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Thermal Transport and Non-Equilibrium Coupling Effects in Molecular Liquids and Solutions

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Statement of Originality

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Abstract

Thermal gradients in molecular liquids and solutions generate coupled transport phenomena such as thermodiffusion, thermoelectricity, and thermal polarization, where temperature differences induce concentration gradients or electric fields. This thesis investigates these effects using non-equilibrium molecular dynamics (NEMD) simulations of water, aqueous electrolyte solutions, and ethanol across a wide range of thermodynamic conditions.

First, thermal transport and polarization in supercooled water are examined using the TIP4P/2005 model. A minimum in thermal conductivity coincides with extrema in the isobaric thermal expansion coefficient, isothermal compressibility, and speed of sound, linking anomalous heat transport to the hypothesized liquid–liquid phase transition (LLPT). Thermal gradients also induce polarization coefficients of several mV/K, with a non-monotonic temperature dependence arising from competing dipolar and quadrupolar contributions.

The study is then extended to supercooled NaCl and LiCl aqueous solutions. Complex thermodiffusive behavior emerges, including multiple thermophilic–thermophobic transitions and Soret coefficient minima between 220 and 250 K. These anomalies correlate with structural transformations between low- and high-density liquid forms of water. Increasing salt concentration disrupts the hydrogen-bond network and weakens these signatures while preserving the underlying thermodynamic anomalies. The influence of pressure up to 2 GPa is subsequently explored for 1 m NaCl and LiCl solutions. Thermal conductivity increases with pressure, whereas the Soret coefficient transitions from thermophilic to thermophobic behavior as the hydrogen-bond network collapses.

Finally, simulations of liquid and supercritical ethanol reproduce experimental thermal conductivity trends and reveal thermally induced polarization with a sign inversion near 400 K. Near the critical point, polarization is significantly enhanced, similar to the behavior observed in water.

Overall, this thesis provides a unified molecular-level understanding of how temperature gradients couple to mass, charge, and polarization fluxes in liquids, connecting transport properties to structural order, hydrogen bonding, and thermodynamic state.

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Nomenclature

A	Cross-sectional area of the simulation box [m^2]
C_P	Isobaric heat capacity [J K^{-1}]
C_V	Isochoric heat capacity [J K^{-1}]
D	Inter-diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]
D_T	Thermal diffusion coefficient [$\text{m}^2 \text{s}^{-1} \text{K}^{-1}$]
$\mathbf{E}$	Electric field [V m^{-1}]
$\mathbf{F}$	Force [N]
$\mathbf{J}_q$	Heat flux [W m^{-2}]
K	Kinetic energy [J]
L_x, L_y, L_z	Simulation box lengths along the x -, y -, and z -axes [m]
M	Molar mass [kg mol^{-1}]
N	Number of particles
P	Pressure [Pa]
S_E	Seebeck coefficient [V K^{-1}]
S_{TP}	Thermal polarization coefficient [V K^{-1}]
T	Temperature [K]
U	Potential energy [J]
V	System volume [m^3]
$\mathbf{a}$	Acceleration [m s^{-2}]
b	Solute molality [mol kg^{-1}]
c_s	Isentropic speed of sound [m s^{-1}]
k_B	Boltzmann constant [J K^{-1}]
m	Particle mass [kg]

$\mathbf{p}$	Momentum [kg m s^{-1}]
q	Charge [C]
$\mathbf{r}$	Position [m]
r_c	Cutoff distance [m]
s_T	Soret coefficient [K^{-1}]
$\mathbf{v}$	Velocity [m s^{-1}]
w	Weight fraction
x	Mole fraction

Greek Symbols

Δt	Simulation timestep [s]
Λ	Thermal de Broglie wavelength [m]
∇T	Temperature gradient [K m^{-1}]
α	Isobaric thermal expansion coefficient [K^{-1}]
β	Inverse thermal energy, $1/k_B T$ [J^{-1}]
ρ	Mass density [kg m^{-3}]
ε	Lennard-Jones energy parameter [J]
ε_0	Vacuum permittivity [F m^{-1}]
κ_T	Isothermal compressibility [Pa^{-1}]
λ	Thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$]
μ	Chemical potential [J mol^{-1}]
ϕ	Electrostatic potential [V]
ρ_q	Charge density [C m^{-3}]
σ	Lennard–Jones size parameter [m]

List of Abbreviations

CN	Coordination Number
CSVR	Canonical Sampling through Velocity Rescaling thermostat
EMD	Equilibrium Molecular Dynamics

EOS Equation of State

HDL High-Density Liquid

IK1 First-order truncated Irving–Kirkwood expression

LDL Low-Density Liquid

LLCP Liquid–Liquid Critical Point

LLPT Liquid–Liquid Phase Transition

LNETH Linear Non-equilibrium Thermodynamics

MSD Mean Square Displacement

NEMD Non-equilibrium Molecular Dynamics

NPT Isothermal-isobaric ensemble

NVE Microcanonical ensemble

NVT Canonical ensemble

PCM Phase Change Material

PPPM Particle–Particle Particle–Mesh method

RDF Radial Distribution Function

SDF Spatial Distribution Function

TMD Temperature of Maximum Density

μ VT Grand canonical ensemble

Chapter 1

Introduction

The purpose of this introduction is to provide the essential background on the topics explored in this thesis. It first discusses thermal transport in fluids, with particular emphasis on the microscopic origin of thermal conductivity. It then reviews the background and applications of the thermal coupling effects investigated in this work, namely thermodiffusion, thermoelectricity, and thermal polarization. Additionally, this introduction provides a brief overview of the specific liquid systems examined in this thesis, including supercooled water, aqueous alkali halide solutions, and ethanol. Finally, the objectives and structure of the thesis are outlined.

1.1 Thermal Transport in Fluids

Thermal transport in fluids plays a key role in many natural processes and technological applications. In geophysical contexts, heat transport by magmatic fluids is a fundamental process in subduction zones, affecting volcanic activity, mantle dynamics, and geophysical properties [1]. In biological systems, heat transfer in synovial fluid supports lubrication and the healthy functioning of human joints [2]. In technological applications, efficient thermal management is essential in electric vehicles, where liquid-based cooling systems are widely employed to regulate battery temperatures and maintain performance, durability, and safety [3, 4]. Additionally, phase change materials (PCMs) exchange heat with surrounding liquids as they undergo reversible melting and solidification, allowing them to store and release significant amounts of thermal energy within a narrow temperature interval. PCMs are widely employed in refrigeration and

cold storage systems that use liquid refrigerants, in domestic hot water storage systems, and in industrial waste heat recovery systems that rely on circulating liquid heat transfer media [5, 6]. Furthermore, the inherently low thermal conductivity of most PCMs motivates the development of liquid-based approaches designed to enhance thermal exchange with the molten PCM [7, 8].

Recently, significant attention has been directed toward nanofluids, in which nanoparticles are dispersed within a base liquid to enhance its thermal transport efficiency [9, 10], as shown schematically in Figure 1.1. These engineered fluids are being explored across a broad range of energy technologies, including microelectronic cooling [11] and solar water heating systems [12]. Nanofluids have also shown considerable promise in nuclear power systems as coolants in reactor loops and emergency core-cooling systems [13, 14]. In addition, they are being investigated for biomedical technologies, including targeted drug delivery and controllable hyperthermia in cancer treatment [15]. Taken together, these diverse applications highlight the broad technological relevance of liquid-phase thermal transport and have motivated extensive scientific interest in understanding the microscopic mechanisms governing heat transfer in both pure liquids and nanoparticle suspensions.

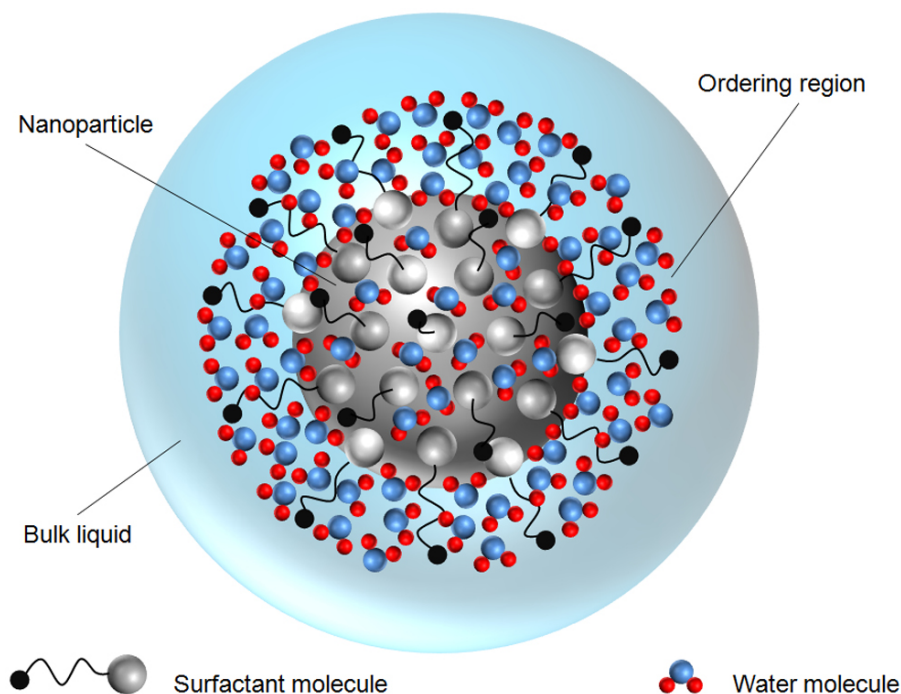


Figure 1.1: Schematic illustration of liquid layering around a surfactant-coated nanoparticle dispersed in water. Reproduced from Reference [10] under the Creative Commons CC BY 4.0 license.

In many of the applications discussed above, liquids operate under sustained thermal gradients rather than near-equilibrium conditions. Such gradients are intrinsic to practical heat-transfer processes, arising from spatially heterogeneous heat generation, dissipation, or external thermal loads [16]. Under these conditions, heat transport in liquids is influenced by temperature-dependent changes in local structure, density, and interfacial organization [17–19].

A central thermophysical property governing heat transport in both pure liquids and suspensions is their thermal conductivity. In liquids, this coefficient quantifies the efficiency of microscopic heat transfer driven by a temperature gradient, which relates the resulting heat flux to the imposed temperature difference. Thermal conductivity has been measured extensively using a range of experimental techniques [20], with the transient hot-wire method emerging as the most widely applied approach for liquids [21, 22]. In this technique, a thin wire immersed in the sample is subjected to a controlled heat flux, and the resulting time-dependent temperature rise is analyzed to yield an absolute and accurate determination of the conductivity. Alternative steady-state techniques, such as concentric cylinder [23] or guarded parallel plate [24] arrangements, establish a constant temperature difference across the sample and measure the resulting heat flux. Although effective, these methods generally require longer equilibration times and precise control of boundary conditions to reduce extraneous heat losses.

Because experimental determinations of liquid thermal conductivity are often scarce and time-consuming, there is a strong motivation to complement them with theoretical models and computer simulations. Bridgman introduced a particularly influential early approach in 1923, who modeled liquids as molecules arranged on a cubic lattice and assumed that energy is transmitted across successive planes at the velocity of sound in the fluid of interest [25]. This led to a phenomenological expression for the thermal conductivity λ ,

$$\lambda = ak_B v^{-2/3} c_s, \tag{1.1}$$

where a is an empirical constant, k_B is the Boltzmann constant, v is the molar volume, and c_s is the isentropic (adiabatic) speed of sound.

Biddle *et al.* [26] demonstrated that the Bridgman model provides an accurate description

of the low-temperature behavior of supercooled water, reproducing the anomalous decrease in thermal conductivity and its association with anomalies in the speed of sound and the isothermal compressibility. More broadly, the strength of the Bridgman equation is the physical insight it offers by expressing thermal conductivity in terms of acoustic and thermodynamic properties. Its quantitative performance, however, is constrained by the assumptions of its derivation, which neglects the internal degrees of freedom and directional interactions present in polyatomic and hydrogen-bonded liquids [27]. As a result, the complex interplay of intermolecular interactions and structural heterogeneity continues to make accurate prediction of liquid thermal conductivity a persistent challenge. Recently, it has been shown that nuclear quantum effects, together with the temperature-dependent balance between low-density and high-density liquid structures, play a central role in determining the anomalous thermal conductivity of water [28].

Despite decades of research, we still lack theoretical models that can reliably predict the thermal conductivity of liquids across different thermodynamic conditions. These challenges motivate the use of molecular simulations, which give direct access to microscopic dynamics and enable a quantitative assessment of liquid thermal transport. A common route is the Green-Kubo formalism, where thermal conductivity is obtained from the time integral of the equilibrium heat-flux autocorrelation function [29]. In practice, however, this approach often requires long simulation runs to achieve statistical convergence, and recent studies have highlighted further limitations associated with its implementation [30, 31]. Additionally, according to non-equilibrium thermodynamics, coupling between heat and other fluxes must be incorporated consistently within the Green-Kubo framework, as is already the case for binary mixtures where thermodiffusion is present [32]. Hence, non-equilibrium molecular dynamics provides a complementary route to evaluate thermal conductivity, with the advantage of naturally incorporating additional coupling effects. In this thesis, boundary-driven non-equilibrium molecular dynamics (NEMD) are employed to compute the thermal conductivity of liquids, with the detailed methodology and calculations presented in Chapter 2.

1.2 Non-Equilibrium Coupling Effects

In addition to heat conduction, thermal gradients in fluids induce a range of non-equilibrium coupling effects. These effects, which couple heat fluxes with mass, charge, or polarization fluxes, give rise to phenomena such as thermodiffusion (Ludwig–Soret effect) [33, 34], thermoelectricity (Seebeck effect) [35], and thermal polarization [36]. Linear non-equilibrium thermodynamics (LNET) [32] provides the theoretical foundation for these effects through phenomenological equations that connect the magnitude of a thermal gradient with the resulting mass separation or electrostatic potential difference. The following subsections introduce each of these three coupling phenomena in more detail.

1.2.1 Thermodiffusion

A temperature gradient applied across fluid solutions can drive thermophoresis, the directed motion of solute particles in suspensions, and thermodiffusion, which leads to the separation of mixture components. This phenomenon is commonly referred to as the Ludwig–Soret effect [33, 34], after Carl Ludwig and Charles Soret, and it is often abbreviated simply as the Soret effect. The effect was first reported by Ludwig in 1856 [33], who observed that when a U-shaped tube filled with a salt solution was maintained with one arm in cold water and the other in boiling water, the solute concentration increased near the colder region. Two decades later, Charles Soret [34] carried out systematic studies using both straight and U-shaped tubes and found that solute accumulation occurred in the cold region of the solution, results that were consistent with Ludwig’s earlier observation.

Since its discovery, thermodiffusion has been investigated extensively in both solutions and suspensions, and it remains an active research topic due to its importance in environmental and biological systems. It contributes to diverse natural phenomena, including the thermal stratification of solar ponds [37], double-diffusive circulation in the oceans [38], chemical fractionation during magma convection in volcanic systems [39], and evaporative fractionation of hydrocarbons in deep oil reservoirs [40]. At the molecular scale, thermal gradients can drive thermophoresis in biomolecules, a mechanism shown to enable DNA replication in confined

convection flows [41] and proposed as a factor in early life evolution under submarine conditions [42]. Thermophoretic transport has long been recognized as a potential driver of molecular organization in biological systems [43], and recent studies demonstrate that local temperature gradients arise even within tissues and single cells, where they influence membrane behavior and intracellular transport [44]. Beyond these roles, thermodiffusion also inspired analytical techniques such as microscale thermophoresis, which exploits biomolecular motion in thermal gradients to quantify interactions in complex liquids [45].

The Soret coefficient $s_T = D_T/D$ expresses the relative strength of thermodiffusion, being defined as the ratio of the thermal diffusion coefficient D_T to the interdiffusion coefficient D , and is widely used as a measure of the magnitude of the Soret effect. Typical values of the Soret coefficient are in the range of 10^{-3} to 10^{-2} K^{-1} for organic mixtures and aqueous solutions [46–48], and can reach approximately 10^{-1} K^{-1} for biomolecular systems [49, 50]. To determine the Soret coefficient, several experimental approaches have been developed [51]. Thermal diffusion cells establish a vertical temperature gradient across a liquid sample by imposing heating and cooling boundaries, and monitor the resulting concentration changes through optical or sampling methods. Thermal lens techniques employ a focused laser beam to simultaneously heat and probe the sample, with the induced refractive index gradient revealing concentration changes. Holographic grating methods, also known as thermal diffusion forced Rayleigh scattering, impose a laser-induced temperature grating that drives a coupled concentration grating, which is then detected by the diffraction of a probe beam. Among these techniques, the holographic grating approach has become the most sensitive and widely adopted for liquids and polymer solutions, largely because it overcomes the drawbacks of long equilibration times and convection artifacts [51].

While experiments provide valuable data, predicting whether a solute drifts toward warmer regions (thermophilic) or accumulates in cooler regions (thermophobic) remains a central challenge in developing a microscopic understanding of thermodiffusion. To address this, theoretical models and molecular simulations have played an essential role in interpreting and rationalizing experimental findings. Classical approaches based on Onsager’s formalism and Chapman–Enskog theory describe gaseous mixtures successfully [52], but they fail to capture

the complex behavior of liquids, particularly when strong interactions such as hydrogen bonding are involved [32]. Prigogine *et al.* [53] used a free energy approach to explain sign reversals of the Soret coefficient in associating liquids, attributing them to entropy gains from molecular complex dissociation, though only at a qualitative level.

Molecular dynamics simulations, both equilibrium and non-equilibrium, have become powerful tools for investigating liquid mixtures and aqueous solutions. Equilibrium simulations have accurately reproduced mutual diffusion coefficients in model Lennard-Jones mixtures [54]. Recent non-equilibrium simulations have further shown that these mixtures display a minimum in the Soret coefficient with composition, a feature linked to extrema in the thermodynamic factor and the non-ideality of mixing [55]. In addition, non-equilibrium simulations have successfully reproduced experimental Soret trends in aqueous electrolyte solutions [56, 57]. Furthermore, these studies capture not only the thermophobic behavior of alkali chloride solutions at ambient conditions but also the experimentally observed inversion of the Soret coefficient at around 290 K for 0.5 m KCl solutions [48], where the system changes from thermophilic at low temperature to thermophobic at higher temperature.

1.2.2 Thermoelectricity

Thermoelectricity describes a class of coupling phenomena where a temperature gradient gives rise to an electric potential gradient through charge separation. This effect, commonly known as the Seebeck effect, was first reported in 1821 by Thomas Johann Seebeck [35], who observed the deflection of a magnetic needle when two different metallic wires were joined and subjected to a temperature difference. He interpreted this observation as a “thermomagnetic effect”. A few years later, in 1823, Hans Christian Ørsted [58] clarified that the underlying cause was electrical rather than magnetic: a thermal gradient across heterogeneous conductors induces an electric current, thereby establishing the foundation of thermoelectricity.

The Seebeck effect has been demonstrated across a wide range of systems, from its classical manifestation in metals [59] to nonaqueous and ionic liquid systems that exhibit remarkably large thermal responses [60, 61], and to aqueous electrolytes where water and ion interactions dominate the thermovoltage [62, 63]. The phenomenon underlies numerous technological

applications, including thermocouples for precise temperature sensing and radioisotope thermoelectric generators used in spacecraft such as NASA’s Voyager, which convert the heat released from radioactive decay into electrical power [64]. Beyond aerospace technology, thermoelectric conversion has been explored in a variety of energy-harvesting contexts, such as biothermal batteries for cardiac pacemakers [65] and systems designed to recover waste heat from automobile exhausts [66]. More broadly, the thermoelectric effect is central to the ongoing development of devices for energy conversion and waste-heat recovery [66, 67], and has recently inspired research into ionic conductors as efficient media for generating strong thermally induced voltages in supercapacitors [68, 69] and thermogalvanic cells [70, 71].

The strength of thermoelectricity is quantified by the Seebeck coefficient S_E , defined as the ratio between the induced electric field and the applied temperature gradient under steady-state conditions. From a fundamental perspective, theoretical estimates of the Seebeck coefficient have been derived for electrolytes at infinite dilution [72]. Although these predictions neglect finite-concentration effects relevant to experiments, they provide a valuable reference for assessing the magnitude and sign of thermoelectric responses in ionic solutions. These theoretical concepts have also been applied to interpret thermophoretic drift in colloidal suspensions, where the direction of particle migration along a thermal gradient correlates with the sign of the Seebeck coefficient [73, 74]. Furthermore, thermoelectric effects in aqueous systems are known to modulate the thermophoretic motion of macromolecules and colloids [75–77] and have also been implicated in biological sensory contexts, including electroreception in fishes and insects [78–80].

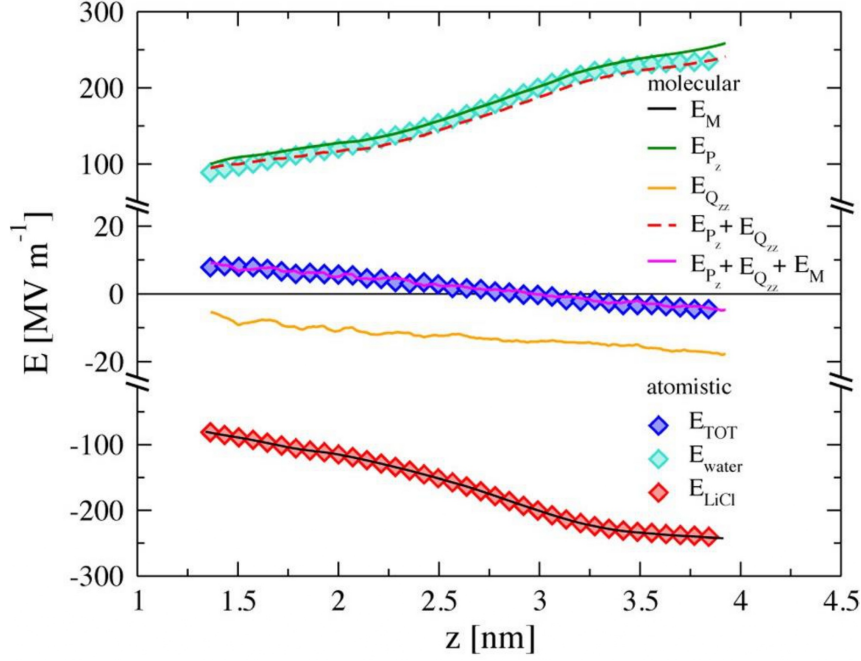


Figure 1.2: Electrostatic field induced by a thermal gradient in a 1 m LiCl solution, decomposed into water and ion contributions. Reproduced from Reference [62] with permission.

Recent studies have revealed that alkali halide aqueous solutions exhibit complex Seebeck behavior, including sign reversals with temperature and concentration, arising from coupled ion–water responses [62, 63]. Under the strong thermal gradients typically employed in non-equilibrium simulations, on the order of 10^{10} K/m, the resulting thermoelectric fields reach magnitudes of 10^6 – 10^7 V/m [62], as shown in Figure 1.2 for 1 m LiCl solution. These fields correspond to Seebeck coefficients on the order of 10^{-4} V/K, and the inversion reflects the interplay between temperature-dependent ionic charge separation and the electrostatic response of the surrounding water. Hence, systematic investigations of the Seebeck effect in aqueous electrolytes are essential to establish a unified framework for thermal coupling phenomena and to elucidate how the molecular properties of water govern both thermodiffusive and thermoelectric responses.

1.2.3 Thermal polarization

Ionic charge separation is not the sole mechanism responsible for the buildup of thermoelectric fields in solutions. Thermal gradients can also induce orientation effects, which have been observed in colloidal systems [81, 82], as well as nonpolar [83, 84] and polar fluids [36, 85]. In

polar liquids, such orientation leads to polarization and the emergence of a net electrostatic field, an effect known as thermal polarization, whose magnitude scales with the applied temperature gradient [36]. Beyond simple liquids, thermally induced polarization and orientation phenomena have been reported in a wide variety of systems. In quantum fluids, heat flux can drive molecular ordering through nuclear quantum effects [86], while in colloidal and soft matter systems, localized temperature gradients enable optothermoelectric strategies for particle manipulation [87, 88] and can induce orientational alignment in anisotropic colloids [82]. Even in applied technologies such as microwave drying of porous materials, polarization has been identified as a key factor coupling heat and mass transfer [89]. In electrolyte solutions such as aqueous alkali halides, water thermal polarization has likewise been shown to play a dominant role in determining the thermoelectric field [62, 63].

Similarly to thermoelectricity, the strength of the thermal polarization effect is quantified by the thermal polarization coefficient, S_{TP} , defined as the ratio between the induced electrostatic field and the applied thermal gradient. The behavior of water under thermal fields is particularly complex: simulations have revealed that the polarization field can invert its sign with temperature, as illustrated in Figure 1.3, a phenomenon arising from the competition between dipolar and quadrupolar contributions [90, 91]. Theoretical analyses further highlight the importance of the dipole-to-quadrupole ratio, which serves as a key parameter for assessing the accuracy of water force fields [92] and for rationalizing the emergence of inversion points in the thermal polarization response [91]. Enhancement of the thermal polarization response has also been observed as water approaches its liquid–vapor critical point, an effect likely driven by the divergence of the thermal expansion coefficient in this regime [93].

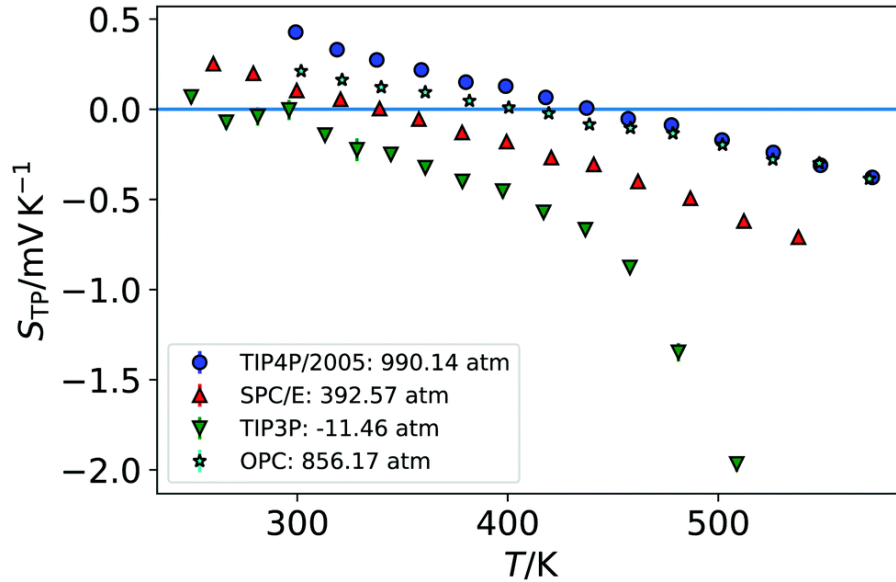


Figure 1.3: Thermal polarization coefficient S_{TP} of water as a function of temperature for various rigid water models, showing a clear inversion of the polarization response. Reproduced from Reference [91] under the Creative Commons CC BY 4.0 license.

Linear non-equilibrium thermodynamics (LNET) predicts that the coupling effects generally lower the effective thermal conductivity of liquids [32], a prediction supported by molecular simulations for both the Soret effect [94] and thermal polarization [85]. In the latter case, simulations of acetonitrile, an aprotic solvent, demonstrate that thermal polarization leads to a measurable reduction in thermal conductivity by about 2–5% at typical liquid densities and temperatures between 300 and 700 K, when compared with the conductivity predicted in the absence of polarization [85]. Extending such investigations to other molecular solvents would help build a more complete understanding of the mechanisms underlying thermally induced electrostatic fields and their influence on the thermal transport properties of liquids. Furthermore, deeper insight into how thermal polarization governs heat transfer at the nanoscale could provide design principles for more efficient nanodevices, since huge electrostatic fields can arise from modest temperature differences [95].

It is equally important to recognize that different coupling phenomena can also influence one another, as they arise from shared microscopic mechanisms such as correlated molecular motion, orientational ordering, and density fluctuations, which contribute to multiple transport processes simultaneously. Within the framework of LNET, such cross effects are captured by off-diagonal Onsager coefficients and generally lead to a suppression of individual transport

contributions compared to the uncoupled case [32]. Molecular simulation offers a powerful approach to isolating these coupled effects. For example, mass transport contributions can be selectively suppressed by equalizing solvent and solute masses, an approach closely related to previous simulation studies that systematically varied ionic masses to assess their influence on thermodiffusion [56]. Similarly, electrostatic coupling can be systematically attenuated or suppressed by modifying partial charges, an approach widely used in molecular simulations to isolate electrostatic contributions [96, 97]. By systematically filtering individual mechanisms in this manner, simulations enable the isolation and quantification of distinct coupling effects.

1.3 Liquids and Solutions Investigated in this Thesis

1.3.1 Supercooled Water and Its Anomalous Properties

Water, as the most prevalent liquid on Earth, occupies a fundamental position in natural and technological processes across the physical, chemical, and biological sciences [98]. In contrast to simple liquids, water exhibits a density maximum near 4 °C, where its thermal expansion coefficient changes sign, together with a range of anomalous behaviors. These include the unusual increase of its isothermal compressibility and heat capacity upon cooling (see Figure 1.4), as well as distinctive structural and thermodynamic responses that are closely linked to the nature of hydrogen bonding [99, 100].

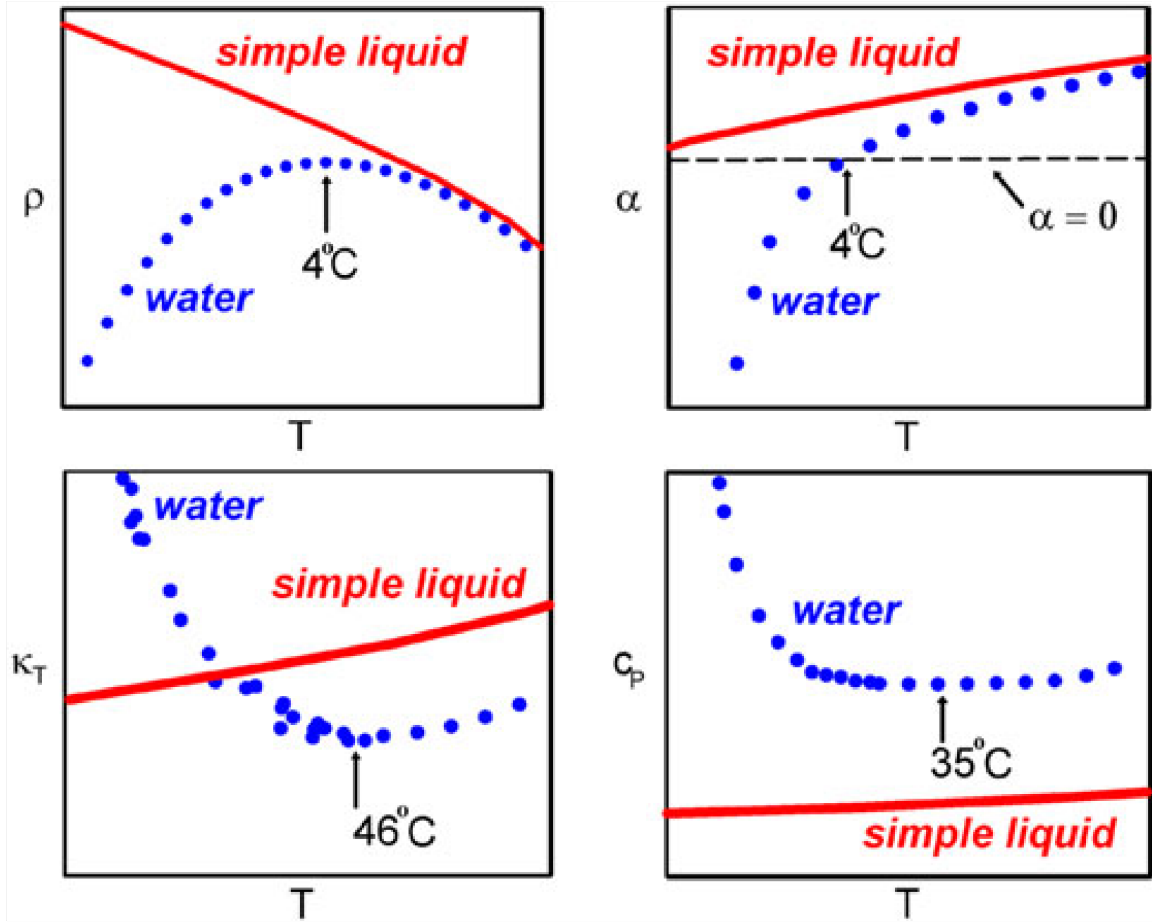


Figure 1.4: Comparison of the anomalous temperature dependence of water's density ρ , isobaric thermal expansion coefficient α , isothermal compressibility κ_T , and isobaric heat capacity C_P with those of a simple liquid. Reproduced from Reference [101] with permission.

These anomalies become increasingly pronounced in the supercooled regime [101–103], where water remains in a metastable liquid state below its freezing point. As illustrated schematically in Figure 1.5, supercooling is bounded by kinetic limits associated with homogeneous ice nucleation, such that liquid water can persist well below the equilibrium melting temperature while remaining thermodynamically metastable [104]. In this deeply supercooled regime, thermodynamic response functions exhibit rapid growth and apparent divergence upon cooling, reflecting increasingly large fluctuations in density and entropy that precede crystallization [101]. Additionally, extremely rapid cooling, at rates on the order of 10^6 K s^{-1} , can suppress crystallization altogether and instead produce glassy, amorphous states of water [105, 106]. Supercooled water occurs naturally in atmospheric clouds, where it plays a crucial role in modulating Earth's radiation balance [98]. It has also been observed in the tissues of woody plants, where deep supercooling of cellular water constitutes a biological adaptation that suppresses ice formation and enables survival

under subzero temperatures [107].

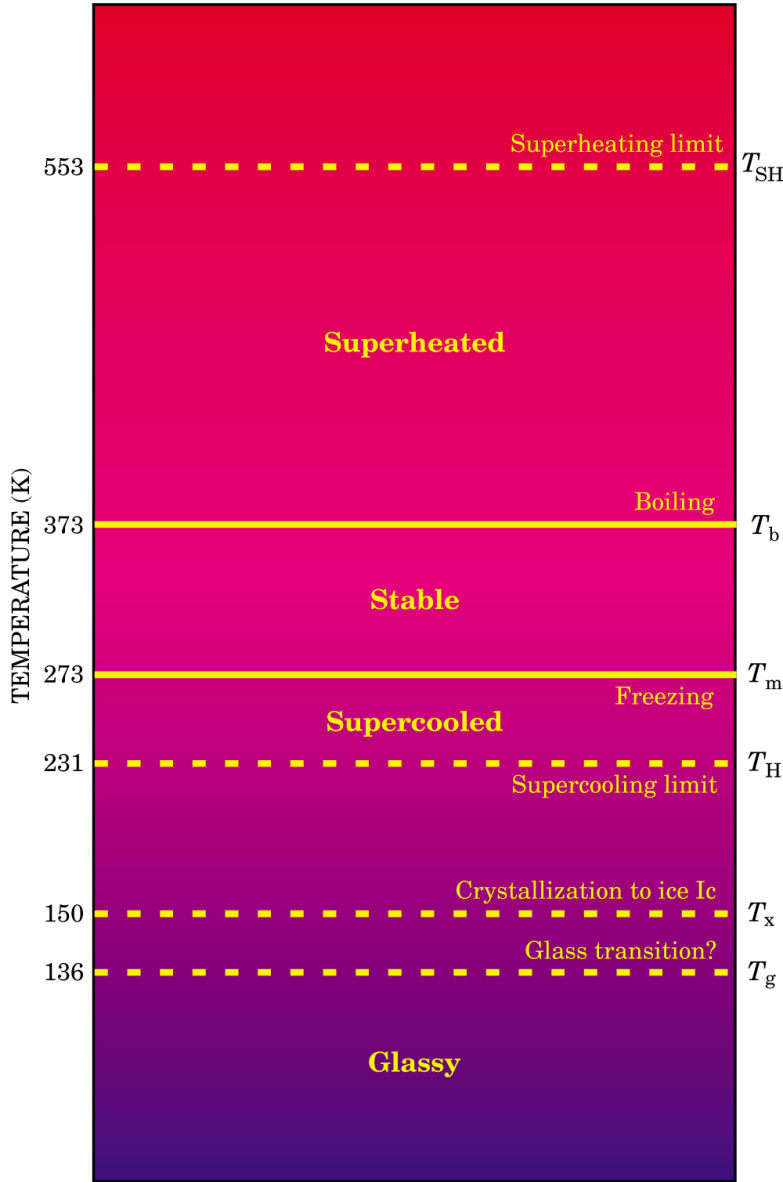


Figure 1.5: Temperature ranges of liquid water at atmospheric pressure, illustrating stable, metastable (superheated and supercooled), and glassy regimes. Reproduced from Reference [101] with permission.

To rationalize the anomalies of supercooled water, several theoretical interpretations have been proposed, including the stability-limit conjecture [108] and the singularity-free scenario [109], among which the liquid–liquid phase transition (LLPT) hypothesis [110] has emerged as one of the most influential. Based on molecular dynamics simulations of the ST2 water model, Poole *et al.* observed sharp discontinuities in the isothermal compressibility curves at low temperatures, analogous to the experimentally observed phase transitions between amorphous ices. They

therefore proposed a first-order transition between two metastable liquid states of different densities, typically associated with a more tetrahedrally ordered low-density liquid (LDL) and a less ordered high-density liquid (HDL), terminating at a liquid–liquid critical point (LLCP) [110]. A schematic P - T representation of this scenario is shown in Figure 1.6, where a first-order LLPT between LDL and HDL is proposed to extend into the deeply supercooled regime and to terminate at a hypothesized second critical point C' , in analogy with the liquid-vapor critical point C . The diagram also shows the correspondence between the liquid states and their amorphous solid counterparts, low-density amorphous (LDA) and high-density amorphous (HDA) ice. The LLPT scenario thus provides a unifying explanation for the anomalous thermodynamic response functions in the supercooled regime and relates them to the critical fluctuations near the LLCP [18, 104].

The enduring question of whether liquid water hosts a second critical point has kept supercooled water at the center of sustained research activity since the 1970s [101]. Experimental investigations have provided tentative support for the existence of a second critical point in supercooled water. Early evidence arose from decompression-induced melting of high-pressure ices, where a kink in the metastable melting curve was interpreted as crossing a liquid–liquid coexistence locus [111]. At near-ambient pressure, scattering on deeply supercooled microdroplets revealed maxima in the isothermal compressibility κ_T , behavior consistent with traversal of a Widom line emanating from a critical point [112]. More direct pump–probe experiments combine femtosecond infrared heating of amorphous ice with X-ray probing, resolving discontinuous changes in the liquid structure factor and transient LDL–HDL coexistence on nanosecond to microsecond timescales before crystallization [113, 114]. More recently, ultrafast X-ray measurements on deeply supercooled water droplets have identified a dynamic fragile-to-strong crossover near 233 K, consistent with a temperature-dependent shift in the populations of HDL- and LDL-like local structures [115]. Nevertheless, rapid crystallization on microsecond timescales still severely constrains direct experimental access to bulk supercooled water in the no-man’s-land region (roughly 232–160 K) [18].

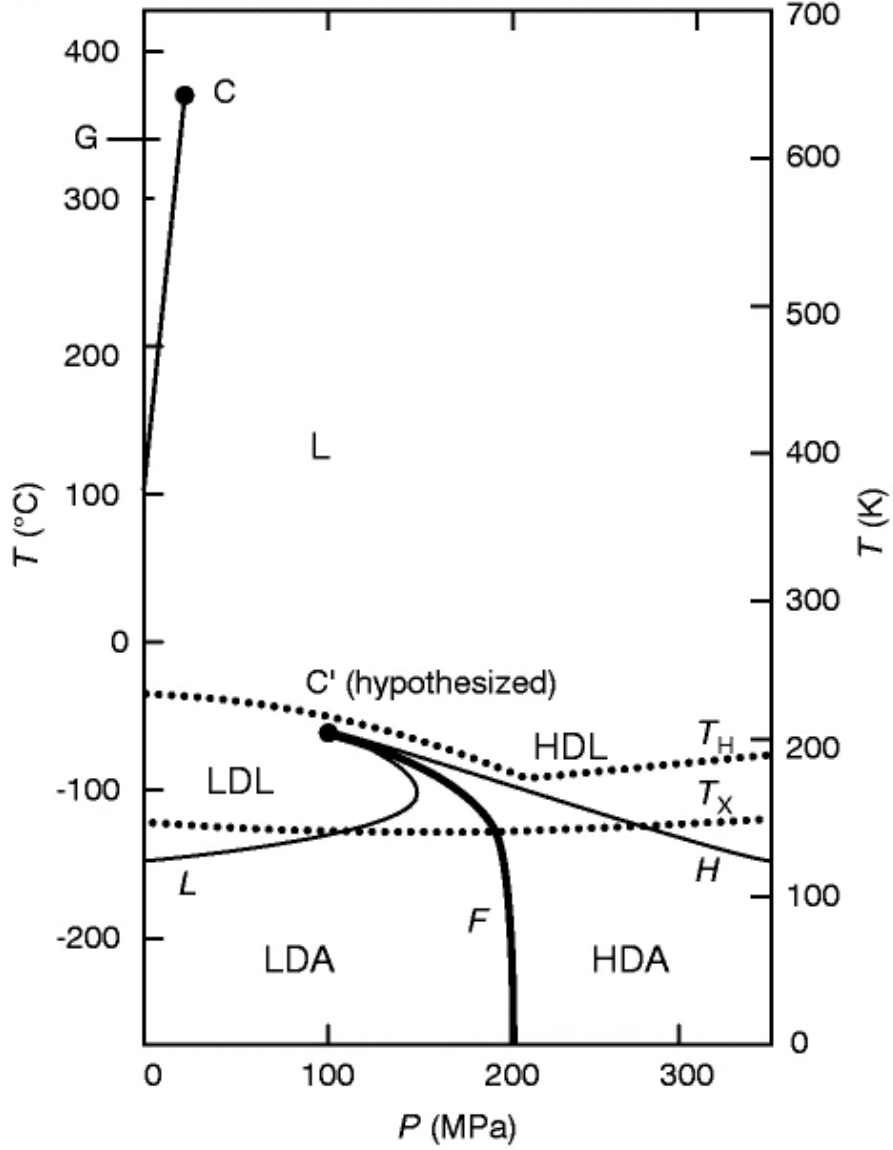


Figure 1.6: Schematic phase diagram of water illustrating the behavior of liquid and amorphous phases under supercooled conditions. Reproduced from Reference [104] with permission.

In contrast to bulk experiments, molecular simulations can routinely access deeply supercooled states because the relaxation time of molecular water models remains faster than crystal nucleation, enabling equilibration of metastable liquids before crystallization [116]. Recent simulation studies across empirical models [117, 118], *ab initio* trained force fields [119], and machine learning-based potentials [120] increasingly support the LLPT picture. These studies collectively tighten LLCP estimates to $T \approx 190\text{--}210$ K and $P \approx 400\text{--}1500$ bar for state-of-the-art models, whereas classical ST2 model places the LLCP at higher temperature and pressure [121]. Taken together, these simulations suggest practical experimental routes, including the use of nanodroplets and externally controlled pressure, to access and probe the predicted critical

conditions [119, 120].

Supercooled water exhibits anomalous thermal transport: at atmospheric pressure, its thermal conductivity decreases upon cooling below the melting point and continues to fall across the experimentally accessible supercooled range. This behavior is captured by the IAPWS correlating equation, which fits conductivities inferred from thermal diffusivity measurements on metastable water down to roughly 250 K [122]. Building on theoretical analyses [26], non-equilibrium molecular dynamics (NEMD) simulations with the TIP5P model [123] and equilibrium Green-Kubo calculations with the TIP4P/2005 model [124] have both reported a local minimum in the thermal conductivity of water. The temperature of this minimum shifts with pressure and coincides with the temperature at which the isothermal compressibility reaches a maximum, while the speed of sound exhibits a minimum [124]. The emergence of such a minimum is also anticipated by the Bridgman relation (see Equation 1.1). Subsequent simulation work based on Green-Kubo formalism reached the opposite conclusion, finding no evidence for a minimum in the thermal conductivity of supercooled TIP4P family water models [125]. Taken together, the scarcity of experimental data in the deeply supercooled regime and the debate surrounding Green-Kubo calculations of thermal conductivity, including their slow convergence and the need to account consistently for couplings between heat and other fluxes (see Section 1.1), motivate complementary approaches. Accordingly, in this thesis, we determine thermal conductivity via NEMD, which naturally incorporates these coupling effects, to probe thermal transport at low temperatures.

1.3.2 Aqueous Alkali Halide Solutions

As the principal solvent on Earth, water is more often encountered in solution than as a pure liquid in both natural and technological contexts. This thesis focuses on aqueous solutions of sodium chloride (NaCl) and lithium chloride (LiCl). NaCl is the dominant salt in seawater, with sodium and chloride together accounting for more than 90% of dissolved ions and thereby shaping marine chemistry and related geophysical processes [126]. Lithium is central to modern energy technologies, most notably rechargeable lithium-ion batteries, whose high energy density underpins portable electronics, electrified transport, and grid-scale storage [127]. Additionally,

alkali chloride salts are prominent constituents of deep crustal fluids and exert a major influence on heat and mass transport within Earth’s interior [128].

In many cases, dissolution facilitates deeper supercooling than in pure water, because alkali halide solutes depress the homogeneous ice nucleation temperature and further delay crystallization to the point of vitrification upon compression, thereby extending the experimentally accessible metastable liquid range [129]. Molecular dynamics simulation studies of aqueous alkali halides consistently indicate that adding salt can stabilize the liquid–liquid critical point (LLCP) while shifting its location in the pressure–temperature plane [130–132]. For a 0.67 m NaCl solution modeled with TIP4P water and Jensen-Jorgensen alkali halide parameters, an LLCP was identified using isochore convergence and maxima in the isothermal compressibility, appearing at higher temperature and lower pressure relative to pure water [130]. Extending the analysis to higher NaCl concentrations (1.36 and 2.10 m), the same protocol revealed a monotonic shift of the LLCP toward higher temperature and more negative pressure, together with a pronounced shrinkage of the LDL stability region [131], as illustrated in Figure 1.7. For LiCl solution, simulations with TIP4P/2005 water and the Madrid-2019 ion force field identified an LLCP at low concentration (0.678 m), whereas at 2.034 m no critical point was detected and the isothermal compressibility maxima became notably broader and weaker, suggesting the disappearance of LLCP at higher salinity [132]. These results motivate a systematic examination of how ion type and concentration modulate the location of the LLCP, and whether the associated structural changes are linked to the anomalies observed in supercooled aqueous electrolyte solutions.

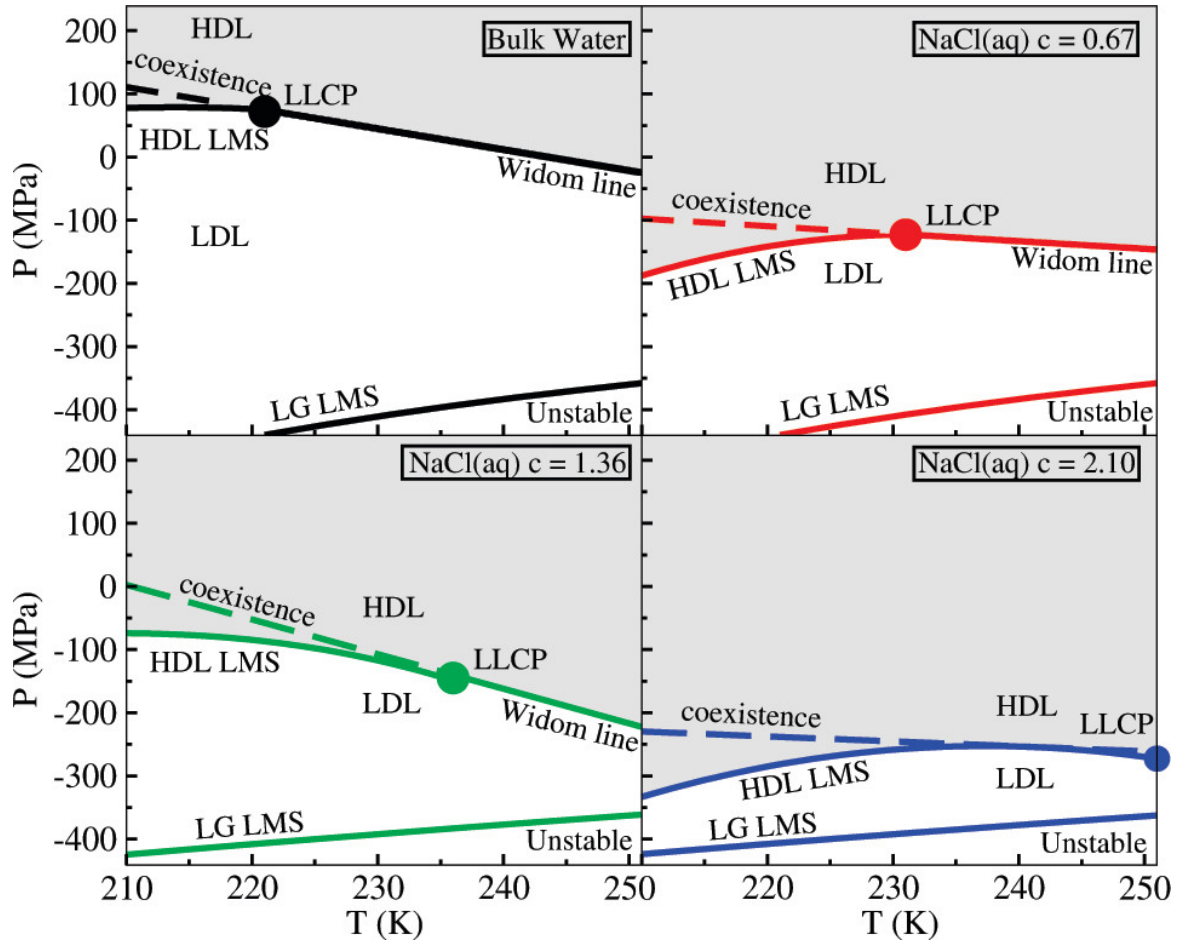


Figure 1.7: Schematic liquid-liquid phase diagrams for bulk water and NaCl aqueous solutions at increasing salt concentrations. Reproduced from Reference [131] with permission.

