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Polarization of ethanol under thermal fields

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ABSTRACT

Thermal fields induce thermal polarization and the buildup of a stationary net electric field in polar liquids. While the thermal polarization effect in water has been studied before, the coupling effects between heat and polarization fluxes remain unexplored in most polar fluids. Here, we investigate thermal transport and thermal polarization in liquid and supercritical ethanol through non-equilibrium molecular dynamics simulations using the TraPPE force field. We discuss the thermal conductivity of ethanol under various thermodynamic conditions and its correlation with other thermophysical properties, such as isothermal compressibility and specific heat capacity. Furthermore, we demonstrate that thermal gradients polarize liquid and supercritical ethanol. We report an inversion in the sign of the polarization field along the liquid branch of the liquid–vapor saturation line and discuss the microscopic origin of this inversion. Near the critical point, the thermal polarization effect increases significantly, as observed in water. Finally, we show a correlation between the sign reversal of the thermal polarization and the minimum in the liquid–vapor surface potential of ethanol.

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I. INTRODUCTION

Understanding thermal transport in fluids is crucial for both industry and fundamental research. Fluids are particularly valuable for thermal management in electrical devices and vehicles^{1–3} and energy storage solutions.^{4,5} There is also a growing interest in enhancing thermal transport capabilities through nanofluids, which are created by adding nanoparticles to base fluids.⁶ A key thermophysical property of both pure fluids and suspensions is their thermal conductivity.

While there are established methods for measuring the thermal conductivity of fluids,⁷ modeling the thermal transport of liquids is challenging. Bridgmann introduced an empirical equation that provides a physical foundation for understanding thermal transport in relation to parameters such as the speed of sound or the molecular volume.^{8,9} Despite these early advancements, we still lack comprehensive theoretical models that can accurately predict the thermal conductivity of liquids.

Previous studies have demonstrated that thermal gradients induce non-equilibrium coupling effects, resulting in the formation of a stationary electrostatic field that varies linearly with the strength of the thermal gradient.^{10,11} This phenomenon, known as *Thermal Polarization* (TP), aligns with the principles of Linear Non-Equilibrium Thermodynamics (LNET),¹² and the TP effect arises

from the coupling of a displacement current and a heat flux. A well-known example of a non-equilibrium coupling effect is thermodiffusion, initially observed by Ludwig and Soret in ionic solutions.^{13–15} Thermodiffusion results from the coupling of mass and heat fluxes in mixtures, and it causes a reduction in the thermal conductivity of the mixtures.¹⁶ According to LNET, any coupling effect, including TP, contributes to a decrease in thermal conductivity.

Recent studies analyzed the effects of thermal polarization in polar fluids, such as water and acetonitrile, across a wide range of thermodynamic states.^{11,17,18} The thermal polarization of acetonitrile, an aprotic solvent, results in a measurable reduction of thermal conductivity (by approximately 2%–5%) at typical liquid densities and temperatures from 300 to 700 K, relative to the thermal conductivity that would be obtained in the absence of the thermal polarization effect. Additionally, molecular orientation induced by thermal gradients has been reported in non-polar fluids.^{19–21} In these cases, the orientation results from the coupling of a mass dipole with the heat flux.

The thermal polarization effect in water is quite complex. There is an inversion in the direction of the thermally induced electrostatic fields when a thermal field is applied in liquids and high-density supercritical water.^{11,22} Atomistic non-equilibrium molecular dynamics simulations also indicate a divergence in the electrostatic field response at the critical point.²³ Dipolar and

quadrupolar interactions play a significant role in determining the water properties. Theoretical studies have highlighted the importance of these electrostatic moments, showing that the molecular dipole-to-quadrupole ratio can be used as a parameter that correlates with the accuracy of water force fields.²⁴ This dipole–quadrupole ratio is also fundamental for understanding the emergence of inversion points in the thermal polarization field of water.^{11,22}

Understanding the role of thermal coupling effects in polar fluids, and in particular thermal polarization, is essential in various fields, including energy and optothermal materials,²⁵ electroporation,²⁶ electrochemistry,²⁷ and the behavior of electrodes under non-equilibrium conditions.^{28,29} In this study, we expand our investigation of thermal polarization to another important hydrogen-bonded fluid: ethanol. This solvent is significant in numerous applications. It is employed as a co-solvent with water in catalysis,^{30,31} oxidation processes using nanomaterials,³² nanoscale phase separation induced by the heating of nanoparticles,³³ or nanofluids.³⁴

Both water and ethanol form strong hydrogen bonds and have similar dipole moments in the gas phase.³⁵ However, the thermal conductivity of ethanol is significantly lower [0.17 W/(K m)]

compared to that of water [0.60 W/(K m)] under standard conditions.^{36,37} This difference indicates that the non-polar alkyl chain and reduced hydrogen bonding in ethanol hinder heat conduction.

