium cations paired with the bis(trifluoromethanesulfonfyl)imide ([Tf₂N]⁻) anion [26], and seven different triazolium-based compounds [25]. For this broad range of ILs, calculated enthalpies of vaporization for ion pairs ranged from 148–238 kJ/mol. Enthalpies of vaporization were lowest for imidazolium cations with short alkyl chains. The enthalpy of vaporization increased as alkyl chain length increased, and decreased as temperature increased. In general, imidazolium cations had lower enthalpies of vaporization than pyridinium cations, which had lower enthalpies of vaporization than triazolium cations. The [Tf₂N]⁻ anion served to lower the enthalpy of vaporization relative to other anions studied. Wang and co-workers [106, 107] have also used atomistic simulations to determine the enthalpies of vaporization of imidazolium-based ILs, and their results generally agree with those from our lab. Importantly, it was assumed in all these calculations that the volatile species is a neutral ion pair.

Very recently, direct measurement of enthalpies of vaporization have been performed for a series of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonfyl)-
imides ([Rₙmim][Tf₂N]⁻) [174]. The experimental enthalpies of vaporization were consistent with previous indirect measures of the enthalpy of vaporization [154, 192, 224] and ranged from 136–192 kJ/mol at 298 K. These authors also calculated the enthalpies of vaporization for these systems using atomistic simulations, assuming the volatile species was a neutral ion pair. The simulations matched the experimental enthalpies of vaporization reasonably well; computed values at 298 K were about 17% too high for [C₂mim]+[Tf₂N]⁻ (i.e. [emim]+-[Tf₂N]⁻) but only 4% too high for [C₈mim]+[Tf₂N]⁻ (i.e. [omim]+[Tf₂N]⁻). Agreement was similar at 578 K, with simulated enthalpies ranging from 23% to 7% too high. Consistent with the previous simulations mentioned above, the enthalpy of vaporization was found to increase with increasing chain length and decrease with increasing temperature.

The fact that all these simulations match experimental trends and yield enthalpies of vaporization that are within 20% or so of experimental values suggests that the volatile species are indeed neutral ion pairs. This mechanism is consistent with a recent gas chromatography - mass spectrometry study [200] and photoelectron spectrum measurements [189]. To date, however, there have been no calculations of the enthalpy of vaporization of clusters larger than an ion pair, nor have calculations been performed on non-neutral ion clusters. As such, one cannot definitively say that the simulations confirm that the dominant volatile species is a single ion pair. In this chapter we will digress from the theme of this dissertation and look at this vaporization process of ILs and look at the nature of the vapor phase for ILs. Specifically, we wish to know answers to the following questions. Do simulations predict that other species such as clusters of two or three ion pairs show similar (or lower) enthalpies of vaporization? Is the computed
enthalpy of vaporization of non-neutral clusters significantly higher than that of neutral clusters, thereby precluding these species as a possible volatile product? Can classical simulations, in which enthalpies are probably only accurate to at best 5–10 kJ/mol, discriminate between different vaporization mechanisms?

In this study, we answer these questions by carrying out vaporization simulations on a series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Rₙmim][Tf₂N⁻]) ILs (abbreviated as [Cₙmim][Tf₂N⁻], where n is the number of carbon atoms in the alkyl chain). We show that for this IL, the only reasonable mechanism consistent with the simulations is one in which single neutral ion pairs volatilize. Larger neutral clusters exhibit much higher enthalpies of vaporization, and the enthalpy of vaporization of non-neutral species is so high that these events will rarely take place. One can also refer to our publications [87, 189] for the details of these simulations and for the additional supporting information. In the Supporting Information of the publication [87], we summarize all of the previous enthalpy of vaporization data computed in our lab for ion pairs, which can be compared against future experimental measurements to assess if other ILs have a similar vaporization mechanism.

9.2 Simulation Details

To model the ILs, we used a classical forcefield of a form consistent with our prior work [24–26, 136] given by Eq. 3.16. With the exception of the partial charges for [C₆mim]⁺ and [C₈mim]⁺ cations, the parameters for the imidazolium cations were taken from the work of Cadena et al. [24]. The parameters for the [Tf₂N⁻] anion were taken from the work of Lopes and Paduá [110]. The partial charges for [C₆mim]⁺ and [C₈mim]⁺ cations were obtained from ab-


\textit{initio} calculations of separate ions in the gas phase, at the B3LYP/6-311++G* level of theory [50] (explained in Chapter 3). The CHELPG [21] algorithm was used to determine the partial charge assignment for the individual atom centers.