Having outlined the supercooled phase behavior of these electrolytes, we now turn to their thermal transport and coupling responses under temperature gradients. In electrolyte solutions, dissolved salts generally reduce the thermal conductivity of water. Experimental measurements show that the thermal conductivity decreases with increasing salt concentration [21, 133], and the magnitude of this reduction grows with the solute’s molecular weight [134], although the microscopic origin of this trend remains unresolved. Recent simulations reproduce this concentration-dependent reduction in thermal conductivity across $\{\text{Li}^+, \text{Na}^+, \text{K}^+\}\{\text{Cl}^-, \text{I}^-\}$ and show that thermal conductivity depends strongly on the anion mass, while the cation type has a comparatively weaker effect [57].

The thermodiffusive response of aqueous alkali halide solutions is quite complex. At near-ambient conditions (around 300 K and above), NaCl and KCl are thermophobic with positive Soret coefficients on the order of 10^{-3} K^{-1} . Upon cooling, the Soret coefficient decreases and

ultimately inverts its sign. Thermal diffusion forced Rayleigh scattering measurements place the inversion near 283 K for NaCl and 293 K for KCl at 0.5 m, with Soret coefficient decreasing with concentration at higher temperatures and increasing at lower temperatures [48]. By contrast, LiCl solutions are more thermophilic: holographic-interferometry experiments in the supercooled regime report consistently negative Soret coefficient down to about 213 K, with a pronounced minimum as a function of concentration in the intermediate molality range [135]. These behaviors have been reproduced in molecular dynamics simulations across various water–ion force fields [48, 56, 136]. Additionally, recent simulations decompose the thermoelectric response of aqueous alkali halides into an ionic thermodiffusion contribution and a solvent-driven thermal polarization term, showing that water thermal polarization can dominate the Seebeck response while ionic contributions modulate its magnitude [62, 63].

1.3.3 Ethanol as a Comparative Hydrogen-Bonded Liquid

In this thesis, we further investigate ethanol, a hydrogen-bonded polar liquid beyond aqueous systems, as a comparative framework for understanding the microscopic origins of thermal transport and coupling effects. Ethanol is a widely used solvent across science and engineering. As a water co-solvent, ethanol–water mixtures are routinely employed to tune polarity, hydrogen bonding, and transport in catalytic systems, including green solvothermal routes that control catalyst morphology and performance [137, 138]. In oxidation chemistry using nanomaterials, noble-metal nanoparticles catalyze alcohol electro-oxidation relevant to direct alcohol fuel cells [139]. Optical heating of plasmonic nanoparticles can also drive phase behavior in ethanol–water mixtures, enabling light-induced distillation and phase separation that bypass the ethanol–water azeotrope [140]. In addition, ethanol is often used as a base fluid for nanofluids, where interfacial adsorption layers with partial solid-like ordering have been linked to enhanced heat transfer [141].

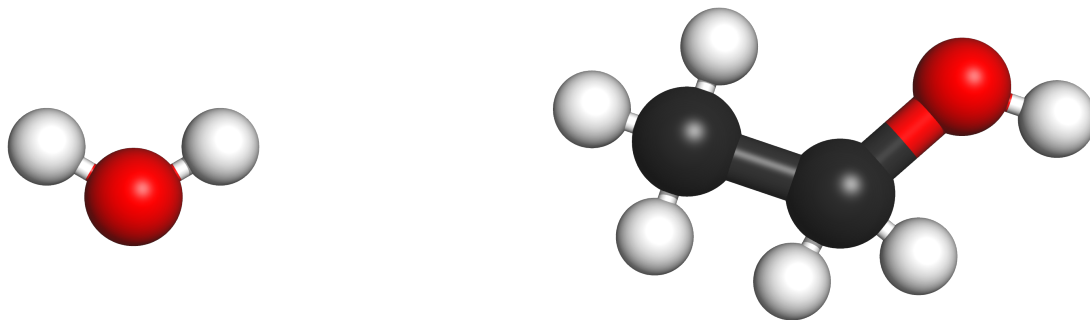


Figure 1.8: Molecular structures of water (left) and ethanol (right) represented in the ball-and-stick model and visualized using PyMOL [142]. Oxygen atoms are shown in red, hydrogen in white, and carbon in black.

Both water and ethanol are hydrogen-bonded polar liquids with comparable gas-phase dipole moments [143]. Nevertheless, under standard conditions the thermal conductivity of ethanol ($\lambda \approx 0.17 \text{ W m}^{-1} \text{ K}^{-1}$) [144, 145] is much lower than that of water ($\lambda \approx 0.60 \text{ W m}^{-1} \text{ K}^{-1}$) [122]. This contrast is consistent with the presence of the nonpolar ethyl group (see Figure 1.8) and the comparatively weaker, less connected hydrogen-bond network in ethanol, which together limit energy transport pathways relative to water.

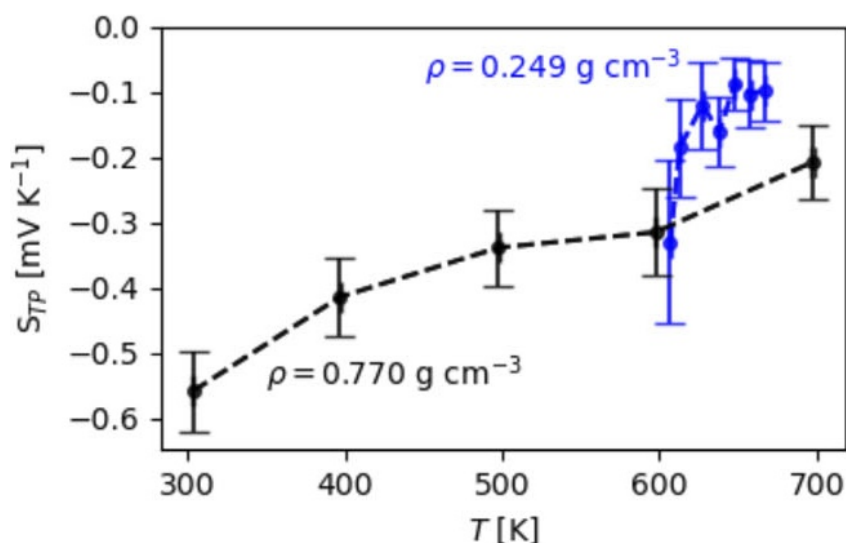


Figure 1.9: Thermal polarization coefficient S_{TP} of acetonitrile as a function of temperature for liquid-density (black) and critical-density (blue) isochores. Reproduced from Reference [85] with permission.

Recent non-equilibrium molecular dynamics simulations show that the aprotic solvent acetonitrile exhibits a consistently negative thermal polarization coefficient, with $S_{TP} < 0$ across both liquid and supercritical states and values on the order of -0.6 mV/K near ambient

conditions [85], as shown in Figure 1.9. In contrast, water displays an inversion of the thermally induced field depending on thermodynamic state (see Section 1.2.3). Motivated by this difference, it is important to examine another hydrogen-bonded polar liquid, ethanol, to clarify how the presence or absence of thermal polarization inversion relates to the structure and connectivity of the hydrogen-bond network.

1.4 Objective of This Thesis

The preceding sections have outlined the background of the main topics in this thesis and highlighted that understanding thermal transport and coupling effects in liquids is essential for interpreting a wide range of natural and technological processes. Building on this foundation, we consider three representative systems: (i) water, with a focus on thermal transport and thermal polarization in the supercooled regime and their connection to the thermodynamic anomalies of water; (ii) aqueous alkali halide solutions (NaCl and LiCl), where salt identity and concentration modulate thermal conductivity and thermodiffusion across ambient, supercooled, and high-pressure conditions; (iii) ethanol, a hydrogen-bonded polar liquid that serves as a comparative benchmark for studying the microscopic origins of thermal transport and thermally induced polarization.

This thesis is organized as follows. Chapter 2 presents the theoretical and computational background, including equilibrium and non-equilibrium molecular dynamics (EMD and NEMD), together with the methods for computing thermal conductivity, the Soret coefficient, and the thermal polarization coefficient. In Chapter 3, we employ NEMD to investigate the thermal transport and thermal polarization of supercooled water along multiple isobars, identifying a local minimum in thermal conductivity and an enhancement in polarization magnitude. Taken together, these features mirror anomalous thermodynamic behavior and are consistent with the hypothesized liquid–liquid critical point (LLCP). Chapter 4 extends the analysis to supercooled aqueous NaCl and LiCl solutions at different concentrations, showing that anomalous thermal transport depends on salinity and weakens with salt addition. Structural characterization further links water’s tetrahedral order to the observed thermodiffusion responses. Chapter 5

examines NaCl and LiCl solutions under pressures up to 2 GPa, quantifying the pressure dependence of thermal conductivity and the Soret coefficient and reinforcing the connection between tetrahedral order and thermodiffusion. Chapter 6 provides a systematic study of thermally induced polarization in ethanol, demonstrating a finite polarization field under temperature gradients and comparing its behavior with that of water and acetonitrile to isolate the role of hydrogen bonding. Finally, Chapter 7 summarizes the main conclusions and offers directions for future research.

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Chapter 2

Computational Methods and Theoretical Background

2.1 Molecular Dynamics Simulations

In this thesis, classical molecular dynamics simulations are employed to investigate thermal transport and thermally induced coupling effects. The theoretical foundation of the method is presented in this section. Molecular dynamics provides access to molecular-scale information, enabling the calculation of thermodynamic, transport, and structural properties. The approach generates a sequence of configurations by integrating Newton’s equations of motion [1]. This sequence, known as the trajectory of the system, describes how the positions and velocities of the particles in the simulation box evolve with time.

2.1.1 Equations of Motion

The motion of particles in a molecular dynamics simulation can be described through Newton’s equations. The second law of motion is expressed as

$$\mathbf{F}_i = m_i \mathbf{a}_i = m_i \frac{d^2 \mathbf{r}_i}{dt^2}, \quad (2.1)$$

where $\mathbf{F}_i$ is the force acting on particle i , m_i is its mass, $\mathbf{a}_i$ is the acceleration, $\mathbf{r}_i$ denotes the position vector, and t is the time.

The force can also be expressed as the gradient of the potential energy U ,

$$\mathbf{F}_i = -\frac{dU}{d\mathbf{r}_i}. \quad (2.2)$$

The potential energy depends on the interactions between particle i and the surrounding particles, which will be discussed in more detail in Section 2.1.6.

By combining Equations 2.1 and 2.2, the following relation is obtained:

$$-\frac{dU}{d\mathbf{r}_i} = m_i \frac{d^2\mathbf{r}_i}{dt^2}. \quad (2.3)$$

Equation 2.3 establishes the connection between the particle positions and the potential energy. Its integration provides the updated trajectories and energetic state of the system. Several algorithms have been developed to perform this integration, which will be introduced in the next section.

2.1.2 Time Integration Algorithms

In molecular dynamics simulations, the equations of motion must be integrated numerically to generate the particle trajectories. One of the most widely used methods is the Verlet algorithm [2], which is based on the Taylor expansion of the particle positions around time t . Expanding forward and backward in time gives

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \frac{1}{2} \Delta t^2 \mathbf{a}_i(t) + \frac{1}{6} \Delta t^3 \frac{d^3\mathbf{r}_i}{dt^3} + O(\Delta t^4), \quad (2.4)$$

$$\mathbf{r}_i(t - \Delta t) = \mathbf{r}_i(t) - \Delta t \mathbf{v}_i(t) + \frac{1}{2} \Delta t^2 \mathbf{a}_i(t) - \frac{1}{6} \Delta t^3 \frac{d^3\mathbf{r}_i}{dt^3} + O(\Delta t^4). \quad (2.5)$$

By adding Equations 2.4 and 2.5, the odd terms cancel and one obtains

$$\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \Delta t^2 \mathbf{a}_i(t) + O(\Delta t^4). \quad (2.6)$$

Equation 2.6 enables the computation of new positions at time $t + \Delta t$ from the positions at t and $t - \Delta t$. The velocity $\mathbf{v}_i$ can be estimated using

$$\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t - \Delta t)}{2\Delta t}. \quad (2.7)$$

The integration timestep Δt was set to 1 fs for most of the simulations in this thesis. The accuracy of the numerical solution depends directly on the choice of Δt : smaller values improve precision. The error associated with Equation 2.6 scales as Δt^4 , whereas that of Equation 2.7 scales as Δt^2 .

Despite its simplicity, the Verlet scheme has notable limitations. First, it is not self-starting, since the calculation at $t + \Delta t$ requires knowledge of $\mathbf{r}_i(t - \Delta t)$. At the beginning of a simulation, only $\mathbf{r}_i(0)$ is known, so an additional initialization step is needed. Second, it requires storing two sets of positions, $\mathbf{r}(t)$ and $\mathbf{r}(t - \Delta t)$. Finally, velocities are not obtained explicitly and must be estimated from finite differences such as Equation 2.7. This additional approximation introduces extra numerical error and can lead to small inaccuracies in the kinetic energy.

An alternative approach that resolves these issues is the velocity Verlet algorithm [3], which directly incorporates velocities. Its formulation is given by

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \frac{1}{2} \Delta t^2 \mathbf{a}_i(t), \quad (2.8)$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{1}{2} \Delta t [\mathbf{a}_i(t) + \mathbf{a}_i(t + \Delta t)]. \quad (2.9)$$

The velocity Verlet scheme requires less storage, is easy to implement, and provides both positions and velocities in a self-consistent manner. Like the original Verlet method, it is a second-order integrator with a global truncation error of order Δt^2 , but it generally exhibits improved energy conservation because the integration scheme is both time-reversible and symplectic. For these reasons, it is one of the most widely adopted integration algorithms.

Another commonly used method is the leap-frog algorithm [4], in which velocities are computed at half-integer timesteps while positions are updated at integer timesteps. The update

rules are

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t \mathbf{v}_i \left(t + \frac{1}{2} \Delta t \right), \quad (2.10)$$

$$\mathbf{v}_i \left(t + \frac{1}{2} \Delta t \right) = \mathbf{v}_i \left(t - \frac{1}{2} \Delta t \right) + \Delta t \mathbf{a}_i(t). \quad (2.11)$$

The leapfrog scheme is named after its alternating update pattern, in which positions and velocities are evaluated in a staggered manner that resembles overlapping jumps. It has the advantage of explicitly including velocities, is straightforward to implement, and has a global truncation error of order Δt^2 . Because the scheme is symplectic and time-reversible, it generally provides good long-term energy conservation. However, positions and velocities are offset by half a time step, which can complicate trajectory analysis and the computation of instantaneous kinetic quantities, as velocities must be shifted back to integer times.

In this thesis, the velocity Verlet algorithm was used for simulations performed with LAMMPS [5], while the leap-frog algorithm was employed in GROMACS [6].

2.1.3 Physical Basis

The microscopic state of a system containing N particles is specified by their positions $\mathbf{r}^N = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$ and momenta $\mathbf{p}^N = \{\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N\}$, which together form a point in a $6N$ -dimensional phase space. The system evolves according to the Hamiltonian

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}^N), \quad (2.12)$$

where the first term is the kinetic energy K and $U(\mathbf{r}^N)$ is the potential energy. The corresponding Hamilton's equations of motion are

$$\frac{\partial H}{\partial \mathbf{p}} = \frac{d\mathbf{r}}{dt}, \quad (2.13)$$

$$\frac{\partial H}{\partial \mathbf{r}} = -\frac{d\mathbf{p}}{dt}. \quad (2.14)$$

A thermodynamic property A is thus a function of both the phase point $(\mathbf{r}^N, \mathbf{p}^N)$ and time t ,

i.e., $A(\mathbf{r}^N, \mathbf{p}^N, t)$. In molecular dynamics, its time average along a trajectory of length $t - t_0$ is

$$\overline{A}(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{t - t_0} \int_{t_0}^t A(\mathbf{r}^N, \mathbf{p}^N, \tau) d\tau. \quad (2.15)$$

The ergodic hypothesis asserts that, for sufficiently long simulations, the time average of a property is equal to its ensemble average,

$$\overline{A}(\mathbf{r}^N, \mathbf{p}^N) = \langle A(\mathbf{r}^N, \mathbf{p}^N) \rangle, \quad (2.16)$$

which implies that the trajectory explores all relevant regions of phase space. In general, the ensemble average of a property A can be expressed in terms of a statistical weight $\rho(\mathbf{r}^N, \mathbf{p}^N)$ as

$$\langle A \rangle = \frac{\int_{\Gamma} A(\mathbf{r}^N, \mathbf{p}^N) \rho(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N}{\int_{\Gamma} \rho(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N}, \quad (2.17)$$

where Γ denotes the full phase space. Specific forms of ρ define the different ensembles, which will be introduced in the following subsection. This connection between time and ensemble averages is fundamental to molecular dynamics, as it allows equilibrium properties to be computed from finite trajectories.

2.1.4 Statistical Ensembles

In statistical mechanics, different ensembles are defined by fixing a combination of macroscopic properties, typically chosen from the number of particles (N), the system volume (V), the chemical potential (μ), the temperature (T), the pressure (P), and the total energy (E). The most commonly employed ensembles in molecular dynamics are the microcanonical (NVE), the canonical (NVT), the grand canonical (μ VT), and the isothermal-isobaric (NPT) [7].

The **microcanonical ensemble** (NVE) describes an isolated system with constant N , V , and E . All accessible states have equal probability because they share the same energy. At thermodynamic equilibrium, the system arranges itself to maximize the number of accessible microscopic configurations, corresponding to a maximum of the entropy $S(N, V, E)$. The

microcanonical partition function, often called the density of states, is

$$\omega(N, V, E) = \frac{1}{N! h^{3N}} \int d\mathbf{r}^N \int d\mathbf{p}^N \delta(E - H(\mathbf{r}^N, \mathbf{p}^N)), \quad (2.18)$$

where h is Planck's constant, and the factor $1/N!$ accounts for indistinguishability.

The **canonical ensemble** (NVT) corresponds to a system at constant N , V , and T . The system is in thermal equilibrium with a heat bath, and energy can fluctuate while the temperature remains fixed. At thermodynamic equilibrium, the system adopts the state that minimizes the Helmholtz free energy $F(N, V, T)$ under these conditions. For the canonical ensemble, $\rho \propto e^{-\beta H}$ with $\beta = 1/(k_B T)$, which leads to the partition function:

$$Z(N, V, T) = \frac{1}{N! h^{3N}} \int d\mathbf{r}^N \int d\mathbf{p}^N e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)} = \frac{1}{N! \Lambda^{3N}} \int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}, \quad (2.19)$$

where $\Lambda = h/\sqrt{2\pi m k_B T}$ is the thermal de Broglie wavelength for a single species of mass m and potential energy U . The second equality follows from analytical integration over momenta.

The **grand canonical ensemble** (μ VT) allows exchanges of matter and energy with a reservoir while μ , V , and T are fixed. The number of particles fluctuates, and the probability of each state depends on both its energy and particle number. Thermodynamic equilibrium in the μ VT ensemble is characterized by a minimum of the grand thermodynamic potential $\Omega(\mu, V, T)$. The grand canonical partition function is

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z(N, V, T). \quad (2.20)$$

The **isothermal-isobaric ensemble** (NPT) maintains constant N , P , and T . This ensemble is particularly useful because it closely mimics experimental conditions where pressure and temperature are controlled. The equilibrium behavior of the system is governed by the minimization of the Gibbs free energy $G(N, P, T)$. Its partition function can be written as

$$\Delta(N, P, T) = \int_0^\infty dV e^{-\beta P V} Z(N, V, T) = \frac{1}{N! \Lambda^{3N}} \int_0^\infty dV e^{-\beta P V} \int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N; V)}. \quad (2.21)$$

In equilibrium, the statistical-mechanical description provided by each ensemble is linked to thermodynamics through the corresponding partition function, from which the relevant thermodynamic potential is obtained. Macroscopic thermodynamic properties can then be derived from derivatives of this potential with respect to the conserved or controlled variables of the ensemble. For instance, in the canonical ensemble, the Helmholtz free energy is related to the partition function via $F(N, V, T) = -k_B T \ln Z(N, V, T)$, and equilibrium properties such as the pressure and entropy follow from derivatives with respect to volume and temperature, respectively. Analogous relations hold for the Gibbs free energy in the NPT ensemble and for the grand thermodynamic potential in the μVT ensemble.

In this thesis, simulations were performed using the NVE, NVT, and NPT ensembles.

2.1.5 Temperature and Pressure Control

Thermostats

For a system with N_{dof} independent degrees of freedom, the kinetic definition of temperature follows from equipartition,

$$\frac{1}{2} N_{\text{dof}} k_B T = K = \frac{1}{2} \sum_{i=1}^N m_i \mathbf{v}_i^2, \quad (2.22)$$

so the instantaneous temperature can be computed from the particle velocities.

A straightforward way to impose a target temperature T_0 is to rescale velocities,

$$\mathbf{v}'(t) = \mathbf{v}(t) \sqrt{\frac{T_0}{T}}, \quad (2.23)$$

which sets the kinetic energy K to the desired value in a single step. However, this method suppresses natural kinetic energy fluctuations and does not generate the canonical distribution. Moreover, the bias in ensemble averages decreases only with increasing system size.

The Berendsen thermostat [8] couples the system to a weak heat bath, relaxing the kinetic temperature toward the target temperature with time constant τ ,

$$\frac{dT}{dt} = \frac{T_0 - T}{\tau}, \quad (2.24)$$

which yields the velocity update

$$\mathbf{v}'(t) = \mathbf{v}(t) \sqrt{1 + \frac{\Delta t}{\tau} \left(\frac{T_0}{T} - 1 \right)}. \quad (2.25)$$

This scheme is effective for equilibration of the average temperature but, like simple rescaling, it does not reproduce the correct canonical fluctuations.

To recover proper canonical statistics, canonical sampling velocity rescaling (CSV) [9] augments velocity rescaling with a stochastic term so that the kinetic energy follows the Maxwell-Boltzmann distribution. In compact form, the kinetic energy evolves as

$$dK = \frac{\bar{K} - K}{\tau} dt + \sqrt{\frac{2K\bar{K}}{N_{\text{dof}} \tau}} dW, \quad (2.26)$$

where $\bar{K} = \frac{1}{2} N_{\text{dof}} k_B T_0$ and dW denotes a Wiener process increment. Exact integration over a timestep Δt yields a random velocity scaling that preserves the canonical distribution of kinetic energy. CSV maintains tight temperature control while accurately sampling the canonical ensemble.

The Langevin thermostat [10, 11] models coupling to a heat bath through both friction and random forces,

$$m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{F}_i - \gamma m_i \mathbf{v}_i + \mathbf{R}_i(t), \quad (2.27)$$

where $\mathbf{R}_i(t)$ is a stochastic force acting on particle i . Its statistical properties are

$$\langle \mathbf{R}_i(t) \rangle = \mathbf{0}, \quad (2.28)$$

$$\langle R_{i,k}(t) R_{j,l}(t') \rangle = 2\gamma m_i k_B T \delta_{ij} \delta_{kl} \delta(t - t'), \quad (2.29)$$

where i, j label particles and $k, l \in \{x, y, z\}$ denote Cartesian components. The friction coefficient γ controls the coupling strength to the heat bath: small γ yields nearly Hamiltonian dynamics, whereas large γ overdamps the motion. Because the fluctuation-dissipation relation is enforced by Equation (2.29), Langevin dynamics samples the NVT ensemble correctly.

The Nosé-Hoover thermostat [12, 13] is a deterministic and time-reversible method that

generates the canonical ensemble provided the dynamics are ergodic. It introduces an auxiliary variable ζ acting as a dynamical friction coefficient,

$$m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{F}_i - \zeta(t) m_i \mathbf{v}_i, \quad \frac{d\zeta}{dt} = \frac{1}{Q} \left[\sum_{i=1}^N \frac{m_i \mathbf{v}_i^2}{2} - \frac{N_{\text{dof}}}{2} k_B T_0 \right], \quad (2.30)$$

where Q is a mass-like parameter controlling the coupling timescale. An appropriate choice of Q is essential to ensure stable dynamics, preventing unphysical oscillations or systematic temperature drifts.

In this thesis, the Nosé-Hoover thermostat was employed for equilibrium NVT and NPT simulations, whereas non-equilibrium molecular dynamics simulations used the CSVr thermostat for pure liquids (water and ethanol) and Langevin dynamics for electrolyte solutions. The CSVr thermostat acts globally and preserves collective dynamics with minimal perturbation of vibrational spectra and heat flux correlations [9, 14], making it well suited for homogeneous systems where transport properties are governed by collective molecular motion. However, due to its global nature, CSVr does not act locally on individual species, which can limit its effectiveness in spatially or compositionally heterogeneous systems and may lead to slower equilibration of subsystems with distinct dynamical timescales. In contrast, the Langevin thermostat introduces local friction and stochastic forces acting on individual particles [10, 11], providing efficient temperature control in multi-component systems such as electrolyte solutions. As shown in References [14, 15], overly strong Langevin coupling may perturb vibrational densities of states and heat flux relaxation dynamics, leading to biased thermal transport properties. For this reason, Langevin dynamics was avoided for pure liquids and employed for solutions using sufficiently weak coupling to minimize dynamical perturbations.

Barostats

In analogy with thermostats that regulate temperature, barostats are used to control pressure in molecular dynamics simulations. The instantaneous pressure P of a system at temperature T can be computed from the virial theorem as

$$PV = Nk_B T + \frac{1}{3} \left\langle \sum_{i < j}^N \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \right\rangle, \quad (2.31)$$

where $\mathbf{r}_{ij}$ is the separation vector between particles i and j , and $\mathbf{f}_{ij}$ is the force exerted by particle j on particle i .

The Berendsen barostat [8] rescales the simulation box vectors and particle coordinates so that the instantaneous pressure relaxes exponentially toward a target value P_0 with a time constant τ_P ,

$$\frac{dP}{dt} = \frac{P_0 - P}{\tau_P}. \quad (2.32)$$

This scheme equilibrates the system volume rapidly and is therefore often employed during initial equilibration. However, like its thermostat analogue, it suppresses natural pressure fluctuations and does not rigorously sample the isothermal-isobaric ensemble.

The Nosé-Hoover method was later extended to pressure control [16] by introducing auxiliary dynamical variables that couple the system volume to an external pressure bath. In principle, this approach yields the correct NPT ensemble, assuming the system samples phase space ergodically. Compared to the Berendsen method, it reproduces the proper pressure fluctuations, though convergence may depend sensitively on the choice of coupling parameters.

The Parrinello-Rahman barostat [17] generalizes pressure control by allowing the simulation cell to fluctuate not only in volume but also in shape. The box vectors evolve dynamically under equations of motion coupled to the full pressure tensor, enabling anisotropic deformations and shear fluctuations. This makes it particularly well-suited for studies of crystals, phase transitions, or systems with anisotropic stresses.

In this thesis, the Nosé-Hoover barostat was employed in LAMMPS equilibrium NPT simulations, while in GROMACS the Berendsen barostat was used during the initial equilibration stage and the Parrinello-Rahman barostat during the production runs.

2.1.6 Interaction Potentials

The potential energy of a molecular system is described by a force field, which employs analytical functions and empirical parameters to represent the interactions between particles. The total

potential energy is commonly divided into bonded and non-bonded contributions,

$$U_{\text{total}} = U_{\text{bonded}} + U_{\text{non-bonded}}. \quad (2.33)$$

Bonded interactions. The bonded term U_{bonded} accounts for intramolecular interactions between atoms that are chemically connected. These interactions are usually categorized as bond stretching (two atoms), angle bending (three atoms), and torsional or dihedral interactions (four atoms). In practice, bond stretching is often constrained using rigid bonds, since at ambient conditions molecules typically remain near their vibrational ground state. These rigid bonds are enforced numerically using constraint algorithms, with the SHAKE [18] and RATTLE [19] algorithms employed in this thesis.

Non-bonded interactions. The non-bonded term $U_{\text{non-bonded}}$ represents intermolecular interactions as well as intramolecular interactions between atoms not directly bonded. These pairwise interactions depend on the distance between atoms i and j ,

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|, \quad (2.34)$$

and vanish as $r_{ij} \rightarrow \infty$. To reduce computational cost, a cutoff distance r_c is applied, beyond which interactions are neglected. The non-bonded potential generally includes van der Waals and electrostatic contributions.

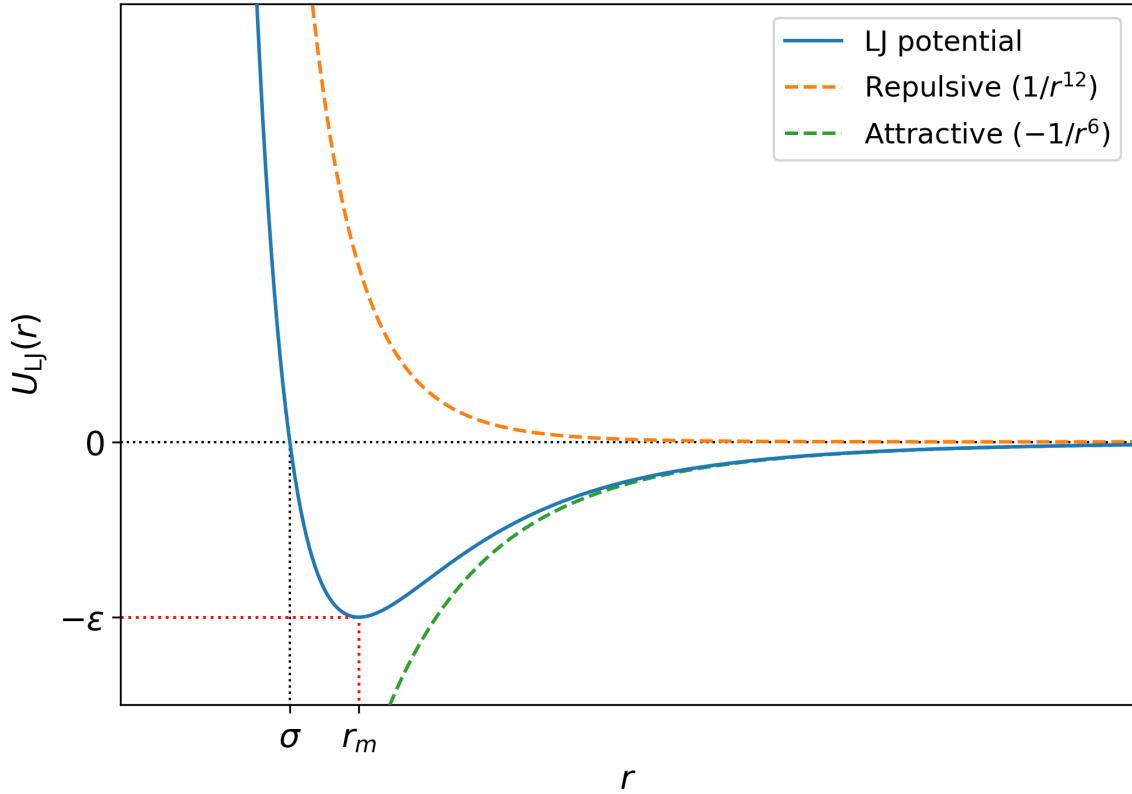


Figure 2.1: Lennard-Jones potential and its components. The solid blue curve shows the full potential, while the dashed orange and green curves represent the repulsive and attractive terms, respectively. The dotted red lines mark the minimum of the potential, which occurs at r_m , where the energy reaches $-\varepsilon$. The black vertical line at σ marks the distance where the potential crosses zero.

The van der Waals interaction is represented as the sum of a short-range repulsion and a long-range dispersion term. A widely used form is the Lennard–Jones potential [20], introduced in 1924 to describe noble gases,

$$U_{LJ}(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (2.35)$$

where ε_{ij} is the depth of the potential well, measuring the interaction strength between particles i and j , and σ_{ij} is the distance at which the potential crosses zero. The first term, proportional to $1/r_{ij}^{12}$, describes the strong repulsion at short distances, while the second term, proportional to $-1/r_{ij}^6$, accounts for the attractive dispersion. The potential has a minimum at $r_m = 2^{1/6}\sigma_{ij}$, where $U_{LJ}(r_m) = -\varepsilon_{ij}$. See Figure 2.1 for the Lennard-Jones potential and its repulsive and attractive contributions.

For systems with multiple particle types, the Lennard–Jones parameters are obtained using the Lorentz–Berthelot combination rules [21, 22],

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \quad \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}. \quad (2.36)$$

Charged particles interact via electrostatic forces, described by the Coulomb potential. For two atoms carrying charges q_i and q_j , the interaction energy at separation r_{ij} is

$$U_{\text{coul}}(r_{ij}) = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j e^2}{r_{ij}}, \quad (2.37)$$

where ε_0 is the vacuum permittivity and e is the elementary charge. These forces are attractive for oppositely charged particles and repulsive for like charges. In both cases, the potential decays as $1/r$, reflecting its long-range nature.

Because Coulomb interactions decay slowly, they remain significant at distances far beyond the typical cutoffs used for van der Waals interactions. A naive truncation at a cutoff radius leads to large artifacts, so alternative methods are required. A common strategy is to decompose the potential into short- and long-range components, treating each with an appropriate numerical scheme.

In this thesis, the particle-particle particle-mesh (PPPM) method [23, 24] is used to evaluate electrostatic interactions. The method splits the Coulomb interaction into a short-range component, treated by direct particle summation, and a smooth long-range component, evaluated on a mesh by solving Poisson’s equation.

The short-range part is given by

$$U_s(r_{ij}) = A_{ij}r_{ij}^{-12} - B_{ij}r_{ij}^{-6} + \frac{q_i q_j e^2}{4\pi\varepsilon_0\varepsilon_1} \frac{\text{erfc}(\eta r_{ij})}{r_{ij}}, \quad (2.38)$$

where A_{ij} and B_{ij} are the Lennard–Jones coefficients that describe the repulsive and dispersive interactions, respectively, and ε_1 is the uniform dielectric constant of the explicit medium. The parameter η sets the range of the complementary error function that screens the Coulomb interaction, corresponding to a Gaussian charge distribution used in the PPPM method. This

screened form defines the rapidly decaying real-space contribution, which can be evaluated efficiently using a finite cutoff.

Screening is implemented by subtracting from each point charge a Gaussian charge distribution of width η^{-1} ,

$$\gamma(\mathbf{r}) = \frac{\eta^3}{\pi^{3/2}} \exp(-\eta^2 r^2), \quad (2.39)$$

where $\mathbf{r}$ denotes the position vector and $r = |\mathbf{r}|$ is its magnitude. The normalization factor $\eta^3/\pi^{3/2}$ ensures that the Gaussian integrates to unity, preserving charge neutrality. Applying this smoothing to all charges produces the long-range charge density

$$\rho(\mathbf{r}) = \sum_j q_j \gamma(\mathbf{r} - \mathbf{r}_j), \quad (2.40)$$

which is suitable for solution on a mesh.

The remaining long-range electrostatic potential is then obtained by solving Poisson's equation,

$$-\nabla^2 \phi_1(\mathbf{r}) = \frac{\rho(\mathbf{r})}{\varepsilon_0 \varepsilon_1}, \quad (2.41)$$

using fast Fourier transforms on a regular grid. The resulting potential is interpolated back to the particle positions to compute the forces. This real-space and mesh-based decomposition yields an overall $N \log N$ scaling and eliminates artifacts associated with truncating the Coulomb interaction. Long-range dispersion interactions were treated using the same mesh-based PPPM method [25, 26]. Despite their r^{-6} decay, truncation of dispersion forces can introduce systematic errors in thermodynamic properties. The reciprocal-space treatment therefore provides an accurate and cutoff-independent description of dispersion contributions to the potential and forces.

2.1.7 Periodic Boundary Conditions

Molecular dynamics simulations aim to reproduce bulk properties of macroscopic systems. In practice, however, simulations are restricted to a finite number of particles, which by themselves are insufficient to capture bulk behavior. To mitigate this limitation, periodic boundary

conditions [7] are commonly employed. In this scheme, the simulation box is replicated infinitely in all directions, so that each real particle is surrounded by translational copies of the system. Although only the particles in the primary simulation cell are explicitly simulated, their periodic images evolve consistently, ensuring that the system mimics an effectively infinite medium.

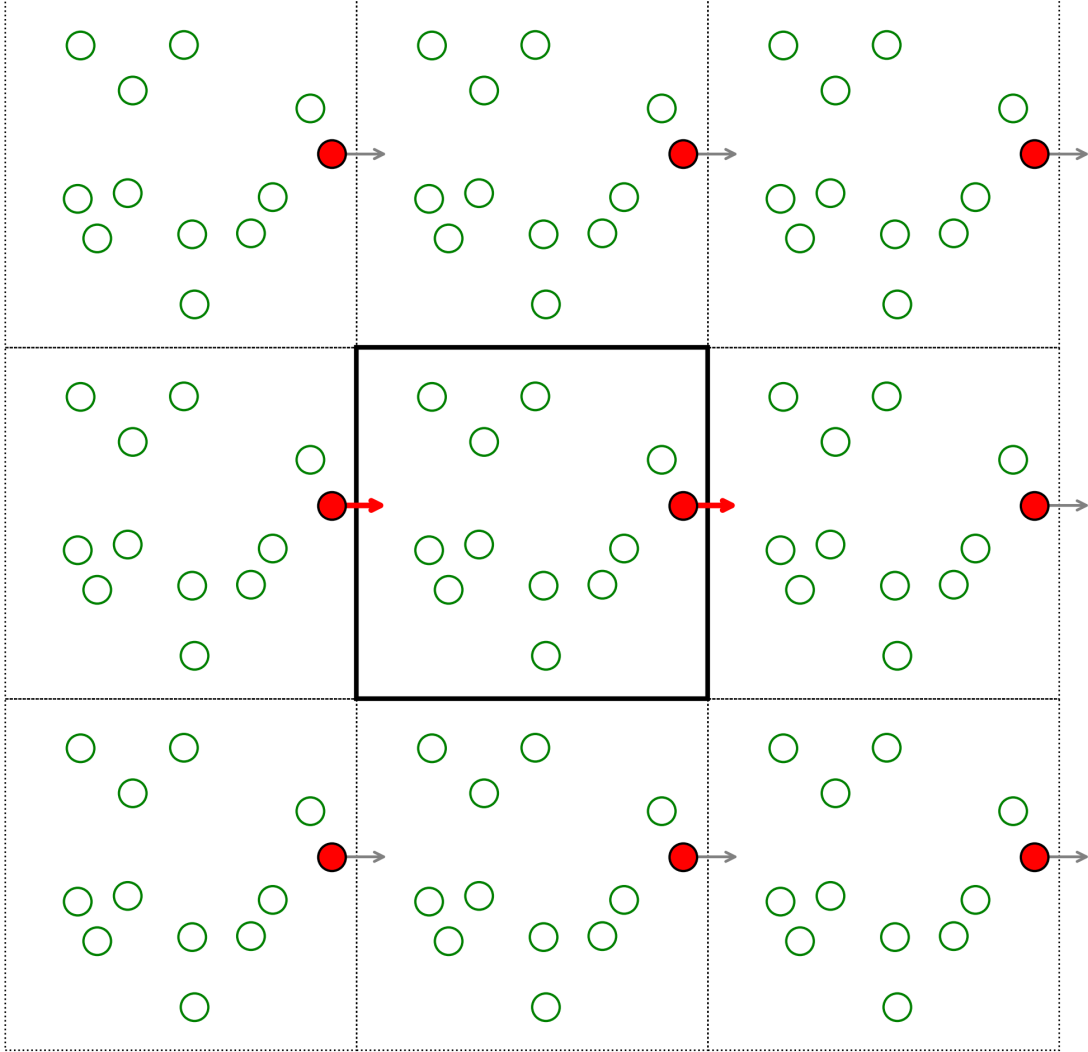


Figure 2.2: Two-dimensional schematic illustration of periodic boundary conditions. The central simulation cell (solid border) is surrounded by its periodic images (dotted borders). When a particle (red) exits the cell through one boundary, its periodic image simultaneously enters from the opposite side, ensuring conservation of particle number and mimicking an infinite system.

When a particle crosses one boundary of the simulation cell, it re-enters through the opposite boundary with the same velocity, thereby conserving the number of particles inside the box. For example, if a particle undergoes a displacement Δx and crosses the boundary in the x -direction,

its position is updated as $x + \Delta x - L_x$, where L_x is the box length along the x -axis. More generally, a particle i located at $\mathbf{r}$ represents an infinite set of periodic images i' positioned at

$$\mathbf{r}' = \mathbf{r} + n_x L_x \hat{\mathbf{x}} + n_y L_y \hat{\mathbf{y}} + n_z L_z \hat{\mathbf{z}}, \quad (2.42)$$

where $n_x, n_y, n_z \in \mathbb{Z}$ are integers, and L_x , L_y , and L_z denote the box dimensions along the Cartesian axes. As a result, particles interact not only with others inside the primary cell but also with their periodic replicas, allowing bulk-like conditions to be approximated while minimizing surface effects.

2.2 Non-equilibrium Thermodynamics

Non-equilibrium thermodynamics extends classical equilibrium thermodynamics to systems subject to external fields or gradients, where inhomogeneous and irreversible processes arise. As introduced in Chapter 1, these processes are described by linear relations between thermodynamic forces and their corresponding fluxes [27]. This framework accounts not only for transport phenomena such as heat conduction, diffusion, and viscosity, but also for cross-coupling effects between multiple non-equilibrium processes within the same system.

2.2.1 Linear Laws

In non-equilibrium thermodynamics, fluxes are driven by thermodynamic forces such as temperature, concentration, or potential gradients. The linear law relates a flux $\mathbf{J}$ to its conjugate force X through a proportionality constant, often associated with a transport coefficient,

$$\mathbf{J}_1 = L_{11} X_1, \quad (2.43)$$

where L_{11} is the phenomenological coefficient.

When multiple processes occur simultaneously, the flux of a given process can depend not only on its own driving force but also on other forces present in the system. The linear law is

then generalized as

$$\mathbf{J}_i = \sum_j L_{ij} X_j, \quad (2.44)$$

where L_{ij} are phenomenological coefficients. The diagonal terms L_{ii} describe direct transport processes (e.g., thermal conductivity or diffusion coefficients), while the off-diagonal terms L_{ij} with $i \neq j$ quantify cross-coupling effects such as the Soret or Seebeck effects.

For a system with two fluxes, the relations take the explicit form

$$\mathbf{J}_1 = L_{11}X_1 + L_{12}X_2, \quad (2.45)$$

$$\mathbf{J}_2 = L_{21}X_1 + L_{22}X_2. \quad (2.46)$$

Here, L_{12} and L_{21} describe the strength of the coupling between the two processes. According to the Onsager reciprocal relations, these coefficients are symmetric [27],

$$L_{ij} = L_{ji}, \quad (2.47)$$

which reduces the number of independent coefficients that need to be determined.

Within the framework of linear non-equilibrium thermodynamics (LNET), the entropy flux is expressed in terms of heat and mass fluxes using the Gibbs relation, allowing the local entropy production σ to be written as a sum of products of irreversible fluxes and their conjugate thermodynamic forces [27],

$$\sigma = \sum_i \mathbf{J}_i X_i \geq 0. \quad (2.48)$$

The non-negativity of σ reflects the second law of thermodynamics and quantifies the irreversibility of the process. In the non-equilibrium molecular dynamics simulations presented in this thesis, the thermodynamic forces appearing in Equation 2.48 are defined as gradients of intensive variables such as temperature, chemical potential, or electrochemical potential. These gradients are imposed through externally applied hot and cold thermostating regions, with the detailed simulation setup described later in Section 2.2.3. They correspond to spatial variations of intensive thermodynamic variables, which are derivatives of the local free energy density, and thus represent gradients of the local free energy that drive irreversible transport. The resulting

steady-state fluxes measured in the simulations can therefore be directly interpreted within the LNET framework as responses to the imposed thermodynamic forces.

2.2.2 Local Equilibrium Hypothesis

The local equilibrium hypothesis is a central assumption of non-equilibrium thermodynamics. It states that, although the system as a whole is out of equilibrium, sufficiently small subregions can be regarded as being in local equilibrium. Consequently, the Gibbs relation between entropy and state variables, valid for equilibrium systems, also applies locally at each position $\mathbf{r}$ and time t . For a mass element, this relation can be written as

$$T \frac{ds}{dt} = \frac{de}{dt} + P \frac{dv}{dt} - \sum_{i=1}^n \mu_i \frac{dc_i}{dt}, \quad (2.49)$$

where s is the specific entropy, e the internal energy, v the specific volume, P the equilibrium pressure, c_i the mass fraction of component i , and μ_i its chemical potential.

In this thesis, we verified the validity of the local equilibrium hypothesis by comparing equations of state obtained from equilibrium and non-equilibrium simulations. As demonstrated in Section 3.3.1, the equations of state extracted from non-equilibrium molecular dynamics simulations agree with those obtained from equilibrium simulations. In addition, transport coefficients computed under strong thermal gradients (on the order of 1 K/Å) are consistent, within numerical uncertainty, with those calculated under smaller imposed gradients, indicating that the system remains within the linear response regime. Similar consistency was observed across all studied systems, confirming that the local equilibrium assumption remains reliable for describing local transport properties even under large imposed gradients.

2.2.3 Boundary-Driven Non-equilibrium Molecular Dynamics

Non-equilibrium molecular dynamics (NEMD) simulations provide a direct approach to study transport properties and coupling effects under thermal gradients. Three main classes can be distinguished: transient methods [28], synthetic methods [29], and boundary-driven methods [30]. Among these, boundary-driven NEMD is most widely employed in practice, as it most closely

mimics experimental setups by imposing explicit boundary conditions. In transient simulations, the relaxation toward equilibrium following a perturbation is analyzed, while in synthetic approaches, a fictitious external field is introduced into the equations of motion to generate a homogeneous flux. In contrast, boundary-driven methods establish non-equilibrium steady states by imposing thermodynamic gradients through thermostatted regions acting as heat reservoirs.

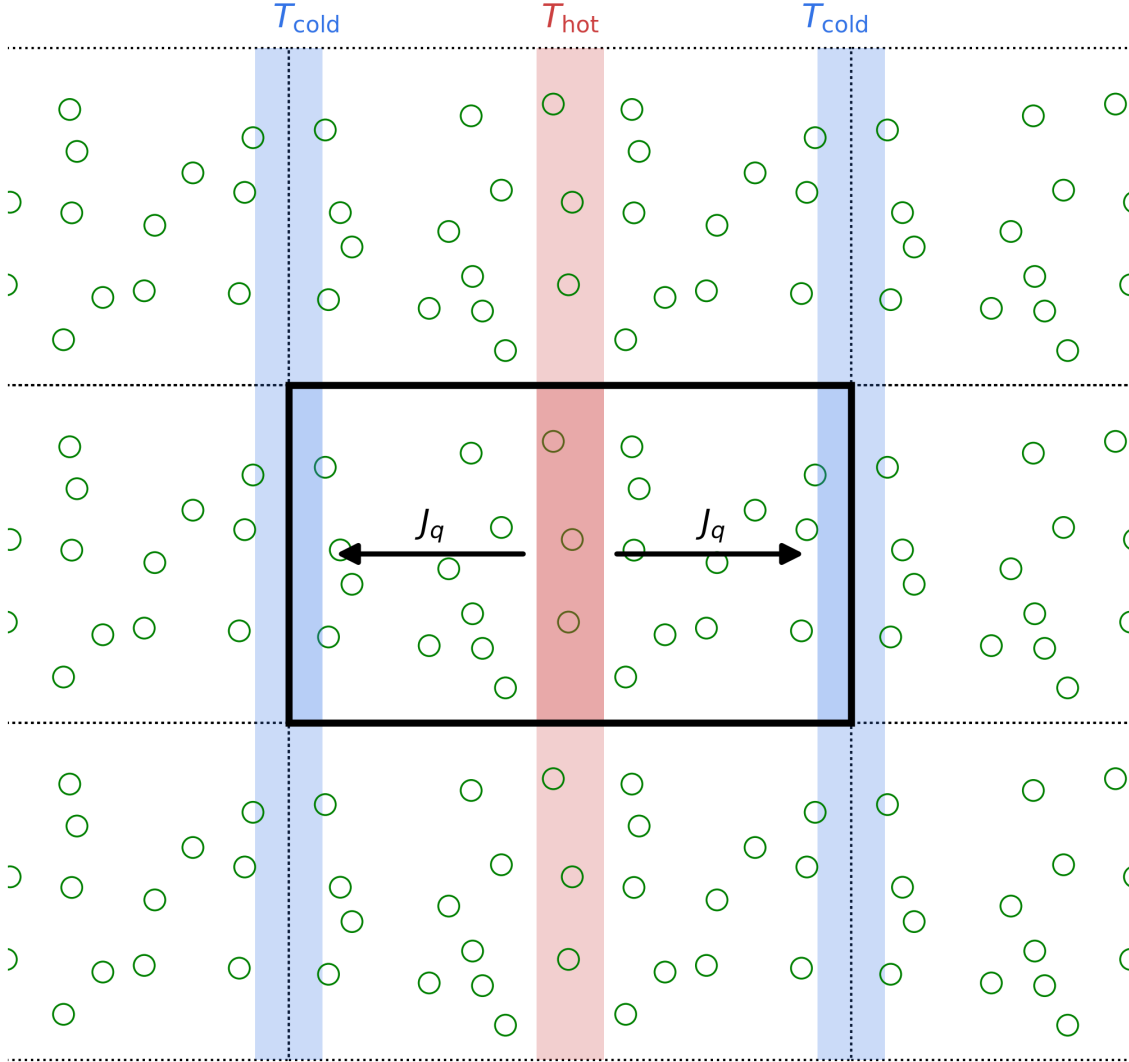


Figure 2.3: Schematic representation of the simulation box in boundary-driven NEMD. The central red region is thermostatted to T_{hot} and the two blue regions to T_{cold} . The solid black line marks the unit-cell boundary; dotted outlines show periodic replicas. Arrows labeled J_q indicate the heat fluxes from the hot region toward the cold regions.