In this study, we use Non-Equilibrium Molecular Dynamics (NEMD) simulations to examine the thermal transport and thermal polarization of ethanol. We model the ethanol molecules using the Transferable Potentials for Phase Equilibria (TraPPE) force field, which applies a united-atom approach to represent alkyl groups.³⁸ This force field accurately predicts various thermophysical properties, including the critical point, and has been used in studies of supercritical ethanol.^{39,40} Our findings indicate that ethanol is polarized by thermal gradients. Notably, when the liquid is heated along its saturation line or at a constant volume, it exhibits an inversion of the thermal polarization field. This behavior is similar to the phenomenon previously reported for water.^{11,22,23}

II. METHODS

We conducted boundary-driven Non-Equilibrium Molecular Dynamics (NEMD) simulations using LAMMPS (version from

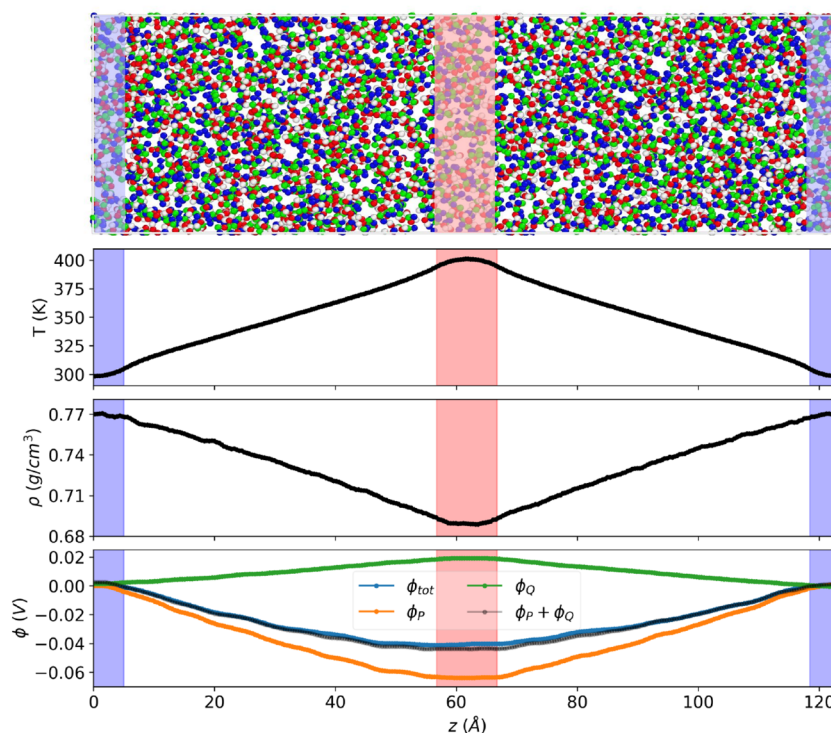


FIG. 1. The top panel displays the snapshot of the simulation cell used in the Non-Equilibrium Molecular Dynamics (NEMD) simulations of ethanol. The snapshot was created using OVITO.⁴⁷ The spheres are color-coded: blue represents CH_3 , green represents CH_2 , red represents oxygen (O), and white represents hydrogen (H). The bottom panels display the temperature, density, and electrostatic potential profiles. The local curvature in the profiles emerges from spatial variations in the thermal conductivity and thermal expansion across different thermodynamic states sampled in the non-equilibrium simulations. The lowest panel shows the total electrostatic potential, alongside the dipolar and quadrupolar contributions. The sum of the dipolar and quadrupolar terms is shown in black and compared against the total potential to evaluate the accuracy of the decomposition. The dipolar and quadrupolar contributions were computed using the molecular center of mass as the reference point for calculations. See Sec. III for a discussion on how the choice of molecular reference affects the calculation of the electrostatic moments. The regions maintained at high and low temperatures are indicated in red and blue, respectively.