The molar enthalpy of vaporization, $\Delta h_{\text{vap}}$, was calculated as

$$\Delta h_{\text{vap}}(T, P) = \langle h_{\text{gas}}(T) \rangle - \langle h_{\text{liq}}(T, P) \rangle$$

(9.1)

where $\langle h_{\text{gas}}(T) \rangle$ and $\langle h_{\text{liq}}(T, P) \rangle$ are the ensemble average molar enthalpies of an ideal gas and neat liquid, respectively, at temperature $T$ and pressure $P$. Note that lower case symbols refer to molar (intensive) energies while upper case symbols refer to total (extensive) energies.

These molar enthalpies are given by

$$\langle h_{\text{gas}}(T) \rangle = \langle u_{\text{gas}}(T) \rangle + R T$$

(9.2)

$$\langle h_{\text{liq}}(T, P) \rangle = \langle u_{\text{liq}}(T, P) \rangle + P v$$

(9.3)

where $u$ is the molar internal energy, $R$ is the universal gas constant, $P$ and $v$ are the pressure and molar volume of the liquid phase, and the gas was assumed to be ideal. The value of the pressure-volume work is negligible for the liquid when compared to the internal energies, and hence can be neglected. The ideal gas internal energy was calculated by simulating a non-interacting cluster and ensemble averaging the internal energy. Separate gas phase simulations were conducted for each type of cluster examined.

Eq. 9.1 can be written as

$$\Delta h_{\text{vap}}(T, P) = \langle u_{\text{gas}}(T) \rangle + R T - \langle u_{\text{liq}}(T, P) \rangle$$

(9.4)
or,

\[ \Delta h_{vap}(T, P) = \Delta u_{vap}(T, P) + R T \]  

(9.5)

where \( \Delta u_{vap} \) is the molar internal energy of vaporization of the entity assumed to be vaporizing.

To compute \( \Delta h_{vap}(T, P) \) for a single ion pair, one simply must compute the average total extensive internal energy of the liquid and an ideal gas at the conditions of interest and divide by the total number of ion pairs. If the vaporizing entity is assumed to be neutral ion dimers, then the extensive energy is divided by the total number of dimers (or one half the number of ion pairs).

To compute the enthalpy of vaporization of non-neutral species, the potential energy is split into different parts. The total internal energy due to cations in the liquid or gas phase is given by

\[ \mathcal{U}^+ = \mathcal{U}^+[+] + \mathcal{U}^+_{\text{intra}} + 0.5 \mathcal{U}^+[\text{-}] \]  

(9.6)

where, \( \mathcal{U}^+[+] \) is the cation-cation non-bonded potential energy, \( \mathcal{U}^+[\text{-}] \) is the cation-anion non-bonded potential energy and \( \mathcal{U}^+_{\text{intra}} \) is the intramolecular energy of the cations. Likewise, the portion of the total internal energy due to anions is

\[ \mathcal{U}^- = \mathcal{U}^-[\text{-}] + \mathcal{U}^-_{\text{intra}} + 0.5 \mathcal{U}^+[\text{-}] \]  

(9.7)

where the symbols have similar meaning. The internal energy of an ion cluster is computed by adding the energies for each ion in the cluster. For example, the internal energy of a cluster containing two cations and one anion, abbreviated as \( \{[+]_2[-]\}^+ \), is

\[ \mathcal{U}^\{[+]_2[-]\}^+ = 2 \mathcal{U}^+[+] + \mathcal{U}^-[\text{-}] \]  

(9.8)
The molar internal energy of a cluster containing $p$ cations and $q$ anions is

$$u_{\{[+]^p[-]^q\}^+} = \frac{p \mathcal{U}_{[+]}}{n_+} + \frac{q \mathcal{U}_{[-]}}{n_-}$$  \hspace{1cm} (9.9)$$

where $n_+$ and $n_-$ are the total number of cations and anions present in the system, respectively. Note that *mole* refers to a mole of the species one is computing the energy for (whether that be ion pairs, a \{[+][−]\} + cluster, or some other entity). Eq 9.9 is equally valid for computing the internal energy of neutral clusters (*i.e.* when $p = q$).