In boundary-driven simulations, external perturbations are applied locally by manipulating

particle velocities or energies within designated hot and cold regions. A widely used approach is the heat exchange algorithm [31, 32], in which kinetic energy is systematically added to the hot region and removed from the cold region, while leaving the potential coordinates unchanged. Particles within these reservoirs are thus thermostatted to predefined target temperatures, whereas the rest of the system evolves under Newtonian dynamics. Through collisions and interactions, particles exchange energy with those in the thermostating regions, giving rise to a stationary temperature gradient across the system.

When combined with periodic boundary conditions, care must be taken to prevent the hot and cold reservoirs from becoming adjacent, which would otherwise cancel the imposed gradient. A common solution is to place hot regions at the center of the simulation cell and cold regions at the boundaries, ensuring symmetry and preserving periodicity. This configuration establishes two thermal gradients of equal magnitude but opposite direction, as illustrated schematically in Figure 2.3.

2.3 Calculations of Transport Properties

This section outlines the procedures used to evaluate the transport properties considered in this thesis, based on NEMD simulations. Particular attention is given to the determination of the thermal conductivity, the Soret coefficient, and the thermal polarization coefficient, each of which plays a central role in characterizing transport behavior and coupling phenomena under thermal gradients.

2.3.1 Thermal Conductivity

To determine the thermal conductivity λ , we applied Fourier's law,

$$\lambda = -\frac{J_q}{\nabla T}, \quad (2.50)$$

where ∇T is the imposed temperature gradient and J_q the corresponding heat flux. As discussed in Section 2.2.3, the thermostats act only on particle velocities, leaving the molecular coordinates

unchanged and thus not affecting the potential energy. Consequently, the heat flux can be evaluated from the change in kinetic energy K using the continuity equation,

$$J_q = \pm \frac{\langle \Delta K \rangle}{2A \Delta t}, \quad (2.51)$$

where ΔK is the amount of kinetic energy added (+) or removed (-) from the hot and cold reservoirs, A is the cross-sectional area of the simulation box perpendicular to the heat flux, and Δt is the simulation timestep.

The NEMD simulations presented in this thesis were performed using elongated simulation cells with a sufficiently large unthermostatted region (approximately 40–60 Å on each side along the direction of the thermal gradient) to ensure fully developed steady-state heat transport. The chosen box lengths are consistent with prior finite-size convergence tests, which demonstrated that the thermal conductivity becomes insensitive to further increases in the simulation length once this regime is reached [33].

In this work, the evaluation of the heat flux using Equation 2.51 depends on how the energy exchanged with the thermostats is determined. For the CSVN thermostat, ΔK is obtained at each timestep from Equation 2.26, where the stochastic differential dK represents the instantaneous increment and its timestep average defines the exchanged energy. In the case of the Langevin thermostat, the exchanged energy is calculated as the work performed by the thermostat forces,

$$\Delta E = \sum_i \mathbf{F}_i^{\text{Langevin}} \cdot \mathbf{v}_i, \quad (2.52)$$

where $\mathbf{F}_i^{\text{Langevin}}$ is the total Langevin force acting on particle i and $\mathbf{v}_i$ its velocity, with the summation restricted to particles in the hot or cold thermostating regions. The Langevin force itself consists of a deterministic frictional drag and a random noise contribution, as expressed in Equation 2.27.

In addition to the continuity expression for the heat flux, the first-order Irving–Kirkwood approximation (IK1) provides an alternative microscopic expression for the heat flux [34]. IK1 represents the leading-order truncation of the full Irving–Kirkwood series and is closely related to the method of planes formulation developed for inhomogeneous fluids [35]. The instantaneous

heat flux across a plane normal to the z direction is expressed as the sum of kinetic and potential contributions:

$$J_q^{\text{IK1}}(z, t) = \frac{1}{A} \sum_{i=1}^N (\mathbf{v}_i - \mathbf{u}(z)) e_i \delta(z - z_i) - \frac{1}{4A} \sum_{i=1}^N \sum_{j \neq i} [(\mathbf{v}_i - \mathbf{u}(z)) \cdot \mathbf{F}_{ij}] [\text{sgn}(z - z_i) - \text{sgn}(z - z_j)], \quad (2.53)$$

where $\mathbf{v}_i$ is the particle velocity, $\mathbf{u}(z)$ the local streaming velocity at the plane, e_i the per particle internal energy, and $\mathbf{F}_{ij}$ the intermolecular force.

In practice, the potential (virial) term in Equation 2.53 includes contributions from both short-range interactions (pairwise and bonded terms) and long-range electrostatics. The short-range part is computed using the centroid atomic stress formulation [36, 37], while the long-range electrostatic component is obtained from the reciprocal-space (k-space) virial using per-atom energy and virial decomposition [38, 39].

2.3.2 Soret Coefficient

The Soret effect is analyzed within the framework of linear non-equilibrium thermodynamics [27]. As introduced in Equation 2.48, entropy production can be written as a bilinear form of fluxes and their conjugate thermodynamic forces. For a binary mixture, this expression becomes

$$\sigma = -\frac{1}{T^2} \mathbf{J}_q \cdot \nabla T - \frac{1}{T} \sum_{i=1}^2 \mathbf{J}_i \cdot \nabla_T \mu_i, \quad (2.54)$$

where $\mathbf{J}_i$ is the mass flux of component i , and $\nabla_T \mu_i$ is the chemical potential gradient at constant temperature.

In a solution where x_1 denotes the solute molar fraction and x_2 the solvent molar fraction, the chemical potentials are not independent but satisfy the Gibbs-Duhem relation at constant pressure and temperature,

$$x_1 d\mu_1 + x_2 d\mu_2 = 0, \quad (2.55)$$

which allows us to eliminate one of the chemical potential gradients, given that $x_1 + x_2 = 1$.

To connect the thermodynamic forces to composition, we express the chemical potential gradient in terms of the mole fraction gradient,

$$\nabla_T \mu_1 = \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,P} \nabla x_1. \quad (2.56)$$

Combining Equations 2.55 and 2.56, the thermodynamic force driving diffusion can be written as

$$\begin{aligned} \nabla_T(\mu_1 - \mu_2) &= \nabla_T \mu_1 - \nabla_T \mu_2 \\ &= \nabla_T \mu_1 + \frac{x_1}{x_2} \nabla_T \mu_1 \\ &= \frac{1}{x_2} \nabla_T \mu_1 \\ &= \frac{1}{x_2} \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,P} \nabla x_1. \end{aligned} \quad (2.57)$$

Imposing mass conservation in the binary mixture, which requires that the total mass flux vanishes ($\mathbf{J}_1 + \mathbf{J}_2 = 0$), and using the entropy production expression in Equation 2.54 together with Equation 2.57, leads to the following explicit form of the phenomenological relations:

$$\mathbf{J}_q = -L_{qq} \frac{\nabla T}{T^2} - \frac{L_{q1}}{T} \nabla_T(\mu_1 - \mu_2) = -L_{qq} \frac{\nabla T}{T^2} - \frac{L_{q1}}{T x_2} \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,P} \nabla x_1, \quad (2.58)$$

$$\mathbf{J}_1 = -L_{1q} \frac{\nabla T}{T^2} - \frac{L_{11}}{T} \nabla_T(\mu_1 - \mu_2) = -L_{1q} \frac{\nabla T}{T^2} - \frac{L_{11}}{T x_2} \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,P} \nabla x_1, \quad (2.59)$$

where the Onsager coefficients satisfy the reciprocal relation $L_{1q} = L_{q1}$, quantifying the coupling between heat and mass transport. The diagonal coefficients L_{qq} and L_{11} correspond, respectively, to the uncoupled thermal conductivity and the interdiffusion coefficient associated with the solute in the absence of cross-coupling.

For clarity, the Onsager coefficients can be recast in terms of transport coefficients that more directly describe heat and mass transport. These are the uncoupled thermal conductivity, the diffusion coefficient, the Dufour coefficient, and the thermal diffusion coefficient, defined as follows.

The uncoupled thermal conductivity, which measures the heat conduction response in the

absence of any contribution from mass diffusion or heat–mass coupling, is

$$\lambda = \frac{L_{qq}}{T^2}. \quad (2.60)$$

The interdiffusion coefficient is

$$D = \frac{L_{11}}{\rho x_2 T} \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,P}. \quad (2.61)$$

The Dufour coefficient, describing the contribution of concentration gradients to the heat flux, is

$$D_F = \frac{L_{q1}}{\rho x_1 x_2 T}. \quad (2.62)$$

The thermal diffusion coefficient, which quantifies the mass flux induced by a temperature gradient, is

$$D_T = \frac{L_{1q}}{\rho x_1 x_2 T^2}. \quad (2.63)$$

The phenomenological Equations 2.58 and 2.59 can be rewritten in terms of the transport coefficients as

$$\mathbf{J}_q = -\lambda \nabla T - \rho \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,P} x_1 D_F \nabla x_1, \quad (2.64)$$

$$\mathbf{J}_1 = -\rho D \nabla x_1 - \rho x_1 x_2 D_T \nabla T, \quad (2.65)$$

where ρ is the density of the solution.

In steady state, the solute flux vanishes ($\mathbf{J}_1 = 0$), and Equation 2.65 reduces to

$$s_T = \frac{D_T}{D} = - \frac{1}{x_1 x_2} \left(\frac{\nabla x_1}{\nabla T} \right)_{\mathbf{J}_1=0}, \quad (2.66)$$

where s_T denotes the Soret coefficient, defined as the ratio between the thermal diffusion coefficient and the interdiffusion coefficient.

For aqueous solutions, it is often convenient to express s_T in terms of the solute molality b [40], defined as

$$b = \frac{m_1}{M_1 m_{\text{H}_2\text{O}}}, \quad (2.67)$$

where m_1 is the solute mass, M_1 its molar mass, and $m_{\text{H}_2\text{O}}$ the mass of water. The solute molar fraction can then be related to the molality through

$$\frac{x_1}{1 - x_1} = b M_{\text{H}_2\text{O}}, \quad (2.68)$$

with $M_{\text{H}_2\text{O}}$ the molar mass of water. Differentiating Equation 2.68 gives

$$dx_1 = M_{\text{H}_2\text{O}}(1 - x_1)^2 db. \quad (2.69)$$

Substituting Equations 2.68 and 2.69 into Equation 2.66 yields the final expression in terms of molality,

$$s_T = -\frac{1}{b} \left(\frac{db}{dT} \right)_{\mathbf{J}_1=0}. \quad (2.70)$$

2.3.3 Thermal Polarization Coefficient

The thermal polarization coefficient S_{TP} quantifies the strength of the electric field induced by a thermal gradient. It is defined as [41]

$$S_{TP}(z) = \frac{E_z(z)}{\nabla T(z)}, \quad (2.71)$$

where E_z is the electrostatic field projected along the z -direction, corresponding to the direction of the imposed heat flux in our non-equilibrium simulations. A closely related quantity, the Seebeck coefficient, can be obtained analogously from the ratio of the electrostatic field to the thermal gradient. In this thesis, the Seebeck coefficient is evaluated for aqueous electrolyte solutions, where the presence of mobile ions leads to thermoelectric responses under thermal gradients.

The electric field is calculated by integrating the microscopic charge density,

$$E_z(z) = \frac{1}{\varepsilon_0} \int_0^z \rho_q(z') dz', \quad (2.72)$$

where ε_0 is the vacuum permittivity. The charge density is defined as

$$\rho_q(z) = \frac{1}{A} \left\langle \sum_{i=1}^{N_{\text{charges}}} q_i \delta(z - z_i) \right\rangle, \quad (2.73)$$

with q_i and z_i the charge and z -coordinate of site i , respectively, and A the cross-sectional area of the simulation box. The angular brackets denote a time average, and the Dirac delta function is evaluated using discrete binning of the simulation cell along the z -direction.

In addition, the electrostatic potential profile was obtained from

$$\phi(z) = - \int_0^z E_z(z') dz', \quad (2.74)$$

which provides an alternative expression for the thermal polarization coefficient,

$$S_{TP}(z) = - \frac{\partial \phi(z)}{\partial T(z)}. \quad (2.75)$$

To analyze the microscopic origin of $\rho_q(z)$, we decomposed the charge density into dipolar and quadrupolar contributions [42]:

$$\rho(z) = - \frac{\partial}{\partial z} P_z(z) + \frac{\partial^2}{\partial z^2} Q_{zz}(z) + \dots, \quad (2.76)$$

where $P_z(z)$ and $Q_{zz}(z)$ are the dipole and quadrupole moment densities along z , defined as

$$P_z(z) = \frac{1}{A} \left\langle \sum_{m=1}^{N_m} \delta(z - z_m) \sum_{i \in m}^{N_{\text{charges}}} q_{i,m} z_{i,m} \right\rangle, \quad (2.77)$$

$$Q_{zz}(z) = \frac{1}{A} \left\langle \sum_{m=1}^{N_m} \delta(z - z_m) \frac{1}{2} \sum_{i \in m}^{N_{\text{charges}}} q_{i,m} z_{i,m}^2 \right\rangle, \quad (2.78)$$

with $q_{i,m}$ and $z_{i,m}$ the charge and z -coordinate of site i in molecule m , and z_m the chosen molecular reference point. Throughout this thesis, we use the dummy site carrying the negative partial charge in the TIP4P/2005 water model [43] and the center of mass for ethanol molecules.

From these definitions, the dipolar and quadrupolar contributions to the thermal polarization

coefficient are given by

$$S_{TP,P} = \frac{E_{P,z}}{\nabla T}, \quad (2.79)$$

$$S_{TP,Q} = \frac{E_{Q,z}}{\nabla T}, \quad (2.80)$$

where $E_{P,z}$ and $E_{Q,z}$ are the electric fields generated by the dipolar and quadrupolar terms, respectively.

The influence of the chosen reference point on the evaluation of electrostatic moments has been examined in recent work [44]. In Section 6.3.3, we compare the total electrostatic potential with its dipolar and quadrupolar contributions, calculated using different molecular reference points for ethanol. That analysis shows that although the individual dipolar and quadrupolar components exhibit some dependence on the chosen reference, their combined contribution remains consistent with the total thermal polarization coefficient S_{TP} . Consequently, in this thesis, we focus on the magnitude of the total S_{TP} , which is independent of the reference point. Comparisons of the dipolar and quadrupolar components are instead limited to their relative trends at different thermodynamic states using the same reference point.

2.4 Calculations from Fluctuations

This section presents the evaluation of thermodynamic response functions from equilibrium fluctuations obtained in NPT simulations.

The isobaric thermal expansion coefficient α was calculated using the fluctuation relation [7]:

$$\langle \delta V \delta H \rangle_{NPT} = k_B T^2 V \alpha, \quad (2.81)$$

where V is the system volume, H the enthalpy, T the temperature, and k_B the Boltzmann constant.

The isothermal compressibility κ_T was obtained from the volume fluctuations,

$$\langle \delta V^2 \rangle_{NPT} = V k_B T \kappa_T. \quad (2.82)$$

Here, the fluctuation $\delta\mathcal{P}$ is defined as the deviation of a property $\mathcal{P}$ from its ensemble average, $\delta\mathcal{P} = \mathcal{P} - \langle\mathcal{P}\rangle$.

The isobaric heat capacity was computed as

$$C_P = \frac{\langle\delta H^2\rangle}{k_B T^2}, \quad (2.83)$$

and the isochoric heat capacity as

$$C_V = C_P - \frac{VT\alpha^2}{\kappa_T}. \quad (2.84)$$

Finally, the isentropic (adiabatic) speed of sound was determined from the relation

$$c_s = \sqrt{\frac{C_P}{C_V} \frac{1}{\rho\kappa_T}}, \quad (2.85)$$

where ρ is the mass density.

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Chapter 3

Thermal Transport and Polarization in Supercooled Water

This chapter is reproduced from the article *Thermal Transport and Thermal Polarization of Water in the Supercooled Regime* by G. Zhao and F. Bresme, *J. Phys. Chem. Lett.* **2024**, 15, 9774–9779 [1], which is published under the Creative Commons CC BY 4.0 license.

The behavior of water in the deeply supercooled regime has long been of fundamental interest, largely due to the proposed existence of a second critical point. One expression of this anomalous behavior is the occurrence of a minimum in the thermal conductivity, previously observed in both experiments and simulations. In this chapter, we employed non-equilibrium molecular dynamics simulations with the TIP4P/2005 water model to investigate thermal transport along four isobars (1, 200, 700, and 1200 bar). Our results confirm the presence of thermal conductivity minima that coincide with the maximum in the isothermal compressibility and the minima in the isobaric thermal expansion coefficient and the speed of sound, thereby linking these transport anomalies to the hypothesized second critical point of water. In addition, we find that thermal gradients induce a measurable polarization in supercooled water, with a thermal polarization coefficient on the order of several mV/K. This effect can be interpreted within a recent theoretical framework that relates thermal polarization to the isobaric thermal expansion coefficient.

3.1 Introduction

Water is a ubiquitous liquid that supports countless physical, chemical, and biological processes. Beyond its central role in life, it exhibits unusual thermodynamic behavior that sets it apart from most simple liquids. Well-known anomalies include the density maximum at 4 °C and extrema in isothermal compressibility [2, 3]. In recent decades, attention has increasingly focused on water cooled below its melting point without crystallization. While extremely rapid cooling at rates on the order of 10^6 K/s produces glassy states [4], water can also persist in a metastable liquid form when cooled more moderately. Such supercooled water occurs naturally in atmospheric droplets [5] and has also been observed in the tissues of woody plants, where deep supercooling represents an adaptation for surviving extreme cold [6].

Supercooled water exhibits pronounced anomalies in its thermodynamic response functions, including increases in isothermal compressibility and heat capacity [7, 8]. A widely discussed explanation is the liquid–liquid phase transition (LLPT) hypothesis, which proposes a first-order phase transition between high- and low-density liquid states terminating at a liquid-liquid critical point (LLCP) [9]. Evidence for this scenario has been reported in both experiments [10, 11] and computer simulations [12, 13], though its validity remains debated [14, 15]. Recent experimental advances have extended access to the deeply supercooled regime [16, 17], yet rapid crystallization still imposes severe limitations. In this context, molecular simulations are particularly effective, as the relaxation times of water models are much shorter than the timescales for ice nucleation [18].

In this chapter, we employ non-equilibrium molecular dynamics (NEMD) simulations to investigate the thermal transport of supercooled water. Experimental studies show that the thermal conductivity decreases anomalously upon cooling below the melting point [19], yet its behavior in the deeply supercooled regime remains poorly characterized. Theoretical analyses [20] and molecular dynamics simulations [21, 22] have suggested the presence of a local minimum in the thermal conductivity, with the temperature of this minimum depending on pressure and coinciding with anomalies in the isothermal compressibility and the speed of sound, in agreement with the Bridgman relation (Equation 1.1). However, later equilibrium simulations challenged these findings and reported no evidence for such a minimum [23]. These contrasting results,

together with the scarcity of reliable experimental data at very low temperatures, highlight the need for complementary simulation strategies. In particular, non-equilibrium approaches offer an attractive alternative to equilibrium Green-Kubo formalism, as they allow direct probing of thermal transport under applied thermal gradients and naturally account for coupling effects, including thermal polarization.

The strength of the thermal polarization effect is quantified by the thermal polarization coefficient, S_{TP} , defined as the ratio between the induced electrostatic field and the applied thermal gradient (Equation 2.71). In polar liquids such as water, this effect arises because a thermal gradient promotes preferential molecular orientation, leading to a net polarization field [24]. As discussed in Chapter 1, the thermal polarization response of water may change sign with temperature, a phenomenon attributed to the balance of dipolar and quadrupolar contributions [25, 26]. Furthermore, an enhancement of the thermal polarization effect has been reported near the liquid–vapor critical point, consistent with the divergence of the thermal expansion coefficient in this regime [27].

Here, we employ the TIP4P/2005 model to perform molecular dynamics simulations of supercooled water. The TIP4P/2005 potential is a rigid four-site model consisting of three atomic sites (two hydrogens and one oxygen) and an additional massless dummy site located along the bisector of the H–O–H angle, where the negative charge is placed to better reproduce the molecular electrostatics of water [28]. This model was parameterized to reproduce the temperature of maximum density, the stability of several ice polymorphs, and other key thermodynamic properties across a broad range of temperatures and pressures. It is widely recognized as one of the most accurate non-polarizable, rigid water models [29]. Previous studies have demonstrated that TIP4P/2005 successfully reproduces many of water’s anomalous thermodynamic and dynamic properties, including the density maximum, the minimum in isothermal compressibility [30], and the pressure and temperature dependence of viscosity [31]. Moreover, it has been extensively used to explore the properties of supercooled water [13, 32] and ice polymorphs [33].

3.2 Simulation Details

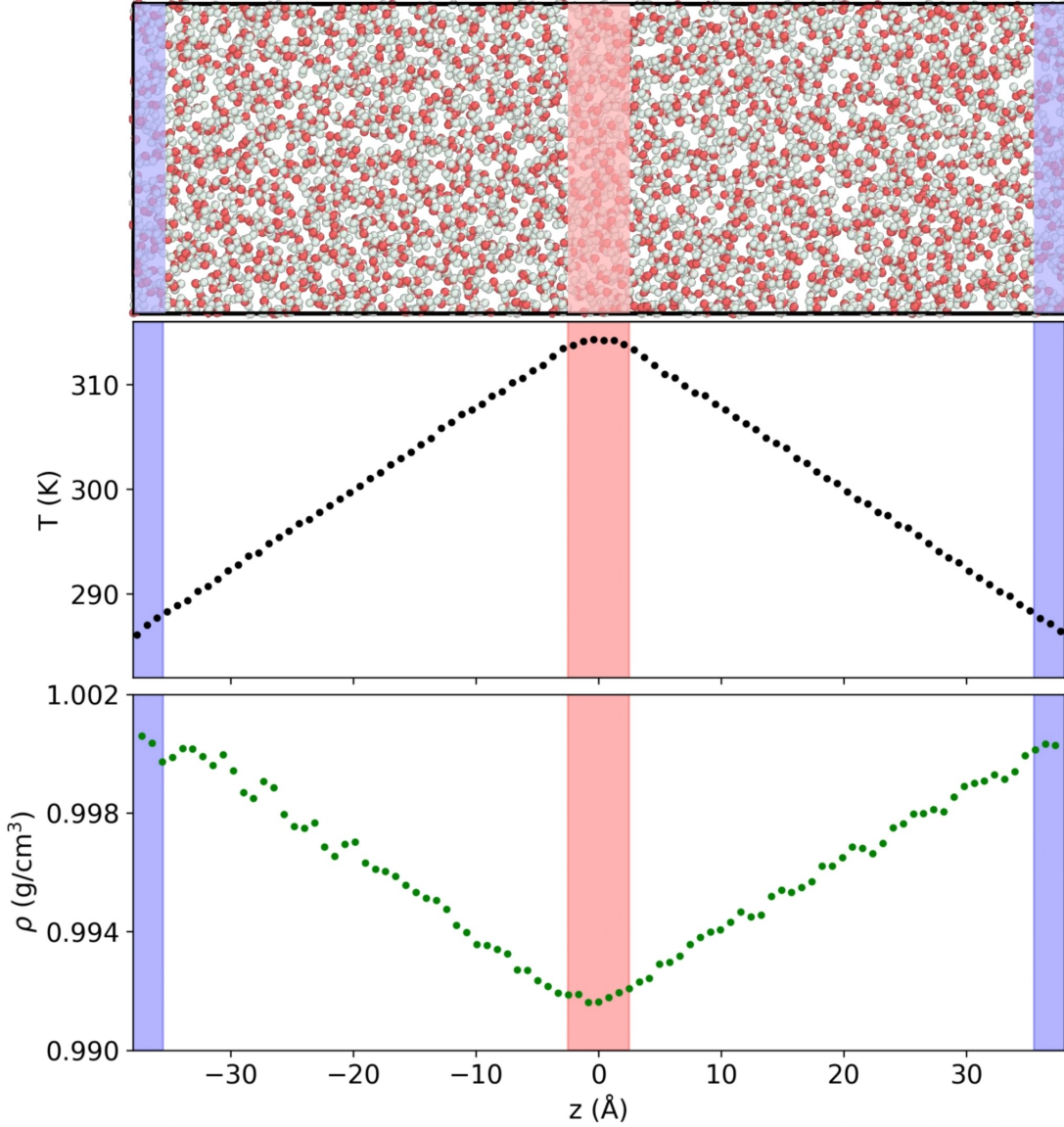


Figure 3.1: (Top) NEMD setup for simulating water, where white and red spheres represent hydrogen and oxygen atoms, respectively. The box configuration was visualized using OVITO [34]. (Middle) Representative temperature and (bottom) density profiles from an NEMD run performed at an average temperature of 300 K and a density of 0.997 g/cm³. The hot and cold thermostating regions (red and blue) were maintained at $T_{\text{hot}} = 315$ K and $T_{\text{cold}} = 285$ K, respectively.

Boundary-driven non-equilibrium molecular dynamics (NEMD) simulations were performed using a rectangular simulation cell with dimensions $\{L_x : L_y : L_z\} = \{1 : 1 : 3\}$, where $L_x \approx 25$ Å, depending on the system density. Each NEMD simulation cell contained 2100 water molecules, and all simulations were carried out using LAMMPS (version 3 Mar 2020) [35].

The simulation box contained three thermostating regions along the z -axis: two cold zones located at the cell boundaries, each with a thickness of 2.5 nm, and a central hot zone of 5 nm (see top panel in Figure 3.1), maintained at T_{cold} and T_{hot} , respectively. This configuration generates two thermal gradients of equal magnitude but opposite direction between the hot and cold regions. The magnitude of the thermal gradient was obtained from a linear fit to the steady-state temperature profile (middle panel in Figure 3.1). Local temperature and density profiles were computed by spatial averaging over 100 bins along the z -axis, corresponding to a bin width of approximately 0.75 Å, as illustrated in the middle and bottom panels of Figure 3.1.

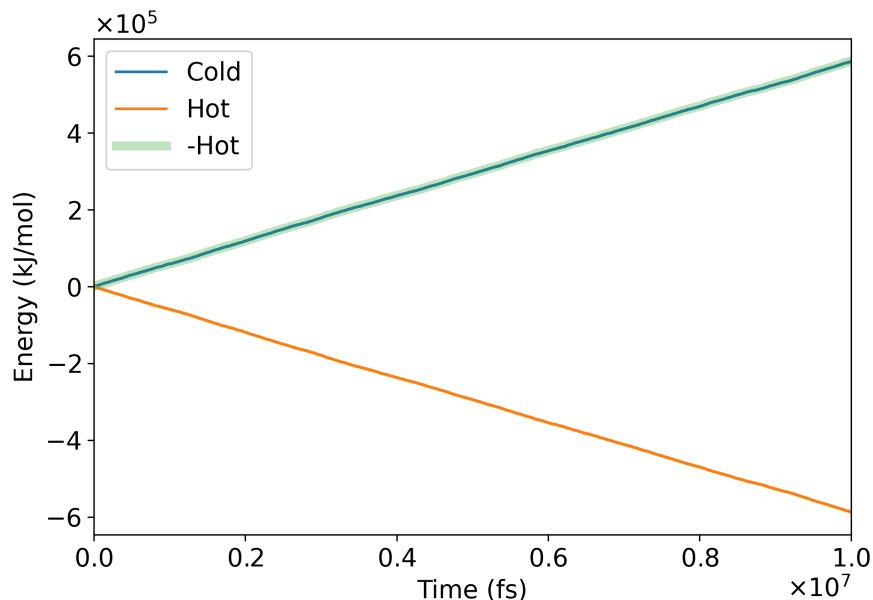


Figure 3.2: Cumulative energy exchanged by the hot and cold thermostats during the same representative NEMD simulation shown in Figure 3.1. The orange and blue lines correspond to the energy exchanged at the hot and cold thermostats, respectively, while the green line represents the negative of the energy in the hot region, included to highlight the excellent energy conservation achieved during the simulation.

During the NEMD simulations, temperature control was achieved using canonical sampling velocity rescaling (CSVR) thermostats [36] applied to the thermostatted regions at every timestep of 1 fs, with a coupling constant of 500 fs. Figure 3.2 shows the cumulative energy exchanged by the hot and cold thermostats during a representative 10 ns NEMD simulation. The close agreement between the two energy curves confirms that energy conservation is well maintained throughout the run. The total center-of-mass momentum of the simulation cell was removed

at each timestep to prevent drift. Long-range electrostatic interactions were treated using the particle–particle particle-mesh (PPPM) algorithm [37] with a relative error of 10^{-5} . The same PPPM scheme was also employed to account for long-range dispersion interactions [38, 39], using accuracy thresholds of 10^{-4} kcal/(mol Å) for the real-space contribution and 2×10^{-4} kcal/(mol Å) for the reciprocal-space term.

To initialize the NEMD simulations, equilibrium molecular dynamics runs were first performed in the isothermal–isobaric (NPT) ensemble at the target pressure and at a temperature corresponding to the average of T_{hot} and T_{cold} . Each system was equilibrated for at least 1 μs with a timestep of 1 fs, using the GROMACS simulation package (version 2021.3) [40]. The equilibrium simulations were conducted in a cubic box containing 500 water molecules. Temperature and pressure were controlled with a Nosé–Hoover thermostat [41, 42] and a Parrinello–Rahman barostat [43], employing coupling time constants of 2 and 4 ps, respectively. Fluctuation properties were computed from these equilibrium simulations using the methods described in Section 2.4, by averaging over data collected every 200 million timesteps, corresponding to a sampling time of 200 ns. In addition, the average density obtained from the NPT simulation was used to rescale the NEMD simulation box volume to achieve the target pressure. The subsequent NEMD simulations were then performed in the microcanonical (NVE) ensemble, keeping the system volume fixed.

The NEMD simulations were run for at least 200 ns, and only the steady-state portion of the trajectories was used for analysis. The thermal conductivity and its associated uncertainty were evaluated using Equations 2.50 and 2.51, based on data collected from a minimum of three independent simulations initialized with different random seeds for the thermostats. Reported values represent the mean and standard deviations computed across these independent replicas. The trajectories from the final 10 ns of each production run (190–200 ns), saved every 100 timesteps, were subsequently used to calculate the electrostatic properties required for the thermal polarization analysis, following the procedures described in Section 2.3.3.

3.3 Results

3.3.1 Simulation Convergence and Equation of State

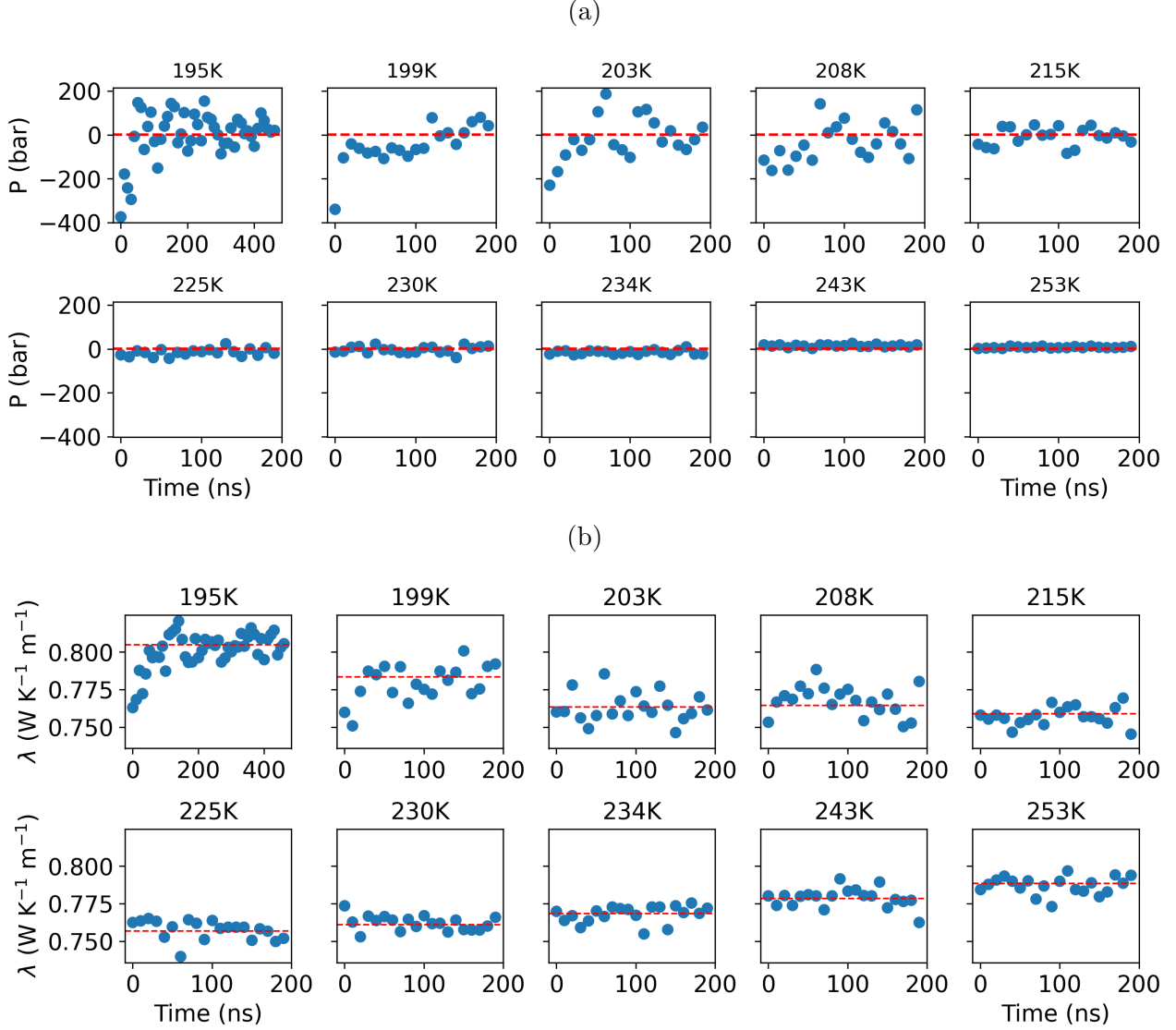


Figure 3.3: Time evolution of (a) pressure and (b) thermal conductivity for NEMD simulations of water at 1 bar across the temperature range 195–253 K. For each temperature, the time series shown corresponds to a single representative replica. For the lowest temperature case (195 K), the simulation was extended to 460 ns to ensure convergence, while all other runs were performed up to 200 ns. The red dashed lines in panels (a) and (b) indicate the target pressure (1 bar) and the average thermal conductivity obtained from the production runs, respectively.

Figure 3.3 shows the time evolution, averaged over 10 ns intervals, of the pressure and thermal conductivity obtained from NEMD simulations at 1 bar. At low temperatures, the system exhibits markedly slower dynamics as it approaches the glass transition [4, 44], requiring

extended simulation times to achieve equilibrium. While convergence is readily obtained at higher temperatures, the simulations at $T < 210$ K required approximately 50–100 ns to reach pressures consistent with the average temperature and density profiles. Consequently, the initial 100 ns of each trajectory was discarded from the production analysis.

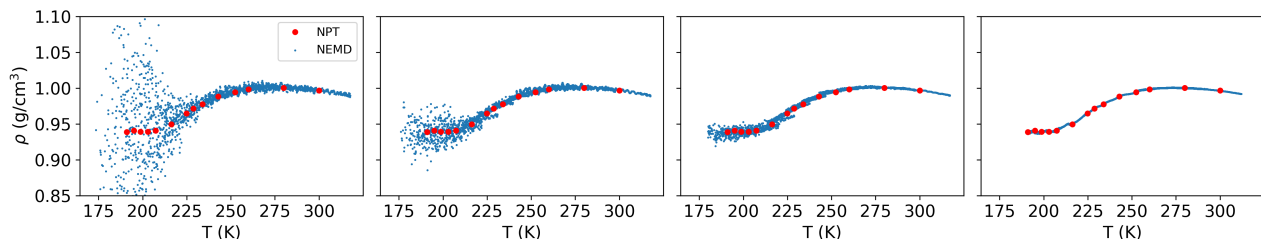


Figure 3.4: Equations of state obtained from equilibrium NPT simulations (red circles) and NEMD runs (blue circles) at 1 bar. The NPT data points represent averages over three independent replicas. Different moving average window sizes were applied to the NEMD data, shown from left to right as 0, 5, 20, and 50 data point averages.

To construct the NEMD equation of state (EOS), the local temperature and density values from each spatial bin were treated as individual data points and aggregated across all replicas and temperatures. The resulting dataset contained more than 5000 points, necessitating the application of a moving-average window to minimize statistical noise. Figure 3.4 illustrates the EOS at 1 bar obtained from NEMD simulations, where raw data are compared with smoothed results using window sizes of 5, 20, and 50. At low temperatures, the EOS displays stronger fluctuations due to slower dynamics and sensitivity to the bin size. Hence, applying the running average procedure effectively suppresses these variations and yields a reliable estimation of the EOS in the deeply supercooled regime.

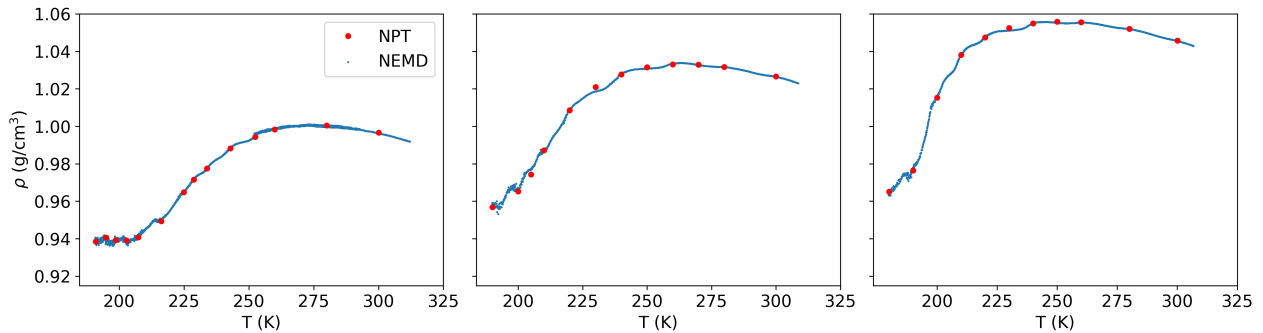


Figure 3.5: Equations of state obtained from equilibrium NPT simulations (red circles) and NEMD runs (blue circles) at three isobars. A moving average filter was applied to the NEMD data to reduce noise (see Figure 3.4). Panels from left to right correspond to pressures of 1, 700, and 1200 bar.

Figure 3.5 presents the EOS of TIP4P/2005 water obtained from both equilibrium and non-equilibrium simulations at three isobars: 1, 700, and 1200 bar. The NEMD data were averaged using a 50-point moving window. The close agreement between the NPT and NEMD results supports the validity of the local equilibrium assumption [45] and confirms that the applied thermal gradients remain within the linear response regime under the investigated conditions. This consistency, together with the convergence demonstrated in long-time simulations (Figure 3.3), confirms that the systems were well equilibrated. Moreover, the EOS obtained here agrees closely with previous results for TIP4P/2005 water [22, 46]. Notably, the EOS curves exhibit an inflection in density at low temperatures, reflecting the characteristic thermodynamic anomalies of supercooled water.

3.3.2 Thermal Conductivity Minimum in Supercooled Water

Figure 3.6 shows the temperature dependence of the thermal conductivity for the three isobars discussed earlier, together with an additional isobar at 200 bar. As illustrated in Figure 3.3 (b), the thermal conductivity converges rapidly at temperatures above 220 K, whereas at lower temperatures the relaxation dynamics become considerably slower, requiring simulation times of at least 100 ns to remove residual drift (see the 195 K case in Figure 3.3 (b)). This behavior is consistent with previous findings [22], which highlighted the need for extended simulations to obtain reliable averages in supercooled water.

As shown in Figure 3.6 (left), all investigated pressures exhibit a distinct minimum in

thermal conductivity within the supercooled region. The temperature corresponding to this minimum, $T_{\min}$, decreases systematically with increasing pressure. Because $T_{\min}$ shifts to lower temperatures at elevated pressures, accessing these states is computationally demanding. To bridge this gap, an additional simulation at an intermediate pressure of 200 bar was performed, revealing a clear minimum at $T_{\min} \approx 215$ K, shifted to a lower temperature relative to the ambient pressure result.

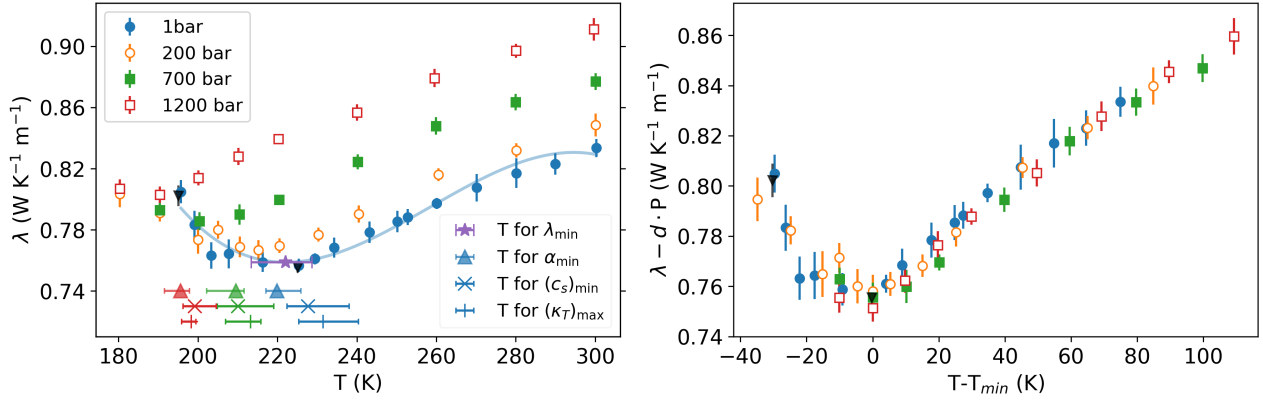


Figure 3.6: (Left) Thermal conductivity along different isobars in the 180–300 K temperature range. Weighted cubic spline fits accounting for the statistical uncertainty of the data were performed to determine the local minima in thermal conductivity. For clarity, only the 1 bar isobar is shown with its spline fit (blue curve) and corresponding minimum (purple star). Horizontal error bars denote 95% bootstrap confidence intervals for the spline-determined minimum, obtained by resampling the data 500 times, refitting the weighted spline, and recalculating the minimum for each realization. The temperatures corresponding to the minimum isobaric thermal expansion coefficient, the minimum isentropic speed of sound, and the maximum isothermal compressibility at 1 bar are marked by the symbols $\triangle$, $\times$, and $+$, respectively. These characteristic temperatures were obtained from spline fits to the corresponding fluctuation properties, as shown later in Figure 3.7. (Right) Thermal conductivity values linearly corrected using a scaling factor of $d = 0.0429 \text{ mW K}^{-1} \text{bar}^{-1}$, plotted as a function of $T - T_{\min}$ for all isobars. The inverted black triangles in both panels indicate thermal conductivities obtained from NEMD simulations at 1 bar using smaller thermal gradients ($\sim 0.36 \text{ K m}^{-1}$), approximately half of those applied in the other runs ($\sim 0.74 \text{ K m}^{-1}$). All reported NEMD results represent averages over at least three independent simulation replicas, each evaluated over successive 10 ns time intervals of the production run, with the corresponding error bars aggregated.

The observed minimum in thermal conductivity points to a thermodynamic origin, as anticipated by the Bridgman Equation [47]. To explore this connection, we analyze the isobaric thermal expansion coefficient, the isentropic (adiabatic) speed of sound, and the isothermal compressibility in Figure 3.7. Our thermal expansion coefficient α , computed from fluctuation analysis of equilibrium simulations (top row), agrees well with the value obtained from the

equation of state via

$$\alpha = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P. \quad (3.1)$$

Moreover, the isothermal compressibility and speed of sound are consistent with previous simulation results [22]. All fluctuation properties examined display clear extrema as a function of temperature, which can be attributed to enhanced density fluctuations associated with the hypothesized second critical point, in line with the LLPT scenario.

At 1 bar, the temperature of the thermal conductivity minimum $T_{\min} \approx 225$ K coincides, within uncertainty, with the temperatures of other anomalies, including the minima in the isobaric thermal expansion coefficient and the speed of sound, as well as the maximum in the isothermal compressibility (see markers in Figure 3.6 (left)). Similar correlations are observed for the 700 and 1200 bar isobars.

Figure 3.6 (right) presents the correlation between thermal conductivity and temperature after accounting for the approximately linear dependence of thermal conductivity on pressure. Following the procedure described in Reference [22], the data were rescaled using the temperature and conductivity at their respective minima. The rescaled data align along a single master curve, indicating a universal behavior across the investigated pressures. The pressure dependence, quantified by the parameter d (see Figure 3.6 (right)), agrees closely with values previously obtained from Green–Kubo calculations [22]. This alignment reinforces the link between the conductivity minimum and the anomalous behavior of thermodynamic response functions.

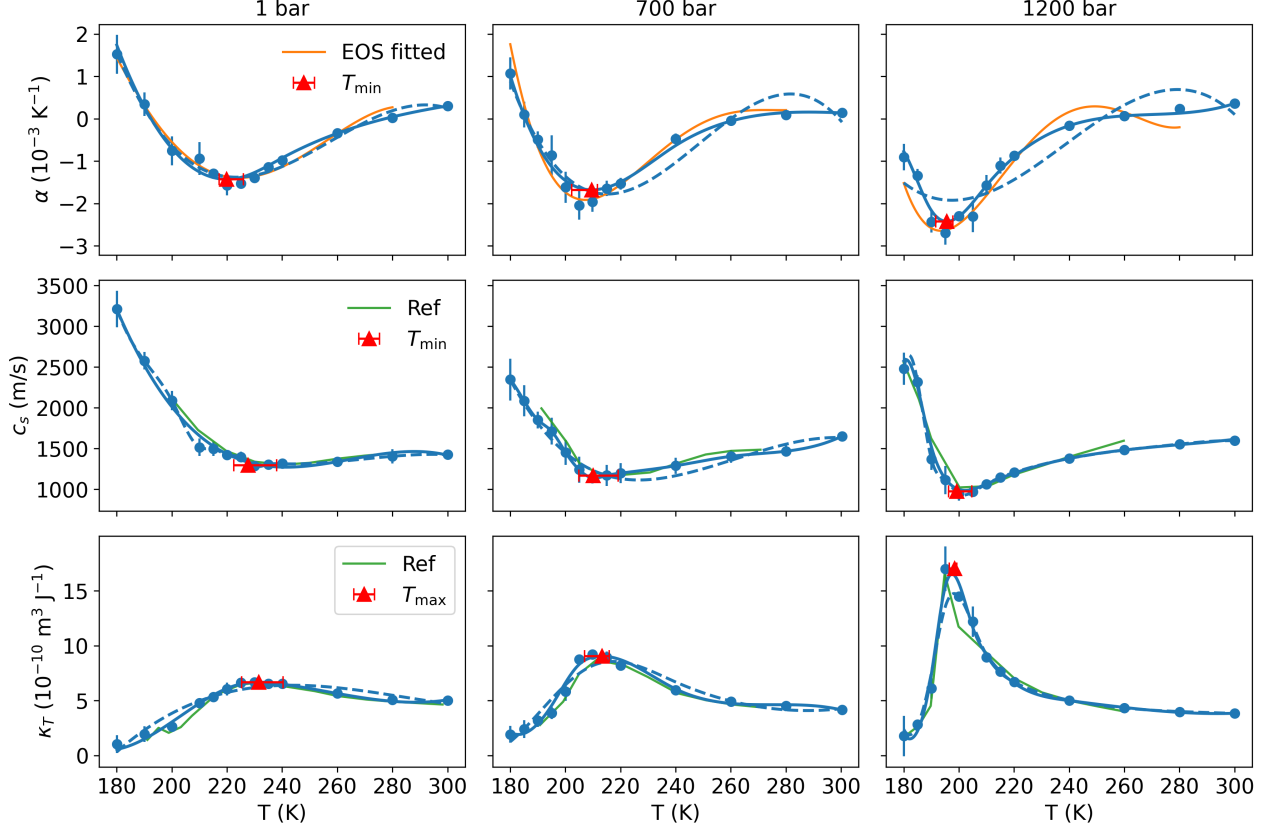


Figure 3.7: Isobaric thermal expansion coefficient (α), adiabatic speed of sound (c_s), and isothermal compressibility (κ_T) of TIP4P/2005 water obtained from equilibrium simulations as a function of temperature. All reported fluctuation properties represent averages over three independent equilibrium NPT simulation replicas. The properties are shown from top to bottom rows as α , c_s , and κ_T , and from left to right columns for the 1, 700, and 1200 bar isobars. The triangles mark the temperatures corresponding to the extrema of each property, representing minima in the top two rows and maxima in the bottom row, as determined from cubic spline fits to the simulation data. Solid blue curves correspond to weighted spline fits that account for the statistical uncertainty of the data, while dashed blue curves show unweighted spline fits included for comparison. Horizontal error bars denote 95% bootstrap confidence intervals for the spline-determined extrema, obtained using the resampling procedure described in Figure 3.6. The orange curves in the top panels show thermal expansion coefficients derived from a fifth-degree polynomial fit to the EOS from NPT simulations using Equation 3.1. The green curves in the remaining panels display speed of sound and compressibility data reported in previous work [22].