2 Aug 2023)^{41,42} to investigate the thermal transport and polarization properties of ethanol. To establish thermal gradients within the simulation box, we applied thermostats to the ethanol molecules located in regions at the edges and the center of the box, maintaining pre-defined hot (T_{hot}) and cold (T_{cold}) temperatures in those regions (see Fig. 1). Each thermostat region had a thickness of 0.1 nm, and the size and shape of the simulation box were defined with the ratios $\{L_x : L_y : L_z\} = \{1 : 1 : 3\}$ and $L_x \sim 40 \text{ \AA}$.

We employed two Canonical Sampling Velocity Rescaling (CSVR) thermostats⁴³ to regulate the temperature of ethanol at each timestep (1 fs) with a coupling constant of 100 fs. Additionally, we reset the center of mass momentum of the entire simulation at every timestep. To compute the electrostatic interactions, we used the Particle-Particle Mesh (PPPM) method,⁴⁴ targeting a force accuracy of $5 \times 10^{-5} \text{ kcal}/(\text{mol \AA})$. We also applied the PPPM method for long-range dispersion interactions.^{45,46} For computing the real and reciprocal space contributions in long-range dispersion interactions, we set accuracies of 10^{-4} and $2 \times 10^{-4} \text{ kcal}/(\text{mol \AA})$, respectively.

A typical NEMD simulation cell contained 2000 ethanol molecules modeled using the TraPPE potential.³⁸ We use the same Lennard-Jones, bending, and torsion parameters as in the original potential. We model the molecule with flexible bonds using a harmonic potential, $U_b = k(r - r_0)^2$, where r_0 is the equilibrium bond length, taken from the original TraPPE force field. We use the following force constants: $k_{\text{CH}_3-\text{CH}_2} = 309.93$, $k_{\text{CH}_2-\text{O}} = 320.08$, $k_{\text{O}-\text{H}} = 552.99 \text{ kcal}/(\text{mol \AA}^2)$. Initially, the simulation box was equilibrated at the target temperature, and the simulation cell was gradually rescaled in the x, y, and z directions to achieve the target density of the liquid phase along the liquid coexistence line.³⁹ The system was then pre-equilibrated at the same temperature using the global canonical CSVR thermostat⁴³ for 5 nanoseconds (ns).

NEMD simulations were conducted using thermostats set to T_{hot} and T_{cold} . We simulated density and temperature state points along the liquid saturation line and various isochores within the liquid region. After an additional 1 ns of simulation, the system reached a steady state, after which we computed the density and temperature profiles. All properties were calculated by averaging over 300 bins along the z-axis, resulting in bin sizes of around 0.4 Å, depending on the density. These values were subsequently used to obtain the equation of state and thermal conductivity. NEMD production runs lasted for a minimum of 10 ns and averaged over 10 replicas, each initialized using a different random number seed for the thermostats. The total accumulated sampling time across all replicas was 100 ns. To calculate the thermal polarization field, we computed the charge density every 10^3 steps, collecting a total of 10^6 configurations from 10 replicas for each state point.

The thermal conductivity at position z , $\lambda(z)$, was calculated using Fourier's Law,

$$\lambda(z) = -\frac{J_q}{\nabla T(z)}, \quad (1)$$

where $\nabla T(z)$ is the local temperature gradient in the direction of heat flux J_q . The heat flux was obtained from the continuity equation,

$$J_q = \frac{\dot{Q}}{2A}, \quad (2)$$

where $\dot{Q}$ is the total simulated heat rate, A is the cross-sectional area of the simulation box in the direction perpendicular to the heat flux, and factor "2" is included to account for the two heat fluxes generated within the simulation cell (see Fig. 1). The heat rate was determined by analyzing the energy transfer in the hot and cold regions. In Non-Equilibrium Molecular Dynamics (NEMD) simulations that maintain good energy conservation, the energy transfer between the two thermostats should be equal in magnitude but opposite in sign. As demonstrated in Fig. 8 in Appendix A, our NEMD method ensures excellent energy conservation, and the heat rates from the hot and cold regions agree within the limits of computational accuracy. Additionally, we compare the heat flux calculated using the continuity route [Eq. (2)] with the microscopic Irvin-Kirkwood heat flux expression truncated to first order (IK1) (see Refs. 48 and 49). Our results are presented in Fig. 9 in Appendix B. The agreement between the continuity equation and the IK1 route is excellent.