In the gas phase, the energies in Eq. 9.9 can be computed by direct pairwise summation because periodic boundary conditions are not needed. In the liquid phase where periodic boundary conditions are used, however, care must be taken when computing the energy of non-neutral clusters. This is because one cannot deconvolute the individual cation-anion interactions in the reciprocal space part of the Ewald sum to obtain the energies in Eqs 9.6 and 9.7. To circumvent this, an approximate direct method was used to compute the energies for non-neutral liquid phase clusters. As shown below, this gives essentially the same liquid phase energies as does the rigorous Ewald sum method.

To compute the enthalpies of vaporization for the ILs, both liquid phase and ideal gas phase simulations were performed in different ensembles using the simulation package NAMD [156] and locally developed software (APPS). The details of how these simulations are carried out has been provided in previous chapters and publications [24–26]. Starting from an equilibrated liquid conformation of 200 ion pairs, a 2 ns isothermal-isobaric molecular dynamics simulation was carried out. The resulting configurations were then simulated for 5 ns at constant temperature and density, with data collected during the latter portion of these runs. Gas phase
calculations were performed on non-interacting clusters at constant temperature. Replicate runs were conducted on selected systems, with the computed standard deviations in energy used to estimate uncertainties.

To investigate the effect of temperature on the enthalpy of vaporization, \([C_2\text{mim}]^+\)\([Tf_2N]^−\) was studied at six different temperatures (\(T = 293, 313, 343, 400, 450\) and 500 K). To examine the effect of alkyl chain length on \(\Delta h_{\text{vap}}\), four different ionic liquids (\([C_2\text{mim}]^+\)\([Tf_2N]^−\), \([C_4\text{mim}]^+\)\([Tf_2N]^−\), \([C_6\text{mim}]^+\)\([Tf_2N]^−\), \([C_8\text{mim}]^+\)\([Tf_2N]^−\)) were simulated at 293 K.

In addition to these calculations, cohesive energy densities, molar volumes, and enthalpies of vaporization obtained from our previous work [24–26, 136] have been compiled and are listed in the Supporting Information of the publication [87].

9.3 Results and Discussion

To determine which species has the lowest enthalpy of vaporization, calculations were performed on \([C_2\text{mim}]^+\)\([Tf_2N]^−\) at 293 K. Enthalpies of vaporization were computed for neutral ion pairs, dimers, and trimers using the standard Ewald sum technique. The results are shown in Table 9.1 and are split into non-bonded van der Waals, Coulombic, and intramolecular contributions. Based on the rigorous Ewald sum calculations, the enthalpy of vaporization increases by about 40 kJ/mol for each additional ion pair added to the cluster, suggesting that single ion pairs are much more likely to volatilize from the liquid than larger neutral clusters. Once in the vapor phase, individual ion pairs may recombine into larger clusters, but the dominant species leaving the liquid is predicted to be a single ion pair.
**TABLE 9.1**

Comparison of enthalpies of vaporization of different ion clusters as well as the contribution from van der Waals, Coulombic and intramolecular energies to the enthalpies of vaporization of different ion clusters. The energies for neutral ion clusters were calculated with Ewald sum method as well as with the direct method with the minimum image convention. Energies of non-neutral clusters were calculated with the minimum image convention. The contribution of van der Waals energies were calculated by simple cutoff in all cases.

<table>
<thead>
<tr>
<th>ion cluster</th>
<th>van der Waals (kJ/mol)</th>
<th>Coulombic (kJ/mol)</th>
<th>intra (kJ/mol)</th>
<th>total (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Ewald sum:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>{[C\text{\textsubscript{2}}\text{mim}]}\textsuperscript{+}</td>
<td>41</td>
<td>211</td>
<td>3</td>
<td>250</td>
</tr>
<tr>
<td>{[Tf\text{\textsubscript{2}}\text{N}]}\textsuperscript{−}</td>
<td>52</td>
<td>179</td>
<td>−1</td>
<td>225</td>
</tr>
<tr>
<td>{[C\text{\textsubscript{2}}\text{mim}][Tf\text{\textsubscript{2}}\text{N}]}</td>
<td>74</td>
<td>74</td>
<td>2</td>
<td>146</td>
</tr>
<tr>
<td>{[C\text{\textsubscript{2}}\text{mim}]\textsubscript{2} [Tf\text{\textsubscript{2}}\text{N}]}\textsuperscript{+}</td>
<td>102</td>
<td>186</td>
<td>−1</td>
<td>282</td>
</tr>
<tr>
<td>{[C\text{\textsubscript{2}}\text{mim}][Tf\text{\textsubscript{2}}\text{N}]\textsubscript{2}}\textsuperscript{−}</td>
<td>106</td>
<td>158</td>
<td>−5</td>
<td>255</td>
</tr>
<tr>
<td>{[C\text{\textsubscript{2}}\text{mim}]\textsubscript{2} [Tf\text{\textsubscript{2}}\text{N}]\textsubscript{2}}</td>
<td>121</td>
<td>71</td>
<td>−4</td>
<td>184</td>
</tr>
</tbody>
</table>