To further confirm that the results lie within the linear response regime, we conducted additional simulations at two representative state points: one at a low temperature and another near the conductivity minimum. In these tests, the applied thermal gradient was reduced by half. The results, included in Figure 3.6, closely match those obtained with the larger gradient, confirming that the calculated conductivities are independent of the gradient magnitude and

therefore correspond to the linear response regime.

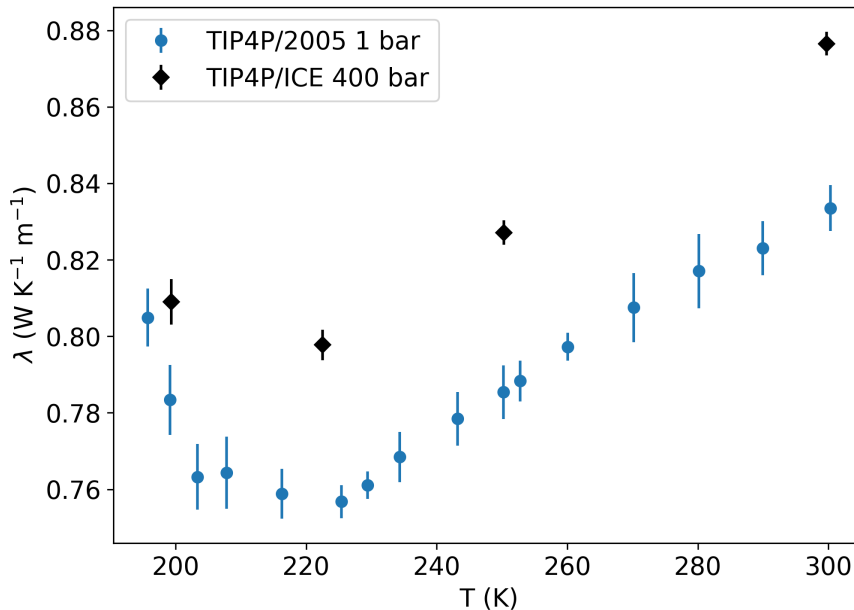


Figure 3.8: Thermal conductivity of the TIP4P/Ice water model at 400 bar (black diamonds) over the temperature range 200–300 K compared with the TIP4P/2005 results at 1 bar (blue circles). Error bars represent statistical uncertainties obtained by averaging over at least three independent replicas at each state point.

Recently, Espinosa et al. [48] performed simulations of the TIP4P/Ice water model and showed that the isobar at 400 bar accurately reproduces the experimental isothermal compressibility and the liquid equation of state at ambient pressure. Their analysis also identified the presence of an LLPT in this model. Motivated by these findings, we carried out additional NEMD simulations of TIP4P/Ice at 400 bar to explore the existence of a minimum in the thermal conductivity. The results, shown in Figure 3.8, together with the TIP4P/2005 data at 1 bar, indicate that the thermal conductivity of TIP4P/Ice is significantly higher, consistent with the elevated pressure conditions. The obtained conductivities are comparable to those from TIP4P/2005 simulations at 700 bar. Our results confirm the presence of a thermal conductivity minimum in TIP4P/Ice near 225 K, consistent with the temperature of maximum isothermal compressibility reported by Espinosa et al. [48]. These findings further reinforce the thermodynamic origin of the conductivity minimum and the anomalous heat transport behavior of supercooled water, both of which support the existence of an LLCP.

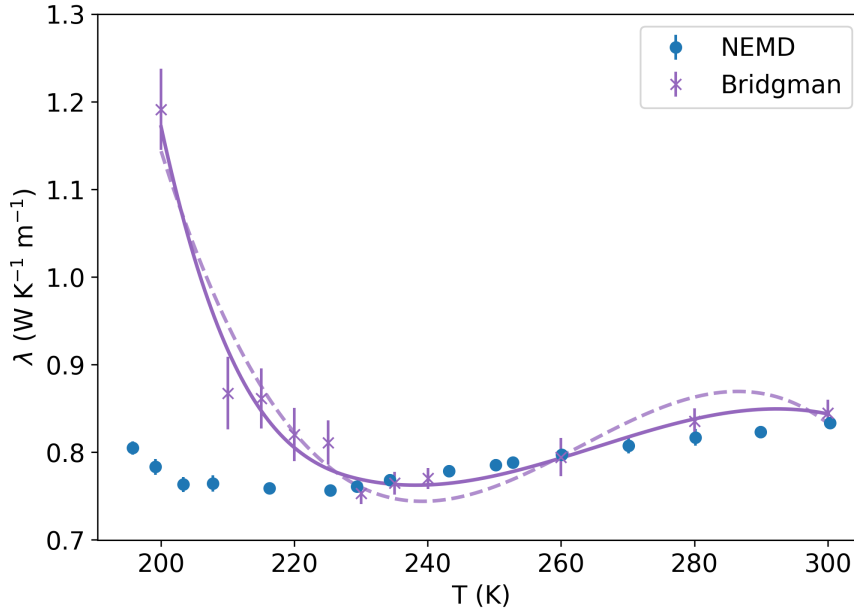


Figure 3.9: Comparison between the thermal conductivity of water at 1 bar obtained from NEMD simulations (blue circles) and values estimated using the Bridgman equation (purple crosses) with an empirical constant of $a = 4.2$. All data points represent averages over at least three independent replicas. The solid purple curve corresponds to a cubic spline fit weighted by the standard deviation of the data, while the dashed purple curve shows an unweighted cubic spline fit included for comparison.

Additionally, to further examine the connection between thermal transport and thermodynamic anomalies, and to assess the applicability of the Bridgman relation [47], we employed the speed of sound data from the NPT simulations to estimate the corresponding thermal conductivities using Equation 1.1. The results are shown in Figure 3.9. By setting the empirical constant to $a = 4.2$, the Bridgman equation reproduces the NEMD conductivities at 1 bar reasonably well above 230 K, and likewise predicts a local minimum in the conductivity near this temperature. However, at temperatures below the minimum, the estimated conductivities increase sharply, driven by the rise in the speed of sound (see the middle row of Figure 3.7). This rapid increase results in a strong divergence in the deeply supercooled regime, where the Bridgman-predicted conductivities become unrealistically large. These results suggest that while the Bridgman relation offers valuable physical insight by linking heat transport to thermodynamic response functions, its quantitative accuracy is limited for polyatomic and hydrogen-bonded liquids such as water, particularly in the deeply supercooled regime, since it was originally formulated for a monatomic rigid-sphere model.

3.3.3 Anomalous Thermal Polarization of Supercooled Water

Figure 3.10 shows the thermal polarization coefficient, S_{TP} , obtained from NEMD simulations at 1, 700, and 1200 bar. Along with the total S_{TP} , the corresponding dipolar and quadrupolar contributions are also displayed. These components were evaluated using the dummy site in the TIP4P/2005 model as the reference point. As discussed in Section 2.3.3, the dipolar and quadrupolar terms may vary depending on the choice of reference, but their sum remains consistent with the total thermal polarization, which is independent of the reference because it accounts for all charged sites in the system. In the TIP4P/2005 model, the charged sites consist of the two hydrogen atoms ($q_H = +0.5564e$) and the massless dummy site ($q_M = -1.1128e$).

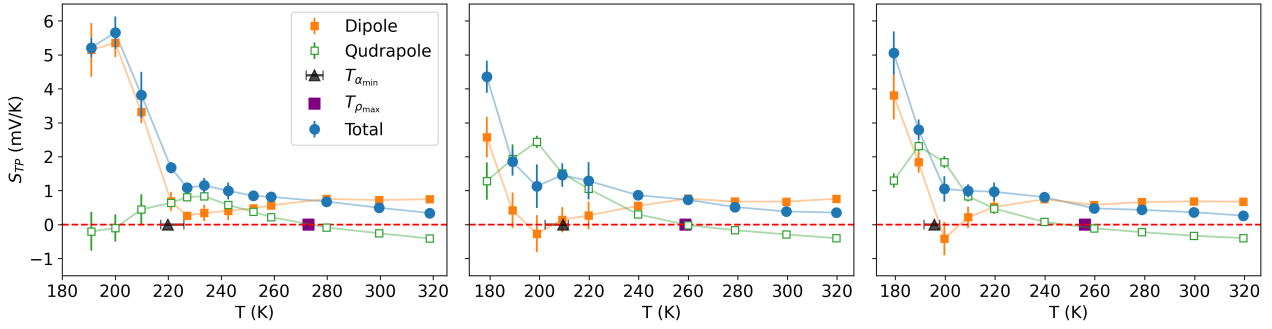


Figure 3.10: Thermal polarization coefficient and its dipolar and quadrupolar contributions for TIP4P/2005 water. The panels from left to right correspond to the 1, 700, and 1200 bar pressures. Solid lines connecting the data points are shown as visual guides, while error bars correspond to statistical uncertainties estimated from at least three independent NEMD simulation replicas. The horizontal red dashed line indicates where the thermal polarization coefficient equals zero. The markers denote the temperatures of the density maximum (squares) and the thermal expansion minimum (triangles) for each isobar.

The dipolar contribution remains approximately constant at temperatures above 240 K, whereas the quadrupolar term exhibits a clear temperature dependence across all three isobars investigated. These behaviors are consistent with previous simulations of water at ambient temperature [25, 27]. The balance between the weakly temperature-dependent dipolar term and the varying quadrupolar contribution explains the inversion of the total thermal polarization previously reported for TIP4P/2005 water at higher temperatures, around 420 K and 1000 bar [26].

A recent theoretical formulation has established a direct connection between the quadrupolar contribution to the thermal polarization and the isobaric thermal expansion coefficient, α .

Specifically, the thermal polarization coefficient can be expressed as [26]:

$$S_{TP} = -\frac{1}{\varepsilon_0} \left(\frac{P_z}{\nabla T} + \frac{1}{3} \rho \text{Tr}[\mathbf{Q}_{\text{mol}}] \alpha \right), \quad (3.2)$$

where P_z denotes the dipolar contribution to the electrostatic field, ρ the molecular density, and $\text{Tr}[\mathbf{Q}_{\text{mol}}]$ the trace of the molecular quadrupole moment.

To examine the correlation suggested by Equation 3.2, Figure 3.11 compares the temperature dependence of α with that of the quadrupolar component of the thermal polarization at 1 bar. The quadrupolar contribution is negative when $\alpha > 0$ and becomes positive when $\alpha < 0$, vanishing near the temperature of maximum density where $\alpha = 0$. At lower temperatures, where α reaches its minimum, the quadrupolar term exhibits a corresponding maximum. Moreover, in the deeply supercooled regime, as the thermal expansion coefficient returns from negative to positive values, the quadrupolar term changes sign accordingly, consistent with the inversion near 200 K observed in Figure 3.11, indicating a strong coupling between molecular quadrupole alignment and the anomalous thermal expansivity of supercooled water.

This coupling can be rationalized by noting that the quadrupolar contribution to the thermal polarization is governed primarily by molecular density gradients, which under local equilibrium conditions are directly proportional to the isobaric thermal expansion coefficient. As established in the theoretical formulation of Chapman and Bresme [26], the traced quadrupole contribution is effectively isotropic and therefore depends weakly on molecular orientation or dipole alignment, in contrast to the dipolar term. Consequently, anomalies in the thermal expansion coefficient are directly reflected in the quadrupolar component of the thermal polarization. In the deeply supercooled regime, where the hydrogen-bond network is increasingly stabilized and water adopts a more tetrahedrally ordered local structure, enhanced orientational correlations may also arise. Such structural reorganization could contribute to the temperature dependence of the dipolar term, while leaving the quadrupolar contribution largely controlled by density variations.

This correspondence is also observed at higher pressures (see markers in Figure 3.10), although this secondary sign reversal is not detected at 700 and 1200 bar, likely because the accessible temperature range does not extend sufficiently into the deeply supercooled region. This

intricate behavior is mirrored in the total thermal polarization, which varies non-monotonically with temperature and displays local extrema or inflection points coinciding with the minima of α . These correlations reinforce the view that the anomalous polarization response of water originates from the same thermodynamic anomalies that characterize the LLCP region.

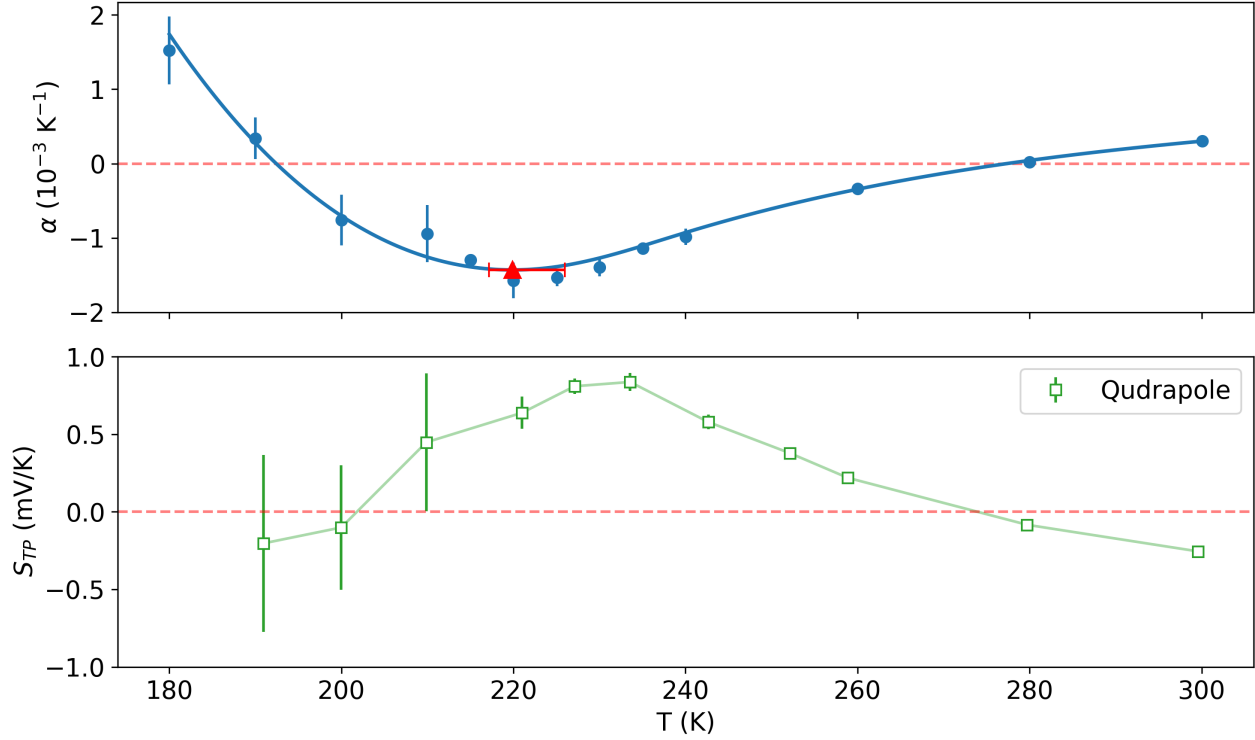


Figure 3.11: Top panel reproduced from Figure 3.7 showing the isobaric thermal expansion coefficient, and bottom panel reproduced from Figure 3.10 showing the quadrupolar contribution to the thermal polarization coefficient of TIP4P/2005 water at 1 bar. The red dashed lines indicate the zero reference for both properties. Error bars indicate statistical uncertainties based on at least three independent replicas.

The thermal polarization of supercooled water is notably strong. At ambient pressure, the thermal polarization coefficient reaches values of S_{TP} up to approximately 5 mV/K at around 200 K. These large responses arise from the combined enhancement of both the quadrupolar and, in particular, the dipolar contributions in the supercooled regime (see Figure 3.10). The magnitude of S_{TP} is comparable to that reported previously for TIP4P/2005 water under conditions close to the liquid-vapor critical point [27], indicating that the application of thermal gradients can induce a substantial polarization in supercooled water and further supporting the existence of a second critical point.

3.4 Conclusions

Using non-equilibrium molecular dynamics simulations, we have demonstrated that the thermal conductivity of supercooled water modeled with the TIP4P/2005 and TIP4P/Ice potentials exhibits local minima. The observed minima in thermal conductivity coincide with the temperature of maximum isothermal compressibility, as well as with the minima in the isobaric thermal expansion coefficient and the speed of sound. These correlations support the thermodynamic origin of the conductivity minimum and its connection to the liquid–liquid critical point (LLCP) of supercooled water. Moreover, we have shown that applying a thermal gradient polarizes supercooled water, inducing an electrostatic field within the liquid. Within the framework of non-equilibrium thermodynamics, this coupling between heat and polarization fields directly influences thermal transport, highlighting the importance of accounting for such effects when evaluating transport properties. The explicit use of thermal gradients in non-equilibrium simulations thus provides a natural and comprehensive route to incorporate these coupled non-equilibrium processes.

The extrema in the isobaric thermal expansion coefficient give rise to a non-monotonic temperature dependence of the thermal polarization response. The polarization exhibits a pronounced enhancement around temperatures corresponding to the thermal conductivity minimum, reflecting the microscopic coupling between dipolar and quadrupolar electrostatic contributions in the deeply supercooled regime. Further insight into the origin of this enhancement could be gained by investigating structural metrics such as the tetrahedral order parameter, which quantifies the local hydrogen-bond network organization in supercooled water. In this region, the magnitude of the thermal polarization is comparable to that reported in previous simulations of supercritical water [27]. Based on our results, we estimate that thermal gradients achievable at the nanoscale (10^6 – 10^8 K/m) could generate polarization fields on the order of 10^3 – 10^6 V/m in supercooled water. Overall, our findings indicate that thermally induced coupling effects play a central role in determining the thermal transport properties of water, and that further studies of these phenomena will advance our understanding of heat transport mechanisms in the supercooled regime.

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Chapter 4

Anomalous Thermal Transport and Coupling Effects in Supercooled Electrolyte Solutions

This chapter is reproduced from the article *Thermal Transport Anomalies of Electrolyte Solutions in the Water Supercooled Regime: Signatures of the Liquid-Liquid Water Phase Transition* by G. Zhao and F. Bresme, *J. Chem. Phys.* **2025**, 163 (22), 224505 [1], which is published under the Creative Commons CC BY 4.0 license.

Water displays a remarkable range of anomalies when supercooled, which are often attributed to a proposed liquid–liquid phase transition (LLPT) separating low-density (LDL) and high-density (HDL) liquid states. In this chapter, non-equilibrium molecular dynamics simulations are used to investigate thermal transport and coupling effects in aqueous NaCl and LiCl solutions with concentrations between 1 and 4 m over the temperature range 200–300 K. At 1 m, the thermal conductivity shows a distinct minimum near 220 K, which coincides with a maximum in the isothermal compressibility and a minimum in the speed of sound, both characteristic of critical fluctuations. As the solute concentration increases, these anomalies gradually weaken and eventually disappear at 4 m, indicating that the LLPT is suppressed under high salinity conditions.

The Soret coefficient exhibits a pronounced temperature dependence. It is thermophobic

at high temperatures (>280 K), where the solute migrates toward the colder region, becomes thermophilic upon cooling as the solute preferentially moves toward the warmer region, and returns to thermophobic behavior below 220 K. This sequence of transitions reflects significant structural changes within the hydrogen bonding network of water. The deep minima in the Soret coefficient, corresponding to the strongest thermophilic response observed for both NaCl and LiCl, occur in thermodynamic states characterized by a low fraction of HDL-like structures and a predominance of tetrahedrally ordered, LDL-like environments. Moreover, the Seebeck coefficient shows sign reversals in the range 220–230 K, demonstrating its pronounced sensitivity to structural and thermodynamic transformations. Overall, the results presented in this chapter highlight that thermal transport and its coupled effects serve as effective probes of the anomalies of supercooled water, and that electrolyte solutions retain these anomalies deep within the supercooled regime.

4.1 Introduction

The previous chapters have discussed in detail the anomalous thermodynamic and thermal transport properties of water in the supercooled regime and their connection to the proposed liquid–liquid phase transition (LLPT) between low- and high-density liquid states. Having established a fundamental understanding of these anomalies in pure water, we now broaden our investigation to include its electrolyte solutions, which are more representative of natural and technological environments. In such contexts, water rarely exists as a pure liquid but instead acts as a universal solvent. The presence of dissolved salts can facilitate deeper supercooling than in pure water, as ionic solutes depress the homogeneous nucleation temperature and delay crystallization [2]. Molecular dynamics simulations of aqueous NaCl and LiCl solutions have also shown that ion addition shifts the location of the liquid–liquid critical point (LLCP) toward higher temperatures and lower pressures [3–5], whereas at high concentrations, such as 2 m LiCl, the LLCP may vanish altogether [5].

In addition to the thermal polarization effect discussed for pure water in Section 3.3.3, electrolyte solutions exhibit further non-equilibrium coupling phenomena under temperature

gradients [6]. Thermal gradients induce mass and charge separation processes, giving rise to thermodiffusion (the Ludwig–Soret effect) [7, 8] and thermoelectricity (the Seebeck effect) [9]. In the Soret effect, a temperature gradient generates a concentration gradient as solute species migrate toward either the hot or cold region, depending on their thermophilic or thermophobic character, respectively. Simultaneously, the Seebeck effect arises when the same temperature gradient causes charge separation, leading to the development of an electrostatic potential difference. This phenomenon has been observed in metallic systems as well as in both aqueous and non-aqueous electrolyte solutions [10–13]. The Seebeck effect has attracted growing interest for its role in converting low-grade thermal energy into electrical energy, offering new possibilities for ionic thermoelectric and electrochemical devices.

The Soret effect represents a particularly fascinating example of coupled transport in fluids [14, 15]. Beyond its fundamental relevance, it has become an increasingly valuable experimental tool, especially for quantifying biomolecular interactions such as protein–ligand binding affinities [16–18]. The Soret effect has been interpreted in terms of underlying thermodynamic driving forces that govern species separation under thermal gradients. Theoretical models proposed that particles accumulate in regions where their Gibbs free energy is reduced, establishing a connection between the Soret coefficient and the temperature dependence of the solvation free energy under conditions of local thermodynamic equilibrium [19]. Within this framework, thermodiffusion is linked to the entropy of solvation. However, recent studies have shown that such free-energy-based models fail to quantitatively reproduce Soret coefficients in many mixtures, including Lennard-Jones fluids and aqueous solutions, and do not capture important dependencies such as mass effects [20]. These findings indicate that while solvation free energy provides qualitative insight, it is not a sufficient predictor of thermodiffusive behavior.

Accordingly, despite extensive research, a unified theoretical framework capable of predicting the direction of solute migration under a thermal gradient remains elusive. The temperature dependence of the Soret coefficient is often complex and non-monotonic, making its microscopic interpretation challenging. Both experimental measurements and molecular simulations of electrolyte solutions have revealed pronounced minima in the Soret coefficient, which correlate closely with the overall thermodiffusive response [21–23]. Additionally, thermophobicity in

aqueous solutions has been linked to modifications in the hydrogen bonding network of water [18, 24].

In this chapter, non-equilibrium molecular dynamics (NEMD) simulations are employed to investigate the thermal transport behavior of aqueous NaCl and LiCl solutions and the associated thermally induced coupling effects across the supercooled regime. The selection of sodium and lithium ions was motivated not only by their relevance in natural aqueous environments and modern energy storage technologies [25], but also by their distinct solvation behavior and systematically varying ion–water interactions across the alkali series. Li^+ forms a well-defined first hydration shell, reflecting its high charge density and strong electrostatic coupling to surrounding water molecules [26, 27]. In contrast, Na^+ exhibits larger ion–oxygen distances and broader hydration features, while larger alkali ions such as K^+ and Cs^+ exhibit progressively weaker and more diffuse hydration structures [26, 28]. Focusing on Li^+ and Na^+ therefore enables a systematic investigation of how increasingly strong ion–water coupling perturbs the thermal transport and thermally induced coupling behavior of supercooled water relative to the pure solvent, whose anomalous response is discussed in Chapter 3.

In all simulations, water molecules are represented using the TIP4P/2005 model [29], a rigid, non-polarizable potential that has been extensively validated for its ability to reproduce the thermodynamic properties of supercooled water and a range of ice polymorphs [30, 31]. The ions are described using the Madrid-2019 force field [32], which was specifically optimized for compatibility with TIP4P/2005 through the use of scaled ionic charges. This combination has been shown to capture the experimental trends in the thermal transport behavior of NaCl and LiCl under ambient conditions [24], and to accurately reproduce the structural and thermodynamic properties of supercooled aqueous electrolyte solutions [5, 33]. Furthermore, this chapter examines both thermophysical and structural properties, with particular attention to the isothermal compressibility and the tetrahedral order parameter, which serve as key indicators for exploring the hypothesized LLPT and the associated LDL–HDL structural bimodality.

4.2 Simulation Details

We conducted boundary-driven non-equilibrium molecular dynamics (NEMD) simulations using LAMMPS (version released on 29 August 2024) [34, 35] to investigate the thermal transport behavior and associated coupling effects in aqueous alkali halide solutions. The simulations employed thermostatted slabs placed at the center and boundaries of the simulation box to establish and maintain predefined hot (T_{hot}) and cold (T_{cold}) temperature regions, as shown in Figure 4.1. Each thermostatted zone was 8 Å thick, and the simulation cell dimensions followed the ratio $\{L_x : L_y : L_z\} = \{1 : 1 : 3\}$, with L_x typically about 40 Å, depending on the system density.

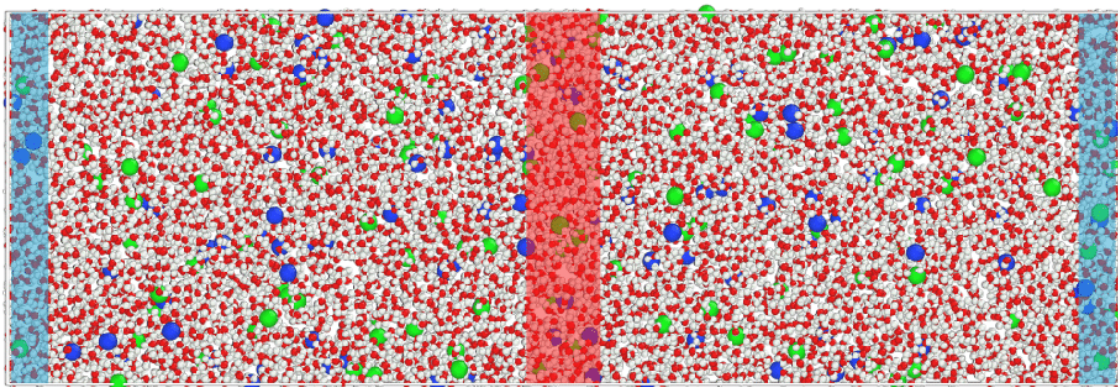


Figure 4.1: Representative snapshot of the simulation box for a 1 m NaCl aqueous solution under NEMD conditions, rendered with OVITO [36]. Oxygen and hydrogen atoms are shown as red and white spheres, whereas Na^+ and Cl^- ions are depicted in blue and green, respectively. The thermostatted zones are marked in red (hot region at the box center) and blue (cold regions at the box boundaries).

During the NEMD production runs, Langevin thermostats [37, 38] were used to control the temperature of molecules and ions within the regions highlighted in Figure 4.1. The thermostats were applied at each timestep of 1 fs with a coupling constant of 500 fs, thereby maintaining a constant temperature gradient across the system. Figure 4.2 displays the cumulative energy exchanged between the hot and cold thermostating regions over a representative 5 ns NEMD trajectory. The exchanged energy was obtained from the work performed by the Langevin forces, as defined in Equation 2.52. The nearly identical energy exchange profiles at both thermostats demonstrate the excellent energy conservation achieved in our NEMD simulations.

To avoid overall drift, the center-of-mass momentum of the system was removed at each timestep. Long-range electrostatic and dispersion interactions were computed using the particle–particle particle-mesh (PPPM) approach [39], employing the same precision settings as those outlined in Section 3.2.

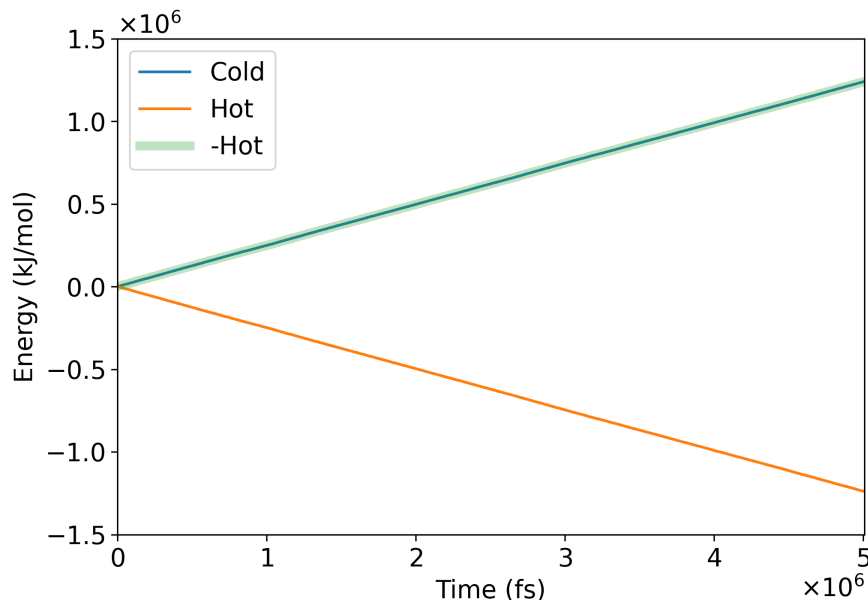


Figure 4.2: Cumulative energy exchanged between the thermostating regions during a representative NEMD simulation of a 1 m NaCl solution at an average temperature of 280 K and density of 1.042 g/cm³. The hot and cold thermostats were maintained at 330 K and 230 K, respectively. Blue and orange lines represent the energy exchanged with the cold and hot regions, while the green line corresponds to the negative of the energy exchanged at the hot thermostat, facilitating the visual assessment of energy conservation.

Each simulation cell was composed of 6663 water molecules, together with 120, 240, or 480 ion pairs, corresponding to concentrations of 1, 2, and 4 m, respectively. Before initiating the NEMD simulations, the systems were equilibrated for 5 ns in the isothermal–isobaric (NPT) ensemble at 1 bar and at a temperature equal to the mean of T_{hot} and T_{cold} . The NPT equilibration employed a Nosé-Hoover thermostat and barostat with relaxation times of 100 fs and 1000 fs, respectively [40, 41]. Following equilibration, the thermostats were activated, and the NEMD simulations proceeded under constant volume conditions.

Extended simulations were performed for the supercooled systems to ensure adequate equilibration and statistical convergence. Figure 4.3 illustrates the evolution of pressure and thermal conductivity at the lowest investigated temperature of 200 K, for which the total

simulation time was extended to 300 ns to explicitly verify convergence of the thermodynamic and transport properties. Consistent with the results discussed for supercooled pure water in Section 3.3.1, the alkali halide aqueous solutions exhibit markedly slow dynamics at low temperatures, requiring extended simulation times to attain equilibrium. Consequently, each simulation was run for at least 200 ns, with the first 150 ns discarded to ensure that only steady-state data were included in the analysis.

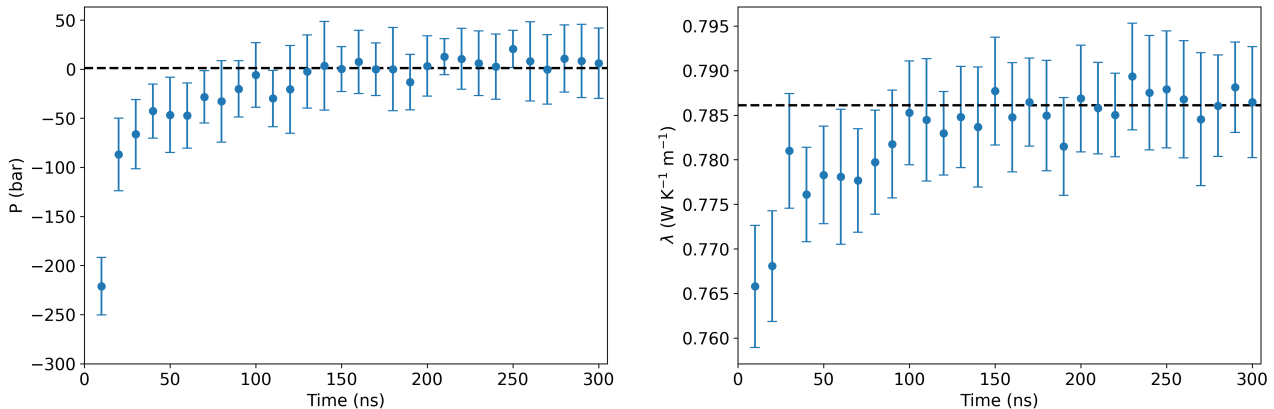


Figure 4.3: Time evolution of pressure (left) and thermal conductivity λ (right) during a 0–300 ns NEMD simulation of 1 m NaCl aqueous solution. All data are averaged over 10 independent NEMD simulation replicas, with error bars representing the standard deviations. The hot and cold thermostats were maintained at 250 K and 150 K, respectively, corresponding to an average temperature of 200 K and a density of 1.009 g/cm³. The dashed black lines indicate the target pressure of 1 bar (left) and the mean thermal conductivity obtained from the steady-state regime (right).

After equilibration, the local temperature and concentration profiles were computed by averaging over 200 spatial bins along the z -axis, corresponding to a bin width of approximately 0.6 Å. These profiles were further averaged over a production run of at least 50 ns from 10 independent replicas, each initialized with a different random seed for the thermostats, yielding a total sampling time of 0.5 μ s. Trajectories from at least the final 10 ns of each production run were saved every 1000 timesteps, yielding 10^5 configurations used to calculate tetrahedral order parameters and electrostatic potential profiles. The equations used to determine the thermal conductivity are provided in Section 2.3.1.

To evaluate thermoelectric properties, the local electrostatic potential, $\phi(z)$, was obtained by integrating the charge density and the corresponding electric field along the direction of the imposed temperature gradient, following Equations 2.72 and 2.74. Representative electrostatic

potential profiles for the 1 m NaCl solution in the supercooled regime (170–270 K) are shown in Figure 4.4. The Seebeck coefficient was then evaluated from the negative temperature derivative of $\phi(z)$, as defined in Equation 2.75.

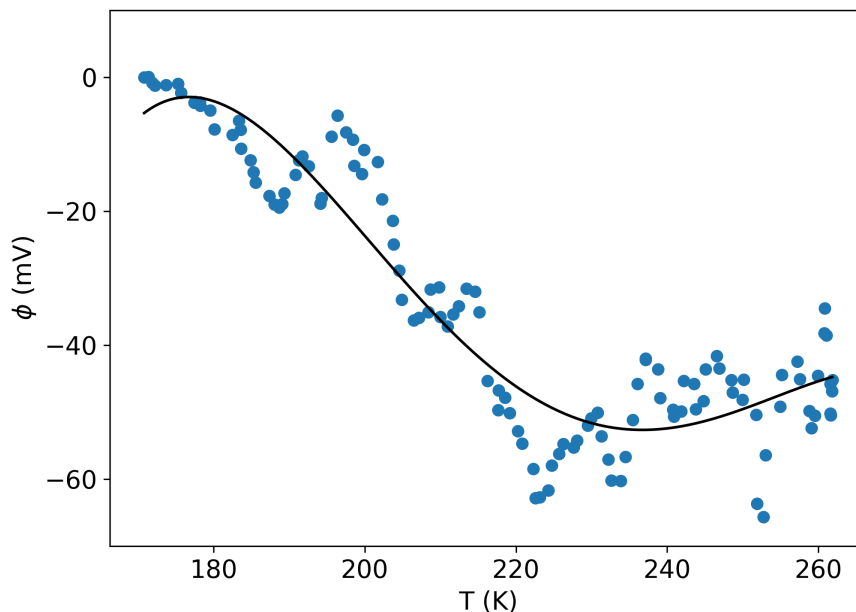


Figure 4.4: Electrostatic potential profiles obtained from representative NEMD simulations of the 1 m NaCl solution in the temperature range of 170–270 K. The blue dots represent the simulated data corresponding to an average temperature of 220 K and a density of 1.028 g/cm³. The solid black line shows a smoothed fit using a fourth-order polynomial, which was subsequently employed to compute the temperature derivatives.

To obtain a smooth and numerically stable derivative, the electrostatic potential profiles were fitted using a fourth-order polynomial. Because fluctuations in the electrostatic potential become more pronounced at low temperatures due to slower dynamics in the deeply supercooled regime, the analysis for simulations below 220 K was based on 25 ns trajectories to improve statistical convergence. Furthermore, the individual contributions of water and ions to the total Seebeck coefficient were separated and quantified for the 1 m NaCl solution at 300 and 200 K. These contributions were evaluated from trajectories of extended NEMD simulations lasting 100 and 200 ns, respectively, to ensure adequate sampling and reliable decomposition of the electrostatic response.

The Soret coefficient, s_T , was evaluated from the local temperature and molar fraction obtained in the NEMD production runs, following the definition provided in Equation 2.66.

For each simulated state, the salt mole fraction and temperature profiles were fitted linearly within a range of ± 5 K around the target temperature to determine s_T . The reported values and corresponding uncertainties represent the mean and standard deviations computed from ten independent simulation replicas. Figure 4.5 presents representative local molar concentration profiles as a function of temperature for a 1 m NaCl aqueous solution obtained from NEMD simulations. The Soret coefficient can be determined from the temperature derivative of these profiles, following Equation 2.70. The left and right panels correspond to simulations conducted at average temperatures of 220 and 280 K, respectively. Due to strong fluctuations, abrupt concentration variations, and large statistical uncertainties near the glass-transition regime below 200 K, data from these low-temperature simulations were excluded from the evaluation of the Soret coefficient.

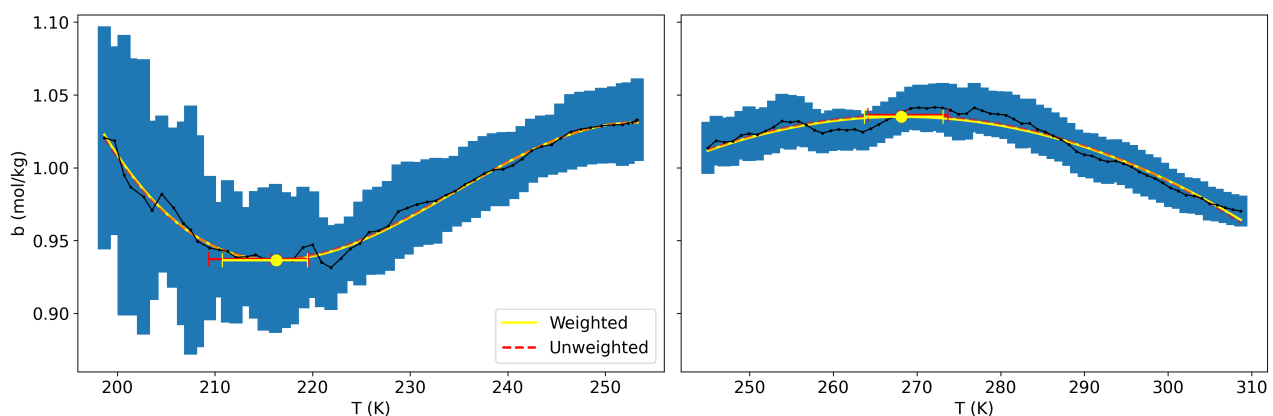


Figure 4.5: Local salt molality as a function of temperature from representative NEMD simulations of a 1 m NaCl aqueous solution, shown for two temperature ranges: 170–270 K (left) and 230–330 K (right). Black symbols represent simulation data averaged over all NEMD replicas, corresponding to mean temperatures and densities of 220 K and 1.028 g/cm³ for the left panel, and 280 K and 1.042 g/cm³ for the right panel. The shaded blue regions denote the statistical uncertainties in the concentration profiles, computed as the standard deviations from 10 independent NEMD simulation replicas. Weighted and unweighted cubic spline fits to the data are shown as solid yellow and dashed red curves, respectively. The corresponding spline-determined minima are indicated by a yellow circle (weighted) and a red cross (unweighted). Horizontal error bars denote 95% bootstrap confidence intervals for the weighted minimum, obtained by resampling the data 500 times, refitting the spline, and recalculating the minimum for each bootstrap realization.

Additionally, the tetrahedral order parameter ξ was computed from the NEMD trajectories to assess local structural variations in the supercooled electrolyte solutions, following the

definition [42]:

$$\xi = 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 \left(\cos \psi_{jk} + \frac{1}{3} \right)^2, \quad (4.1)$$

where ψ_{jk} denotes the angle between the vectors connecting a central water oxygen atom to its four nearest oxygen atoms.

According to Equation 4.1, $\xi = 1$ corresponds to a perfect tetrahedral arrangement ($\psi_{jk} = 109.47^\circ$), while a molecule with three tetrahedrally arranged neighbors and one disordered neighbor yields $\xi \approx 0.5$. In contrast, $\xi \approx 0$ corresponds to an ideal-gas-like random angular distribution. At ambient conditions, liquid water exhibits a bimodal distribution of ξ , with a low- ξ population associated with less structured local environments and a high- ξ population corresponding to more tetrahedrally ordered, ice-like configurations. Upon cooling, the distribution shifts toward larger ξ , indicating enhanced tetrahedral ordering and a stronger hydrogen-bond network [42].

Figure 4.6 shows the normalized probability density distributions, $P(\xi)$, obtained from NEMD trajectories according to Equation 4.1. To quantify the relative abundance of local structural motifs, each distribution was divided at the local minimum between peaks, separating the less tetrahedrally ordered, high-density liquid-like (HDL) configurations from the more tetrahedrally ordered, low-density liquid-like (LDL) ones. The position of this minimum was used as the integration limit to evaluate the fractional area associated with each structural population.

In LiCl solutions, an additional peak appears at low ξ values ($\xi \lesssim 0.2$), reflecting highly disordered local environments. For consistency, this contribution was included in the HDL region rather than treated as a distinct category. Accordingly, the HDL region encompasses all values up to the second minimum, while the LDL region corresponds to values beyond it. The fractions of HDL and LDL structures were determined by integrating their respective regions and normalizing by the total area of the distribution.

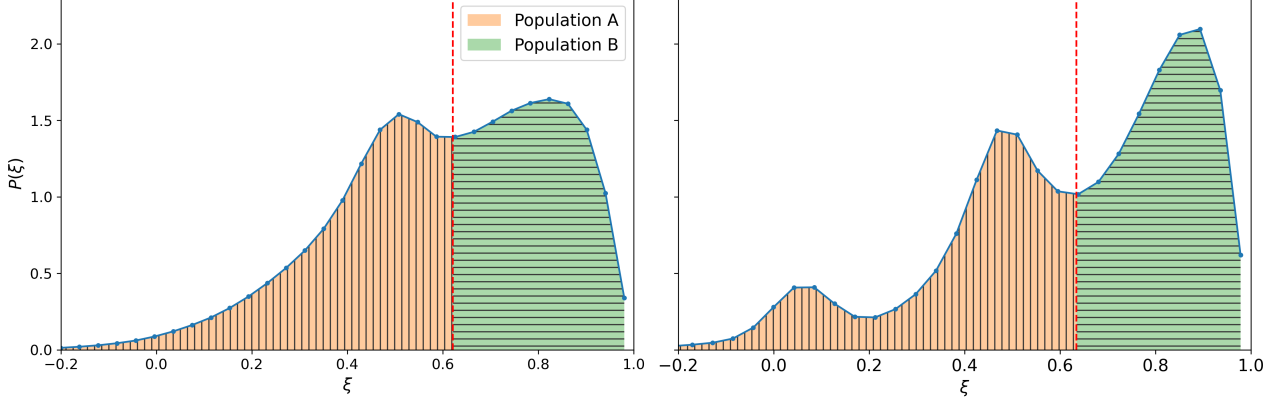


Figure 4.6: Representative probability density distributions, $P(\xi)$, for aqueous NaCl (left) and LiCl (right) solutions at 4 m concentration and an average temperature of 200 K. The distributions are averaged over 10 independent NEMD simulation replicas at this representative state point. The two structural subpopulations are identified as high-density liquid-like (Population A, orange with vertical hatching, less tetrahedrally ordered) and low-density liquid-like (Population B, green with horizontal hatching, more tetrahedrally ordered). Red dashed lines mark the minima between the two main peaks for both NaCl and LiCl solutions.

To examine the thermophysical behavior of the electrolyte solutions, equilibrium molecular dynamics simulations were performed in the isothermal-isobaric (NPT) ensemble using GRO-MACS (version from January 2024) [43]. Each simulation cell was cubic and contained 926 water molecules together with 17, 34, or 67 ion pairs, corresponding to concentrations of 1, 2, and 4 m, respectively. The production simulations were run for at least 200 ns with a timestep of 1 fs to ensure sufficient sampling. The fluctuation-derived thermodynamic quantities were evaluated following the procedures described in Section 2.4.

The radial distribution functions (RDF) between ions and water oxygen atoms were also computed from the equilibrium NPT simulation trajectories using the following relation [44]:

$$g(r) = \frac{1}{N\rho} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \delta(r - r_{ij}) \right\rangle, \quad (4.2)$$

where ρ is the number density of the system, N is the total number of particles, r denotes the position of the reference particle, and r_{ij} is the distance between particles i and j . The coordination number, corresponding to the number of water oxygen atoms in the first hydration shell of an ion, was obtained by integrating $g(r)$ up to its first minimum. This analysis provides quantitative insight into the local hydration structure of ions in the electrolyte solutions.

4.3 Results

4.3.1 Equation of State Validation

Figure 4.7 presents the equations of state for aqueous NaCl and LiCl solutions at concentrations of 1, 2, and 4 molal (m), evaluated along the 1 bar isobar. The local temperatures and densities were extracted from Non-Equilibrium Molecular Dynamics (NEMD) simulations. Temperature–density data were collected from all spatial bins across ten independent replicas, with each bin providing one data point used to construct the equation of state. The resulting data exhibit excellent agreement with both our equilibrium NPT simulations and previously reported molecular dynamics results [45]. This consistency confirms the reliability of the simulation setup and demonstrates that the systems attain local equilibrium under thermal gradients of approximately $1 \text{ K}/\text{\AA}$. In accordance with earlier findings, the presence of dissolved salts shifts the temperature of maximum density (TMD) to lower values. As discussed by Reference [45], the TIP4P/2005–Madrid-2019 force field combination closely reproduces the experimental TMDs of NaCl and LiCl solutions within the 0–2 m concentration range.

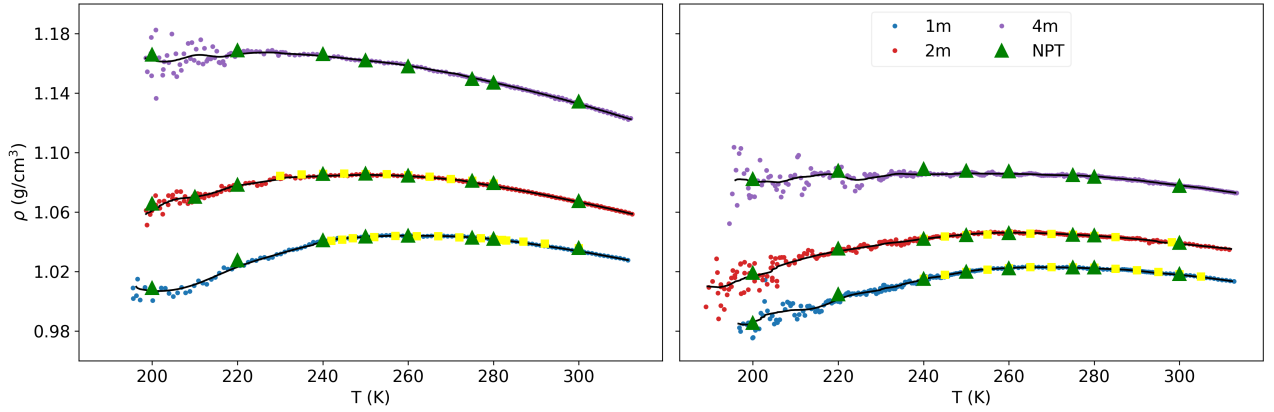


Figure 4.7: Equations of state obtained from equilibrium NPT simulations at 1 bar are shown as green triangles, with each data point representing an average over three independent replicas. Results from NEMD simulations are plotted in blue, red, and purple for concentrations of 1, 2, and 4 m, respectively. The black curves represent running averages over ten consecutive data points, while the yellow squares indicate reference data from Reference [45]. The left and right panels correspond to NaCl and LiCl solutions, respectively. The numerical results from the NEMD and NPT simulations are presented in Tables B.1 and B.2, respectively, in the Appendix.

4.3.2 Thermal Conductivity Minimum in Supercooled Electrolyte Solutions

Figure 4.8 presents the thermal conductivity of aqueous NaCl and LiCl solutions as a function of temperature between 200 and 300 K, for concentrations ranging from 1 to 4 m. The thermal conductivity generally decreases upon cooling. At the lowest concentration (1 m), however, a clear minimum appears near 220 K. Over the examined temperature range, the data also reveal that the thermal conductivity decreases as the liquid density increases, indicating an anomalous thermal response in these solutions. As discussed later, this reduction correlates with a decrease in the speed of sound throughout most of the supercooled regime investigated.