To quantify the polarization coupling induced by a thermal gradient, we calculated charge density $\rho_q(z)$,

$$\rho_q(z) = \frac{1}{A} \left\langle \sum_{i=1}^{N_{\text{charges}}} q_i \delta(z - z_i) \right\rangle. \quad (3)$$

The angular brackets represent the binned time average of the sum over all charged sites, where q_i and z_i are the charge and z-coordinate of site i , respectively. In the case of the ethanol molecule modeled using the TraPPE force field,³⁸ the charged sites include the CH_2 group ($q_{\text{CH}_2} = 0.265e$), the oxygen atom ($q_{\text{O}} = -0.7e$), and the hydrogen atom ($q_{\text{H}} = 0.435e$). The electrostatic field associated with the heat flux was projected in the direction of the heat flux, E_z , and was calculated by integrating the charge density,

$$E_z(z) = \frac{1}{\epsilon_0} \int_0^z \rho_q(z') dz', \quad (4)$$

where ϵ_0 represents the vacuum permittivity. The thermopolarization coefficient, S_{TP} , quantifies the strength of the field induced by the thermal gradient, and it was calculated using the equation

$$S_{TP}(z) = \frac{E_z(z)}{\nabla T(z)}. \quad (5)$$

We also integrated the electric field to obtain the induced electric potential ($\phi(z) = -\int_0^z E_z(z') dz'$). In this case, S_{TP} is obtained from $S_{TP}(z) = -\partial\phi(z)/\partial T(z)$ (see Fig. 10 in Appendix C).

Additionally, we calculated the dipolar (P_z) and quadrupolar (Q_{zz}) contributions to the electrostatic charge density,⁵⁰

$$\rho(z) = -\frac{\partial}{\partial z} P_z(z) + \frac{\partial^2}{\partial z^2} Q_{zz}(z) + \dots, \quad (6)$$

where the dipolar and quadrupolar terms are defined as

$$P_z(z) = \frac{1}{A} \left\langle \sum_m^{N_m} \delta(z - z_m) \sum_{i \in m}^{N_{\text{charges}}} q_{i,m} z_{i,m} \right\rangle, \quad (7)$$

$$Q_{zz}(z) = \frac{1}{A} \left\langle \sum_m^{N_m} \delta(z - z_m) \frac{1}{2} \sum_{i \in m}^{N_{\text{charges}}} q_{i,m} z_{i,m}^2 \right\rangle. \quad (8)$$

In the equations above, z_m is the z -coordinate of the reference point selected for a specific ethanol molecule, which is defined as the molecular center of mass throughout the main text. We provide a comparison of the electrostatic moments calculated using alternative reference points in [Appendix G](#). The effects of using various reference points in water have been discussed recently.⁵¹ The terms $q_{i,m}$ and $z_{i,m}$ represent the charge and z -coordinate, respectively, of the i th charged site in the m th ethanol molecule. The summations in Eqs. (7) and (8) are over all molecules in the system, and the inner sums are over every charged atom within them.

In our previous work on water, we established a correlation between the inversion of the thermopolarization field and the change in the sign of the gradient of the electrostatic potential of the liquid–vapor interface as a function of temperature.¹¹ To further investigate this correlation, we performed equilibrium NVT simulations of the liquid–vapor interface of ethanol. We started with a pre-equilibrated simulation box, which was then elongated by 100 Å on each side in the z direction (perpendicular to the interface plane). The setup is illustrated in [Fig. 11](#) in [Appendix D](#). The system was equilibrated for 1 ns, followed by 10 ns of simulation to calculate the electrostatic potential. The bottom panels in [Fig. 11](#) show representative density and electrostatic potential profiles.

We conducted equilibrium simulations using Gromacs (ver. January 2024)^{52,53} to calculate fluctuation properties and evaluate the influence of thermal polarization coupling on the thermal conductivity of ethanol. Each simulation box contained 1728 ethanol molecules arranged in a cubic configuration, and the simulations were carried out for a minimum of 20 ns with a timestep of 1 fs. Following the simulations, we determined the dielectric permittivity (ϵ_r) and the Debye relaxation time (τ_D) to assess the change in thermal conductivity ($\delta\lambda$) due to the thermopolarization effect. This change in thermal conductivity is defined as follows:¹⁷

$$\delta\lambda = -\frac{S_{TP}^2 T}{\tau_D} \left(\frac{\epsilon_0 \epsilon_r^2}{\epsilon_r - 1} \right). \quad (9)$$

Additional information regarding the calculation of dielectric permittivity and Debye relaxation time can be found in [Appendix E](#).