*Continued on next page*
To compute the enthalpy of vaporization for non-neutral clusters, the minimum image convention was used to calculate the Coulombic interactions in the liquid phase, while the normal cutoff with tail corrections were applied to van der Waals interactions. As mentioned above, this is necessary because the standard Ewald sum cannot be used in Eq. 9.9. As can be seen in Table 9.1, the use of this approximate treatment of the charged interactions gives the same enthalpy of vaporization of neutral ion pairs as the exact result, within the uncertainty of the calculations. This is to be expected, given that the simulation box is relatively large. It is also expected that the non-neutral species values are of the same accuracy as the neutral cluster enthalpies. There are three interesting conclusions that can be drawn from the results in Table 9.1. First, non-neutral clusters/ions have a much higher enthalpy of vaporization than neutral clusters of similar size. This is due mostly to the increased Coulombic enthalpy of the non-neutral clusters. Second, small neutral clusters have a lower enthalpy of vaporization than larger...
clusters consisting of two and three pairs of ions. Nearly all of the increase in enthalpy of vaporization which occurs with increasing cluster size is due to non-bonded energies; Coulombic and intramolecular energies are roughly the same for the different cluster sizes. Taken together, this suggests that single neutral ion pairs are the dominant volatile species. The third finding is that the enthalpies of vaporization of a negative cluster ($\{[+][-]_2\}^-$) is lower than that of a positive cluster ($\{ [+2][-] \}^+$). In fact, the enthalpies of vaporization of a single anion is about 25 kJ/mol lower than that of a single cation. Most of this difference is due to Coulombic interactions, suggesting that the somewhat smaller and more flexible anion does a better job solvating the charge on the cation than does the cation solvating the charge on the anion.

Table 9.2 shows the molar enthalpy of vaporization for ion pairs of $[C_2mim]^+$-$[Tf_2N]^- \text{ as a function of temperature. From these results, the enthalpy of vaporization is estimated to be } 143 \pm 3 \text{ kJ/mol at } 298 \text{ K and } 124 \pm 3 \text{ kJ/mol at } 578 \text{ K. This compares reasonably well with the experimental values [174, 224] of } 136 \pm 6 \text{ and } 110.4 \pm 2.4 \text{ kJ/mol, respectively. Using a different forcefield, Santos et al. computed the enthalpy of vaporization as } 159 \pm 10 \text{ and } 136 \pm 20 \text{ kJ/mol at these same two temperatures. Thus both sets of simulations appear to be in fair agreement with the experimental data. The calculations suggest that the internal energy of vaporization drops about 15\% over this temperature range, as the molar volume increases by about 14\%. Clearly, much of the drop in the enthalpy of vaporization is due to the thermal expansion of the liquid reducing the favorable attractive interactions present in the liquid phase. This causes a relatively large reduction in the cohesive energy density of the system with increasing temperature.}
TABLE 9.2
Cohesive energy density \((c)\), molar volume \((v)\), internal energy of vaporization \((\Delta u_{vap})\) and enthalpy of vaporization \((\Delta h_{vap})\) for \([C_{2}mim]^{+}[Tf_{2}N]^{-}\) as a function of temperature at 1 bar. Note that ion pairs were assumed to be the volatile species. Uncertainties in the internal energy and enthalpy of vaporization were estimated to be 3 kJ/mol.