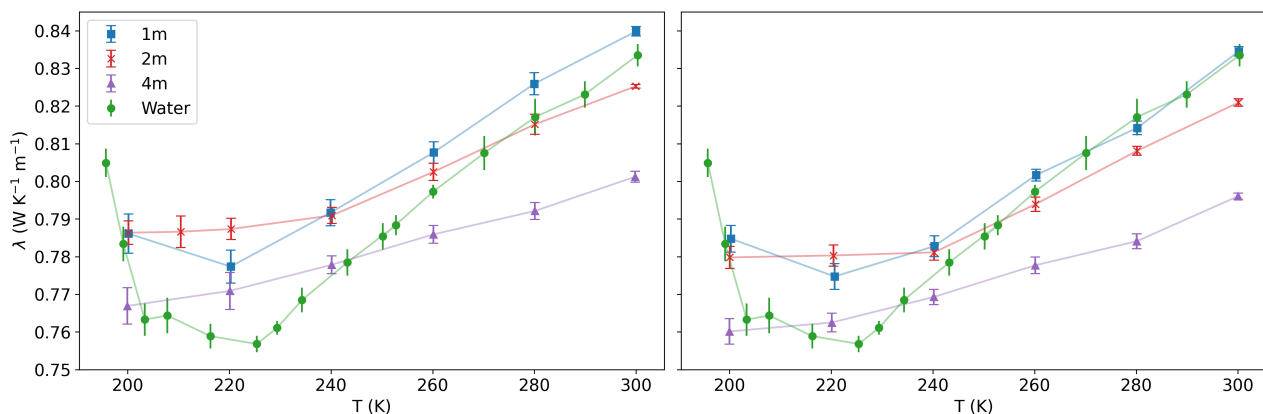


Figure 4.8: Thermal conductivity of NaCl (left) and LiCl (right) aqueous solutions at different concentrations in the 200–300 K temperature range. Green dots represent the thermal conductivity values of pure water using the TIP4P/2005 model obtained from Section 3.3.2. Lines connecting the data points are shown as visual guides. All reported NEMD results correspond to averages over ten independent simulation replicas, with each replica evaluated over successive 10 ns segments of the production trajectory. The error bars reflect the aggregated statistical uncertainty.

The thermal conductivities of NaCl and LiCl solutions are almost identical across the studied temperature and concentration ranges. This similarity agrees with previous simulation studies, which reported that the thermal conductivity of alkali halide solutions is primarily governed by the anion’s mass and composition rather than by the cation species [24]. At 300 K, both 1 m NaCl and LiCl solutions exhibit conductivities comparable to that of pure water, whereas at higher concentrations a marked reduction is observed.

For both NaCl and LiCl solutions at 1 m, a local minimum in thermal conductivity emerges

around 220 K, consistent with the behavior observed for pure TIP4P/2005 water in Section 3.3.2. At higher concentrations (2 m and 4 m), this minimum disappears, indicating that the addition of salt suppresses the thermal conductivity anomaly characteristic of the supercooled regime.

The presence of a thermal conductivity minimum suggests a thermodynamic origin. To investigate this connection, we examined the isothermal compressibility, which is directly related to the speed of sound (see Equation 2.85). The compressibility was determined from equilibrium NPT simulations and then used to evaluate the isentropic (adiabatic) speed of sound. As shown in the top panels of Figure 4.9, the calculated isothermal compressibilities are in good agreement with experimental measurements and previous simulation results under both ambient and supercooled conditions [24, 33, 46].

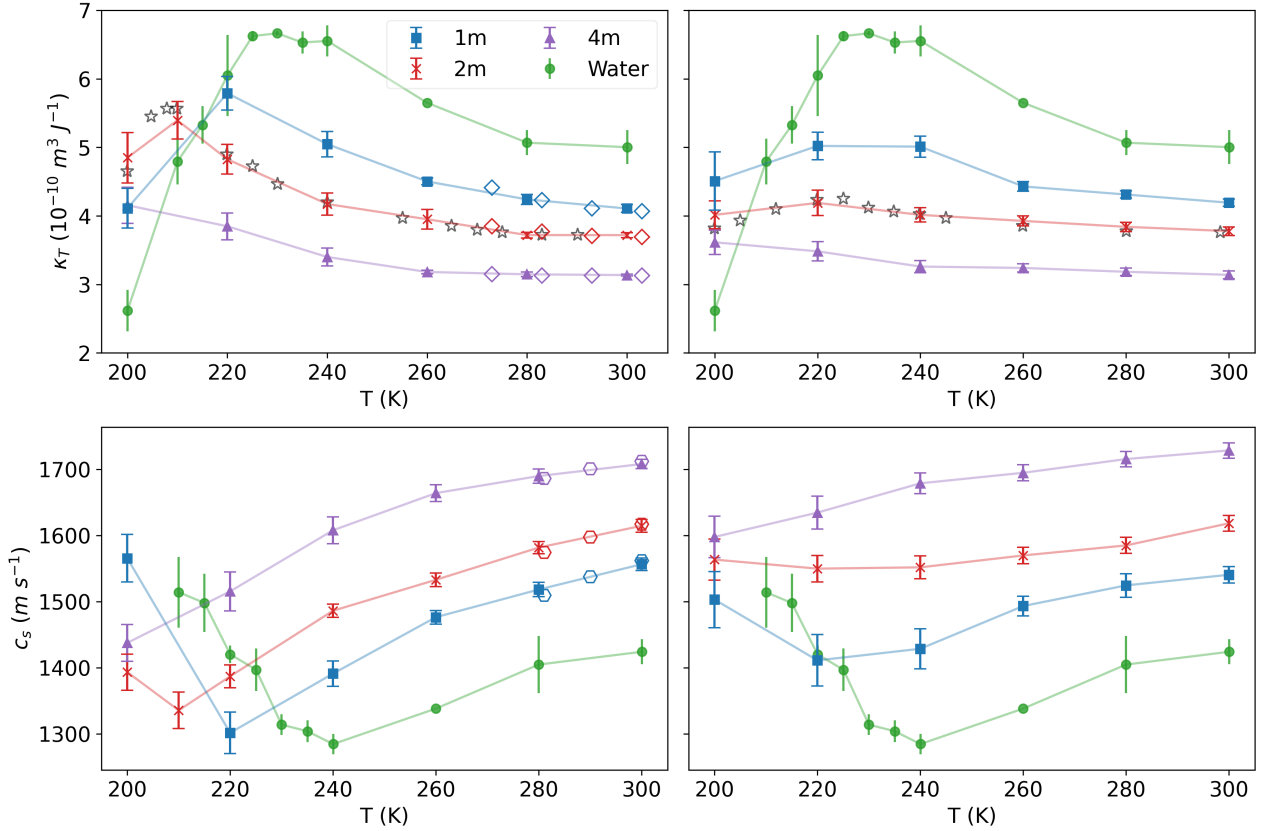


Figure 4.9: Isothermal compressibility (top) and speed of sound (bottom) for 1, 2, and 4 m NaCl (left) and LiCl (right) solutions as functions of temperature. The data points represent averages over three independent equilibrium NPT simulation replicas. Green dots correspond to pure water data obtained from Section 3.3.2. In the top left panel, open diamonds represent experimental measurements of NaCl from Reference [46], while open stars in both top panels indicate simulated compressibilities for 2 m NaCl and LiCl reported in Reference [33]. In the bottom left panel, open hexagons show the speed of sound for NaCl derived from the correlation equations presented in Reference [47] based on experimental data.

The isothermal compressibility of 1 m and 2 m NaCl and LiCl solutions exhibits pronounced maxima, similar to the behavior reported for pure water in previous studies [48]. With increasing salt concentration, these maxima shift to lower temperatures and diminish in magnitude. This trend is consistent with prior findings [5, 33] and strongly influences the temperature dependence of the speed of sound (see bottom panels of Figure 4.9). The computed sound velocities for NaCl agree well with experimental data [47]. They decrease with temperature in the moderately supercooled regime ($T > 240$ K) and display minima for the 1 m NaCl and LiCl solutions at temperatures corresponding to the compressibility maxima. These minima coincide with the temperatures where the thermal conductivity also reaches its minimum (see Figure 4.8). The link between the speed of sound and thermal conductivity was previously identified by Bridgman in his empirical relation (Equation 1.1) [49].

At higher concentrations, particularly at 4 m, the speed of sound no longer exhibits a distinct minimum. The absence of clear minima within the examined temperature range likely results from a shift of these extrema to lower temperatures beyond the scope of the present study, combined with a further weakening of the anomalies in more concentrated solutions. Overall, these observations indicate that thermal transport in supercooled alkali halide solutions remains influenced by underlying thermodynamic anomalies. This interpretation connects the minimum in thermal conductivity to the presence of a liquid–liquid critical point (LLCP), which is apparent in the 1 m solution. At higher concentrations, however, these anomalies become progressively weaker or vanish entirely, consistent with previous findings showing that the LLCP is suppressed or absent in highly concentrated LiCl solutions [5].

The analysis of the speed of sound reveals a clear correlation with the disappearance of thermal conductivity minima in highly concentrated solutions. This relationship suggests that both the overall decrease in thermal conductivity across all salts and concentrations, and the distinct minima observed for the 1 m solutions, are governed by the temperature dependence of the sound velocity. Ultimately, this behavior originates from the temperature dependence of the isothermal compressibility in the supercooled regime.

4.3.3 Thermodiffusion and Structural Correlations in Supercooled Electrolyte Solutions

Having identified the thermodynamic signatures associated with structural transitions, we next examine thermodiffusion to clarify the coupling between thermal gradients and molecular mobility. Figure 4.10 presents the Soret coefficients of aqueous NaCl and LiCl solutions as functions of temperature for different concentrations. At 300 K, our results agree well with previous simulation studies, accurately reproducing both the magnitude and temperature dependence of the Soret effect [24]. A clear inversion of the Soret coefficient is observed, transitioning from thermophobic behavior at high temperatures to thermophilic behavior at low temperatures. This sign reversal occurs near 300 K for LiCl and around 260 K for NaCl, and is largely independent of concentration. Similar trends have also been reported in experimental measurements and simulations employing different force fields [28, 50–53].

We note that for the 1 m NaCl solution, within statistical uncertainty, the inversions of the Soret coefficient near 215 and 270 K are consistent with the positions of the local extrema identified in the corresponding molar concentration profiles (see Figure 4.5). Because the concentration profiles exhibit relatively large statistical fluctuations, particularly below 220 K in the deeply supercooled regime, we assessed the robustness of the extracted extrema using both a weighted spline fit, which accounts for uncertainties across simulation replicas, and an unweighted fit for comparison. Although the unweighted analysis yields broader confidence intervals for the extrema and inversion temperatures, both approaches consistently locate the inversion within the same temperature window, further supporting the statistical significance of the observed sign change.

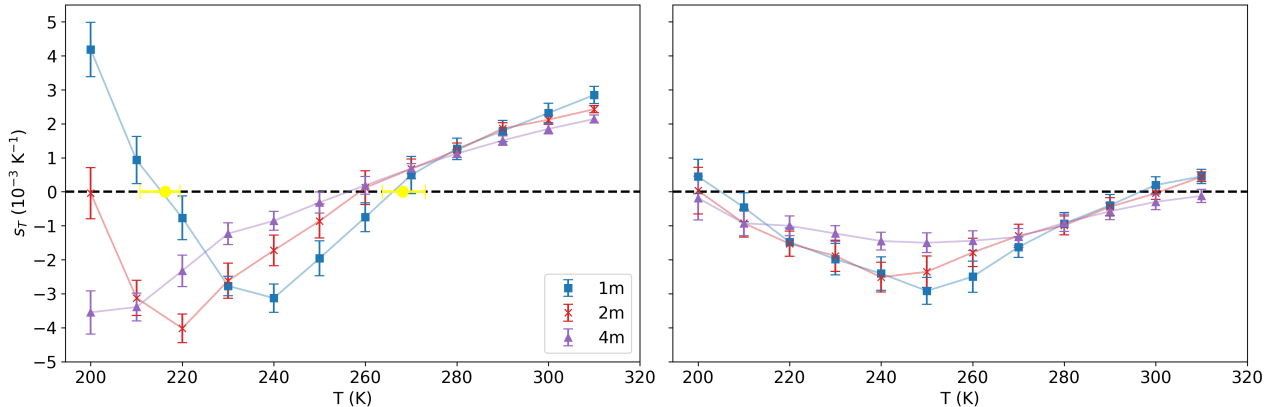


Figure 4.10: Soret coefficients of NaCl (left) and LiCl (right) aqueous solutions at concentrations of 1, 2, and 4 m in the 200–300 K temperature range. The horizontal dashed black line indicates the zero value of the Soret coefficient. The data points represent averages over 10 independent NEMD simulation replicas. Yellow circles in the left panel denote the local extrema in the molar concentration profiles for the 1 m NaCl solution, as shown in Figure 4.5.

A notable feature of our results is the intersection of the Soret coefficient curves for different concentrations near 280 K. Above this temperature, the coefficient decreases with increasing concentration, whereas below it the trend reverses. Experimental studies have reported a similar crossover around 315 K [28], while simulations of LiCl solutions using the SPC/E water model found crossings between 260 and 280 K [22, 52], in close agreement with our results. This contrasting temperature dependence across concentrations has been attributed to two competing effects: at high temperatures, entropy dominates, whereas at low temperatures, enhanced hydrogen bonding strengthens ion–water interactions, promoting salt accumulation in the hot region. Our findings reproduce these behaviors and further show that this interplay persists in the supercooled regime.

In the deeply supercooled region, both NaCl and LiCl solutions at 1 m and 2 m display a pronounced local minimum in the Soret coefficient between 220 and 250 K (see Figure 4.10). As the concentration increases from 1 to 2 m, this minimum shifts toward lower temperatures. At 4 m, no clear minimum is detected for NaCl within the examined temperature range, and for LiCl, the minimum becomes noticeably less distinct compared to the lower concentrations.

When comparing the two electrolytes, NaCl shows a stronger temperature dependence of the Soret coefficient than LiCl, developing a more pronounced and sharper minimum upon cooling. In addition, a second sign reversal emerges near 200 K for both NaCl and LiCl solutions

at 1 m and 2 m. This feature is especially prominent in the 1 m NaCl solution, where the Soret coefficient reaches values above $4 \times 10^{-3} \text{ K}^{-1}$ at 200 K, indicating a strong thermophobic response. Overall, the results suggest that increasing salt concentration makes the supercooled solutions less thermophilic in the 230–280 K range and less thermophobic at temperatures above 280 K, reflecting an overall suppression of the thermodiffusive response with increasing salt concentration.

The complex temperature dependence of the Soret coefficient suggests alterations in the hydrogen-bond network of water. To investigate the structural origin of this behavior, we examined the tetrahedral order parameter, whose probability distribution is shown in Figure 4.11. The emergence of a bimodal distribution agrees with previous studies on supercooled pure water, indicating the coexistence of distinct local environments [42, 54]. The two main peaks correspond to highly ordered, low-density liquid-like (LDL) structures ($\xi \approx 0.8\text{--}1$) and less tetrahedrally ordered, high-density liquid-like (HDL) configurations ($\xi \approx 0.4\text{--}0.6$). The relative degree of tetrahedral ordering is quantified by integrating the low- ξ and high- ξ regions of the distribution, with the resulting fractions summarized in Table 4.1. We observe that increasing salt concentration reduces the fractional area associated with highly tetrahedral environments, consistent with progressive disruption of the hydrogen-bond network, whereas cooling enhances the population of these ordered configurations.

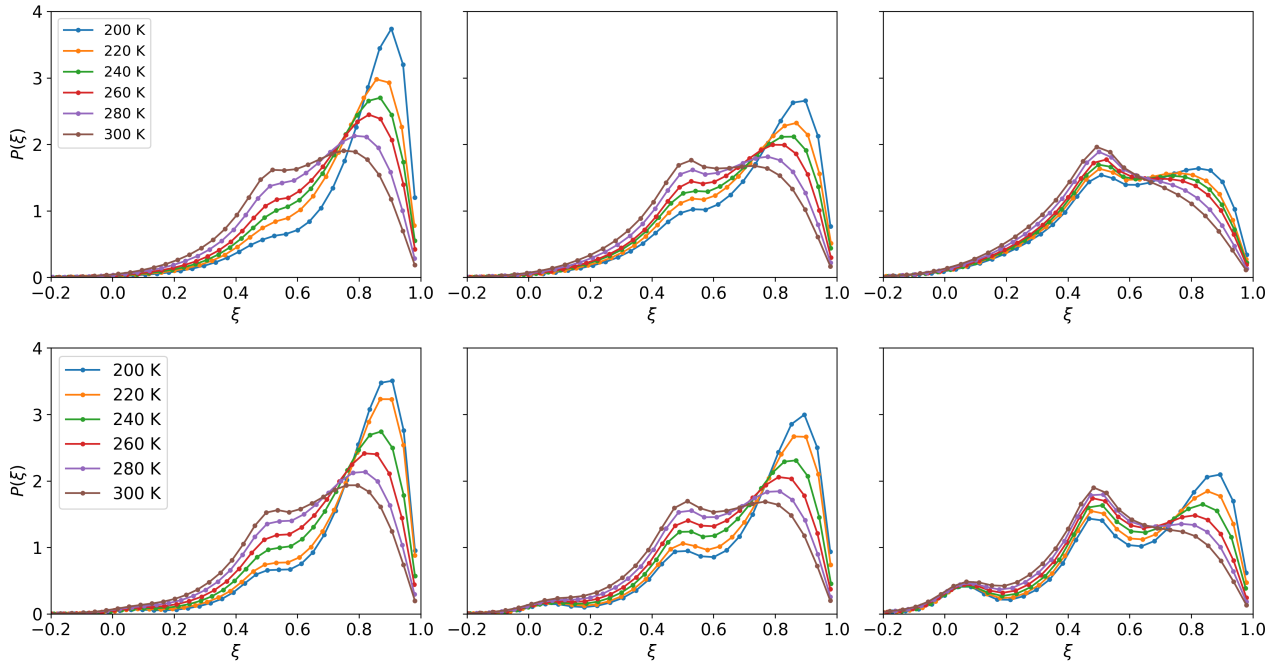


Figure 4.11: Probability density distributions of the tetrahedral order parameter (ξ) for aqueous NaCl (top row) and LiCl (bottom row) solutions at temperatures between 200 and 300 K. From left to right, the columns correspond to concentrations of 1, 2, and 4 m, respectively. Each probability density distribution is averaged over 10 independent NEMD simulation replicas.

Notably, all LiCl solutions display an additional peak at $\xi < 0.2$, revealing the presence of highly disordered local configurations. This multimodal feature is not observed in NaCl solutions, implying that LiCl induces greater structural heterogeneity, leading to a stronger distortion of the water tetrahedral network.

Because of its small ionic radius, lithium generates a strong electrostatic field and is surrounded by a stable hydration shell composed of four to five water molecules, resulting in a high heat of hydration [26, 27]. Both classical molecular dynamics and *ab initio* calculations predict a first solvation shell formed by four water molecules arranged in a tetrahedral configuration [32, 55]. Experimental studies further indicate that the hydration number remains largely independent of ion concentration [27]. These observations are consistent with our calculated lithium–oxygen (Li–O) coordination numbers (CN) (see Table B.2 in the Appendix). Our simulations show that the Li–O CN remains nearly constant throughout the supercooled temperature range, in agreement with recent findings [5]. In contrast, the coordination numbers for sodium–oxygen (Na–O) and chloride–oxygen (Cl–O) vary more noticeably with both temperature and concentration. Accordingly, the progressive increase in the height of the main

peak between 1 and 4 m (see Figure 4.11) likely reflects a growing population of $[\text{Li}(\text{H}_2\text{O})_4]^+$ complexes as the salt concentration increases.

Table 4.1: Average tetrahedral order parameter ($\bar{\xi}$), fraction of the high-density liquid-like (HDL) structure, and Soret coefficient (s_T) for NaCl and LiCl aqueous solutions at 1, 2, and 4 m in the temperature range of 200–300 K. The quantities $\bar{\xi}$ and HDL fraction were obtained from the tetrahedral order parameter distributions, whereas s_T values were computed from NEMD simulations. Standard deviations from independent replicas are shown in parentheses. Bold entries indicate the local minima of s_T and the corresponding HDL fractions used for the correlation analysis.

	1 m			2 m			4 m		
T [K]	$\bar{\xi}$	HDL [%]	s_T [10^{-3} K^{-1}]	$\bar{\xi}$	HDL [%]	s_T [10^{-3} K^{-1}]	$\bar{\xi}$	HDL [%]	s_T [10^{-3} K^{-1}]
NaCl									
200	0.773	16.5	4.187(0.8)	0.708	24.2	-0.040(0.8)	0.608	48.5	-3.549(0.6)
220	0.738	21.1	-0.767(0.6)	0.683	27.1	-4.018(0.4)	0.592	48.8	-2.325(0.5)
240	0.707	24.7	-3.129(0.4)	0.661	31.6	-1.726(0.5)	0.578	54.9	-0.855(0.3)
260	0.683	28.9	-0.747(0.4)	0.637	33.3	0.122(0.5)	0.564	68.1	0.193(0.3)
280	0.654	35.3	1.266(0.3)	0.615	40.3	1.221(0.2)	0.549	72.1	1.122(0.1)
300	0.628	34.3	2.316(0.3)	0.594	51.4	2.120(0.1)	0.534	75.5	1.850(0.1)
LiCl									
200	0.766	16.8	0.449(0.5)	0.719	25.3	0.035(0.7)	0.625	45.7	-0.186(0.6)
220	0.750	19.6	-1.479(0.4)	0.700	27.2	-1.529(0.4)	0.606	49.8	-1.000(0.3)
240	0.717	24.8	-2.407(0.5)	0.672	30.4	-2.513(0.4)	0.586	54.7	-1.450(0.3)
260	0.688	29.9	-2.499(0.5)	0.646	37.1	-1.785(0.4)	0.565	59.2	-1.442(0.3)
280	0.658	35.6	-0.937(0.3)	0.620	40.1	-0.991(0.3)	0.545	67.6	-0.914(0.2)
300	0.632	36.2	0.199(0.2)	0.597	48.4	-0.042(0.2)	0.524	73.5	-0.297(0.2)

We analyzed the fraction of HDL-like structures obtained from the probability distributions in Figure 4.11 and examined its relationship with the Soret coefficient. The corresponding numerical values are reported in Table 4.1. Between 240 and 300 K, the Soret coefficient for both NaCl and LiCl solutions at all concentrations exhibits a decreasing trend with cooling, indicating that the systems become increasingly thermophilic, with ions migrating preferentially toward the hot region. This behavior is consistent with previous studies [18]. Around 240 K, where the 1 m and 2 m NaCl and LiCl solutions display local minima in the Soret coefficient, the calculated HDL structural fraction is approximately 25–30%. This indicates that thermophilic

behavior is associated with a more strongly connected hydrogen-bond network, characterized by enhanced orientational ordering and a larger proportion of LDL-like local environments. Indeed, more than 70% of the systems examined in this study exhibit HDL fractions below 30%. The most pronounced thermophilic responses (negative Soret coefficients) are observed in the low-HDL regime, where the hydrogen-bond network is strengthened relative to ambient conditions.

However, changes in the hydrogen-bond network alone do not fully account for the inversion and subsequent increase in the Soret coefficient observed upon further cooling. In the deeply supercooled regime, additional competing effects become relevant, possibly including enhanced density fluctuations that modify the local molar concentration and thermodynamic response of the ions. The resulting Soret behavior therefore reflects a balance between solvent structural ordering and these competing contributions, with the latter becoming increasingly important at lower temperatures. In this context, the more pronounced isothermal compressibility maximum observed in Figure 4.9 for the dilute 1 m NaCl solution is consistent with its stronger thermophobic behavior at low temperature compared with higher concentrations. In contrast, LiCl exhibits a less significant concentration dependence of thermophobicity in the deeply supercooled regime, which may be associated with the comparatively smaller variation in the $\text{Li}^+\text{--O}$ coordination number (see Table B.2). Figure 4.12 provides a graphical representation of the correlation between the Soret coefficient and the HDL fraction, complementing the data summarized in Table 4.1.

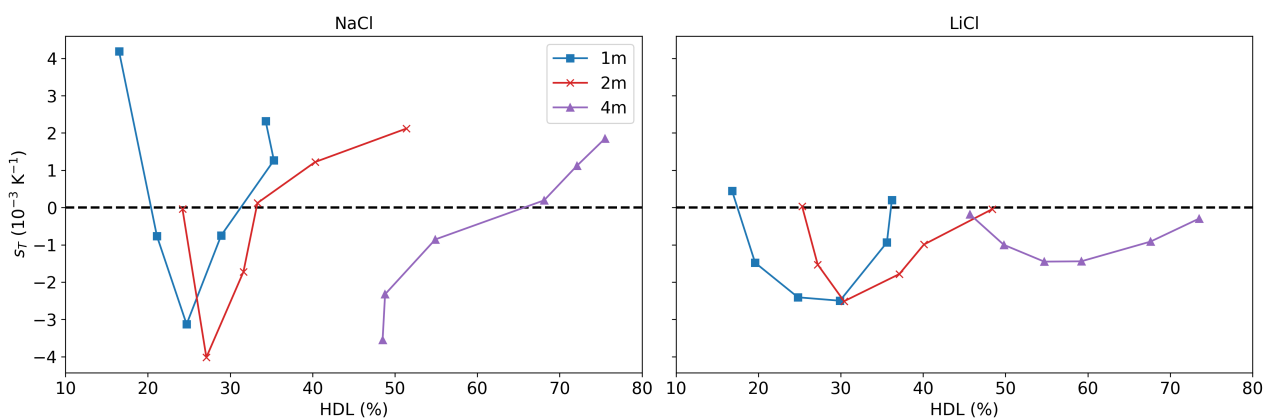


Figure 4.12: Correlation between the Soret coefficient, s_T , and the fraction of high-density liquid-like (HDL) structures in aqueous NaCl (left) and LiCl (right) solutions at concentrations of 1, 2, and 4 m.

Upon entering the deeply supercooled regime, the Soret coefficient increases sharply, reaching strongly positive values of approximately $+4 \times 10^{-3} \text{ K}^{-1}$ for the 1 m NaCl solution and around $+0.5 \times 10^{-3} \text{ K}^{-1}$ for the LiCl solution. These observations indicate the emergence of an additional competing mechanism affecting thermodiffusion under these conditions. It is also plausible that the tetrahedral order parameter considered here may lack the sensitivity to capture additional structural rearrangements taking place in supercooled aqueous solutions.

4.3.4 Anomalous Thermoelectric Response in Supercooled Electrolyte Solutions

The link between the microscopic structure of water and its thermodiffusive behavior also extends to other transport processes. In particular, the Seebeck coefficient serves as an additional probe for examining how structural rearrangements influence thermal transport in the supercooled regime (see Figure 4.13). Above 240 K, the Seebeck coefficients of NaCl and LiCl solutions are virtually identical across all investigated concentrations. For the 1 m NaCl solution at 300 K, our results closely match previous simulation data and remain within the reported uncertainties, even though different force fields were employed [13]. Upon further cooling into the deeply supercooled regime, the Seebeck coefficient changes sign near 220 K and subsequently exhibits a sharp increase in magnitude, consistent with the representative electrostatic potential profiles shown in Figure 4.4. At 200 K, this enhancement decreases with increasing salt concentration, reaching approximately 2 mV/K for 1 m and about 1 mV/K for 2 and 4 m solutions. These results demonstrate that ionic solutes strongly modulate the low-temperature thermoelectric response of supercooled water.

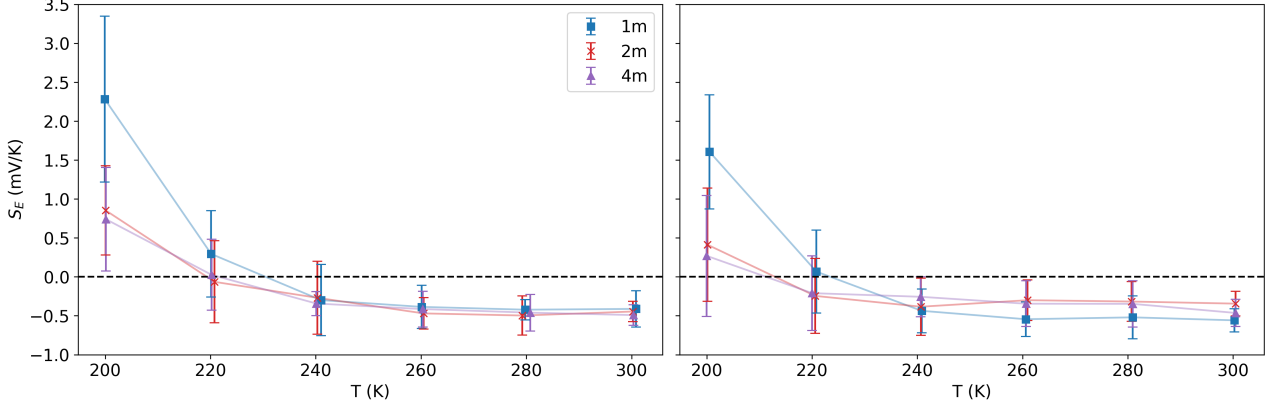


Figure 4.13: Seebeck coefficient of NaCl (left) and LiCl (right) aqueous solutions at concentrations of 1, 2, and 4 m over the temperature range 200–300 K. The horizontal dashed black line represents the zero reference for the Seebeck coefficient. The data points correspond to averages over 10 independent NEMD simulation replicas, and the error bars indicate the standard deviations.

We evaluated the separate contributions of water and ions to the total Seebeck coefficient for the 1 m NaCl solution at 300 and 200 K. The decomposed contributions are summarized in Table 4.2. At 300 K, both the ionic and water components contribute with opposite signs, resulting in a slightly negative total Seebeck coefficient. In contrast, at 200 K, the ionic term increases sharply and dominates over the water contribution, leading to a reversal of the overall sign. This inversion originates from the stronger temperature dependence of the ionic contribution in the supercooled regime, where both components exhibit a pronounced increase in magnitude, collectively enhancing the thermoelectric response of the solution.

Table 4.2: Individual contributions of water and ions to the total Seebeck coefficient, S_E , for the 1 m NaCl solution at 300 and 200 K. All data and statistical uncertainties are obtained from 10 independent NEMD simulation replicas.

T [K]	$S_{E,\text{total}}$ [mV K ⁻¹]	$S_{E,\text{ions}}$ [mV K ⁻¹]	$S_{E,\text{water}}$ [mV K ⁻¹]
300	-0.412 ± 0.233	1.223 ± 0.167	-1.635 ± 0.163
200	2.284 ± 1.065	69.150 ± 0.760	-66.866 ± 0.748

4.4 Conclusions

We have performed nonequilibrium molecular dynamics simulations to explore the thermal transport properties of NaCl and LiCl aqueous solutions in the supercooled regime, employing

the TIP4P/2005 and Madrid-2019 force fields. The results provide compelling support for the presence of a liquid–liquid phase transition (LLPT) in electrolyte solutions at moderate salt concentrations of approximately 1 m. At this concentration, the thermal conductivity exhibits a distinct minimum near 220 K, coinciding with a maximum in isothermal compressibility and a minimum in the speed of sound. These coupled anomalies weaken progressively with increasing salt concentration and vanish around 4 m, consistent with the suppression of the hypothesized LLPT by ionic solutes [5]. The close correspondence between transport anomalies and thermodynamic extrema suggests a common underlying structural mechanism governing both phenomena.

Thermodiffusion displays a complex temperature dependence characterized by multiple sign reversals in the Soret coefficient. The solutions evolve from thermophobic behavior at high temperatures (>280 K) to thermophilic behavior upon cooling, before reverting to thermophobic in the deeply supercooled region (<220 K). Local minima in the Soret coefficient emerge between 220 and 250 K, with NaCl showing sharper transitions than LiCl. These features correlate with structural transformations in the hydrogen-bond network, as revealed by the tetrahedral order parameter, which reflects a gradual conversion between high- and low-density liquid (HDL and LDL) structures with temperature. LiCl solutions additionally display a fraction of strongly disordered local configurations ($\xi < 0.2$), absent in NaCl, implying that lithium ions introduce greater structural heterogeneity within the hydrogen-bond network and thereby weaken the thermodiffusive anomalies.

The Seebeck coefficients, on the order of 1 mV/K, also undergo sign reversals near 220–230 K, confirming the sensitivity of thermoelectric properties to structural reorganization and the coupling between heat and charge transport. These results demonstrate that the Seebeck response in supercooled electrolyte solutions arises from competing contributions of ions and water, both of which increase in magnitude as temperature decreases. Future work should aim to elucidate the microscopic origins of this interplay through a detailed analysis of charge–structure correlations.

Overall, this study establishes thermal transport properties as powerful microscopic probes of structural transitions in supercooled electrolyte solutions, offering fresh insights into water’s

anomalous behavior. A clear link is observed between the HDL/LDL structural balance and the thermodiffusive response: systems dominated by HDL configurations (lower tetrahedral order) exhibit thermophobic behavior at higher temperatures, whereas the dominance of LDL structures with stronger tetrahedral order leads to thermophilic responses at lower temperatures.

Further simulations employing alternative force fields, as well as systematic studies of other alkali halide solutions, would provide valuable tests of these predictions and deepen our understanding of water’s phase behavior under extreme conditions. For example, independently varying ionic masses and partial charges would allow separation of mass transport and electrostatic contributions, while the water component of the total Seebeck coefficient could be further decomposed into its intrinsic polarization response and its induced response to ion migration. In addition, systematic analyses of density–concentration correlations and hydration shell stability in the deeply supercooled regime would explicitly test the proposed balance of competing mechanisms underlying thermodiffusion.

From an experimental perspective, probing deeply supercooled pure water remains challenging due to rapid homogeneous nucleation. In contrast, aqueous electrolyte solutions exhibit suppressed nucleation temperatures, allowing access to lower temperatures than those attainable for bulk water [2]. Systematic investigations of mildly supercooled solutions, for example around 240 K, would therefore provide a practical means to examine the predicted thermodiffusive behavior. Structural characterization of hydrogen-bond ordering in this regime, using scattering or spectroscopic techniques, could determine whether changes in the Soret coefficient remain correlated with variations in tetrahedral ordering, as observed in the simulations.

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Chapter 5

Thermal Transport and Thermodiffusion of Alkali Halide Solutions under Pressure

This chapter is reproduced from the article *Alkali Halide Aqueous Solutions Under Pressure: A Non-Equilibrium Molecular Dynamics Investigation of Thermal Transport and Thermodiffusion* by G. Zhao and F. Bresme, *Entropy* **2025**, 27, 193 [1], which is published under the Creative Commons CC BY 4.0 license.

Temperature gradients in aqueous salt solutions drive thermodiffusion, a non-equilibrium phenomenon arising from the coupling between heat and mass fluxes. Although thermal transport has been extensively investigated under ambient conditions, its behavior at elevated pressures and temperatures, representative of environments such as the Earth’s crust, remains far less explored. The combination of non-equilibrium thermodynamics and non-equilibrium molecular dynamics (NEMD) simulations offers an effective framework to characterize these transport processes under extreme conditions and to relate them to microscopic structural changes in the liquid. In this study, we analyze the thermal conductivity and thermodiffusion of 1 molal NaCl and LiCl aqueous solutions over the 300–1000 K temperature range and at pressures up to several gigapascals. The simulations were performed using the Madrid-2019 ion parameters together with the TIP4P/2005 water model. The results reveal a marked

enhancement in thermal conductivity with increasing pressure. Consistent with the behavior at ambient conditions, the conductivity of the electrolyte solutions remains below that of pure water, with reductions of approximately 3% at gigapascal pressures. Under these conditions, both solutions exhibit thermophobic behavior, characterized by ion migration toward the colder region of the simulation cell. The influence of pressure is particularly pronounced for LiCl, which undergoes a transition from thermophilic to thermophobic response at pressures exceeding about 0.2 GPa. This behavior is linked to the progressive disruption of the hydrogen-bond network in water, which leads to a structural arrangement resembling that of simple liquids at high pressure.

5.1 Introduction

In the previous chapter, we examined the thermal transport properties and associated coupling effects in alkali halide aqueous solutions within the supercooled regime. In this chapter, we extend our investigation to explore how these processes behave under high-pressure conditions.

Electrolyte solutions are subjected to pressures on the order of 0.1–1 GPa in geological and planetary environments, such as the Earth’s mantle [2, 3], deep oceanic trenches, and subsurface oceans beneath icy crusts on other celestial bodies [4]. Numerous studies have reported that compression profoundly alters both physicochemical [5] and biological [6] processes occurring under such conditions. Both experimental [7, 8] and simulation-based investigations [9, 10] have revealed that applying pressure in the gigapascal range leads to a significant reorganization of the hydrogen bonding network in liquid water, producing a more densely packed structure that resembles simple liquids. This structural transformation affects the efficiency of energy transfer between water molecules, thereby influencing the liquid’s thermal transport properties [11, 12].

The coupling between heat and mass fluxes gives rise to thermodiffusion, also known as the Ludwig–Soret effect [13, 14], where a temperature gradient induces a concentration gradient in electrolyte solutions. This coupling can be described within the framework of linear non-equilibrium thermodynamics (LNET) [15], which expresses the induced mass flux in terms of the applied thermal field through phenomenological equations. Depending on the sign of the

Soret coefficient, solutes may migrate toward the hot (thermophilic) or cold (thermophobic) regions of the system [16, 17]. Previous experimental and simulation studies have identified both inversions and minima in the Soret coefficient [16, 18–22]. Furthermore, a correlation between thermophobicity and the disruption of water’s structural organization has been reported in References [17, 23] and discussed in Section 4.3.3. Since pressure substantially alters the hydrogen bonding network of water, these effects are expected to play an important role in determining the thermodiffusive behavior of electrolyte solutions under high-pressure conditions.

The behavior of ionic solutions under elevated pressure has attracted considerable attention, as such conditions are prevalent within the Earth’s crust and upper mantle. Numerous investigations have examined the structural, dielectric, and transport properties of aqueous electrolytes, as well as those of pure water, at pressures reaching the gigapascal regime [24–32]. Metamorphic fluids, in which water constitutes a dominant component, play a central role in mass and heat transport processes within the Earth. Their thermophysical properties differ markedly from those of fluids under ambient conditions [33, 34]. Beyond terrestrial relevance, the study of high-pressure aqueous systems also extends to planetary science, where subsurface oceans with pressures approaching 0.1 GPa have been proposed on icy moons such as Europa [4].

In this study, we explore how pressure influences the thermal transport behavior of aqueous NaCl and LiCl solutions. The simulations employ the TIP4P/2005 water model [35] in combination with the Madrid-2019 ion force field [36]. We determine both the thermal conductivity and the Soret coefficient for these systems over a range of pressures and analyze the microscopic origins of the observed trends. Particular attention is given to the pressure-induced modifications in water structure and the hydration shells of ions, which are shown to affect the efficiency of heat and mass transport. Understanding these thermophysical properties of water and electrolyte solutions at high pressure provides valuable insight for thermodynamic modeling of geofluids in the Earth’s upper mantle [33, 34].

5.2 Simulation Details

We performed boundary-driven non-equilibrium molecular dynamics (NEMD) simulations following the setup and procedures described in Section 4.2 (see also Figure 4.1). All NEMD simulations were carried out using LAMMPS (version of 3 March 2020) [37] with a timestep of 1 fs. Each system contained 6663 water molecules and 120 ion pairs, corresponding to a 1 m concentration. The simulations employed Langevin thermostats [38, 39] positioned at the center and edges of the simulation box to impose temperature gradients between predefined hot (T_{hot}) and cold (T_{cold}) regions, using the same thermostat settings as described previously. The validation presented in Figure 5.1 demonstrates that our NEMD setup conserves energy accurately, with the energy exchange between the hot and cold reservoirs remaining consistent within computational uncertainties. The total center-of-mass momentum was removed at each timestep. Long-range electrostatic and dispersion interactions were calculated using the particle-particle particle-mesh (PPPM) method [40] with accuracy parameters consistent with those used in Section 3.2.

Each system was pre-equilibrated for 5 ns in the isothermal-isobaric (NPT) ensemble at the target pressure and the mean temperature $(T_{\text{hot}} + T_{\text{cold}})/2$. The average cell dimensions obtained from this equilibration were then used to define the fixed simulation box for the subsequent NEMD simulations. Following an additional equilibration period of approximately 10 ns, data were collected over production runs lasting at least 50 ns. The thermal conductivity and Soret coefficient were evaluated from the resulting local temperature and concentration profiles using the procedures described in Sections 2.3.1 and 2.3.2.

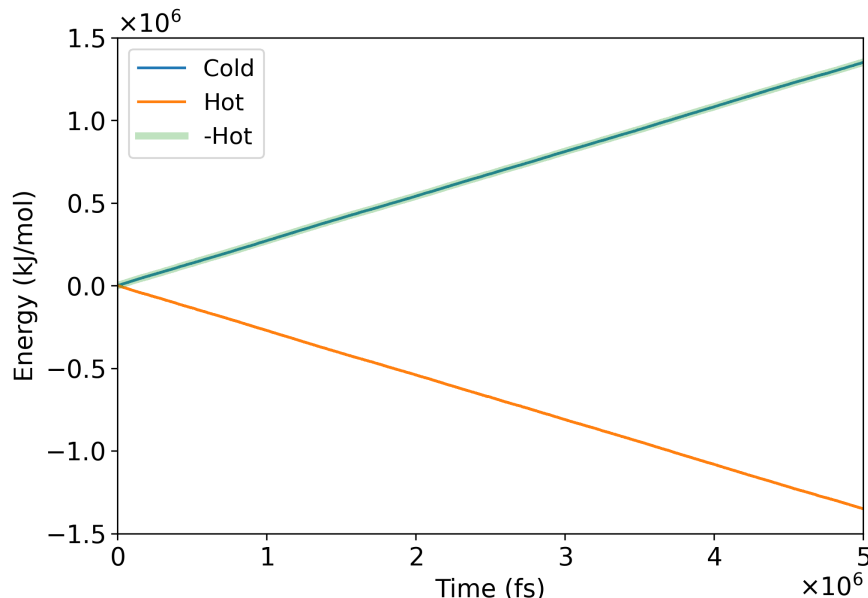


Figure 5.1: Cumulative energy exchange with the hot and cold thermostating regions during a representative NEMD simulation of a 1 m NaCl aqueous solution performed at an average temperature of 290 K, an average pressure of 0.1 GPa, and a density of 1.08 g/cm³. The cold and hot thermostating regions were maintained at 240 K and 340 K, respectively. The energy transferred in the cold and hot zones is shown by the blue and orange lines, respectively, while the green line represents the negative of the hot-region energy to facilitate direct comparison and evaluation of energy conservation.

We additionally performed equilibrium isothermal–isobaric (NPT) simulations using GRO-MACS (version 2021.3) [41] to analyze the structural properties and evaluate the speed of sound of the electrolyte solutions. Each simulation cell contained 926 water molecules and 17 ion pairs, and the production runs were carried out for at least 60 ns with a timestep of 1 fs. The radial distribution functions (RDF) and coordination numbers (CN) were computed from the NPT trajectories following the approach described in Section 4.2. The fluctuation-derived thermodynamic properties, including the isobaric thermal expansion coefficient, isothermal compressibility, and adiabatic speed of sound, were evaluated as discussed in Section 2.4. Furthermore, the spatial three-dimensional density distribution functions (SDF) [42] of hydrogen and oxygen atoms in water were computed using the TRAVIS package [43, 44].

We also computed the self-diffusion coefficients of the ions in solution. In the classical hydrodynamic viewpoint, diffusion in simple molecular liquids is often estimated using the Stokes–Einstein relation, which links the self-diffusion coefficient D_{self} to thermal energy, the solvent viscosity η , and an effective molecular radius a : $D_{\text{self}} \simeq k_{\text{B}}T/(6\pi\eta a)$ [45–47]. In the

molecular dynamics simulations carried out in this chapter, however, self-diffusion coefficients are obtained directly from mean square displacement (MSD) analysis using the Einstein relation [48, 49],

$$D_{\text{self}} = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle, \quad (5.1)$$

where $\mathbf{r}_i(t)$ denotes the position of ion i at time t . This microscopic approach naturally captures molecular and ion-specific mobility beyond the hydrodynamic approximation.

5.3 Results

To assess the accuracy and consistency of the employed force field under elevated pressures, we determined the equation of state (EOS) of pure water along the 290 K isotherm. The simulated densities show excellent agreement with the experimental data [50] up to 0.8 GPa (see Figure 5.2), confirming the reliability of the TIP4P/2005 force field within the high-pressure regime explored in this work. In addition, the EOS derived from non-equilibrium molecular dynamics (NEMD) simulations at ambient conditions (Table C.1 in the Appendix) is in good agreement with previous studies [51] and with the results presented in Section 3.3.1, which employed the same model under equilibrium conditions with smaller system sizes. It should also be noted that the TIP4P/2005 model exhibits a temperature shift relative to the experimental coexistence curve, and the liquid phase remains stable beyond 0.8 GPa.

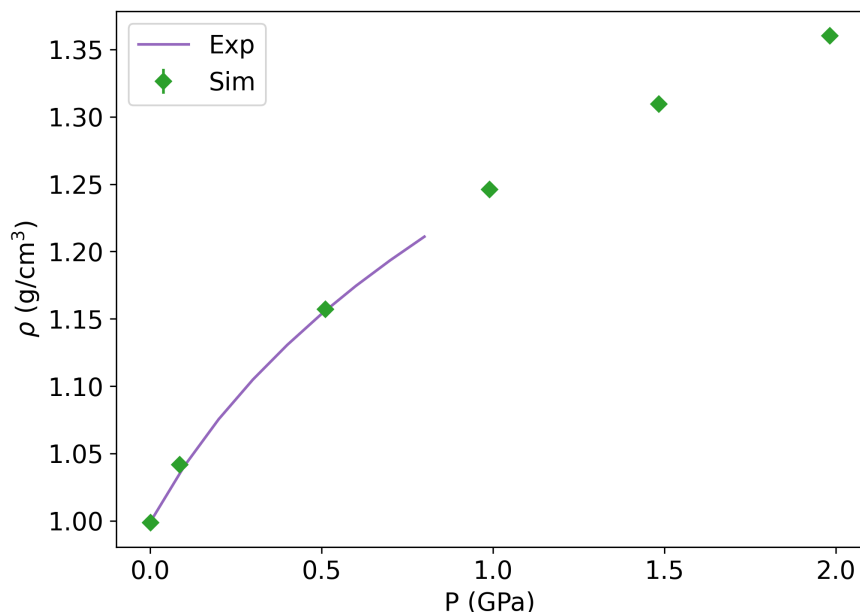


Figure 5.2: Equation of state of water obtained from equilibrium NPT simulations (green symbols representing averages over three independent simulation replicas) at pressures of 10^{-4} , 0.1, 0.5, 1.0, 1.5, and 2.0 GPa along the 290 K isotherm. The simulated densities are compared with experimental data (purple line) reported up to 0.8 GPa [50].

5.3.1 Thermal Transport in Electrolyte Solutions under Pressure

Figure 5.3 shows the pressure dependence of the thermal conductivity for 1 m NaCl and LiCl aqueous solutions along the 290 K isotherm. As illustrated in Figure 3.3 and discussed in Section 3.3.1, the thermal conductivity of TIP4P/2005 water converges within 10–30 ns at temperatures above 230 K. Following this procedure, averages were calculated over the production runs to ensure statistical convergence.

The thermal conductivity of both NaCl and LiCl solutions increases with pressure, and no significant difference is observed between the two electrolytes. This trend is consistent with previous studies conducted near ambient conditions [23], which showed that the thermal conductivity of alkali halide solutions depends more strongly on the anion mass than on the cation type. The conductivities of the salt solutions remain lower than that of pure water (see Figure 5.3), exhibiting a reduction of approximately 1–3%, which becomes more pronounced at higher pressures. This decrease relative to pure water agrees with both experimental and simulation results obtained under standard conditions [23, 52] and in the supercooled regime (see Section 4.3.2). Previous studies [23] attributed the reduction to an increase in the molar

volume upon salt addition and to the disruption of the hydrogen-bond network, with the latter effect becoming more prominent at higher salt concentrations.

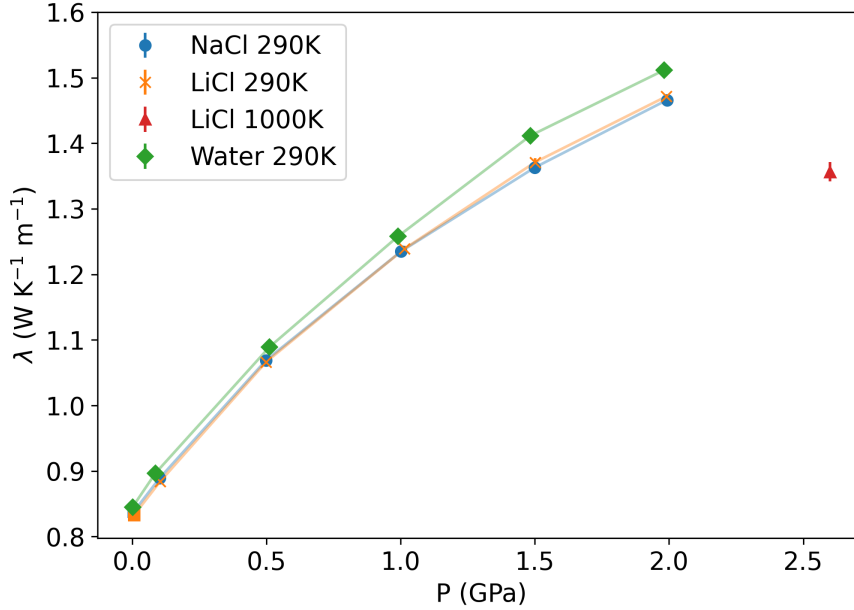


Figure 5.3: Thermal conductivity of 1 m NaCl and LiCl aqueous solutions along the 290 K isotherm at pressures of 10^{-4} , 0.1, 0.5, 1.0, 1.5, and 2.0 GPa. The green symbols correspond to pure water at 290 K, while the red triangle denotes data for a 1 m LiCl solution at 1000 K and 2.6 GPa. The square symbols represent previous simulation results for 1 m NaCl and LiCl solutions at 298 K and approximately 3×10^{-3} GPa, reported in Reference [23]. Lines connecting the data points serve as visual guides. All reported NEMD results correspond to averages over ten independent simulation replicas, with each replica evaluated over successive 10 ns segments of the production trajectory. The error bars represent the aggregated statistical uncertainty. The numerical data are summarized in Table C.1.