III. RESULTS

[Figure 2](#) illustrates the equations of state along the liquid branch of the coexistence diagram, which were derived from the local temperatures and densities of the Non-Equilibrium Molecular Dynamics (NEMD) simulations. The results from these simulations demonstrate excellent agreement with both experimental data³⁶ and previous equilibrium simulations.³⁹ This consistency confirms the accuracy of the TraPPE force field regarding the coexistence properties compared to experimental observations. Furthermore, the consistency of the equilibrium and non-equilibrium simulation results indicates that our simulation reproduces the state of local equilibrium and supports the linear response for thermal gradients employed in this work, ~ 1 K/Å. Additionally, fluctuation properties, such as the isobaric thermal expansion coefficient, isothermal compressibility, and isentropic (adiabatic) speed of sound in ethanol (see [Table I](#)) obtained from equilibrium simulations, are close to the experimental results.^{55–57} However, the TraPPE model is slightly more compressible and features a higher thermal expansion at 300 K and standard pressure.

The thermal conductivities of ethanol, calculated at various thermodynamic states along the saturation line, are shown in [Fig. 3\(a\)](#). As the temperature increases and the system approaches the critical point, the thermal conductivity decreases. This trend is consistent with experimental findings.^{36,58} We report a consistent

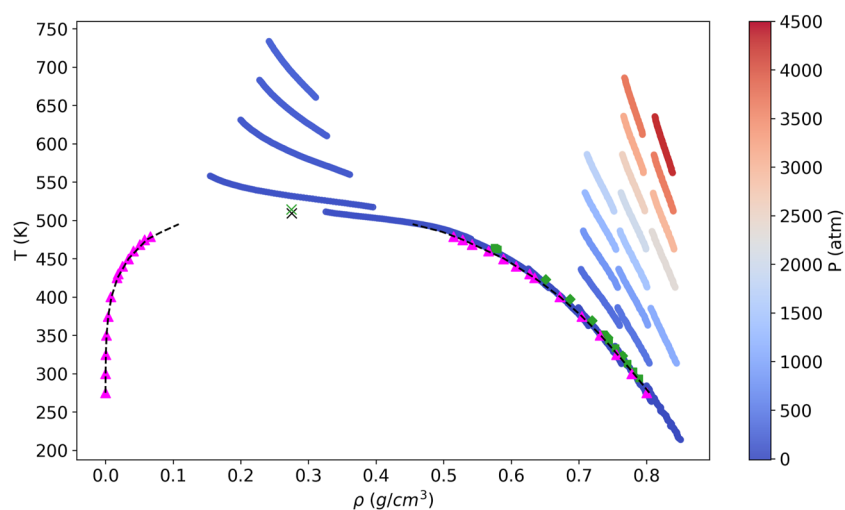


FIG. 2. Equations of state (EOS) calculated using the local temperature and density profiles obtained in the non-equilibrium molecular dynamics (NEMD) simulations. The isobars are color-coded according to their average pressure in the NEMD simulation (see color bar for pressure values). The dashed lines represent the liquid–vapor coexistence lines of the TraPPE model reported in Ref. 39. The black “x” marks the TraPPE critical point (509.1 K, 0.276 g/cm³), compared to the green “x,” which represents the experimental value.⁵⁴ The magenta triangles represent the coexistence lines obtained in this work through direct coexistence simulations of an explicit liquid slab in the NVT ensemble. The green square and diamond markers represent experimental data from Refs. 36 and 55, respectively.

TABLE I. Fluctuation and dielectric properties computed from equilibrium simulations at the thermodynamic states along the saturation curve using Gromacs. T is temperature, ρ is density, α is the isobaric thermal expansion coefficient, κ_T is the isothermal compressibility, c_s is the adiabatic speed of sound, ϵ_r is the static dielectric constant, τ_D is the Debye relaxation time, and $\delta\lambda$ is the difference from the total thermal conductivity λ associated with the thermal polarization effect and calculated using Eq. (9). Values in parentheses represent the standard deviations calculated across independent replicas.