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>(c) (J/cm(^3))</th>
<th>(v) (cm(^3)/mol)</th>
<th>(\Delta u_{vap}) (kJ/mol)</th>
<th>(RT) (kJ/mol)</th>
<th>(\Delta h_{vap}) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>568</td>
<td>251.87</td>
<td>143</td>
<td>2.44</td>
<td>146</td>
</tr>
<tr>
<td>313</td>
<td>530</td>
<td>257.82</td>
<td>137</td>
<td>2.60</td>
<td>139</td>
</tr>
<tr>
<td>343</td>
<td>511</td>
<td>263.18</td>
<td>135</td>
<td>2.85</td>
<td>137</td>
</tr>
<tr>
<td>400</td>
<td>501</td>
<td>271.33</td>
<td>136</td>
<td>3.33</td>
<td>139</td>
</tr>
<tr>
<td>450</td>
<td>458</td>
<td>281.40</td>
<td>129</td>
<td>3.74</td>
<td>133</td>
</tr>
<tr>
<td>500</td>
<td>427</td>
<td>291.63</td>
<td>124</td>
<td>4.16</td>
<td>129</td>
</tr>
</tbody>
</table>
Table 9.3 shows how the computed enthalpy and internal energy of vaporization, cohesive energy density and molar volume change as the length of the alkyl chain is increased at 293 K. Fig. 9.1 shows a comparison of the computed enthalpy of vaporization versus alkyl chain length against the experimental data of Santos et al. [174] and Zaitsau et al. [224], as well as the simulation results of Santos et al. [174]. The experiments predict that the enthalpy of vaporization increases by about 5 kJ/mol for every 2-carbon increment in the alkyl chain. This is similar to the experimental observations of Zaitsau et al. [224]. The experiments and simulations of Santos et al. [174] show a somewhat larger increase in the enthalpy of vaporization of about 19 kJ/mol and 14 kJ/mol for every 2-carbon increase in chain length, respectively. The present simulations suggest that this increase in enthalpy of vaporization is mostly due to the additional van der Waals interactions that arise as chain lengths increase, as suggested by Santos et al. [174]. Similar effects were observed for simulations of pyridinium-based ILs paired with the $[Tf_2N]^{-}$ anion [25], where enthalpies of vaporization increased about 7 kJ/mol for every two-carbon increment in the long alkyl chain. When a methyl group was added to the pyridinium ring, however, the enthalpy of vaporization decreased, due to an increase in the molar volume (see Supporting Information of Kelkar and Maginn [87]).
TABLE 9.3

Results of calculations on \([C_2\text{mim}]^+[Tf_2N]^-\) at 293 K and 1 bar, compared against previous experiments [174, 224] and simulations [174]. Uncertainties in the internal energy and enthalpy of vaporization for the present simulations were estimated to be 3 kJ/mol.

| \(n\) | \(c\) \((\text{J/cm}^3)\) | \(v\) \((\text{cm}^3/\text{mol})\) | \(\Delta u_{\text{vap}}\) \((\text{kJ/mol})\) | \(RT\) \((\text{kJ/mol})\) | \(\Delta h_{\text{vap}}^{\text{sim}}\) \((\text{kJ/mol})\) | \(\Delta h_{\text{vap}}^{\text{sim},[174]}\) \((\text{kJ/mol})\) | \(\Delta h_{\text{vap}}^{\text{expt},[174]}\) \((\text{kJ/mol})\) | \(\Delta h_{\text{vap}}^{\text{expt},[224]}\) \((\text{kJ/mol})\) |
|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 2    | 563             | 254.24          | 143             | 2.44            | 146             | 159             | 136             | 135             |
| 4    | 515             | 288.53          | 149             | 2.44            | 151             | 174             | 155             | 136             |
| 6    | 477             | 323.30          | 154             | 2.44            | 157             | 184             | 173             | 140             |
| 8    | 446             | 358.33          | 160             | 2.44            | 162             | 201             | 192             | 150             |
Figure 9.1. Comparison of the computed enthalpy of vaporization for \([C_2\text{mim}]^+[\text{Tf}_2\text{N}]^-\) at 293 K and 1 bar with the experiments of Santos et al. [174] and Zaitsau et al. [224] at 298 K and 1 bar. Also shown are the simulation results of Santos et al. [174].