At pressures above 0.1 GPa, the characteristic tetrahedral arrangement of water molecules becomes significantly distorted, as will be further discussed in Section 5.3.2. Consequently, the high thermal conductivity observed at elevated pressures cannot be attributed to the hydrogen-bonding network of water.

To further examine the pressure response of the system, we analyzed the isobaric thermal expansion coefficient and the isothermal compressibility. Figure 5.4 presents these simulated properties for pure water and for the 1 m NaCl and LiCl solutions at 290 K, together with experimental reference data extracted from the equation of state of water reported in Reference [50]. The simulated and experimental results show only minor differences between pure water and the electrolyte solutions. In the left panel of Figure 5.4, all systems display a local

maximum in the isobaric thermal expansion coefficient near 0.5 GPa, which corresponds to the pressure range where the orientational tetrahedral order becomes markedly disrupted. With increasing pressure, the difference in thermal expansion between pure water and the salt solutions diminishes. On average, the simulated thermal expansion coefficients are about 15% higher than the experimental values, consistent with the $\sim 9\%$ overestimation previously reported for the TIP4P/2005 model under ambient conditions [35].

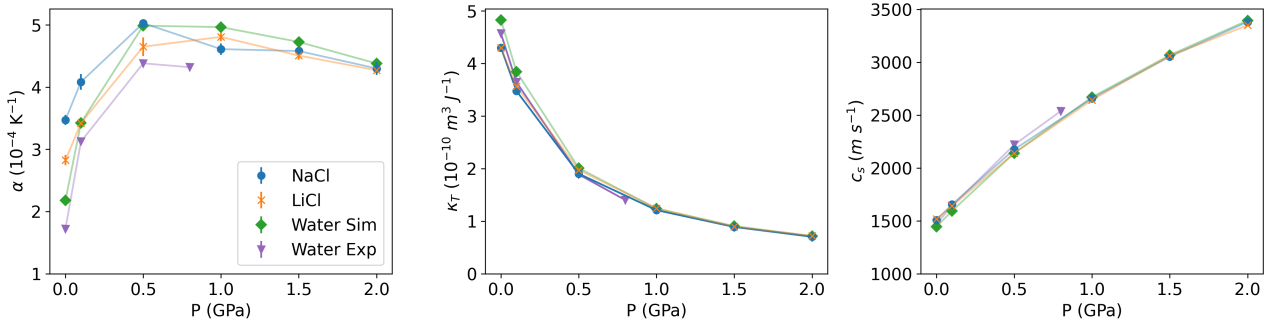


Figure 5.4: From left to right, panels show the isobaric thermal expansion coefficient, isothermal compressibility, and isentropic (adiabatic) speed of sound for pure water and 1 m NaCl and LiCl solutions at 290 K. The data correspond to pressures of 10^{-4} , 0.1, 0.5, 1.0, 1.5, and 2.0 GPa. All fluctuation properties were computed from equilibrium NPT simulations, with each state point averaged over three independent replicas. The purple triangles indicate experimental measurements reported in Reference [50] at 10^{-4} , 0.1, 0.5, and 0.8 GPa and 290 K.

The simulation results reproduce the experimental isothermal compressibility and speed of sound well, confirming the accuracy of the TIP4P/2005 model at high pressure. The isothermal compressibility, shown in the middle panel of Figure 5.4, decreases with increasing pressure, whereas the speed of sound in the right panel increases correspondingly. The thermal conductivity correlates with the speed of sound through the Bridgman equation (Equation 1.1) [53], which, although approximate, captures the main qualitative relationship between these two properties. This relation has also motivated more recent formulations that explicitly incorporate the speed of sound as a governing variable [12]. Furthermore, the weak dependence of the speed of sound on the cation type is consistent with the similar thermal conductivities observed for the NaCl and LiCl solutions.

5.3.2 Thermodiffusion in Electrolyte Solutions under Pressure

The Soret coefficients obtained from NEMD simulations are presented in Figure 5.5. For both NaCl and LiCl solutions, the Soret coefficient increases with pressure up to about 0.5 GPa and then reaches a plateau, becoming nearly independent of pressure at higher values. In this high-pressure regime, water loses its characteristic tetrahedral organization, and the radial distribution functions approach those typical of simple liquids (see Figure 5.6). This interpretation is further supported by the spatial distribution functions of water shown in Figure 5.8.

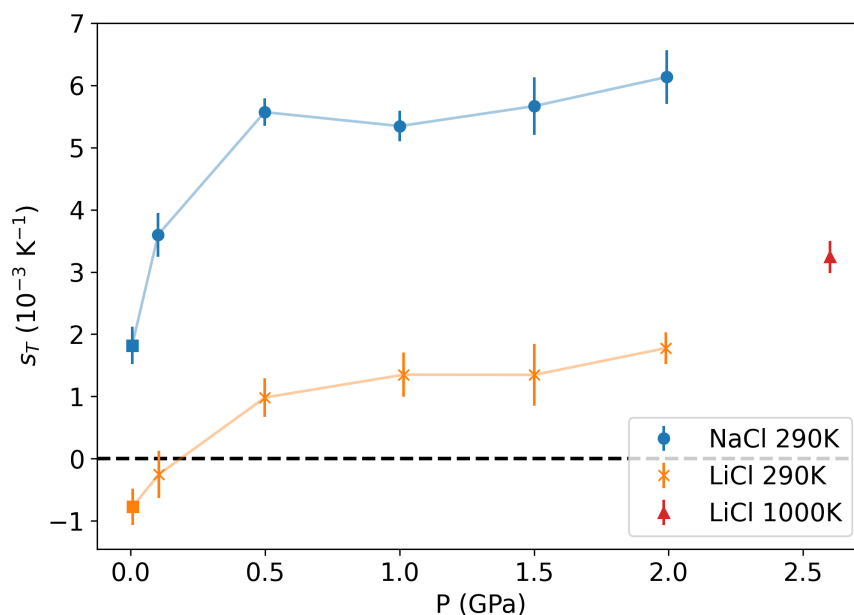


Figure 5.5: Soret coefficients of 1 m NaCl and LiCl aqueous solutions along the 290 K isotherm at pressures of 10^{-4} , 0.1, 0.5, 1.0, 1.5, and 2.0 GPa. The symbols follow the same color and marker scheme as in Figure 5.3: squares denote previous simulation results at 298 K and 3×10^{-3} GPa [23], circles and crosses represent the NaCl and LiCl simulated at 290 K in this work, and the red triangle corresponds to the 1 m LiCl at 1000 K and 2.6 GPa. Each data point corresponds to the average of 10 independent NEMD simulation replicas.

The solutions become increasingly thermophobic with rising pressure. This effect is particularly pronounced for the Li^+ salt, whose Soret coefficient changes sign at approximately 0.2 GPa, indicating a transition from thermophilic to thermophobic behavior. This crossover coincides with the progressive loss of tetrahedral ordering, as shown by the oxygen–oxygen radial distribution functions (see Figure 5.6). The influence of pressure is also evident in the ionic self-diffusion coefficients obtained from NPT equilibrium simulations (see Table C.2 in the Appendix). The values computed under standard conditions agree well with experimental

measurements [54]. For both cations and anions, the self-diffusion coefficients remain nearly constant up to about 0.5 GPa, beyond which they decrease sharply upon compression, reaching roughly half their initial magnitude by 2 GPa.

Zhang et al. recently investigated the thermal transport properties of pure water under extreme conditions using neural network (NN) potentials, covering pressures up to 22 GPa and temperatures between 1000 and 2000 K [12]. These thermodynamic states are relevant to the Earth’s mantle. Their results indicated that the thermal conductivity shows only a weak dependence on temperature but increases with pressure. Understanding the behavior of ionic solutions at comparable high pressures (around 1 GPa) and temperatures (near 1000 K) is therefore essential for modeling deep Earth fluids [34]. To this end, we performed additional NEMD simulations for a 1 m LiCl solution at 1000 K and 2.6 GPa (see the red triangle marker in Figures 5.3 and 5.5). The density predicted by the TIP4P/2005 model for this solution (1.17 ± 0.003 g/cm³) agrees closely with that obtained from NN potential simulations of pure water (1.20 g/cm³) [12]. The corresponding thermal conductivity of the LiCl solution, 1.36 ± 0.02 W m⁻¹ K⁻¹, is comparable to the value reported for pure water under the same thermodynamic conditions using NN potentials (1.14 ± 0.22 W m⁻¹ K⁻¹). Under these extreme conditions, the Soret coefficient becomes more thermophobic than in the 290 K simulations within the 0.1–2 GPa range. This finding supports the view that disruption of the hydrogen bonding structure of water, driven by elevated temperature and pressure, enhances the thermophobic behavior of electrolyte solutions. Overall, our results demonstrate that thermodiffusion constitutes a key coupling mechanism under conditions relevant to the Earth’s mantle.

5.3.3 Pressure-Induced Structural Changes in Electrolyte Solutions

We next examine the structural modifications that occur in the solutions as pressure increases. Figure 5.6 shows the oxygen–oxygen radial distribution functions (RDFs) of pure water at 290 K for pressures ranging from 10^{-4} to 2 GPa. A pronounced disruption of the water structure appears above 0.5 GPa, as indicated by the shift of the second coordination peak, located near $r = 0.45$ nm, toward larger intermolecular separations. At and beyond this pressure, the second peak lies at approximately twice the distance of the main maximum, r_{max} , in the RDF, which

is characteristic of a simple liquid. The O–O RDFs of the NaCl and LiCl solutions display similar behavior, with comparable peak positions and amplitudes as the pressure increases (see Figure 5.7), indicating that pressure exerts a stronger influence on the overall water structure than the presence of ions under the examined conditions.

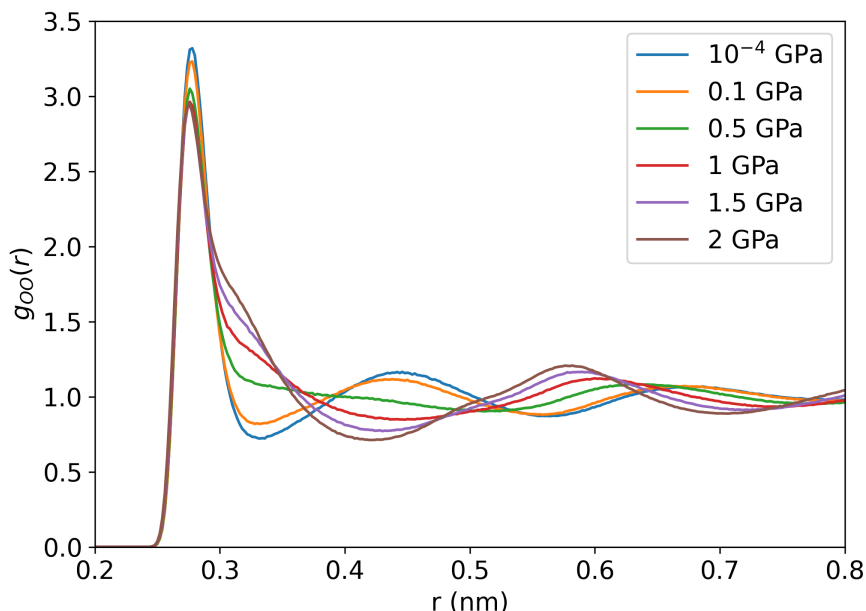


Figure 5.6: Pressure dependence of the oxygen–oxygen radial distribution functions of pure water at 290 K, evaluated at 10^{-4} , 0.1, 0.5, 1.0, 1.5, and 2.0 GPa, with the distributions averaged over three independent equilibrium simulation replicas at each pressure.

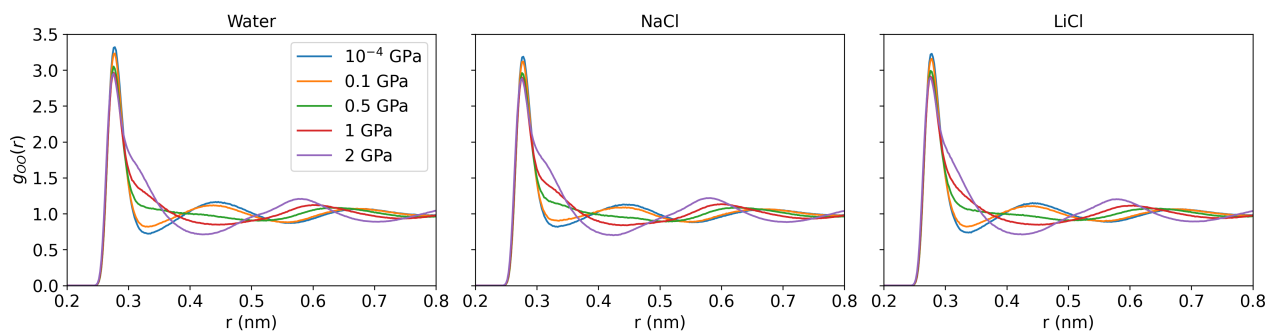


Figure 5.7: Oxygen–oxygen radial distribution functions of pure water and 1 m NaCl and LiCl aqueous solutions at 290 K for pressures of 10^{-4} , 0.1, 0.5, 1.0, and 2.0 GPa. Each distribution function was averaged over three independent simulation replicas.

The spatial distribution functions (SDFs) of the aqueous solutions shown in Figure 5.8 further reinforce the structural trends discussed above. A considerable loss of local tetrahedral ordering in water occurs around 0.5 GPa, and this structural motif is completely absent at

higher pressures. This behavior is observed in both LiCl and NaCl solutions. At 1.5 and 2 GPa, the liquid structure closely resembles that of a simple liquid, consistent with previous findings for pure water under extreme conditions [10] and with SDF analyses from X-ray scattering experiments on aqueous solutions at high pressure [30].

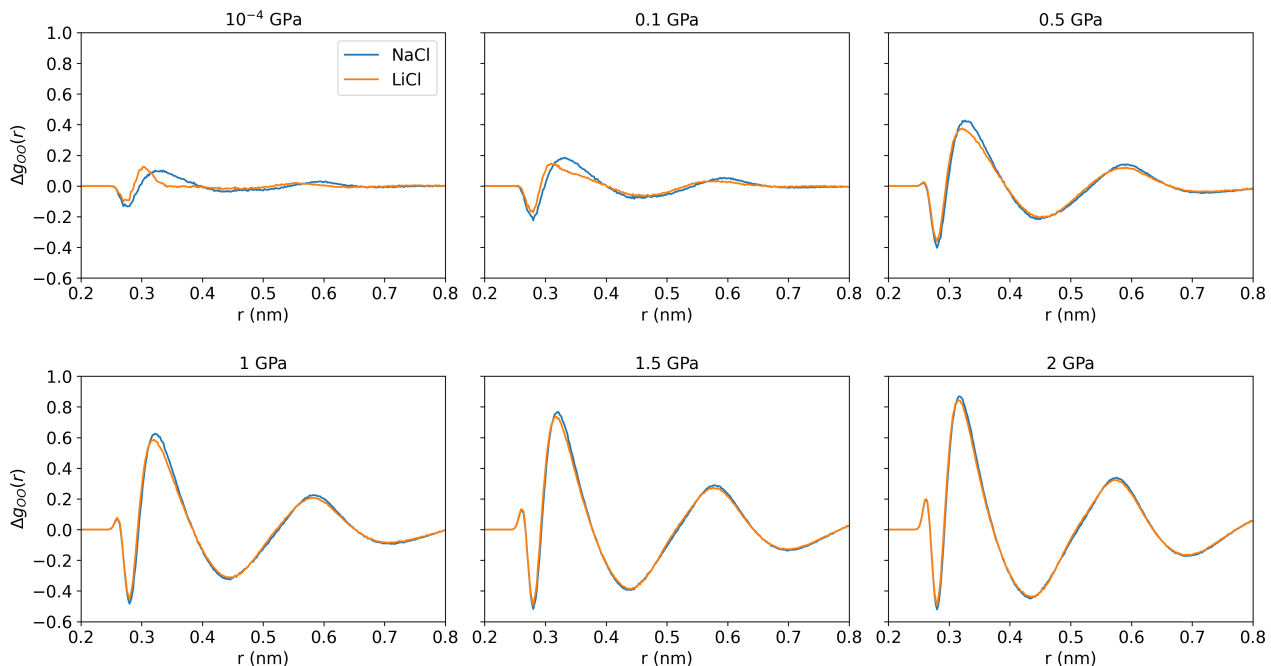


Figure 5.9: Differences in the oxygen–oxygen RDFs of 1 m NaCl and LiCl solutions at 290 K and pressures of 10^{-4} , 0.1, 0.5, 1.0, 1.5, and 2.0 GPa. Each curve represents the deviation from the RDF of pure water at standard pressure, defined as $\Delta g_{OO}(r) = g_{OO,\text{solution}}(r) - g_{OO,\text{pure water}(10^{-4} \text{ GPa})}(r)$. All distribution functions were computed as averages over three independent equilibrium simulation replicas to improve statistical reliability.

To examine how ion–water interactions evolve with increasing pressure, we calculated the differences between the oxygen–oxygen RDFs of the electrolyte solutions and that of pure water at standard pressure (see Figure 5.9). The most pronounced variations occur near the second coordination shell (0.4–0.5 nm) and are associated with the progressive loss of tetrahedral ordering, which becomes increasingly evident at higher pressures. At low pressures (10^{-4} and 0.1 GPa), the presence of LiCl causes only minor perturbations in the O–O correlations, mainly within the first coordination shell, whereas NaCl produces more noticeable changes at distances between 0.35 and 0.5 nm. As the pressure increases, the disruption of the O–O structure in this region intensifies considerably. At 0.5 GPa and above, the orientational hydrogen-bond network of water is no longer preserved (see Figure 5.9), and the resulting structural modifications become

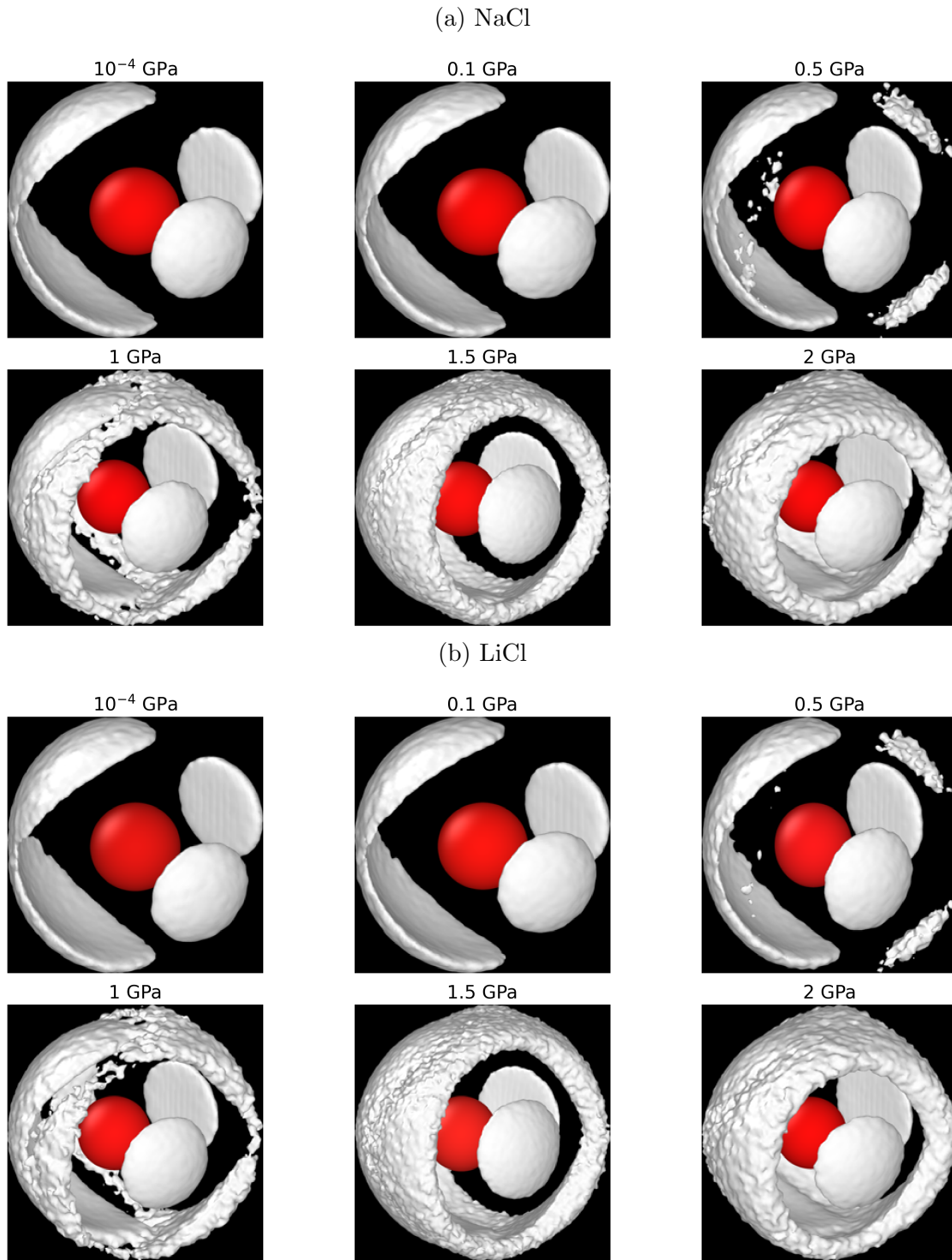


Figure 5.8: Spatial distribution functions $g_{OH}(r, \Omega)$ for 1 m NaCl (a) and LiCl (b) aqueous solutions at 290 K and pressures of 10⁻⁴, 0.1, 0.5, 1.0, 1.5, and 2.0 GPa. Each panel is derived from a representative simulation at the indicated pressure. The central oxygen atom, shown in red, serves as a reference point. Visualization rendered using OVITO [55].

largely independent of the cation species (Li^+ or Na^+). Overall, these results demonstrate a clear correlation between the thermophobic response and the loss of tetrahedral structure, particularly within the 0.35–0.5 nm range, consistent with previous observations for chloride solutions under ambient conditions [23].

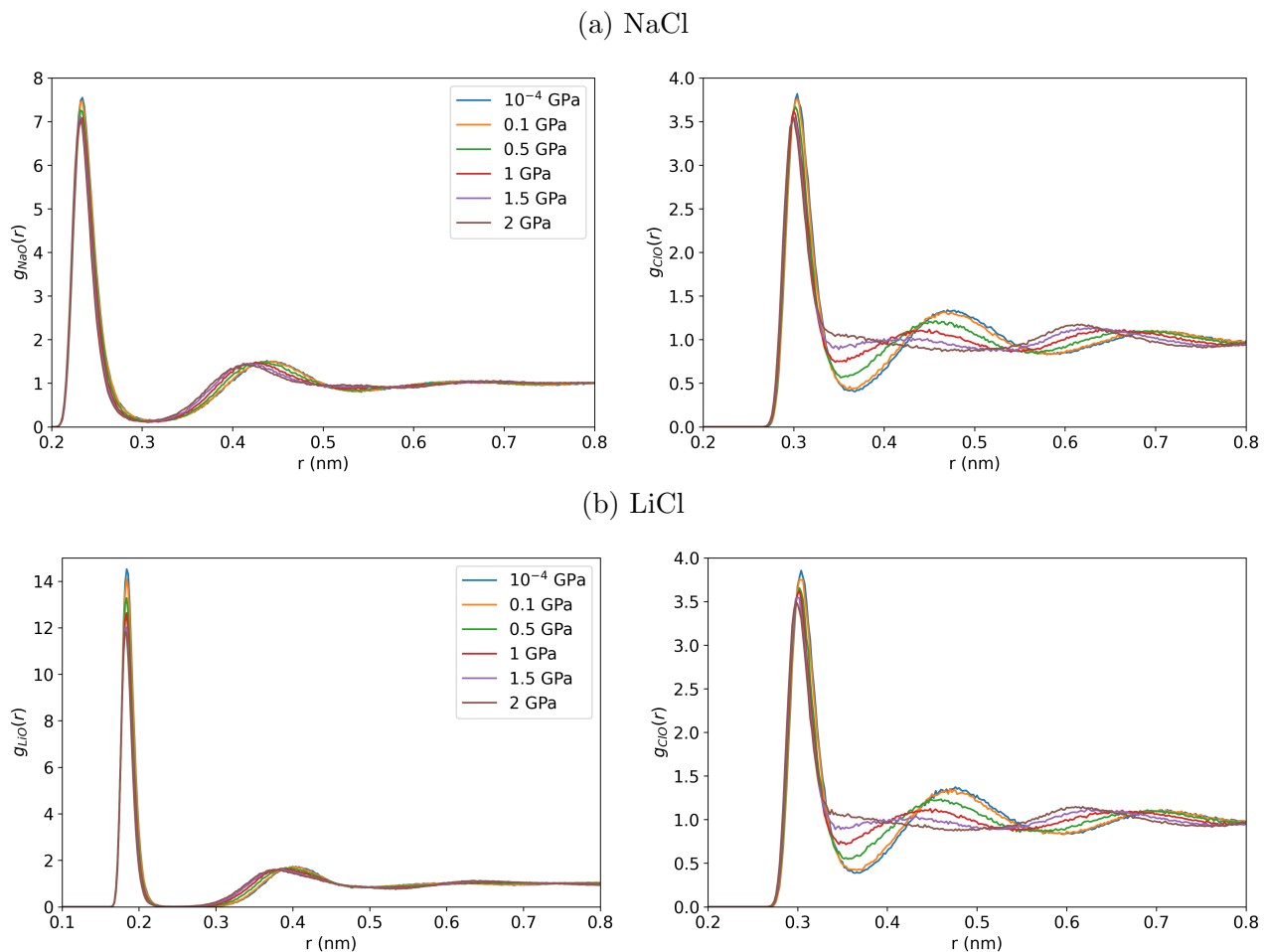


Figure 5.10: Ion–oxygen RDFs for 1 m NaCl (top panels) and LiCl (bottom panels) aqueous solutions at 290 K and pressures of 10^{-4} , 0.1, 0.5, 1.0, 1.5, and 2.0 GPa. The distributions shown are averaged over three independent equilibrium simulation replicas. The left and right panels correspond to the cation–oxygen and anion–oxygen RDFs, respectively.

The ion–oxygen RDFs are shown in Figure 5.10, and the corresponding coordination numbers, obtained by integrating each RDF up to its first minimum, are listed in Table C.2. Pressure exerts only a minor influence on the cation hydration structure, particularly for Li^+ , whose Li–O coordination number remains constant at four across all examined pressures. In contrast, the Cl–O RDFs exhibit pronounced changes upon compression. The second Cl–O peak diminishes from 0.1 GPa onward and disappears above 1.5 GPa, indicating a progressive loss of a well-

defined solvation structure. Meanwhile, the Cl–O coordination number increases markedly, reaching values of approximately 20 at around 2 GPa.

This strong pressure dependence of chloride hydration is consistent with previous molecular dynamics simulations, which report substantial restructuring and coordination growth under compression [56]. Such sensitivity reflects the intrinsic asymmetry between cation and anion solvation. Experimental and simulation studies have shown that Cl^- forms hydrogen-bonded bridges with surrounding water molecules and can be accommodated within the hydrogen-bond network, whereas cations impose stronger orientational ordering by directing water oxygens toward the ion [57, 58]. This substantial increase in chloride coordination, accompanied by a shift of the main Cl–O peak to larger distances, is consistent with X-ray diffraction measurements that reported an increase from 6 to 16 at 1.7 GPa and 300 K [30]. Likewise, the negligible pressure dependence of the cation coordination number observed here agrees with those experimental results. Similar effects on anion hydration were also reported in X-ray absorption studies of RbBr at 2.8 GPa, which revealed a concurrent loss of orientational order within the hydration shells [59].

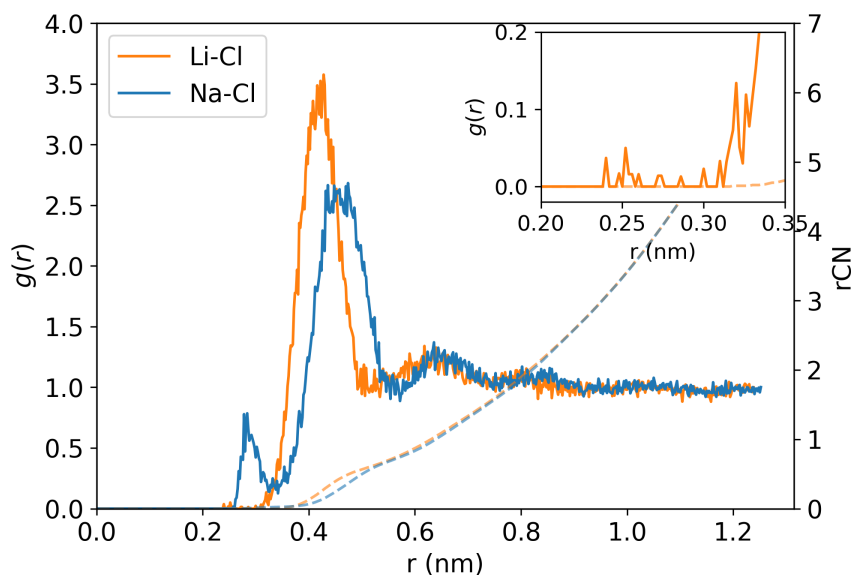


Figure 5.11: Sodium–chloride (blue) and lithium–chloride (orange) RDFs (solid lines) and corresponding running coordination numbers (dashed lines) for NaCl and LiCl aqueous solutions at 290 K and 2 GPa. The reported distribution functions correspond to averages over three independent simulation replicas. The inset highlights the region between 0.2 and 0.35 nm, providing a closer view of the first minimum in the Li–Cl RDF.

We further analyzed the ion–ion correlations to assess the degree of ion association. Figure 5.11 shows the cation–anion RDFs and the corresponding running coordination numbers for the NaCl and LiCl solutions at 2 GPa. The first minima in the Na–Cl and Li–Cl RDFs occur at approximately 0.28 and 0.33 nm, respectively, in agreement with values reported in previous simulation studies [19, 24, 25]. Sakuma and Ichiki investigated NaCl solutions over the 670–2000 K temperature range and up to 2 GPa, and observed that the cation–anion coordination number decreases with increasing pressure and decreasing temperature [24, 25]. Under our conditions (290 K and 2 GPa), no significant ion-pair formation is detected, particularly in the LiCl solutions.

5.4 Conclusions

We have investigated the thermal transport and thermodiffusion behavior of 1 m NaCl and 1 m LiCl aqueous solutions under GPa pressures using non-equilibrium molecular dynamics simulations and state-of-the-art rigid empirical force fields. These conditions are relevant to crustal and upper mantle fluids.

The thermal conductivity of the electrolyte solutions shows little dependence on the cation species. Consistent with experimental and computational studies, the addition of NaCl and LiCl reduces the thermal conductivity of water, with the reduction becoming more pronounced (about 3%) at GPa pressures. In contrast, the overall magnitude of thermal conductivity increases significantly with pressure, reaching nearly twice the value of pure water at ambient conditions. This enhancement correlates with the substantial decrease in compressibility and the accompanying rise in the speed of sound, as illustrated by the comparison between Figures 5.3 and 5.4. Hence, both pure water and the electrolyte solutions become more efficient in heat conduction under GPa pressures.

The Soret coefficients of NaCl and LiCl increase with pressure up to approximately 0.5 GPa, beyond which they reach a plateau. The increasing thermophobicity of the solutions is closely associated with the loss of tetrahedral ordering and the disruption of the hydrogen bonding network in water. Above 0.5 GPa, the liquid structure resembles that of a simple liquid.

The hydration environment of Li^+ remains largely unaffected by compression, maintaining its tetrahedral coordination up to 2 GPa. These results indicate that the transition from thermophilic to thermophobic behavior in alkali halide solutions is governed by the breakdown of the hydrogen-bond structure in water, emphasizing the crucial role of hydrogen bonding in controlling thermodiffusive responses. This interpretation is consistent with previous studies of thermodiffusion under ambient conditions [17] and in concentrated aqueous electrolyte solutions [23].

Furthermore, the high-pressure results reinforce the idea that strong, stable hydrogen bonding favors thermophilic behavior, whereas weakened hydrogen bonding promotes thermophobicity, causing ions to migrate toward cooler regions in crustal fluids. Within a local thermodynamic framework, the Soret coefficient is governed by the temperature derivative of the solvation free energy, and thus by the entropy of the ion–water system [60]. Strong, stable hydrogen-bond networks provide significant enthalpic stabilization to the solvation shell [57]. As temperature increases and hydrogen bonds progressively weaken, the resulting change in hydration entropy enhances the temperature dependence of the solvation free energy, thereby favoring thermophilic migration. In contrast, when the hydration structure is already disrupted and less tetrahedral, its weaker enthalpic stabilization leads to a reduced temperature sensitivity of the chemical potential, promoting thermophobic drift toward cooler regions. Future work should quantify the pressure-induced loss of tetrahedral order, for example through evaluation of the tetrahedral order parameter, to directly correlate structural changes in hydrogen bonding with the observed thermodiffusive response.

All simulations in this work employed rigid water models. Under extreme conditions relevant to the Earth’s mantle, bond-stretching and angular flexibility may become significant and could be incorporated into future studies. Previous simulations using the flexible TIP4P/2005 model have reported slightly higher thermal conductivities than those obtained with the rigid version at 300 K and ambient pressure [61]. Future work employing machine-learning potentials and incorporating quantum corrections [62, 63] may offer deeper insights into thermal transport and coupling phenomena in aqueous systems under extreme conditions. In parallel, experimental validation of the predicted structural changes under GPa compression could be pursued using high-pressure

X-ray and neutron scattering, as well as X-ray absorption spectroscopy techniques [59, 64]. Measurements of pressure-induced modifications in coordination number and hydrogen-bond network structure would offer valuable benchmarks to assess the accuracy of the simulated structural response.

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Chapter 6

Polarization of Ethanol under Thermal Fields

This chapter is reproduced from the article *Polarization of Ethanol under Thermal Fields* by G. Zhao, Y. Xiao, A. Deshmukh, A. Chapman, and F. Bresme, *J. Chem. Phys.* **2025**, 163, 024501 [1], which is published under the Creative Commons CC BY 4.0 license.

Thermal gradients induce polarization and give rise to a steady-state electric field in polar liquids. Although this phenomenon has been extensively analyzed in water, the mutual coupling between heat and polarization fluxes remains largely unexplored in other polar fluids. In this chapter, we employ non-equilibrium molecular dynamics simulations with the TraPPE force field to examine both thermal transport and thermally induced polarization in liquid and supercritical ethanol. The thermal conductivity of ethanol is evaluated over a broad range of thermodynamic states and compared with related thermophysical properties, including the isobaric thermal expansivity and isothermal compressibility. Our simulations reveal that temperature gradients induce polarization in ethanol in both the liquid and supercritical regimes. Along the liquid branch of the vapor–liquid coexistence curve, we identify a reversal in the direction of the polarization field and analyze its microscopic origin. Close to the critical point, the magnitude of the thermal polarization is markedly enhanced, resembling the behavior previously observed in water. Moreover, the change in the sign of the polarization field correlates with the minimum of the liquid–vapor surface potential of ethanol.

6.1 Introduction

Despite decades of experimental and theoretical work, modeling the thermal transport properties of liquids remains a challenging task. Empirical correlations, such as Bridgman’s relation (Equation 1.1), which links thermal conductivity to the speed of sound and molecular volume [2, 3], provide valuable qualitative insight but lack the predictive capability required to describe transport over a broad range of thermodynamic states. Accurate microscopic models are therefore essential for elucidating how heat is conducted in molecular liquids and how it couples with other non-equilibrium fluxes.

One such coupling effect arises when a temperature gradient induces an electrostatic field, a phenomenon known as thermal polarization (TP). Within the framework of Linear Non-equilibrium Thermodynamics (LNET) [4], TP reflects the cross-coupling between the heat flux and the displacement current. Similar coupling effects occur in thermodiffusion (Ludwig–Soret effect) [5, 6], where mass and heat fluxes interact to generate concentration gradients in mixtures [7, 8]. According to LNET, such couplings generally contribute to a reduction in the effective thermal conductivity of the system.

Recent simulation studies have explored thermal polarization in polar liquids such as water and acetonitrile across a broad range of conditions [9, 10]. In acetonitrile, thermal polarization produces a decrease in thermal conductivity of approximately 2–5% relative to the uncoupled value. Water, on the other hand, exhibits a much richer response: the direction of the induced electrostatic field reverses depending on pressure and temperature [9, 11], and a pronounced enhancement is observed near the liquid–vapor critical point [12]. These features have been linked to the interplay between dipolar and quadrupolar contributions to the polarization field, and theoretical analyses indicate that the dipole-to-quadrupole ratio serves as a key parameter governing this behavior [9, 13].

The investigation of thermal coupling effects in other hydrogen-bonded polar liquids remains limited. In particular, ethanol provides an instructive comparison to water: it forms hydrogen bonds yet possesses a nonpolar alkyl group that weakens the hydrogen bonding network and reduces thermal conductivity under ambient conditions [14, 15]. Understanding how these

structural differences influence the interplay between heat transport and polarization is essential for identifying the microscopic factors that govern thermal coupling in molecular systems.

In this chapter, we employ non-equilibrium molecular dynamics (NEMD) simulations with the TraPPE force field [16] to analyze the thermal transport and thermally induced polarization of ethanol in both liquid and supercritical states. The TraPPE model adopts a united-atom representation, in which methyl and methylene groups are treated as single pseudo-atoms interacting through Lennard-Jones and fixed-charge electrostatic potentials, while hydroxyl oxygen and hydrogen atoms are modeled explicitly. This parametrization provides an efficient yet accurate description of molecular interactions, enabling reliable predictions of vapor–liquid equilibria and hydrogen bonding behavior across alcohols [17]. We characterize thermal conductivity over a wide range of thermodynamic conditions and examine its correlation with other thermophysical properties, including the isobaric thermal expansion coefficient and the adiabatic speed of sound. Furthermore, we demonstrate that thermal gradients polarize ethanol and that the sign of the resulting electrostatic field reverses along the liquid branch of the vapor–liquid coexistence line. The origin of this inversion and the enhancement of the polarization near the critical point are discussed in connection with molecular structure and variations in the liquid–vapor surface potential.

6.2 Simulation Details

6.2.1 Non-Equilibrium Molecular Dynamics

To investigate the thermal transport and thermally induced polarization of ethanol, we performed boundary-driven Non-Equilibrium Molecular Dynamics (NEMD) simulations using LAMMPS (version released 2 August 2023) [18, 19]. Thermal gradients were generated by maintaining fixed hot (T_{hot}) and cold (T_{cold}) temperatures for ethanol molecules located within designated thermostat regions of the simulation cell (see Figure 6.1). Each thermostat region, 0.1 nm in thickness, was placed at the cell boundaries and at the center to establish a steady temperature profile along the z -direction. The simulation box dimensions followed the ratio $L_x : L_y : L_z = 1 : 1 : 3$, with $L_x \approx 40 \text{ \AA}$.

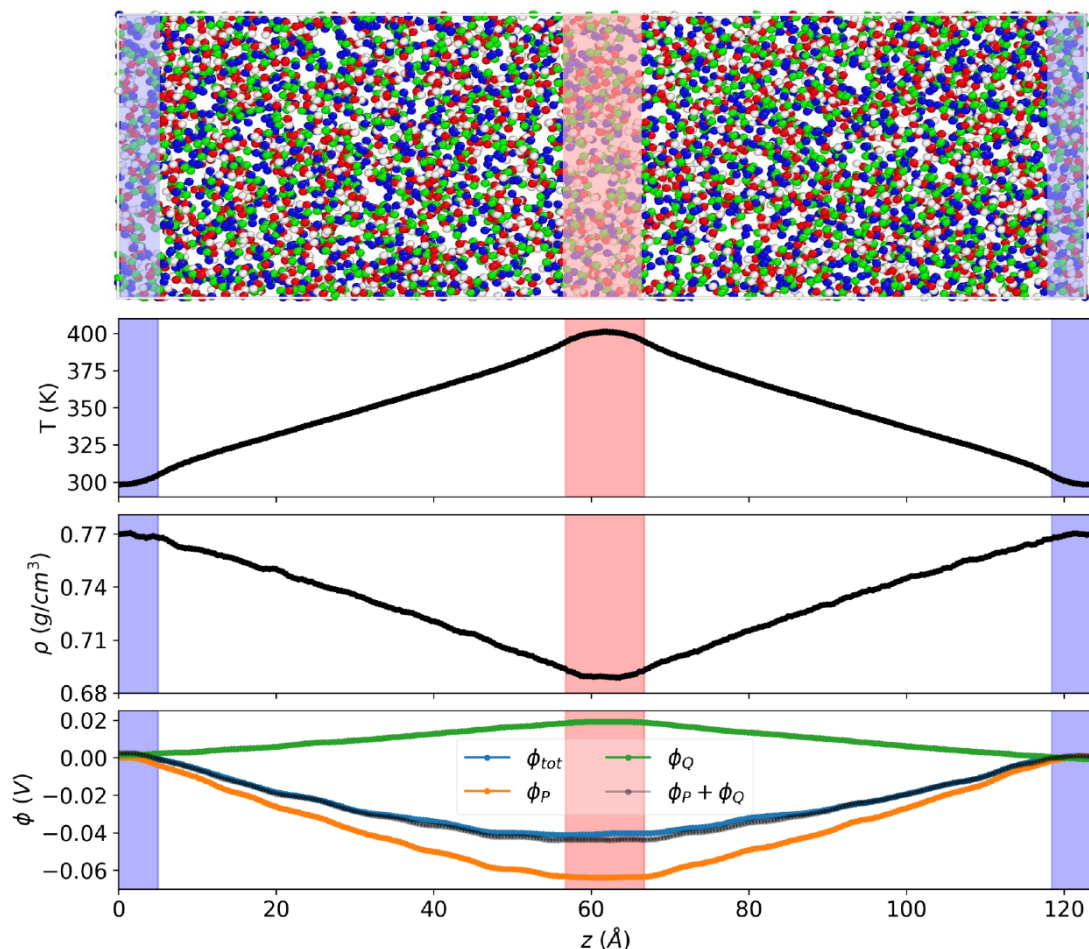


Figure 6.1: The top panel shows a snapshot of the simulation cell used in the Non-Equilibrium Molecular Dynamics (NEMD) simulations of ethanol, rendered with OVITO [20]. Atomistic sites are color-coded as follows: blue for CH_3 , green for CH_2 , red for oxygen (O), and white for hydrogen (H). The lower panels present the temperature, density, and electrostatic potential profiles across the non-equilibrium simulation domain. These profiles correspond to a representative simulation performed at an average temperature of 348 K and a density of 0.732 g/cm^3 , with the thermostatted regions maintained at 300 K (cold) and 400 K (hot). The bottom panel displays the total electrostatic potential together with its dipolar and quadrupolar components. Their sum (black line) is compared with the total potential. The regions thermostatted at high and low temperatures are indicated in red and blue, respectively.

Temperature control was implemented using canonical sampling velocity rescaling (CSVR) thermostats [21], applied to the hot and cold regions at every 1 fs timestep with a coupling constant of 100 fs. Figure 6.2 confirms that the NEMD simulations maintain excellent energy conservation, as indicated by the agreement between the heat rates injected at the hot and extracted at the cold regions. The total center-of-mass momentum of the simulation cell was removed at each timestep to prevent drift. Long-range electrostatic and dispersion interactions were treated using the particle-particle particle-mesh (PPPM) method [22], following the same

accuracy criteria described in Section 3.2.

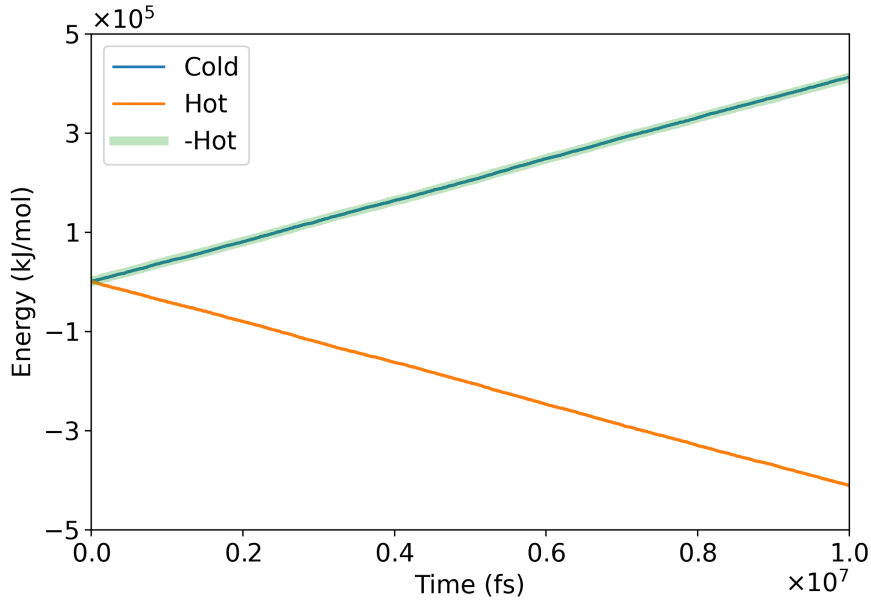


Figure 6.2: Verification of energy conservation in the same representative NEMD simulation of liquid ethanol shown in Figure 6.1. The cumulative energy exchanged with the cold and hot thermostats is shown as blue and orange curves, respectively, while the green curve represents the negative of the energy input at the hot side for clarity.

Each NEMD simulation cell contained 2000 ethanol molecules modeled using the TraPPE force field [16]. The same Lennard–Jones, bending, and torsional parameters as in the original model were employed. Bond flexibility was introduced via a harmonic potential,

$$U_b = k(r - r_0)^2, \quad (6.1)$$

where r_0 and k denote the equilibrium bond length and force constant, respectively, taken from the TraPPE parameterization (Table 6.1). The system was first equilibrated at the target temperature, and the simulation cell dimensions were gradually rescaled in all directions to reproduce the liquid-phase density along the vapor–liquid coexistence line [17]. Subsequent equilibration was performed for 5 ns using a global CSVN thermostat.

Table 6.1: Harmonic bond parameters for TraPPE-UA ethanol.

Bond	r_0 [$\text{\AA}$]	k [$\text{kJ mol}^{-1} \text{\AA}^{-2}$]
$\text{CH}_3\text{--CH}_2$	1.540	1297
$\text{CH}_2\text{--O}$	1.430	1339
O--H	0.945	2314

Non-equilibrium simulations were then performed by applying thermostats at T_{hot} and T_{cold} . State points were sampled along the liquid saturation curve and at selected isochores within the liquid region. After approximately 1 ns, the system reached a steady state, from which temperature and density profiles were obtained. Spatial averages were computed over 300 bins along the z -direction, corresponding to bin widths of about 0.4 $\text{\AA}$, depending on the density. These profiles were used to evaluate the equation of state and to calculate the thermal conductivity using Equations 2.50 and 2.51. A detailed comparison with the microscopic heat flux formulation is provided in Section 6.3.1. Each production run lasted at least 10 ns and was averaged over ten independent replicas, each initialized with a different random thermostat seed, yielding a total sampling time of 100 ns. To determine the thermal polarization field, charge densities were recorded every 10^3 steps, resulting in a total of 10^6 configurations collected from ten replicas for each state point. The corresponding thermal polarization coefficient was obtained following the procedures described in Section 2.3.3.

6.2.2 Equilibrium Simulations

In previous work on water, the inversion of the thermally induced polarization field was shown to correlate with a change in the sign of the electrostatic potential gradient at the liquid–vapor interface as a function of temperature [9]. To further investigate this relationship, we performed equilibrium NVT simulations of the ethanol liquid–vapor interface. Starting from a pre-equilibrated bulk configuration, the simulation cell was elongated by 100 $\text{\AA}$ on both sides along the z -axis, perpendicular to the interfacial plane, to create two independent interfaces. The total center-of-mass momentum of the system was removed at each timestep to prevent drift of the liquid slab. The system was equilibrated for 1 ns and subsequently simulated for an

additional 10 ns to compute the electrostatic potential profiles. A representative configuration of the interfacial setup is shown in Figure 6.3, together with the corresponding density and electrostatic potential profiles. The surface potential, ϕ_{surf} , was determined as the difference between the average electrostatic potentials of the liquid and vapor phases, $\phi_{\text{liq}} - \phi_{\text{vap}}$, indicated by the separation between the blue and orange dashed lines in the figure.

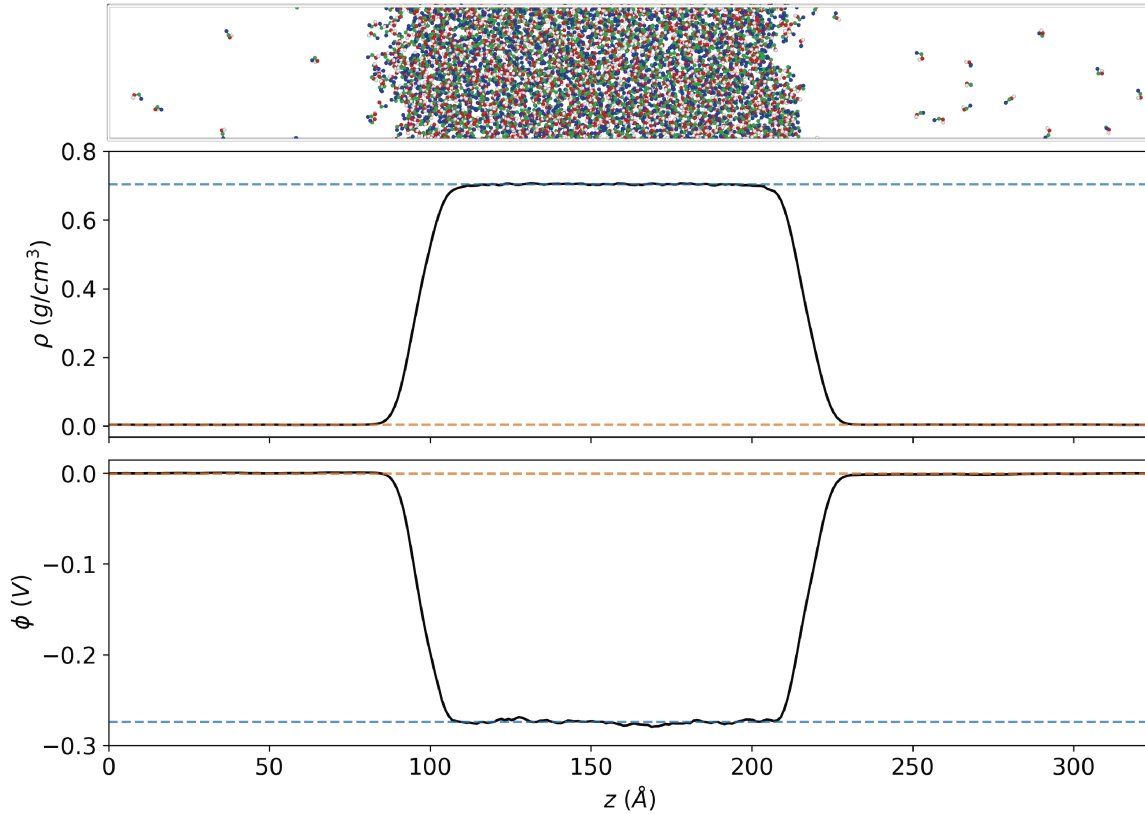


Figure 6.3: (Top) Representative setup of the equilibrium simulation for the ethanol liquid–vapor interface at an average temperature of 375 K. The color scheme for atomic sites is the same as in Figure 6.1. (Bottom) Density and electrostatic potential profiles obtained from the simulations. The dashed blue and orange lines represent the average values corresponding to the liquid and vapor phases, respectively.

To complement the non-equilibrium results and assess the influence of thermal polarization coupling on the thermal conductivity of ethanol, we performed additional equilibrium molecular dynamics simulations using GROMACS (version released January 2024) [23]. Each cubic simulation box contained 1728 ethanol molecules, and all simulations were carried out with a timestep of 1 fs. An initial 20 ns simulation in the isothermal–isobaric (NPT) ensemble was conducted to validate the force field implementation and determine the equilibrium density

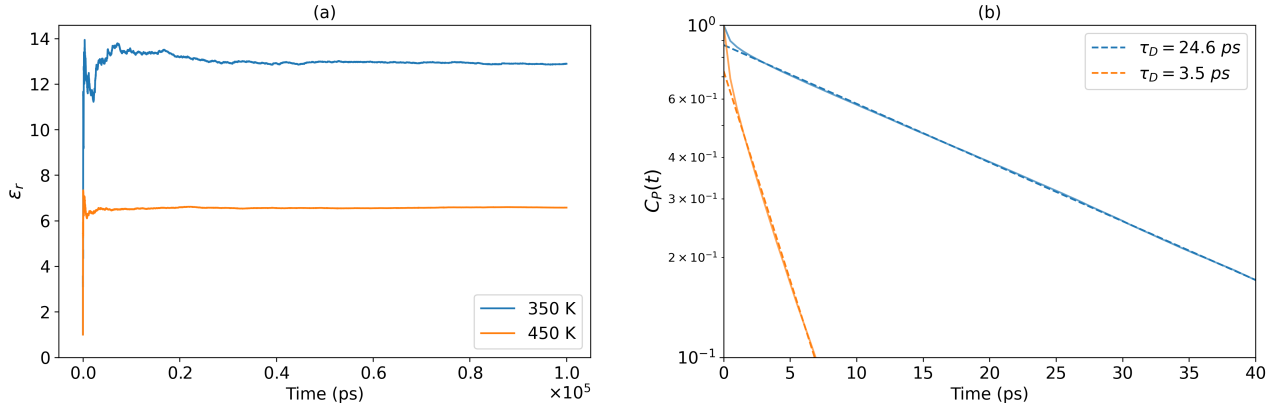


Figure 6.4: (a) Time evolution of the dielectric constant over a 100 ns trajectory at 350 and 450 K along the saturation line. (b) Total dipole moment autocorrelation functions, $C_P(t)$, obtained under the same thermodynamic conditions. The dashed lines represent exponential fits used to determine the Debye relaxation times. Both the dielectric constants and the dipole autocorrelation functions were averaged over three independent equilibrium simulation replicas under each thermodynamic condition.

and thermophysical properties of ethanol, including the isobaric thermal expansion coefficient, isothermal compressibility, and adiabatic speed of sound, following the fluctuation relations described in Section 2.4.

Subsequently, canonical (NVT) simulations were performed at the target density and at temperatures corresponding to the average of T_{hot} and T_{cold} from the NEMD simulations. These simulations were used to evaluate the dielectric properties of ethanol. Dielectric properties of polar fluids obtained from molecular simulations are known to exhibit slow convergence with respect to trajectory length, owing to the long-time correlations of total dipole moment fluctuations [24–26]. To ensure statistical reliability, all dielectric quantities reported here were averaged over three independent equilibrium trajectories of 100 ns each, with only the converged portion (the final 50 ns; see Figure 6.4 (a)) used for analysis to ensure robust sampling of dipolar fluctuations. At ambient conditions, the resulting dielectric constants and relaxation times are consistent with previous experimental and simulation studies [27–29], as discussed in detail in Section 6.3.4. The dielectric permittivity ϵ_r was calculated from the fluctuations of the total dipole moment, $\mathbf{P} = \sum_i q_i \mathbf{r}_i$, determined by summing the the products of atomic charges (q_i)

and their position vectors ($\mathbf{r}_i$) within the simulation cell, using the relation [30]:

$$\epsilon_r - 1 = \frac{\langle \mathbf{P}^2 \rangle - \langle \mathbf{P} \rangle^2}{3Vk_B T \epsilon_0}, \quad (6.2)$$

where the angle brackets denote time averages and V is the simulation box volume.

The Debye relaxation time, τ_D , was obtained from the autocorrelation function of the total dipole moment,

$$C_P(t) = \frac{\langle \mathbf{P}(t) \cdot \mathbf{P}(0) \rangle}{\langle \mathbf{P}(0) \cdot \mathbf{P}(0) \rangle}, \quad (6.3)$$

by fitting its long-time decay to a single exponential, $C_P(t) = A \exp(-t/\tau_D)$, as shown in Figure 6.4 (b). The resulting values of ϵ_r and τ_D were then used to estimate the change in thermal conductivity associated with thermal polarization coupling, $\delta\lambda$, according to [10]:

$$\delta\lambda = -\frac{S_{TP}^2 T}{\tau_D} \left(\frac{\epsilon_0 \epsilon_r^2}{\epsilon_r - 1} \right). \quad (6.4)$$

6.3 Results

6.3.1 Simulation Validation: Microscopic Heat Flux and Equation of State

The overall heat flux was obtained from the time derivative of the cumulative energy using the continuity relation (Equation 2.51). In addition, the microscopic heat flux was evaluated using the first-order Irving–Kirkwood (IK1) formulation [31, 32], as detailed in Section 2.3.1 and given by Equation 2.53. The close agreement shown in Figure 6.5 confirms that the continuity approach provides an accurate evaluation of the heat flux, as validated against the microscopic IK1 method.

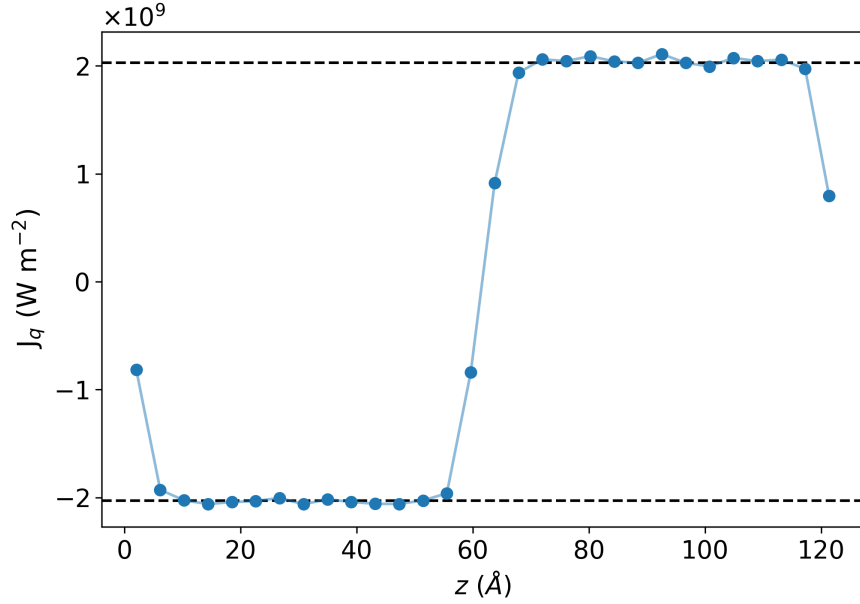


Figure 6.5: Comparison of the microscopic heat flux (blue symbols) along the direction of the thermal gradient, calculated using the IK1 formulation, with the flux derived from the continuity relation shown as a dashed black line. Results correspond to the same representative NEMD simulation shown in Figure 6.2.

Figure 6.6 presents the equations of state (EOS) obtained along the liquid branch of the coexistence curve, derived from the local temperature and density profiles shown in the second and third panels of Figure 6.1. The slight curvature observed in these profiles arises from spatial variations in thermal conductivity and thermal expansivity, reflecting the range of thermodynamic states sampled under non-equilibrium conditions. The simulated EOS data exhibit excellent agreement with both experimental measurements [15] and previous equilibrium simulations using the TraPPE model [17], confirming the reliability of the force field in reproducing the coexistence properties of ethanol. Moreover, the close correspondence between equilibrium and non-equilibrium results indicates that the system maintains local equilibrium under the applied thermal gradients (approximately $1 \text{ K/\AA}$), thereby validating that the simulations were conducted within the linear response regime.

In addition, the fluctuation-derived thermophysical properties obtained from equilibrium simulations, including the isobaric thermal expansion coefficient, isothermal compressibility, and the adiabatic speed of sound (Table 6.2), show overall good agreement with experimental measurements [33–35]. Small discrepancies remain, with the TraPPE model predicting slightly

higher compressibility and thermal expansivity near 300 K and ambient pressure.

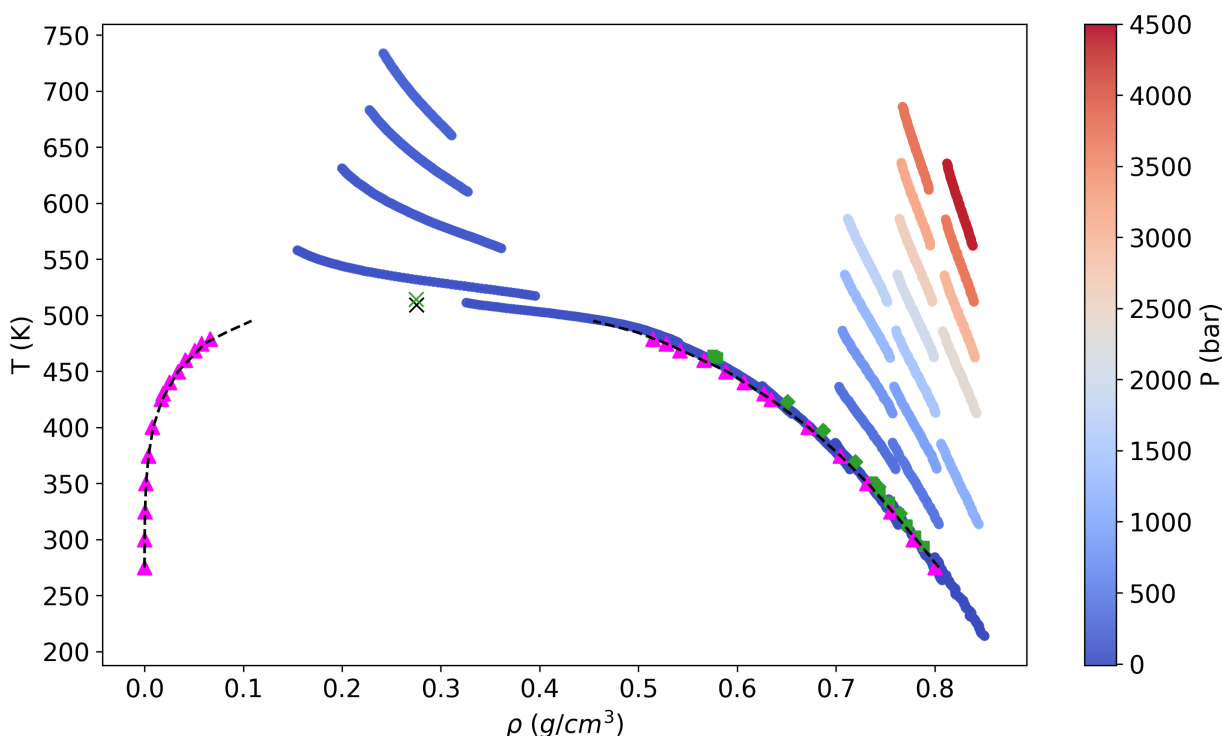


Figure 6.6: Equations of state (EOS) derived from the local temperature and density profiles obtained from the Non-Equilibrium Molecular Dynamics (NEMD) simulations. Each curve corresponds to an isobar, color-coded according to the average pressure determined from the NEMD data (see color bar for pressure values). Coexistence lines from direct liquid–vapor coexistence simulations in the NVT ensemble are shown as magenta triangles. NEMD data were averaged over ten independent replicas, whereas the equilibrium NVT coexistence simulations were averaged over three independent replicas. The dashed lines represent the liquid–vapor coexistence boundaries of the TraPPE model from Reference [17]. The black “x” denotes the TraPPE critical point (509.1 K, 0.276 g/cm³), while the green “x” marks the experimental critical point [36]. Experimental data from References [15, 34] are plotted as green square and diamond symbols, respectively.

6.3.2 Thermal Transport in Ethanol

The thermal conductivities of ethanol obtained from NEMD simulations at different thermodynamic states along the liquid–vapor saturation line are presented in Figure 6.7(a). A gradual decrease in thermal conductivity is observed with increasing temperature as the system approaches the critical point, in line with experimental observations [15, 37]. The simulations systematically underestimate the experimental values, consistent with deviations previously reported for the OPLS force field [38]. Subsequent studies employing the OPLS-AA model

yielded slightly higher conductivities, although they remained below experimental measurements near 300 K [39]. Previous simulations using a rigid, non-polarizable three-site model of ethanol yielded thermal conductivities that were consistent with experimental data [40].

The decrease in thermal conductivity with increasing temperature can be rationalized in terms of the thermal expansion of the liquid. As discussed in Section 1.1, the Bridgman relation [2] (Equation 1.1) provides a phenomenological framework linking the thermal conductivity to the molecular volume and the speed of sound. Along the saturation line, the simulated sound velocity decreases steadily with temperature, primarily due to the increase in isothermal compressibility (see Table 6.2 and Equation 2.85). Simultaneously, the liquid density also decreases with rising temperature. Both effects reduce the efficiency of energy transfer within the liquid, resulting in the observed decrease in thermal conductivity predicted by the Bridgman relation. The simulated sound velocities are approximately 15% lower than the experimental measurements reported by Ahmadi *et al.* [34], which, according to the Bridgman framework, also contributes to the underestimation of the simulated conductivities.

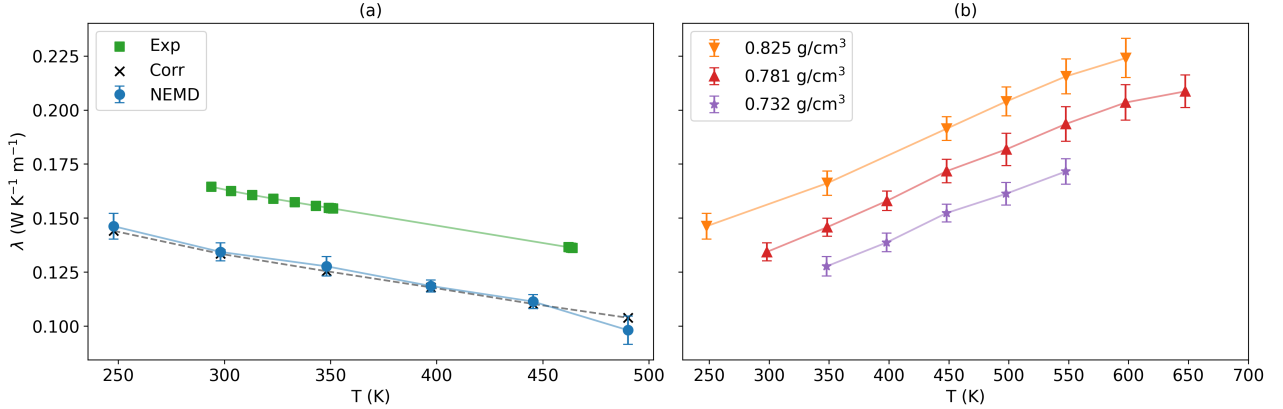


Figure 6.7: (a) Thermal conductivity of ethanol along the liquid–vapor saturation line. Green squares denote experimental data from Reference [15], while blue circles correspond to thermal conductivities obtained from NEMD simulations in this work. All reported NEMD results represent averages over ten independent simulation replicas, with each replica evaluated using successive 10 ns segments of the production trajectory. The error bars reflect the aggregated statistical uncertainty. The “ $\times$ ” symbols represent values predicted by the empirical correlation of Assael *et al.* [37], scaled by a factor of 0.83 to match the average offset between experimental and simulated conductivities. (b) Thermal conductivities from NEMD simulations performed at isochores of 0.825, 0.781, and 0.732 g/cm^3 over the temperature range 250–700 K. The lines in panels (a) and (b) are included as a visual guide.

Assael *et al.* [37] developed a semi-empirical correlation that reproduces the experimental

thermal conductivity of ethanol as a function of temperature and density. When this correlation is scaled by a factor of 0.83, corresponding to the average difference between the simulated and experimental conductivities, it aligns closely with the NEMD results shown in Figure 6.7(a). This scaling factor is consistent with the roughly 15% lower sound velocities predicted by our simulations relative to experiment, further supporting the interpretation based on the Bridgman relation. Although this relation is not expected to provide quantitatively exact values, it captures the essential coupling between thermodynamic properties and thermal transport, providing a physically consistent explanation for the systematic underestimation of the simulated thermal conductivity. This interpretation is further supported by the results for supercooled water presented in Section 3.3.2, where a similar correlation between the speed of sound and thermal conductivity was observed.

Table 6.2: Thermodynamic fluctuation and dielectric properties of ethanol evaluated from equilibrium molecular dynamics simulations along the liquid–vapor saturation line using GROMACS. The quantities reported are: temperature (T), density (ρ), isobaric thermal expansion coefficient (α), isothermal compressibility (κ_T), adiabatic speed of sound (c_s), static dielectric constant (ϵ_r), and Debye relaxation time (τ_D). The term $\delta\lambda$ denotes the deviation between the total thermal conductivity λ and the component arising from coupling with thermal polarization effects, as defined in Equation 6.4. Values in parentheses indicate standard deviations from three independent equilibrium simulation replicas.

T [K]	ρ [g cm ⁻³]	α [10 ⁻⁴ K ⁻¹]	κ_T [10 ⁻¹⁰ m ³ J ⁻¹]	c_s [m s ⁻¹]	ϵ_r	τ_D [ps]	$\delta\lambda$ [mW K ⁻¹ m ⁻¹]	$\delta\lambda$ [%]
300.0	0.781	14.7(1.2)	15.0(0.8)	1033.6(43.4)	17.51(0.10)	110.94(2.33)	-0.13	0.09
350.0	0.732	18.8(1.4)	22.9(0.7)	881.8(21.0)	12.90(0.03)	24.56(0.60)	-0.39	0.30
399.9	0.673	30.4(2.6)	42.9(1.4)	721.0(18.2)	9.24(0.02)	8.10(0.04)	-0.03	0.003
449.9	0.590	48.7(3.4)	104.0(3.3)	528.9(14.4)	6.59(0.01)	3.45(0.01)	-2.60	2.34
495.0	0.452	194.7(6.2)	818.8(9.3)	283.4(19.3)	4.53(0.01)	1.76(0.01)	-65.4	66.7

Figure 6.7(b) shows the thermal conductivity of ethanol along several high-density isochores, extending up to 700 K, where the system reaches pressures as high as 4500 bar. The results reveal that thermal conductivity increases systematically with density, reflecting enhanced molecular packing that facilitates more efficient energy transfer, consistent with the Bridgman framework. Within the dense liquid regime (0.732–0.825 g/cm³), the conductivity increases approximately

linearly with temperature, with a slope of about $0.23 \text{ mW K}^{-2} \text{ m}^{-1}$. This temperature dependence agrees well with experimental data [37], which exhibit a comparable slope of roughly $0.3 \text{ mW K}^{-2} \text{ m}^{-1}$, confirming the consistency between simulated and experimental trends.

6.3.3 Thermal Polarization Inversion and Reference Point Dependence in Liquid Ethanol

Figure 6.8 shows the variation of the thermal polarization coefficient, S_{TP} , along the liquid saturation line of ethanol. The results confirm that a thermal gradient induces a finite polarization in ethanol, with a magnitude comparable to that reported for water [9] and acetonitrile [10]. Around 400 K, the direction of the induced polarization field reverses. This behavior is further illustrated by the temperature dependence of the electrostatic potential shown in Figure 6.9, where S_{TP} corresponds to the negative first derivative of that relation, as defined in Equation 2.75. Above the inversion temperature, the total thermal polarization coefficient becomes negative. A similar sign reversal has also been reported for water, although the exact inversion temperature varies with the force field employed. Based on simulations with the TIP4P/2005 and OPC models, both of which accurately reproduce the experimental thermal expansion, Chapman *et al.* [9] estimated that the inversion in real water would occur between 400 and 500 K, consistent with their phenomenological relation (Equation 3.2).

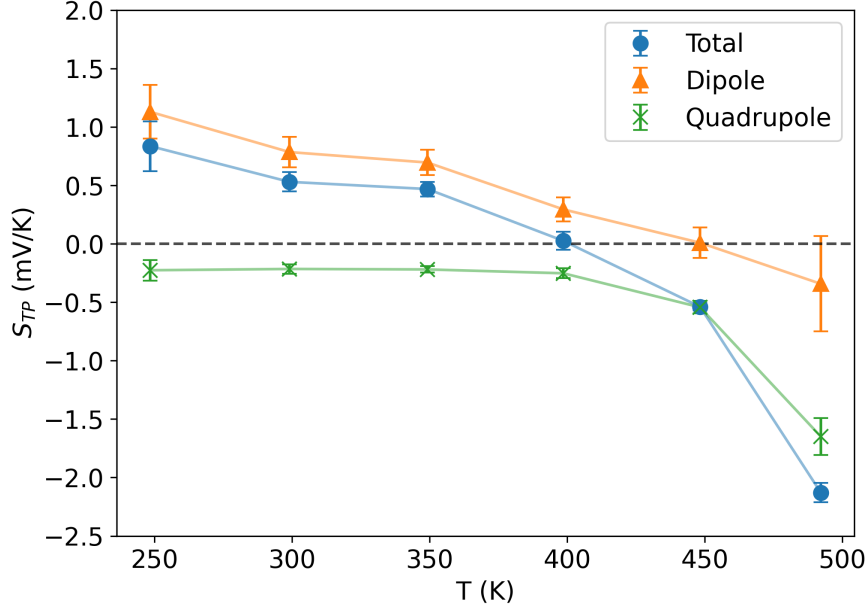


Figure 6.8: Thermal polarization coefficient of liquid ethanol and its decomposition into dipolar and quadrupolar components along the saturation curve. All reported values were averaged over ten independent NEMD simulation replicas. The black dashed line marks the zero reference level at $S_{TP} = 0$ mV/K. Both the dipole and quadrupole contributions were evaluated using the molecular center of mass as the reference. Solid curves are included to guide the eye.

The occurrence of a thermal polarization inversion in water can be rationalized by examining how different contributions combine to form the total electrostatic field. As described in previous theoretical studies [41, 42], the charge density can be expanded in a multipole series that includes dipolar (P), quadrupolar (Q), and higher-order components. Calculating these electrostatic moments requires specifying a molecular reference point. Following the approach in Reference [41], the molecular center of mass is most commonly used for this purpose, although other reference positions are equally valid. The influence of this reference choice on the dipolar contribution in water has been investigated in recent studies [43, 44].

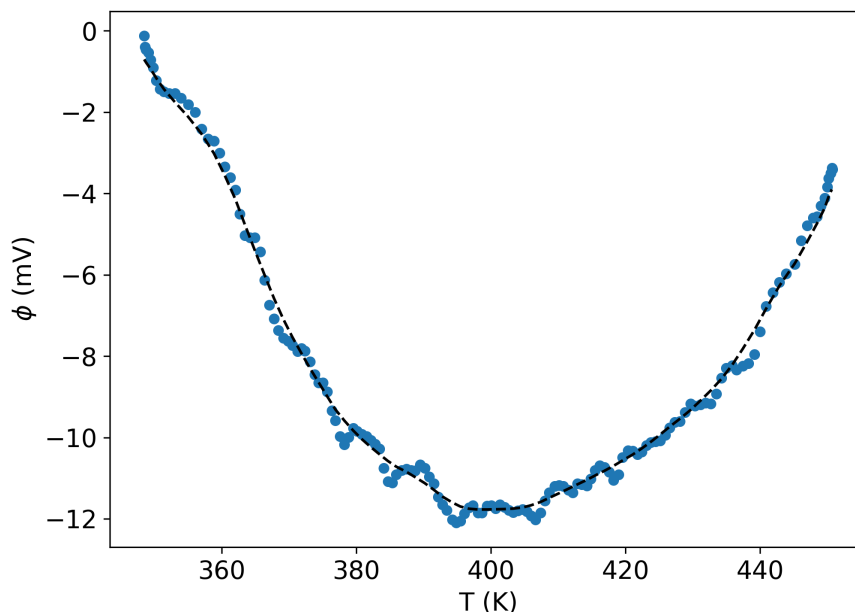


Figure 6.9: Electrostatic potential profile as a function of temperature from a representative NEMD simulation, where the hot and cold thermostats were maintained at 450 K and 350 K, respectively. The system corresponds to an average temperature of 397 K and a density of 0.672 g/cm^3 . The black dashed line represents a smoothed fit obtained using a one-dimensional Gaussian filter with a standard deviation of five sampling intervals for improved visual clarity.

Figure 6.10 presents the total electrostatic potential together with its dipolar and quadrupolar contributions as functions of temperature, calculated for several molecular reference points in ethanol across the ranges 250–350 K and 350–450 K. The selected reference points include the molecular center of mass and the atomic sites corresponding to CH_3 , CH_2 , O, and H. The corresponding thermal polarization coefficients are summarized in Table 6.3.

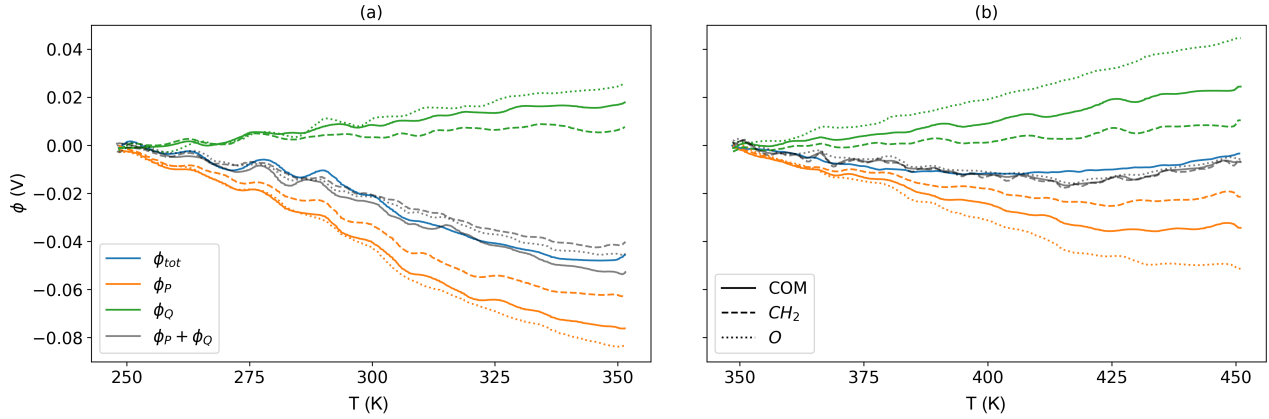


Figure 6.10: Results for the electrostatic potential in liquid ethanol, together with the dipolar and quadrupolar components, from sample NEMD runs over two temperature intervals: (a) 250–350 K and (b) 350–450 K. The mean state points of these simulations correspond to 298 K and 0.781 g/cm³ in panel (a), and 397 K and 0.672 g/cm³ in panel (b). In each case, the sum of the dipolar and quadrupolar terms is shown in black and compared with the full potential, which is plotted in blue. Line styles distinguish different molecular reference choices: center of mass (solid), CH₂ group (dashed), and oxygen atom (dotted).

The dipolar and quadrupolar components show a modest dependence on the choice of reference, reflecting variations in how molecular multipoles are spatially assigned to each bin along the temperature gradient. Nevertheless, the sum of these two contributions remains nearly constant and agrees, within statistical uncertainties, with the total thermal polarization coefficient, $S_{TP,tot}$, obtained directly from integrating the full charge density. The average deviation between the total and the summed dipole–quadrupole ($P + Q$) terms remains within 4–6%. These small differences arise from instantaneous charge density fluctuations, which slightly affect the slopes extracted from linear fits near the target temperature. This minor discrepancy is also observed in the bottom panel of Figure 6.1, which compares the electrostatic potential derived from the charge density integral with that reconstructed from molecular multipoles using the center of mass as the reference point.

Table 6.3: Dipolar and quadrupolar contributions to the thermal polarization coefficient S_{TP} in liquid ethanol, evaluated using different molecular reference points: the center of mass (COM), the CH_3 and CH_2 groups, and the oxygen and hydrogen atoms. The table lists the dipolar term $S_{TP,P}$, quadrupolar term $S_{TP,Q}$, their sum, and the total S_{TP} obtained from the atomic charge density. All values are reported in mV/K and correspond to two representative NEMD simulations performed over the ranges 250–350 K and 350–450 K, with average temperatures of 298 K and 397 K, respectively. Standard deviations across ten independent NEMD simulation replicas are shown after the $\pm$ symbol.

298 K				
Ref	$S_{TP,P}$	$S_{TP,Q}$	$S_{TP,P} + S_{TP,Q}$	$S_{TP,\text{tot}}$
COM	0.785 $\pm$ 0.131	-0.215 $\pm$ 0.040	0.570 $\pm$ 0.137	0.530 $\pm$ 0.083
CH_3	0.844 $\pm$ 0.120	-0.280 $\pm$ 0.042	0.564 $\pm$ 0.127	0.530 $\pm$ 0.083
CH_2	0.683 $\pm$ 0.133	-0.120 $\pm$ 0.088	0.563 $\pm$ 0.159	0.530 $\pm$ 0.083
O	0.889 $\pm$ 0.149	-0.356 $\pm$ 0.096	0.533 $\pm$ 0.177	0.530 $\pm$ 0.083
H	0.674 $\pm$ 0.178	-0.112 $\pm$ 0.089	0.562 $\pm$ 0.199	0.530 $\pm$ 0.083
397 K				
Ref	$S_{TP,P}$	$S_{TP,Q}$	$S_{TP,P} + S_{TP,Q}$	$S_{TP,\text{tot}}$
COM	0.295 $\pm$ 0.104	-0.252 $\pm$ 0.042	0.043 $\pm$ 0.112	0.026 $\pm$ 0.077
CH_3	0.332 $\pm$ 0.063	-0.237 $\pm$ 0.018	0.095 $\pm$ 0.066	0.026 $\pm$ 0.077
CH_2	0.207 $\pm$ 0.024	-0.124 $\pm$ 0.016	0.083 $\pm$ 0.029	0.026 $\pm$ 0.077
O	0.548 $\pm$ 0.054	-0.453 $\pm$ 0.033	0.095 $\pm$ 0.063	0.026 $\pm$ 0.077
H	0.251 $\pm$ 0.040	-0.174 $\pm$ 0.015	0.077 $\pm$ 0.043	0.026 $\pm$ 0.077

For completeness, we also considered the octupole moment density [41],

$$O_{zzz}(z) = \frac{1}{A} \left\langle \sum_{m=1}^{N_m} \delta(z - z_m) \frac{1}{6} \sum_{i \in m}^{N_{\text{charges}}} q_{i,m} z_{i,m}^3 \right\rangle, \quad (6.5)$$

which was evaluated by co-author Aidan Chapman and reported in Reference [1]. The octupolar contribution was essentially uniform at approximately 1.2×10^{-5} V over 250–350 K (with the oxygen atom chosen as the reference), which is three orders of magnitude smaller than the dipolar and quadrupolar components spanning -0.08 to 0.04 V. This confirms that higher-order multipoles have a negligible effect and that truncating the expansion at the dipole–quadrupole

level is sufficient to reproduce the electrostatic potential derived from the full charge density.

Additionally, the dipolar and quadrupolar terms always appear with opposite signs, independent of the molecular reference point used (see Figure 6.10 and Table 6.3). This persistent sign opposition explains the emergence of the inversion temperature as a balance between the P and Q contributions. Since this balance is maintained across all reference points examined, the center of mass is adopted as the reference for all subsequent analyses.

As outlined in classical electrodynamics [41], decomposing the electrostatic response into molecular multipole components provides a useful framework for interpreting the polarization behavior of molecular liquids. Along the liquid saturation line, increasing temperature leads to a clear and progressive reduction of the dipolar contribution (see Figure 6.8), reflecting the gradual disruption of collective dipolar alignment as hydrogen bonding becomes progressively less persistent. Importantly, the molecular dipole magnitude of ethanol is reported to be nearly temperature-independent in commonly used nonpolarizable force fields [26]. The observed decay therefore primarily reflects changes in collective dipolar correlations that govern the dipolar contribution to the thermal polarization. For temperatures below 400 K, the quadrupolar contribution remains comparatively insensitive to temperature outside the near-critical region. Consequently, the polarization inversion in ethanol is primarily driven by the decay of the dipolar term, while the quadrupolar contribution acts as a slowly varying background of opposite sign.

A direct comparison with water highlights a key underlying difference in the origin of the polarization inversion. In water, the dipolar contribution remains nearly constant over most thermodynamic states, including ambient and mildly supercooled conditions (see Figure 3.10 in Chapter 3), and only exhibits a modest weakening as the liquid–vapor critical region is approached [12]. In contrast, the quadrupolar contribution in water displays a pronounced temperature dependence and closely follows the trend of the isobaric thermal expansion coefficient. As a result, the polarization inversion in water arises predominantly from the varying quadrupolar contribution, which progressively counterbalances the nearly constant dipolar component of opposite sign.

In ethanol, this behavior can be traced back to its distinct molecular structure. The presence of a nonpolar ethyl group and a comparatively weaker hydrogen-bond network render dipolar

alignment more susceptible to disruption, even at temperatures well below the critical point. These structural characteristics also limit the sensitivity of the quadrupolar contribution to thermal expansion, such that it remains nearly constant until critical density fluctuations become significant above approximately 450 K.

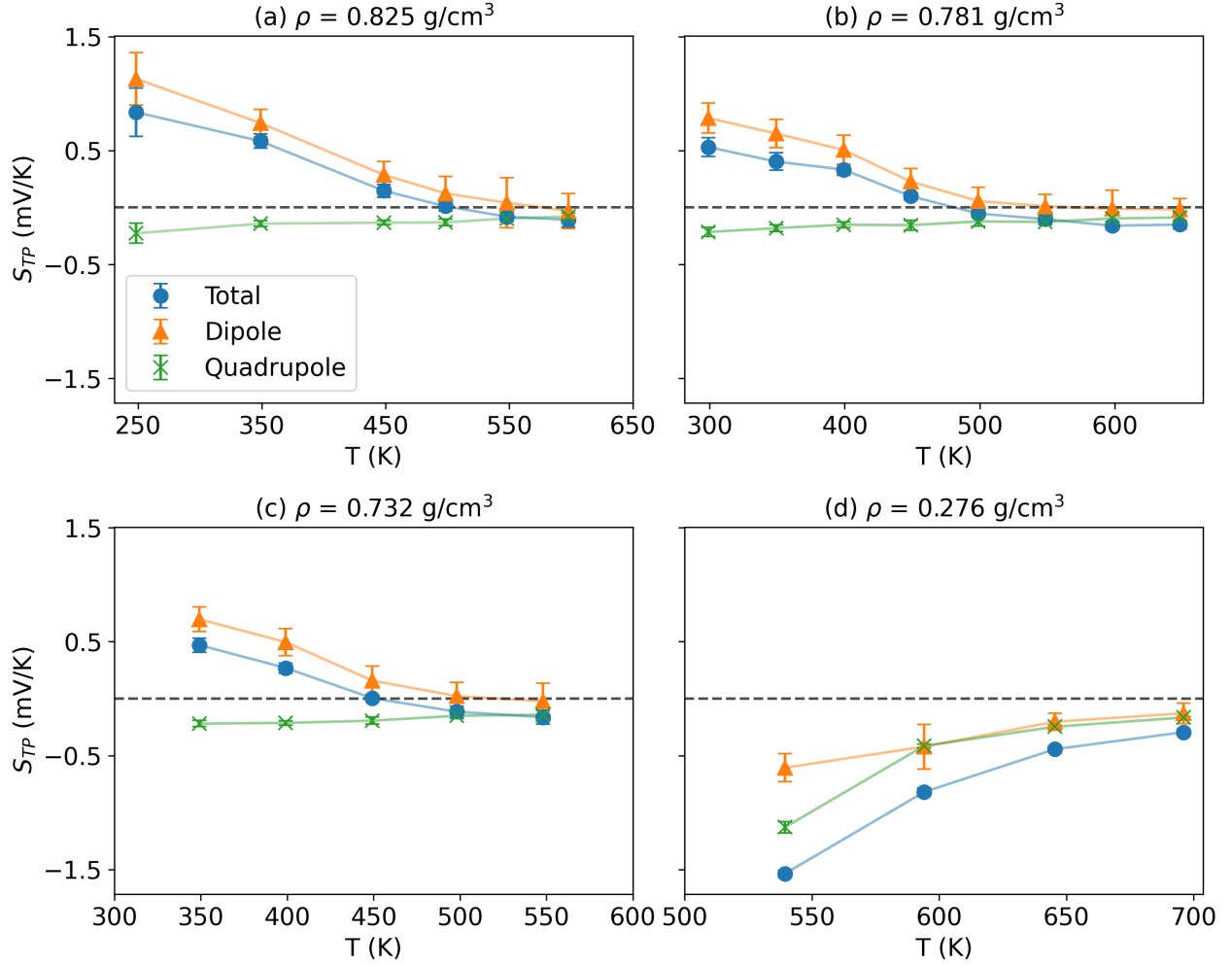


Figure 6.11: Thermal polarization coefficient and its dipolar and quadrupolar components obtained from NEMD simulations performed along several isochores. All values shown represent averages over ten independent NEMD simulation replicas. The black dashed line marks the zero reference level at $S_{TP} = 0$ mV/K. Both dipole and quadrupole terms were evaluated with respect to the molecular center of mass.

Our findings show that thermal polarization increases notably as the liquid approaches its critical point. The magnitude of this enhancement reaches values comparable to those reported near the primary liquid–vapor critical point of water, where $S_{TP} \approx -4$ mV/K [12]. A similar rise in polarization has also been observed in simulations of supercooled water, within the

thermodynamic region associated with the proposed liquid–liquid critical point, as discussed in Section 3.3.3. In ethanol, we observe a comparable strengthening of the total thermal polarization coefficient in the vicinity of the critical region. This enhancement is primarily driven by a pronounced increase in the quadrupolar contribution, consistent with the sharp growth of the isobaric thermal expansion coefficient (see Table 6.2). Upon approaching criticality, enhanced density fluctuations are likely to dominate over the structural constraints imposed by the nonpolar ethyl group and the weaker hydrogen-bond network, thereby shaping the temperature dependence of the quadrupolar contribution.

Figure 6.11 presents the thermal polarization coefficient calculated along several isochores. For the high-density cases shown in Figures 6.11(a)–(c), distinct inversions of the thermal polarization are observed for each isochore, arising from the counterbalance between dipolar and quadrupolar contributions. The corresponding inversion temperatures of 451, 481, and 505 K increase systematically with density, for ethanol densities of 0.732, 0.781, and 0.825 g/cm³, respectively. In contrast to the pronounced enhancement observed along the liquid–vapor coexistence line near the critical point, the liquid isochores exhibit a considerably weaker polarization response above the inversion temperature, with S_{TP} remaining below 0.2 mV/K. Furthermore, along the critical isochore at 0.276 g/cm³, S_{TP} increases sharply with decreasing temperature, as shown in Figure 6.11(d). Together, these results confirm that the thermal polarization effect becomes strongly amplified under near-critical conditions.

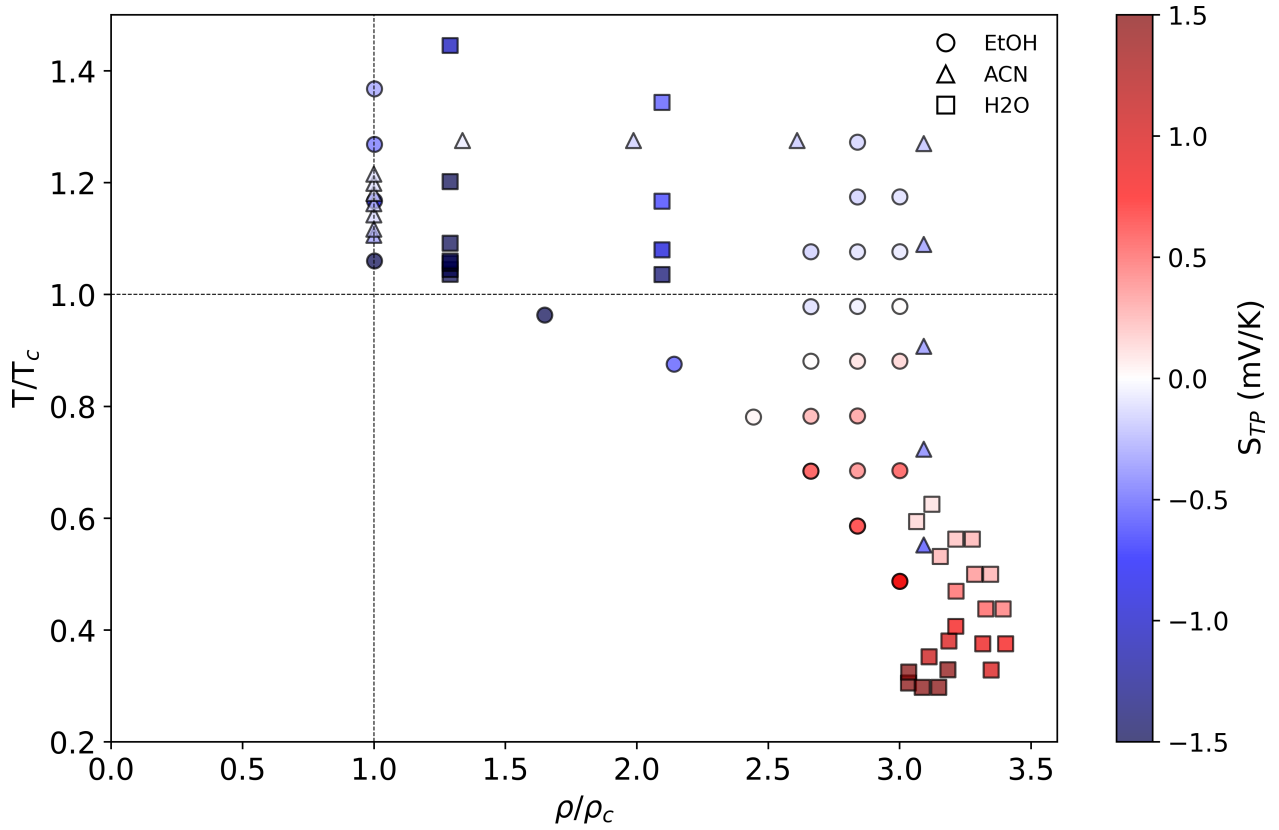


Figure 6.12: Comparison of the thermal polarization coefficient for ethanol (this work, circles), acetonitrile (triangles, data from [10]), and TIP4P/2005 water (squares, data from [12, 45]). The values are presented in the reduced temperature–density plane, normalized by the respective critical properties of each fluid. Critical temperatures and densities were taken from Reference [17] for TraPPE ethanol, Reference [46] for TraPPE acetonitrile, and Reference [47] for TIP4P/2005 water. The color scale represents both the magnitude and sign of S_{TP} .

Figure 6.12 shows a comparison of the thermal polarization coefficients for ethanol, acetonitrile [10], and water [12, 45], expressed in reduced units normalized by their respective critical temperatures and densities. Under subcritical conditions, both water and ethanol display a sign reversal in their thermal polarization coefficients, S_{TP} , changing from positive to negative values as the systems approach the critical region. In water, this inversion has been attributed to a competition between a positive dipolar contribution and a negative quadrupolar contribution, with the quadrupolar term exhibiting a pronounced temperature dependence [9, 11]. An analogous competition between dipolar and quadrupolar contributions of opposite sign is found in ethanol. In this case, however, the inversion of S_{TP} is primarily driven by the temperature dependence of the dipolar contribution. In contrast, acetonitrile maintains a consistently negative S_{TP} across the entire temperature range investigated, and both its dipolar and higher-order contributions

are negative in the liquid phase [10].

This comparison indicates that hydrogen-bond network formation may facilitate a positive dipolar contribution by stabilizing orientational correlations and local polarity. Within this framework, stronger hydrogen bonding (as in water) can sustain a nearly temperature-independent dipolar contribution over a broad range, whereas weaker hydrogen bonding (as in ethanol) is more readily disrupted with increasing temperature, leading to a progressive reduction of the dipolar term under subcritical conditions. By contrast, in non-hydrogen-bonded polar liquids such as acetonitrile, the dipolar contribution remains negative throughout the liquid regime, precluding the emergence of competing opposite-sign terms and therefore preventing an inversion of S_{TP} [10].

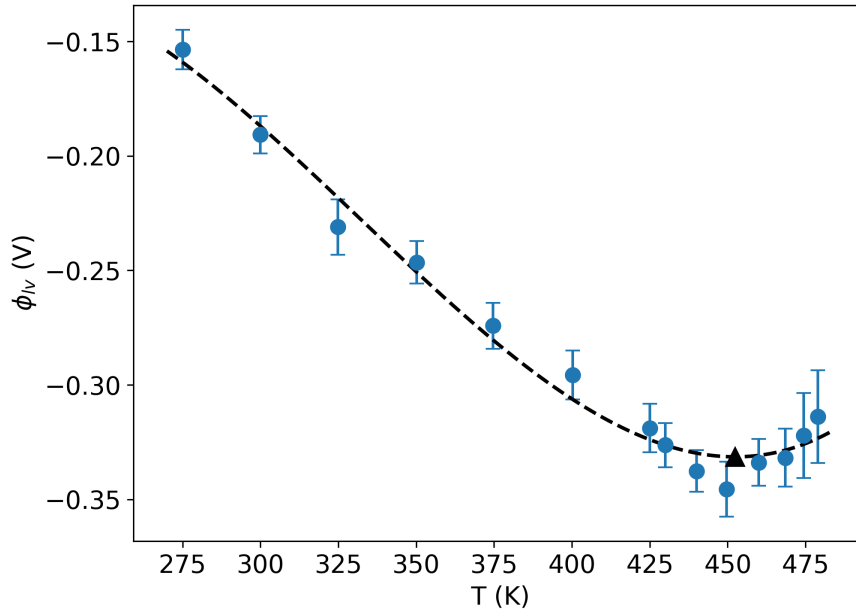


Figure 6.13: Temperature dependence of the surface potential at the ethanol liquid–vapor interface, obtained from equilibrium NVT simulations. The reported data correspond to averages obtained from three independent simulation replicas to ensure statistical reliability. The black dashed curve shows a third-order polynomial fit to the simulation data, expressed as $\phi_{lv} = 3 \times 10^{-8}T^3 - 3 \times 10^{-5}T^2 + 9 \times 10^{-3}T - 0.9$. The black triangle indicates the local minimum of the surface potential, corresponding to the temperature ($T = 452.5$ K) where the derivative with respect to temperature changes sign.

The temperature dependence of the liquid–vapor interfacial surface potential has been analyzed in a previous study [9]. Simulations based on the SPC/E water model [48] reported a surface potential gradient of approximately -1 mV/K, in agreement with experimental

measurements obtained for aqueous solutions [49]. For water, the surface potential exhibits a pronounced minimum between 350 and 425 K. Moreover, a linear correlation was identified between the inversion temperature of the thermal polarization coefficient and the position of this minimum across different water models [9].