9.4 Conclusion

Calculations of the enthalpy of vaporization of ILs comprised of an alkylimidazolium cation paired with the bis(trifluoromethylsulfonyl)imide anion have been performed as a function of temperature and cation alkyl chain length. It is shown that the most energetically favorable volatile species for this class of IL is a single neutral ion pair. Each additional ion pair that is added to a cluster increases the enthalpy of vaporization by about 40 kJ/mol. Non-neutral clusters have even higher enthalpies of vaporization. The calculated enthalpies of vaporization agree with previous experimental and simulation results, and show a trend of increasing enthalpy with increasing alkyl chain length and decreasing temperature.
CHAPTER 10

CONCLUSIONS AND RECOMMENDATIONS

*It’s always helpful to learn from your mistakes because then your mistakes seem worthwhile.*

(.. Garry Marshall

[Wake Me When It’s Funny]

Owing to their exciting properties, ionic liquids have spurred a lot of interest in the industry and in the academia over the past decade. Even though in the beginning these liquids were looked at as a possible replacement for VOCs, the scope of the field has increased tremendously and now span from possible replacement for industrial solvents to heat exchanger fluids to reaction media to lubricants to absorption media and so on. As pointed out by Wishart and Castner [218], a lot of progress has been made in the synthesis of the new ILs and their properties have been measured. However, there is a lack of fundamental understanding of these properties. And this is, in part, hindering the applications of ILs on an industrial scale. As noted many times in this thesis, knowledge of transport properties is necessary to take a lab scale process to the industrial level or for that matter to the pilot plant level. The transport properties can affect the rate of a reaction through the rate of mass transport or dictate the design of a reactor or a heat exchanger. They also control the power consumption in a plant including the cost...
for pumping of the material. In short, transport properties affect the fixed cost to build the plant through sizes of the equipments as well as the variable cost to keep it running. Knowledge and fundamental understanding of these properties and their dependence on the state point or the impurities is thus of a prime importance. The goal of this study was to help provide a better understanding of these transport properties for ILs and to study the effect of various conditions, such as temperature, pressure and water content on these properties with the help of atomistic simulations.

Chapter 2 summarizes key findings and previous work that has been done in the field of ionic liquids while Chapter 3 summarizes few important concepts in the field of atomistic simulations. Chapter 4 builds on these key concepts and outlines the different algorithms developed and used in this study.

In Chapter 5 we implement a previously developed method, known as MIR, to compute the shear viscosities of longer alkanes and a 10 unit bead spring model of polymers. In the process of accurately estimating the shear viscosity of these fluids, we extend this algorithm by deriving a new set of equations of motion which would automatically generate a Gaussian velocity profile. We have also implemented a new averaging and fitting methods, in turn, making this method more robust.

Due to a problem with the operational window of MIR method for highly viscous systems such as ILs, we implement a different method to estimate shear viscosity, known as RNEMD, in Chapter 6. We validate the algorithm by benchmarking the results for four different test cases including argon, \( n \)-hexane, water and molten sodium chloride. We then extend this study and apply the algorithm to five polyhydric alcohols. Shear viscosity for these systems were calculated at four
different pressures. Even though the forcefield parameters from TraPPE forcefield were not optimized based on the experimental data for any of these polyhydric alcohols, the forcefield performs very well resulting in a good agreement with the experiments. The trends in the viscosity were then explained on the basis of structural analysis.

In Chapter 7, we extend this RNEMD method to study the effect of temperature and water content on the viscosity of an IL, \([\text{emim}]^+ [Tf_2N]^−\). A forcefield developed in our research group for the cations and a forcefield from the literature for the anion was used to study this effect. The viscosity of the pure IL was estimated at 5 different temperatures and a good agreement was found. The effect of water content was studied by considering 3 different water loadings. The simulations could not capture the rapid decrease in the viscosity of IL as the water content increases. The simulations predict a lower drop in viscosity than the experiments. These results were then compared with the mixture viscosity models in the literature. It was observed that the ideal mixture (or pseudo colligative) models predict even faster drop in viscosity. The systems were then analyzed in terms of the excess molar volume and the cluster formation. It was observed that the excess molar volume was negative and the non-ideality parameter \((G_{12})\) was found to be around 1. This is a high number, indicating a significant non-ideality. The analysis of the simulation trajectories revealed that water tends to associate more with the anion than with the cation and forms cluster ranging in sizes of up to 5 molecules. This indicates that, even though the interactions between cations and anions are reduced they are not reduced as much as in an ideal mixture and the viscosity does not drop as fast. Most of this drop in viscosity, however, could be associated with the pseudo colligative effect, i.e. large difference in the pure
component viscosities.

Chapter 8 summarizes the study carried out on \(\text{emim}^+\text{[EtSO}_4]^-\) - water system using MD simulations. In this case the forcefield for the anion was modified from what was available in the literature. The system of pure IL was studied at four different temperatures. The effect of water composition on IL was studied at 348 K. Equilibrium properties like heat capacities and enthalpy of vaporization were computed. Where the data was available, the simulations did a good job predicting the pure component properties. The agreement was not as good when the mixture properties were computed. Excess molar volumes and the enthalpies of mixing were determined at many different water loading. It was observed that the simulations overestimate the magnitude of these properties. This was thought to be, in part, due to the over attractive water-IL interactions. The effect of water composition on transport properties was studied at three different water loadings. The simulations agree very well with the experiments for the viscosity of pure IL. As the water content increases, the the viscosity of the mixture decreases. Again, simulations fail to capture the rapid drop in the viscosity observed in the experiments. In this case as well, the ideal mixture models predict even faster drop than observed. The results from the first simulation study on thermal conductivity for ILs are also summarized in this chapter. As expected the thermal conductivity increases as the water loading increases. Although the experimental data was not available to compare against, the estimates are in good agreement with the experimental thermal conductivity of similar ILs.

In Chapter 9 we digress from the determination of transport properties of ILs and study the enthalpy of vaporization of ILs. The effect of temperature and alkyl chain length on the enthalpy of vaporization were studied. Also the enthalpy of
vaporization for different neutral and non-neutral clusters were calculated. Indeed, it was observed that a lone ion pair has the minimum energy penalty for evaporation and therefore most probable way for IL vaporization. As the temperature increased the enthalpy of vaporization decreased. Also, the enthalpy of vaporization increased as the length of the alkyl side chain increased.

It needs to be noted that computation of these properties and the fundamental understanding of the structure-property relationship for ILs is still just a part of the puzzle. Before the ILs can be used on the industrial level, one needs to understand the ecological toxicity effects and biodegradability issues. The efforts in this regard are underway, in fact a research group at the University of Notre Dame is actively working on the same issue. One of the important observations from their study is that imidazolium based ILs have problems in biodegradation. One more thing to be noted here is that as more and more ILs will be used in the industry, the production of the raw materials to prepare ILs will also rise and even though synthesizing ILs may not pose environmental problems, the synthesis of their raw materials may!

In summary, it can be said that the techniques of atomistic simulations can be successfully applied to ionic liquids. These studies can provide a molecular level insight into the system and a fundamental understanding of the structure property relationship. The transport properties like viscosity can be predicted quantitatively using atomistic simulations. At the end, I hope to have convinced the reader that this study has contributed to the knowledge of the field of ionic liquids and helped advanced the field in the positive direction.
10.1 Recommendations for Future Work

Ideally, I would have liked to have this section blank to indicate that I have finished what I was set out to do. However, in the course of carrying out these calculations, some problems have surfaced and we would like to address them as this work is continued in the future. Moreover, as they say, “there is always room for improvements”.

As observed in previous simulation studies, the dynamics of ionic liquids seem to be sluggish. They show glass like behavior. This makes it difficult to get an efficient sampling of the system. The simulations become prohibitively long especially at lower temperatures. Hence, in an attempt to improve this situation one can either improve on the algorithm (i.e. the simulation package) or one can think about improving on the forcefield.

In this study, we have used two different simulation softwares (NAMD and APSS). NAMD is very fast and is available without any cost for academic use, however, it does not carry out all the operations that one would like to. For example, it can not compute the viscosities effectively using nonequilibrium methods. NAMD can simulate long equilibrium trajectories for reasonably big systems in relatively short times, but as indicated in this dissertation, equilibrium methods tend to be less efficient in computing transport properties. This necessitates the use of a different, more specialized simulation packages. In our research group we use a locally developed simulation software known as APSS (which stands for All Purpose Simulation Software). In this simulation software, we have implemented many different algorithms including nonequilibrium methods like MIR and RNEMD. Moreover, this software can take advantage of parallel computing by splitting the work load over many processors. However, the method used to
achieve this (known as replicated data) is one of the less efficient techniques for this purpose. A significant speed-up is expected if we use an algorithm like domain decomposition. Also we can add one more level in the multiple timestepping algorithm to compute van der Waals and electrostatic interactions on two different time scales. In addition, as aptly pointed out by Prof. Gezelter, method used to handle the electrostatic interactions (known as Ewald summation) tend to be the bottleneck of an atomistic simulation. One can think of improving the efficiency of these computation by implementing a recently developed Wolf method [44, 219]. Together with domain decomposition, this method is expected get a speed-up of about 20 times over the current version.