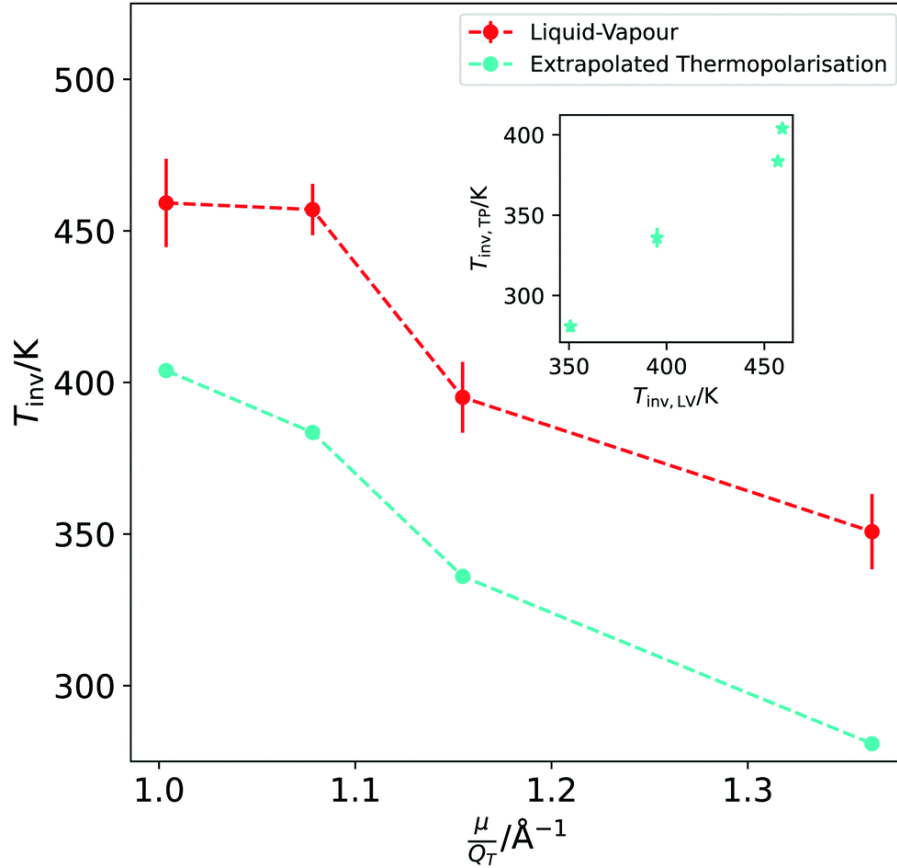


Figure 6.14: Temperature of thermal polarization inversion, $T_{\text{inv,TP}}$, together with the inversion temperature of the temperature derivative of the liquid–vapor surface potential, $T_{\text{inv,LV}}$, for several water models. The inset shows the correlation between $T_{\text{inv,TP}}$ and $T_{\text{inv,LV}}$. Reproduced from Reference [9] under the Creative Commons CC BY 4.0 license.

The temperature dependence of the liquid–vapor interfacial surface potential has been analyzed in a previous study [9]. Simulations based on the SPC/E water model [48] reported a surface potential gradient of approximately -1 mV/K , in agreement with experimental measurements obtained for aqueous solutions [49]. For water, the surface potential exhibits a pronounced minimum between 350 and 425 K. Moreover, a linear correlation was identified between the inversion temperature of the thermal polarization coefficient and the position of this minimum across different water models, as shown in Figure 6.14. Although the absolute inversion temperatures vary among models, the systematic offset between the two characteristic

temperatures is preserved: the inversion temperature of the thermal polarization coefficient is consistently lower by approximately 50 K than the temperature associated with the liquid–vapor surface potential minimum [9]. The persistence of this offset across different force fields suggests a common underlying structural origin linking the two phenomena.

In this chapter, we extend this analysis to ethanol to investigate whether a similar relationship exists between the inversion of thermal polarization and the minimum in its liquid–vapor surface potential. The temperature dependence of the ethanol surface potential was evaluated through equilibrium NVT simulations (see Figure 6.3). The resulting profile is shown in Figure 6.13. At lower temperatures, the surface potential decreases with increasing temperature, with an approximate slope of 1 mV/K, mirroring the behavior of the thermal polarization coefficients presented in Figures 6.8 and 6.11.

A local minimum appears in the surface potential near 450 K, beyond which the slope changes sign, as illustrated in Figure 6.13. The inversion temperature of the thermal polarization coefficient, around 400 K, occurs roughly 50 K below the temperature at which the surface potential reaches its minimum. This behavior is consistent with the trend reported for water [9] (see Figure 6.14), where the thermal polarization inversion temperature similarly lies below the temperature corresponding to the minimum in the surface potential. In ethanol, the comparable offset between these two characteristic temperatures further supports a correlation between bulk thermal polarization inversion and interfacial electrostatic reorganization. The emergence of this pattern in both liquids may reflect their shared structural features, particularly the presence of a hydrogen-bond network that governs molecular orientational ordering in both bulk and interfacial environments.

6.3.4 Coupling Between Thermal Polarization and Heat Transport in Ethanol

Non-equilibrium thermodynamics predicts that cross effects such as thermal polarization can lead to a reduction in the thermal conductivity of a fluid [4]. These coupling effects vanish at the inversion temperature, where the thermal polarization coefficient S_{TP} becomes zero. To

evaluate the influence of thermal polarization on the thermal conductivity of ethanol, we employ Equation 6.4 [10], which incorporates the static dielectric permittivity and the Debye relaxation time.

Table 6.2 lists the values of the static dielectric permittivity and the Debye relaxation times obtained at various thermodynamic states along the liquid–vapor coexistence curve, covering temperatures from 300 to 495 K. At 300 K, the simulated dielectric permittivity is slightly lower than experimental measurements at the same temperature [28, 29], but it agrees well with previous simulations employing the OPLS potential [27]. The approximately 25% deviation from experiments can be partly attributed to the simplicity of the non-polarizable united-atom model. As noted by Saiz *et al.* [27], including the high-frequency dielectric constant ($\epsilon_\infty \approx 1.85$) improves the agreement between simulations and experiments.

The decrease in dielectric constant with increasing temperature reflects the progressive loss of dipolar alignment as thermal motion intensifies. Within linear response fluctuation theory, the static dielectric constant increases with both density and the degree of orientational correlation between neighboring dipoles [50]. As temperature rises and the system approaches critical conditions, the density decreases and the orientational correlations sustained by the hydrogen-bond network are progressively disrupted. This leads to a reduction in the amplitude of total dipole moment fluctuations that determine the dielectric response. The same loss of collective dipolar alignment is reflected in the weakening of the dipolar contribution to the thermal polarization coefficient in Figure 6.8. The Debye relaxation time, determined by fitting the total dipole moment autocorrelation function to an exponential decay, also decreases markedly with temperature. This trend mirrors that observed in water, where relaxation times follow an Arrhenius-type temperature dependence associated with reduced viscosity [51, 52]. The relaxation time obtained at ambient temperature agrees well with experimental values corresponding to bulk reorientational dynamics [28, 29].

The reduction in thermal conductivity arising from the coupling between thermal polarization and heat flux is presented in Table 6.2. The correction, computed using Equation 6.4, remains small at ambient conditions and vanishes at the inversion point where $S_{TP} = 0$. In rapidly rotating molecular liquids such as acetonitrile, this coupling effect is more pronounced, producing

an approximately 4% decrease in thermal conductivity at 300 K [10]. As ethanol approaches its critical region, however, the combination of shorter Debye relaxation times and larger S_{TP} values results in a more substantial suppression of thermal conductivity. Consequently, near-critical conditions amplify the influence of thermal polarization on heat transport.

6.4 Conclusions

Through non-equilibrium molecular dynamics simulations employing accurate empirical force fields, we investigated the mechanisms of heat transport and thermally induced polarization in ethanol across a broad range of thermodynamic states, spanning both liquid and supercritical phases. The TraPPE model accurately reproduces the overall temperature dependence of ethanol’s thermal conductivity. Consistent with experimental observations, the thermal conductivity decreases with increasing temperature along the liquid–vapor coexistence curve, whereas at constant density, it increases almost linearly with temperature.

Ethanol exhibits a substantially lower thermal conductivity than water, a difference that can be attributed to its nonpolar alkyl group, which impedes energy transfer but does not modify the fundamental transport mechanism. The TraPPE force field underestimates the thermal conductivity of ethanol by about 15%, a systematic deviation likely linked to an underestimated speed of sound or an overestimated isothermal compressibility. These results provide useful guidance for refining ethanol force fields by focusing on key thermophysical properties that can be assessed through equilibrium fluctuation analyses.

We also demonstrated that applying a thermal gradient induces a measurable polarization in ethanol. The resulting polarization field undergoes inversion both along the liquid–vapor coexistence line and across multiple liquid isochores. This inversion arises from the counterbalance between dipolar and quadrupolar contributions, which act with opposite signs in determining the total thermal polarization coefficient. The molecular moments were evaluated with respect to the molecular center of mass, the most common reference choice, although their values inherently depend on the selected origin. For ethanol, however, alternative reference points yield nearly identical results, indicating that the observed inversion can be consistently interpreted as

the outcome of two opposing electrostatic moment contributions.

The coupling between thermal polarization and heat flux in ethanol suggests that strong polarization responses reduce the efficiency of heat conduction. This effect becomes particularly significant near the critical region, where the amplified polarization response has a pronounced influence on the calculated thermal conductivity. Therefore, accurate evaluation of the thermal conductivity of molecular liquids requires explicit consideration of this coupling.

Thermal polarization has previously been identified in theoretical investigations of hydrogen-bonded systems such as water and in aprotic solvents like acetonitrile. The present results confirm that ethanol also exhibits this behavior. Extending such analyses to a wider range of molecular liquids would provide a broader understanding of the microscopic mechanisms governing thermally induced electrostatic fields and their impact on heat transport. In particular, systematic studies of both hydrogen-bonded and non-hydrogen-bonded simple liquids would help clarify whether the occurrence of thermal polarization inversion and the emergence of a positive dipolar contribution in the liquid phase are general features of polar fluids or instead characteristic of hydrogen-bonded systems. Furthermore, investigating the coupling between thermal and polarization gradients in water under thermodynamic conditions where the hydrogen-bond network is significantly disrupted, such as under high compression as discussed in Chapter 5, would provide further insight into how network connectivity influences the inversion temperature and its relationship with the minimum in the liquid–vapor surface potential.

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Chapter 7

Conclusions and Future Work

7.1 Conclusions

Thermal gradients in molecular liquids and solutions give rise to a variety of coupling phenomena, including thermodiffusion [1, 2], thermoelectricity [3], and thermal polarization [4], where temperature differences induce mass, charge, and polarization fluxes. This thesis examines these processes through extensive non-equilibrium molecular dynamics (NEMD) simulations, providing a unified microscopic perspective on the coupling between temperature fields and the resulting transport and structural responses in liquids. The work focuses on four representative systems: supercooled water, aqueous NaCl and LiCl solutions studied under both supercooled and high-pressure conditions, and the hydrogen-bonded molecular liquid ethanol, thus covering a wide range of thermodynamic states.

The results reveal that thermal transport and coupling phenomena are strongly linked to the microscopic structure and underlying thermodynamic response functions. By bridging equilibrium and non-equilibrium perspectives, this work demonstrates that the observed anomalies in thermal conductivity and other thermally induced coupling effects stem from structural transformations within the hydrogen-bond network and from critical-like fluctuations characteristic of these liquids.

The first part of this thesis examines the thermal transport and polarization of supercooled water using the TIP4P/2005 model. The simulations reproduce the experimentally observed

decrease in thermal conductivity upon cooling [5] and identify a pronounced minimum near 220 K at 1 bar. This minimum coincides with extrema in several key thermodynamic response functions, including the isothermal compressibility, the isobaric thermal expansion coefficient, and the speed of sound, thereby demonstrating a clear correspondence between anomalous heat transport and the underlying thermodynamic behavior. The correlation among these extrema supports the interpretation that the thermal conductivity anomaly arises from critical fluctuations associated with the hypothesized liquid–liquid phase transition (LLPT) in water [6].

A further important finding addresses the thermal polarization of water under temperature gradients. The NEMD simulations reveal the emergence of measurable electrostatic fields, corresponding to thermal polarization coefficients of several mV/K. The sign and magnitude of this coefficient exhibit a non-monotonic temperature dependence, reflecting a subtle interplay between dipolar and quadrupolar contributions [7, 8]. The quadrupolar term, which scales with the isobaric thermal expansion coefficient, dominates the temperature dependence of the total polarization at temperatures above 240 K, while the dipolar component remains nearly constant. In the deeply supercooled regime, however, the dipolar contribution increases significantly, yielding overall thermal polarization coefficients comparable to those observed near the liquid–vapor critical point of water [9]. These results demonstrate that thermal polarization provides an additional microscopic probe of structural order in liquid water and complements the interpretation of its thermodynamic anomalies.

The second part of this thesis extends the investigation to supercooled aqueous NaCl and LiCl solutions. The simulations show that these electrolyte solutions retain the fundamental anomalies of supercooled water, while the presence of ions gradually weakens these features with increasing concentration. The Soret coefficients display complex temperature dependencies, including multiple thermophilic–thermophobic transitions and distinct minima between 220 and 250 K. At low concentrations (1–2 m), the Soret coefficient becomes strongly negative upon cooling, indicating thermophilic behavior, whereas at lower temperatures it reverts to positive values, revealing a second thermophobic regime. These transitions closely correlate with changes in the structural balance between low-density (LDL) and high-density (HDL) water configurations.

The tetrahedral order parameter distributions demonstrate that thermophilic behavior corresponds to enhanced tetrahedral order and a predominance of LDL-like structures, whereas thermophobicity is associated with higher fractions of disordered HDL-like environments. With increasing salt concentration, the hydrogen-bond network becomes progressively disrupted, suppressing both the tetrahedral ordering and the related transport anomalies. Thus, electrolyte addition effectively modulates the LLPT signatures of water and weakens the coupling between structure and transport.

Furthermore, the Seebeck coefficients of NaCl and LiCl solutions exhibit sign reversals within the same temperature interval as the Soret coefficient minima, underscoring the common structural origin of thermodiffusive and thermoelectric responses. Overall, these findings establish thermodiffusion and thermoelectricity as sensitive microscopic probes of the structural heterogeneity in supercooled aqueous solutions and reinforce the interpretation of thermal transport anomalies as signatures of the LLPT.

The third part of this thesis investigates the effect of pressure on the thermal transport and thermodiffusion of 1 m NaCl and LiCl solutions up to 2 GPa. These conditions are relevant to crustal and mantle aqueous fluids, where dissolved salts play an important role in energy and mass transfer [10, 11]. The simulations show that the thermal conductivity increases steadily with pressure for both salts, consistent with the compression of the liquid structure and the resulting enhancement of molecular packing. In contrast, the Soret coefficient displays a pressure-induced shift toward more thermophobic behavior as the hydrogen-bond network collapses and local tetrahedral order diminishes. At pressures above 0.5 GPa, where the hydrogen-bond network is almost completely disrupted, the Soret coefficient reaches a plateau and becomes largely insensitive to further compression. These observations further reinforce the connection between water’s tetrahedral order and the thermophobicity of aqueous solutions, in agreement with experimental findings under ambient conditions [12]. This part of the work advances the understanding of the thermophysical behavior of aqueous electrolyte solutions under planetary and geophysical conditions [13] and supports the incorporation of transport coefficients into geochemical models of mantle fluids [14, 15].

The final part of this thesis explores thermal transport and thermal polarization in liquid

and supercritical ethanol, another hydrogen-bonded molecular liquid. The computed thermal conductivities reproduce the experimentally observed decrease over a broad temperature range along the liquid–vapor coexistence line as the system approaches the critical point. Importantly, ethanol becomes polarized under thermal gradients, exhibiting a sign inversion of the induced electrostatic field around 400 K. This inversion arises from the competition between dipolar and quadrupolar contributions and coincides with a minimum in the liquid–vapor surface potential, analogous to the mechanism identified for water [8]. Near the critical point, the magnitude of the polarization increases markedly, indicating a strong coupling between molecular orientation and density fluctuations. The close correspondence between water and ethanol underscores the generality of thermal polarization coupling in hydrogen-bonded liquids.

Collectively, this thesis integrates equilibrium and non-equilibrium molecular dynamics simulations with detailed structural analyses to investigate molecular liquids and aqueous solutions. It demonstrates that heat transport and thermally induced coupling effects are governed by the microscopic structure and the thermodynamic response of the fluid. Furthermore, the findings show that non-equilibrium observables such as the thermal conductivity and the Soret and Seebeck coefficients serve as sensitive diagnostic indicators of structural transitions in liquids, including the LLPT in water and its progressive weakening in electrolyte solutions.

7.2 Future Work

Future work can be designed to directly test the hypotheses proposed throughout this thesis regarding the microscopic origins of thermal transport and thermally induced coupling effects. In particular, targeted simulation tests that decouple individual physical contributions would provide robust validation of the proposed mechanisms. For example, in aqueous electrolyte solutions, independently varying ionic masses and partial charges would enable a systematic separation of mass transport and electrostatic effects. Complementary analyses of density–concentration correlations, hydration shell stability, and local structural ordering in the deeply supercooled regime would allow a more explicit evaluation of the competing mechanisms proposed to govern thermodiffusion. Extending structural investigations under compression to quantify changes

in hydrogen-bond connectivity and orientational ordering would further clarify how structural reorganization relates to the observed increase in thermophobic behavior.

Beyond mechanism isolation, broader simulation studies are required to assess the generality of the phenomena identified here. Extending similar analyses to a wider range of molecular liquids, including both hydrogen-bonded and non-hydrogen-bonded simple fluids, would help establish whether thermal polarization inversion in the liquid phase is a generic feature of polar systems or instead characteristic of hydrogen-bonded networks. Furthermore, examining the coupling between heat and polarization fluxes in water under thermodynamic conditions where the hydrogen-bond network is substantially weakened, such as under high compression, would clarify how changes in network connectivity influence the inversion temperature and its relationship with the liquid–vapor surface potential.

In parallel, complementary experimental investigations of aqueous electrolyte solutions could provide valuable validation of the predicted structural and transport behavior. High-pressure X-ray and neutron scattering, as well as X-ray absorption spectroscopy [16, 17], could be employed to examine pressure- and temperature-induced modifications in coordination number and hydrogen-bond network structure, including in mildly supercooled regimes. Furthermore, thermal diffusion forced Rayleigh scattering [18] could be used to measure thermodiffusion under these conditions, thereby enabling a direct comparison between transport coefficients and the underlying structural changes.

Another promising direction involves the use of flexible and polarizable water models, which explicitly account for intramolecular vibrations and electronic polarization, effects that may become significant at high pressures or low temperatures. Previous studies have shown that flexible variants of the TIP4P/2005 model yield slightly higher thermal conductivities and modified hydrogen bond dynamics compared with their rigid counterparts [8]. A systematic exploration of such effects will help quantify the role of molecular flexibility in heat and mass transport processes.

Moreover, the development of machine learning (ML) based force fields trained on *ab initio* potential energy surfaces provides a promising route toward quantitatively accurate simulations of transport phenomena. These ML potentials can capture many-body and anharmonic interactions

beyond classical empirical models, as demonstrated for flexible first principles water potentials and AI-assisted optimization of charge-scaled models [19–22]. Incorporating nuclear quantum effects through quantum corrected thermostats or path integral approaches represents another essential step toward predictive accuracy [23, 24]. Recent work has shown that these effects, particularly the depopulation of librational modes, strongly influence vibrational energy transfer and thermal conductivity in water [25]. Hence, developing force fields capable of describing water under non-equilibrium conditions would be of considerable interest for future studies.

Another important research direction concerns establishing a predictive microscopic framework for the Soret coefficient in electrolyte solutions. While the present results demonstrate that ion type and concentration strongly influence the thermophoretic response, a systematic mapping between solute properties and the resulting Soret coefficient remains to be developed. Molecular dynamics studies of binary Lennard-Jones mixtures have revealed clear scaling relationships with mass, size, and interaction strength, with the mass ratio often emerging as a key control parameter [26]. Extending such systematic analyses to aqueous electrolytes would allow identification of analogous trends in realistic molecular systems. Establishing whether electrolyte solutions follow similar scaling behavior or instead exhibit deviations due to specific ion–water interactions would help bridge simple model systems and complex aqueous environments, enabling more predictive descriptions of thermodiffusion that can be directly compared with experiment.

Overall, these future efforts will deepen the molecular-level understanding of coupled heat, mass, and charge transport under increasingly complex and realistic conditions, bridging atomistic simulations with experimental systems relevant to nanofluidics, geophysics, and thermal management applications. In particular, improved molecular descriptions of heat and mass transfer in liquids will support the development of advanced thermal technologies, including phase change materials for refrigeration and waste heat recovery [27, 28], as well as nanofluid-based heat transfer media for microelectronic cooling [29], vehicle thermal management [30], and solar thermal systems [31].

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Appendix A

Supplementary Data Table for Chapter 3

Table A.1 reports the complete non-equilibrium molecular dynamics (NEMD) simulation results for TIP4P/2005 water discussed in Chapter 3.

Table A.1: NEMD simulation results for water at selected target pressures and temperatures. Reported pressure (P , σ_P) and thermal conductivity (λ , σ_λ) are averages and corresponding standard deviations over at least three independent replicas. Units: pressure in bar, temperature in K, density in g cm^{-3} , thermal conductivity in $\text{W m}^{-1} \text{K}^{-1}$, and time in ns. Entries marked * at $P_{\text{target}} = 1$ bar and $T_{\text{target}} = 195, 225$ K used a smaller thermal gradient (0.36 vs. 0.74 K m^{-1}) and were initialized from the final configurations of the larger gradient runs.

P_{target}	T_{target}	Time	T	T_{hot}	T_{cold}	ρ	P	σ_P	λ	σ_λ
[bar]	[K]	[ns]	[K]	[K]	[K]	[g cm^{-3}]	[bar]	[bar]	[$\text{W m}^{-1} \text{K}^{-1}$]	[$\text{W m}^{-1} \text{K}^{-1}$]
1	195	480	195.7	209.4	180.6	0.941	21.9	67.0	0.805	0.0076
1*	195	280	195.1	202.2	187.9	0.941	13.5	27.6	0.802	0.0067
1	200	200	199.1	213	184.5	0.939	11.8	52.0	0.783	0.0092
1	203	200	203.4	217.4	188.5	0.939	8.8	68.7	0.763	0.0086
1	207	200	207.8	221.9	193	0.941	-10.4	72.3	0.764	0.0094
1	215	200	216.3	230.8	201.7	0.949	-6.9	41.0	0.759	0.0065
1	225	200	225.4	239.5	210.4	0.965	-8.9	16.0	0.757	0.0043
1*	225	180	225.2	232.3	217.7	0.964	-27.5	15.1	0.755	0.0039

APPENDIX A. SUPPLEMENTARY DATA TABLE FOR CHAPTER 3

P_{target}	T_{target}	Time	T	T_{hot}	T_{cold}	ρ	P	σ_P	λ	σ_λ
[bar]	[K]	[ns]	[K]	[K]	[K]	[g cm ⁻³]	[bar]	[bar]	[W m ⁻¹ K ⁻¹]	[W m ⁻¹ K ⁻¹]
1	230	200	229.4	243.3	214.5	0.972	-1.1	17.0	0.761	0.0036
1	235	200	234.3	248.5	219.3	0.978	-12.9	10.8	0.768	0.0065
1	243	200	243.2	257.5	228.3	0.988	16.0	5.3	0.778	0.007
1	252	200	252.8	267	238.1	0.994	8.7	13.0	0.788	0.0053
1	250	200	250.2	264.5	235.5	0.991	-8.0	14.1	0.785	0.007
1	260	200	260.1	274.4	245.7	0.996	-10.1	11.8	0.797	0.0036
1	270	200	270.1	284.3	255.6	1.001	25.3	9.5	0.808	0.009
1	280	200	280.2	294.3	265.7	0.999	-3.9	7.8	0.817	0.0097
1	290	200	289.9	304.2	275.8	0.999	22.4	7.1	0.823	0.0071
1	300	200	300.3	314.3	285.8	0.997	13.0	6.1	0.834	0.006
1	320	200	320.2	334.1	305.8	0.989	7.0	6.0	0.841	0.0067
1	340	200	340	354.2	325.9	0.978	0.1	6.7	0.84	0.0091
1	360	200	360.4	373.8	345.9	0.965	3.0	6.6	0.838	0.0088
1	380	200	379.9	394.1	365.8	0.95	-1.9	7.2	0.824	0.0067
1	400	200	400.1	414.2	385.8	0.933	-4.7	7.0	0.811	0.009
200	180	200	180.3	194.4	165.7	0.943	254.8	15.4	0.803	0.0086
200	190	200	190.4	204.3	175.6	0.941	226.6	30.3	0.791	0.0057
200	200	200	200.1	214.3	185.7	0.945	156.6	51.2	0.774	0.0091
200	205	200	205.1	219.5	190.6	0.948	218.9	37	0.78	0.0059
200	210	200	210.6	224.6	195.7	0.954	164.5	49.9	0.769	0.0068
200	215	200	215.2	229.5	200.7	0.962	200.1	41.3	0.767	0.0064
200	220	200	220.5	234.6	205.6	0.971	182.1	34.6	0.77	0.0048
200	230	200	230.3	244.6	215.7	0.987	213.9	29.2	0.777	0.0045
200	240	200	240.5	254.5	225.6	0.998	212	24.2	0.79	0.0056
200	260	200	260.5	274.4	245.6	1.009	209.6	14.5	0.816	0.0041
200	280	200	280.2	294.3	265.7	1.01	207	10.2	0.832	0.0046
200	300	200	300.1	314.2	285.8	1.006	206.1	8.5	0.849	0.0074

APPENDIX A. SUPPLEMENTARY DATA TABLE FOR CHAPTER 3

P_{target}	T_{target}	Time	T	T_{hot}	T_{cold}	ρ	P	σ_P	λ	σ_λ
[bar]	[K]	[ns]	[K]	[K]	[K]	[g cm ⁻³]	[bar]	[bar]	[W m ⁻¹ K ⁻¹]	[W m ⁻¹ K ⁻¹]
200	320	200	320	334.2	305.8	0.998	206.2	8.1	0.855	0.0086
200	340	200	340	354	326	0.988	207.8	7.9	0.854	0.0055
200	360	200	360.1	373.9	345.8	0.975	199	9.4	0.846	0.0058
200	380	200	380	394.1	365.8	0.961	200.1	9.6	0.837	0.0063
200	400	200	400.1	414.2	385.8	0.944	200.9	9.8	0.831	0.004
700	190	250	190.4	204.6	175.8	0.957	681.7	31.4	0.793	0.0045
700	200	250	200.3	214.5	185.8	0.965	672.5	37.7	0.786	0.0059
700	210	250	210.5	224.6	195.8	0.987	668.7	25.7	0.79	0.0067
700	220	200	220.5	234.6	205.6	1.009	710.9	14.7	0.8	0.0032
700	240	200	240.2	254.4	225.6	1.028	714.9	3.9	0.825	0.0049
700	260	200	260	274.2	245.7	1.034	718.4	2.8	0.848	0.0057
700	280	200	280	294.2	265.9	1.032	707.0	1.8	0.863	0.0054
700	300	200	300.1	314	285.9	1.027	710.0	1.3	0.877	0.0055
700	320	200	319.8	334.1	305.9	1.019	707.9	2.8	0.888	0.0063
700	340	200	340	353.9	325.9	1.008	705.6	1.8	0.885	0.0056
700	360	200	359.8	374	345.9	0.996	703.6	1.2	0.88	0.0088
700	380	200	379.8	393.9	366.1	0.983	698.2	0.9	0.873	0.0089
700	400	200	399.9	414	385.8	0.968	702.5	1.4	0.86	0.0088
1200	180	250	180.4	194.3	165.8	0.965	1195.7	42.0	0.807	0.006
1200	190	200	190.4	204.5	175.8	0.976	1236.7	53.2	0.803	0.0054
1200	200	200	200.2	214.5	185.9	1.015	1195.8	53.1	0.814	0.0049
1200	210	200	210.2	224.5	195.6	1.038	1215.4	34.0	0.828	0.0056
1200	220	200	220.2	234.3	205.7	1.047	1199.2	10.5	0.839	0.0033
1200	240	200	240	254.4	225.8	1.055	1210.5	4.6	0.857	0.0054
1200	260	200	259.5	274.2	245.9	1.056	1208.0	2.9	0.879	0.0059
1200	280	200	280	294	265.8	1.052	1206.6	2.1	0.897	0.0046
1200	300	200	299.7	313.9	285.9	1.046	1206.8	2.3	0.911	0.0073

P_{target}	T_{target}	Time	T	T_{hot}	T_{cold}	ρ	P	σ_P	λ	σ_λ
[bar]	[K]	[ns]	[K]	[K]	[K]	[g cm ⁻³]	[bar]	[bar]	[W m ⁻¹ K ⁻¹]	[W m ⁻¹ K ⁻¹]
1200	320	200	319.7	333.9	305.9	1.037	1205.1	1.0	0.914	0.007
1200	340	200	339.9	353.8	326	1.027	1205.4	1.9	0.92	0.0066
1200	360	200	359.9	374.1	346.1	1.016	1203.7	2.6	0.917	0.0077
1200	380	200	379.4	393.9	366	1.003	1202.2	1.9	0.907	0.0064

Appendix B

Supplementary Data Tables for Chapter 4

B.1 NEMD Simulation Data

Table B.1 compiles the complete NEMD simulation results for NaCl and LiCl aqueous solutions at 1, 2, and 4 m used in the analysis presented in Chapter 4.

Table B.1: NEMD results for NaCl and LiCl aqueous solutions at 1, 2, and 4 m. Values are time averages over steady-state production runs; numbers in parentheses are standard deviations across ten independent replicas. Units: temperature in K, density in g cm^{-3} , pressure in bar, thermal conductivity in $\text{W m}^{-1} \text{K}^{-1}$, and S_E in mV K^{-1} .

T	T_{hot}	T_{cold}	ρ	P	λ	S_E
[K]	[K]	[K]	$[\text{g cm}^{-3}]$	[bar]	$[\text{W m}^{-1} \text{K}^{-1}]$	$[\text{mV K}^{-1}]$
1 m NaCl						
200.2	249.9	150.0	1.009	9.0(22.5)	0.786(0.016)	2.284(1.065)
220.3	270.1	170.1	1.028	-4.3(9.8)	0.777(0.013)	0.294(0.555)
239.9	291.0	190.0	1.041	12.7(3.1)	0.792(0.010)	-0.299(0.458)
260.2	310.1	210.1	1.044	10.7(4.0)	0.808(0.009)	-0.386(0.276)
280.0	329.8	229.9	1.042	4.7(1.8)	0.826(0.009)	-0.422(0.131)
300.0	350.8	249.9	1.036	6.6(2.3)	0.840(0.004)	-0.412(0.233)

Table B.1: (continued)

T	T_{hot}	T_{cold}	ρ	P	λ	S_E
[K]	[K]	[K]	[g cm ⁻³]	[bar]	[W m ⁻¹ K ⁻¹]	[mV K ⁻¹]
2 m NaCl						
200.1	250.1	150.0	1.066	10.4(25.8)	0.786(0.009)	0.853(0.573)
220.4	270.8	170.0	1.078	0.3(7.7)	0.787(0.008)	-0.065(0.527)
240.2	290.3	189.9	1.086	5.0(4.8)	0.791(0.006)	-0.270(0.468)
260.2	310.5	210.0	1.085	4.0(3.7)	0.803(0.007)	-0.470(0.202)
280.1	329.2	229.9	1.080	-1.5(1.2)	0.815(0.008)	-0.497(0.251)
300.0	350.3	249.9	1.067	8.6(1.8)	0.825(0.001)	-0.446(0.131)
4 m NaCl						
200.0	250.1	149.9	1.166	-89.8(34.5)	0.767(0.014)	0.741(0.665)
220.1	270.2	170.1	1.169	-73.0(7.2)	0.771(0.015)	0.025(0.456)
240.1	290.1	189.9	1.166	-64.0(5.0)	0.778(0.007)	-0.343(0.154)
260.1	310.3	209.7	1.158	-67.8(3.0)	0.786(0.007)	-0.414(0.230)
280.1	330.8	229.8	1.147	-67.1(1.0)	0.792(0.007)	-0.461(0.235)
299.8	350.3	249.9	1.134	-33.8(2.2)	0.801(0.004)	-0.491(0.133)
1 m LiCl						
200.3	250.5	149.9	0.985	39.2(16.3)	0.785(0.011)	1.606(0.733)
220.6	270.8	169.9	1.005	7.1(17.0)	0.775(0.010)	0.067(0.533)
240.3	290.8	190.1	1.015	-8.0(4.4)	0.783(0.008)	-0.437(0.281)
260.3	310.6	210.1	1.022	-2.3(2.3)	0.802(0.005)	-0.545(0.224)
280.2	330.9	229.9	1.023	1.1(1.5)	0.814(0.005)	-0.521(0.275)
300.1	350.2	249.9	1.018	1.8(0.8)	0.835(0.004)	-0.559(0.149)
2 m LiCl						
200.0	250.1	149.6	1.019	77.2(18.1)	0.780(0.009)	0.412(0.728)
220.5	270.6	169.9	1.036	-13.0(18.9)	0.780(0.008)	-0.245(0.482)
240.2	290.7	190.1	1.042	-9.5(2.7)	0.781(0.006)	-0.384(0.369)
260.2	311.0	210.0	1.046	-5.4(3.6)	0.794(0.006)	-0.300(0.262)

Table B.1: (continued)

T	T_{hot}	T_{cold}	ρ	P	λ	S_E
[K]	[K]	[K]	[g cm ⁻³]	[bar]	[W m ⁻¹ K ⁻¹]	[mV K ⁻¹]
280.2	330.7	230.2	1.044	-1.7(1.0)	0.808(0.004)	-0.318(0.255)
300.1	350.5	249.9	1.039	4.4(1.1)	0.821(0.003)	-0.345(0.159)
4 m LiCl						
200.0	250.0	149.5	1.082	-50.5(38.1)	0.760(0.010)	0.269(0.777)
220.1	270.0	169.9	1.088	-7.4(14.6)	0.762(0.007)	-0.210(0.479)
240.2	290.6	190.2	1.089	-3.5(4.6)	0.769(0.006)	-0.256(0.257)
260.1	310.6	209.7	1.087	-0.2(2.1)	0.778(0.007)	-0.345(0.294)
280.1	330.9	229.9	1.084	0.4(0.9)	0.784(0.006)	-0.347(0.299)
300.0	350.5	250.0	1.078	-2.2(0.9)	0.796(0.003)	-0.464(0.176)

B.2 Equilibrium NPT Simulation Data

Table B.2 summarizes the equilibrium thermodynamic and structural properties of NaCl and LiCl aqueous solutions obtained from NPT simulations. Reported quantities include the density, isobaric thermal expansion coefficient, isothermal compressibility, adiabatic speed of sound, and ion–oxygen coordination numbers, together with the cutoff radii defined by the first minima of the corresponding radial distribution functions, as used in the analysis of Chapter 4.

Table B.2: Equilibrium NPT results for NaCl and LiCl aqueous solutions at 1, 2, and 4 m over the range 200–300 K. Values are averages from equilibrium trajectories; numbers in parentheses are standard deviations across at least three independent replicas. Units: T in K, ρ in g cm⁻³, α in 10⁻⁴ K⁻¹, κ_T in 10⁻¹⁰ m³ J⁻¹, and c_s in m s⁻¹. Distances are in nm.

T	ρ	α	κ_T	c_s	$n_{\text{cation-O}}$	$r_{\text{cation-O}}$	$n_{\text{Cl-O}}$	$r_{\text{Cl-O}}$
[K]	[g cm ⁻³]	[$\times 10^{-4}$ K ⁻¹]	[$\times 10^{-10}$ m ³ J ⁻¹]	[m s ⁻¹]		[nm]		[nm]
1 m NaCl								
200	1.009	-2.54(0.58)	4.11(0.29)	1565.4(36.0)	5.68	0.31	5.76	0.36
220	1.028	-6.34(0.26)	5.79(0.25)	1301.5(31.4)	5.67	0.31	5.78	0.36

Table B.2: (continued)

T	ρ	α	κ_T	c_s	$n_{\text{cation-O}}$	$r_{\text{cation-O}}$	$n_{\text{Cl-O}}$	$r_{\text{Cl-O}}$
[K]	[g cm ⁻³]	[$\times 10^{-4}$ K ⁻¹]	[$\times 10^{-10}$ m ³ J ⁻¹]	[m s ⁻¹]		[nm]		[nm]
240	1.041	-3.96(0.14)	5.05(0.19)	1391.1(19.4)	5.63	0.31	5.79	0.36
260	1.044	0.79(0.18)	4.50(0.05)	1476.3(10.3)	5.61	0.32	5.80	0.36
280	1.042	2.15(0.13)	4.24(0.07)	1518.2(10.9)	5.57	0.32	5.80	0.36
300	1.036	3.71(0.16)	4.11(0.06)	1556.4(9.4)	5.50	0.31	5.80	0.36
2 m NaCl								
200	1.066	-8.04(0.56)	4.85(0.37)	1393.3(27.3)	5.78	0.32	5.82	0.36
210	1.070	-5.76(0.51)	5.40(0.27)	1335.6(27.6)	5.75	0.32	5.82	0.36
220	1.078	-5.29(0.32)	4.83(0.22)	1386.9(17.1)	5.73	0.31	5.82	0.36
240	1.086	-1.50(0.20)	4.17(0.16)	1486.1(9.9)	5.68	0.32	5.82	0.36
260	1.085	1.83(0.16)	3.95(0.14)	1532.8(10.5)	5.62	0.32	5.89	0.36
280	1.080	3.28(0.07)	3.72(0.04)	1581.6(9.2)	5.56	0.32	5.90	0.36
300	1.067	4.27(0.07)	3.72(0.04)	1614.5(9.8)	5.51	0.32	5.93	0.37
4 m NaCl								
200	1.166	-2.87(0.65)	4.16(0.26)	1437.5(27.9)	5.85	0.32	5.87	0.36
220	1.169	-0.64(0.32)	3.85(0.20)	1515.4(29.3)	5.78	0.32	5.89	0.36
240	1.166	1.67(0.27)	3.40(0.13)	1607.7(20.5)	5.70	0.32	5.90	0.36
260	1.158	2.95(0.19)	3.18(0.03)	1663.9(12.8)	5.61	0.32	5.91	0.36
280	1.147	4.01(0.09)	3.15(0.03)	1689.7(10.7)	5.51	0.31	5.93	0.36
300	1.134	4.77(0.09)	3.14(0.01)	1707.8(7.1)	5.47	0.32	5.94	0.36
1 m LiCl								
200	0.985	-6.33(0.44)	4.51(0.42)	1503.0(42.4)	4.00	0.24	5.62	0.36
220	1.005	-7.32(0.25)	5.02(0.20)	1411.0(38.9)	4.00	0.24	5.71	0.36
240	1.015	-3.89(0.15)	5.01(0.15)	1428.6(30.1)	4.00	0.25	5.71	0.36
260	1.022	-1.72(0.15)	4.43(0.07)	1493.2(14.9)	4.00	0.26	5.76	0.36
280	1.023	1.56(0.29)	4.31(0.05)	1524.4(17.9)	4.00	0.26	5.82	0.37

Table B.2: (continued)

T	ρ	α	κ_T	c_s	$n_{\text{cation-O}}$	$r_{\text{cation-O}}$	$n_{\text{Cl-O}}$	$r_{\text{Cl-O}}$
[K]	[g cm ⁻³]	[$\times 10^{-4}$ K ⁻¹]	[$\times 10^{-10}$ m ³ J ⁻¹]	[m s ⁻¹]		[nm]		[nm]
300	1.018	3.50(0.19)	4.19(0.05)	1540.5(12.5)	4.00	0.26	5.85	0.37
2 m LiCl								
200	1.019	-6.50(0.37)	4.01(0.20)	1563.4(31.3)	4.00	0.23	5.64	0.36
220	1.036	-5.19(0.45)	4.19(0.19)	1549.7(20.1)	4.00	0.24	5.75	0.36
240	1.042	-3.04(0.18)	4.02(0.11)	1551.7(17.1)	4.00	0.25	5.75	0.36
260	1.046	-0.68(0.18)	3.93(0.07)	1569.7(12.4)	4.00	0.25	5.76	0.36
280	1.044	2.19(0.08)	3.84(0.07)	1584.8(12.0)	4.00	0.26	5.83	0.37
300	1.039	3.79(0.12)	3.78(0.06)	1618.3(12.1)	4.00	0.28	5.90	0.37
4 m LiCl								
200	1.082	-2.63(0.51)	3.61(0.18)	1597.6(31.5)	4.00	0.24	5.74	0.36
220	1.088	-0.75(0.43)	3.48(0.14)	1634.4(24.7)	4.00	0.24	5.73	0.36
240	1.089	-0.24(0.37)	3.26(0.09)	1678.7(15.8)	4.00	0.25	5.74	0.36
260	1.087	0.75(0.12)	3.24(0.06)	1694.6(12.0)	4.00	0.25	5.79	0.36
280	1.084	2.55(0.14)	3.18(0.05)	1715.3(11.5)	4.00	0.26	5.81	0.36
300	1.078	4.03(0.11)	3.14(0.06)	1728.4(11.6)	4.00	0.26	5.89	0.37

Appendix C

Supplementary Data Tables for Chapter 5

C.1 NEMD Simulation Data

Table C.1 presents the complete NEMD simulation results for pure water and for 1 m NaCl and LiCl aqueous solutions across the pressure range 0.1–2.6 GPa, as discussed in Chapter 5.

Table C.1: Summary of NEMD simulation results for pure water and 1 m NaCl and LiCl aqueous solutions. P is the pressure in GPa, T in K, ρ in g cm^{-3} , λ in $\text{W m}^{-1} \text{K}^{-1}$, and s_T in 10^{-3}K^{-1} . The quantities $\delta\lambda$ and δs_T denote standard deviations calculated from ten independent replicas.

P	T	ρ	λ	$\delta\lambda$	s_T	δs_T
[GPa]	[K]	[g cm^{-3}]	[$\text{W m}^{-1} \text{K}^{-1}$]	[$\text{W m}^{-1} \text{K}^{-1}$]	[10^{-3}K^{-1}]	[10^{-3}K^{-1}]
1 m NaCl						
0.10	290.1	1.08	0.889	0.001	3.60	0.35
0.50	290.2	1.19	1.069	0.002	5.57	0.22
1.00	290.1	1.28	1.235	0.005	5.35	0.24
1.50	290.2	1.34	1.363	0.004	5.67	0.46
1.99	290.4	1.39	1.466	0.003	6.13	0.43
1 m LiCl						
0.10	290.2	1.06	0.884	0.002	-0.26	0.38

Table C.1: (continued)

P	T	ρ	λ	$\delta\lambda$	s_T	δs_T
[GPa]	[K]	[g cm ⁻³]	[W m ⁻¹ K ⁻¹]	[W m ⁻¹ K ⁻¹]	[10 ⁻³ K ⁻¹]	[10 ⁻³ K ⁻¹]
0.50	290.1	1.17	1.066	0.002	0.98	0.31
1.01	290.1	1.26	1.239	0.005	1.35	0.35
1.50	290.0	1.33	1.371	0.006	1.35	0.50
1.99	290.2	1.37	1.472	0.003	1.78	0.26
2.60	999.9	1.17	1.357	0.002	3.24	0.26

Water				
P	T	ρ	λ	$\delta\lambda$
[GPa]	[K]	[g cm ⁻³]	[W m ⁻¹ K ⁻¹]	[W m ⁻¹ K ⁻¹]
1.70e-03	289.9	1.00	0.845	0.002
0.87	289.6	1.04	0.897	0.002
0.51	289.9	1.16	1.089	0.002
0.99	290.0	1.25	1.258	0.006
1.48	289.2	1.31	1.412	0.001
1.98	289.9	1.36	1.512	0.003

C.2 Equilibrium NPT Simulation Data

Table C.2 summarizes the equilibrium self-diffusion coefficients and ion–water coordination properties obtained from NPT simulations of 1 m NaCl and LiCl aqueous solutions at 290 K and pressures up to 2 GPa, as used in the analysis presented in Chapter 5. The self-diffusion coefficients (D_i) were determined from the mean-squared displacement using the Einstein relation (Equation 5.1). The ion–oxygen coordination numbers ($n_{\text{ion-O}}$) and corresponding cutoff radii ($r_{\text{ion-O}}$) are reported as defined in Appendix B.2.

Table C.2: Self-diffusion coefficients (D_i) and ion–oxygen coordination numbers ($n_{\text{ion-O}}$) with corresponding cutoff radii ($r_{\text{ion-O}}$) for 1 m NaCl and LiCl aqueous solutions at 290 K and pressures of 10^{-4} , 0.1, 0.5, 1, 1.5, and 2 GPa. Diffusion coefficients are given in units of $10^{-10}\text{m}^2\text{s}^{-1}$, with standard deviations in parentheses, derived from at least three independent replicas. Distances are in nm.

P	T	D_{cation}	D_{Cl}	$n_{\text{cation-O}}$	$r_{\text{cation-O}}$	$n_{\text{Cl-O}}$	$r_{\text{Cl-O}}$
[GPa]	[K]	[$10^{-10}\text{m}^2\text{s}^{-1}$]	[$10^{-10}\text{m}^2\text{s}^{-1}$]		[nm]		[nm]
1 m NaCl							
10^{-4}	290.0	5.56 (0.26)	9.64 (0.10)	5.55	0.32	5.94	0.37
0.10	290.0	5.29 (0.46)	9.63 (0.16)	5.64	0.32	5.98	0.36
0.50	290.1	5.77 (0.09)	9.10 (0.09)	5.84	0.31	6.05	0.35
1.00	289.9	5.65 (0.41)	8.51 (0.12)	5.95	0.31	6.20	0.35
1.50	290.0	3.41 (0.43)	5.70 (0.28)	6.03	0.31	23.03	0.52
2.00	290.1	2.82 (0.39)	5.04 (0.38)	6.06	0.30	19.87	0.49
1 m LiCl							
10^{-4}	290.0	5.86 (0.25)	11.93 (0.49)	4.00	0.27	5.81	0.36
0.10	290.0	5.84 (0.47)	10.31 (0.27)	4.00	0.26	5.99	0.37
0.50	290.0	5.75 (0.17)	10.37 (0.69)	4.00	0.25	6.15	0.36
1.00	290.1	4.09 (0.19)	7.08 (0.14)	4.00	0.26	6.55	0.35
1.50	289.9	3.39 (0.55)	6.10 (0.57)	4.00	0.24	22.66	0.51
2.00	290.1	1.86 (0.51)	5.19 (0.28)	4.00	0.24	18.38	0.47

Appendix D

Supplementary Data Table for Chapter 6

D.1 NEMD Simulation Data

The results of the NEMD simulations are summarized in Table D.1. The table reports the quantities obtained for ethanol along the liquid–vapor coexistence curve and at selected isochores, covering both liquid and supercritical conditions, as discussed in Chapter 7.

Table D.1: Results of the non-equilibrium molecular dynamics (NEMD) simulations for ethanol. Reported quantities include temperature (T), density (ρ), pressure (P), thermal conductivity (λ), and thermal polarization coefficient (S_{TP}), together with their corresponding standard deviations (σ_P , σ_λ , and $\sigma_{S_{TP}}$), derived from ten independent replicas.

T	ρ	P	σ_P	λ	σ_λ	S_{TP}	$\sigma_{S_{TP}}$
[K]	[g cm ⁻³]	[bar]	[bar]	[W m ⁻¹ K ⁻¹]	[W m ⁻¹ K ⁻¹]	[mV K ⁻¹]	[mV K ⁻¹]
247.8	0.83	-4.26	3.14	0.146	0.006	0.836	0.21
298.1	0.78	-1.01	1.82	0.134	0.004	0.530	0.08
348.1	0.73	-2.94	1.93	0.128	0.004	0.469	0.06
397.3	0.67	1.22	2.43	0.119	0.003	0.026	0.08
445.4	0.59	14.39	1.22	0.111	0.003	-0.539	0.03
490.1	0.45	48.84	0.61	0.098	0.007	-2.129	0.08
348.5	0.83	1111.0	2.13	0.166	0.006	0.582	0.06

Table D.1: (continued)

T	ρ	P	σ_P	λ	σ_λ	S_{TP}	$\sigma_{S_{TP}}$
[K]	[g cm ⁻³]	[bar]	[bar]	[W m ⁻¹ K ⁻¹]	[W m ⁻¹ K ⁻¹]	[mV K ⁻¹]	[mV K ⁻¹]
448.2	0.83	2363.4	3.55	0.191	0.005	0.147	0.06
498.0	0.83	3033.4	4.86	0.204	0.007	0.011	0.04
547.8	0.83	3707.4	3.45	0.216	0.008	-0.081	0.04
597.7	0.83	4376.1	3.75	0.224	0.009	-0.108	0.06
348.5	0.78	434.4	2.33	0.146	0.004	0.403	0.08
398.4	0.78	933.1	2.74	0.158	0.005	0.332	0.05
448.2	0.78	1474.9	2.03	0.172	0.005	0.099	0.04
498.0	0.78	2041.2	3.34	0.182	0.007	-0.053	0.03
547.7	0.78	2615.7	3.55	0.194	0.008	-0.102	0.04
597.6	0.78	3191.7	2.73	0.203	0.008	-0.160	0.04
647.5	0.78	3751.2	4.66	0.209	0.008	-0.150	0.04
398.1	0.73	360.0	2.63	0.139	0.004	0.269	0.04
448.2	0.73	798.3	2.94	0.152	0.004	0.004	0.03
497.8	0.73	1262.2	2.84	0.161	0.005	-0.115	0.05
547.8	0.73	1742.6	3.75	0.172	0.006	-0.163	0.06
539.4	0.28	68.9	0.71	0.073	0.006	-1.536	0.03
594.1	0.28	134.6	0.61	0.075	0.003	-0.820	0.04
645.5	0.28	195.2	0.91	0.073	0.003	-0.444	0.03
696.0	0.28	252.1	0.81	0.075	0.003	-0.295	0.03