While simulating IL-water systems, one can think of improving on the force-field. As we have pointed out in the previous Chapter 8, that the higher magnitude of partial charges on water molecule may lead to over attractive interactions. Even though we did simulate a reduced charge model to get an estimate of heat of mixing, the densities predicted by that model were incorrect. As a next step, we can use a more realistic water model like TIP5P [116]. It is relatively easier to compute the densities of a given system and match them with the experimental numbers. However, matching the densities, or for that matter vapor-liquid coexistence curve may not give an accurate representation of the dynamics in the system. Self-diffusion coefficients are relatively easy to compute in an atomistic simulation and when developing new forcefield for ionic liquids, one can think of including this parameter as one of the optimization variables. In this way the correct order of atomic or molecular mobilities (and in turn transport properties) can be captured in a simulation. If we do have a fast or an efficient software, we can think of implementing and using polarizable forcefields. For systems like ionic
liquids, where the charge-charge (or electrostatic) interactions dominate, using a polarizable model can provide a better physical insight into the system than using a fixed charge forcefield. Also it has been observed in the literature that incorporating polarizibility in the forcefield may lead to increased mobility in the system [223]. However, these forcefield do come with a time penalty. Moreover, as mentioned in this dissertation, one can optimize the forcefield, even with the fixed charge model, to reproduce the correct order of mobility in the system. Everything being same, however, we would like to use a polarizable forcefield to get a better insight into the system.

It was mentioned in Chapter 7, that MIR method (described in 4.2.2.4) suffers from the problem of operational window in the case of ILs. This problem stems from the imposition of the external velocity field. Even though we use the modified equations of motion, the system is still has memory of only the thermal component of the velocities and not the total velocities. When in the beginning of the production run, the system starts moving with the total velocity, it takes some time adjusting to this new velocity profile. Although, using the equations of motion aid this process, a time lag equivalent to the rotational relaxation time is observed before the response of the system can be tracked as the response to an externally imposed velocity field. Instead of deriving the Hamiltonian equations of motion, if we propose an non-Hamiltonian equations of motion which can produce the Gaussian velocity profile, we can equilibrate the system to the total velocity. In this way, if our postulate is correct, once the production run starts, the system would not exhibit the lag time associated with it and the true response to the external velocity field could be tracked from the beginning. One thing needs to be note, however, before using these equations of motion, one would have to analyze
them and make sure that they do sample from the correct ensemble. If we can propose such equations of motion, one can use this method efficiently to compute the viscosities of highly viscous ILs. Even though this method necessitates the use of larger simulation boxes, the very short time of production runs (on the order of picoseconds instead of nanoseconds) could compensate for that.

Ionic liquids are being investigated as potential lubricants or lubricant additives. This would indicate that the transport properties of ILs, especially shear viscosity, needs to be computed at elevated temperatures and pressures. These experiments, generally, tend to be very difficult to carry out. As pointed out earlier, atomistic simulations could be used to compute the properties of IL systems at elevated temperatures and pressures with minimal cost. By studying these systems at different temperatures, one can compute the viscosity index, a typical measure of performance of a lubricant. Also studies at different pressures can give an estimate of the Barus coefficient. As shown by this work, simulations can be used to compute the relative order of these quantities for many different candidates and short list some potential systems. The experiments can now be performed on a small pool of candidates. Also, atomistic simulation studies can give a molecular level insight into the system which can be used to direct the research activities to synthesize the “task-specific” ILs more effectively.

The literature review reveals that an combination of imidazolium cation and a bis(trifluoromethanesulfonyl)imide can lead to relatively low viscosity ILs. However, many different candidates could potentially be available to reduce the viscosity of the system even further. These ILs could be complicated and could be difficult and expensive to synthesize, hence a molecular simulation study could be performed upfront to screen many different, yet-to-be-synthesized ILs to narrow
down the pool.

As the co-solvents and impurities tend to affect the properties of ILs significantly, different IL-IL mixtures or different IL - co-solvent mixtures could be studied using simulations to figure our the pool of candidates which would perform best for a specific application. Again this means improving the efficiency of “task-specific” ILs concept.

Thus, we can say that, atomistic simulations is a very powerful tool to study different systems on the molecular level. With the ever increasing speed of computations (both through faster processors and efficient algorithms) this field has very big upside. Having said that, these simulations may never replace the actual experiments and we would still have to carry out experiments to put the finishing touches on any research activity. However, it is not the competition between the simulations and experiments, but the collaboration of these two fields that can advance the science and the technology in the positive direction!
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