T (K)	ρ (g/cm ³)	α (10 ⁻⁴ K ⁻¹)	κ_T (10 ⁻¹⁰ m ³ J ⁻¹)	c_s (m/s)	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

underestimation of the thermal conductivity compared to experimental data, resembling the discrepancies reported with the OPLS force field.⁵⁹ Later studies using the OPLS-AA force field reported higher thermal conductivities. However, those values are still below the experimental results at temperatures around 300 K.⁶⁰ Good agreement between simulated and experimental thermal conductivities was achieved using a rigid non-polarizable three-site model of ethanol.⁶¹

The decrease in thermal conductivity with rising temperature can be explained by the thermal expansion of the liquid. The Bridgman equation offers a phenomenological perspective to clarify this behavior,⁸

$$\lambda = Ak_B v^{-2/3} c, \quad (10)$$

where A is a constant, v is the molar volume, and c is the speed of sound. We find that the speed of sound of the liquid consistently decreases along the saturation line as the temperature rises.

This trend is primarily due to the increasing isothermal compressibility [see Table I and Eq. (E1) in Appendix E]. In addition, the density of the liquid also decreases with increasing temperature. Together, these two factors contribute to reducing heat transfer and thermal conductivity, as indicated by Eq. (10). Notably, the simulated speed of sound in Table I is consistently about 15% lower than the experimental values reported by Ahmadi *et al.*⁵⁵ According to Eq. (10), this discrepancy will also lead to a reduction in thermal conductivity.

Assael *et al.* proposed a correlation formula to predict the thermal conductivity of ethanol based on its temperature and density.⁵⁸ This formula accurately reproduces the experimental data. When the correlation is adjusted by a factor of 0.83, calculated from the average difference between experimental and simulated thermal conductivity, it aligns closely with our NEMD simulation results [see Fig. 3(a)]. Notably, this scaling factor is very close to the ~10% underestimation observed in the speed of sound between simulations and

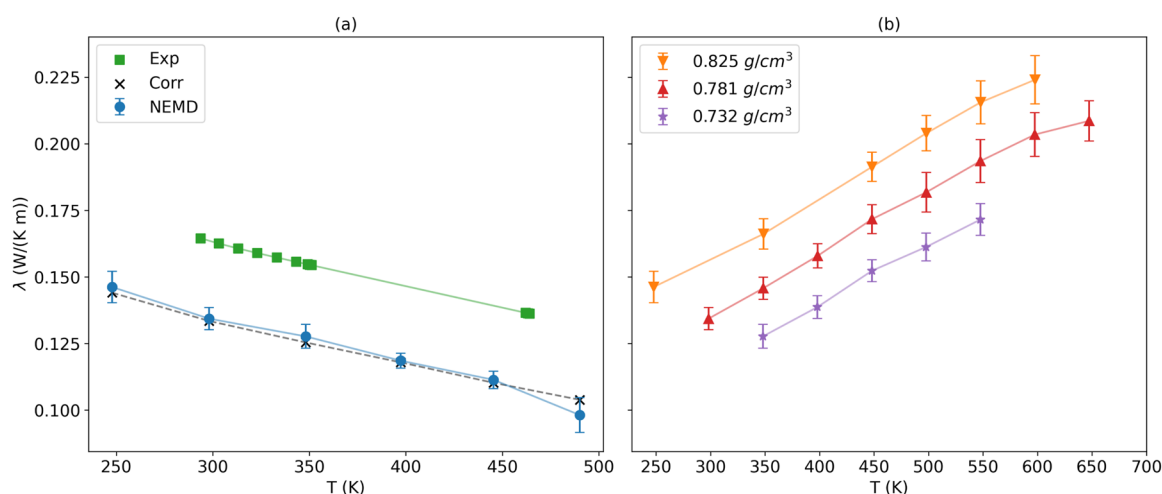


FIG. 3. (a) The thermal conductivity of ethanol along the liquid–vapor saturation line. The green square markers represent the experimental thermal conductivities reported in Ref. 36, and blue circles represent the NEMD data simulated in this work. The error bars represent the standard deviation obtained using ten replicas. The “x” markers represent the thermal conductivity values computed with the correlation equation reported in Ref. 58, scaled by a factor of 0.83 to match the average difference between experimental and simulated conductivities. (b) Thermal conductivities computed from NEMD simulations at 0.825, 0.781, and 0.732 g/cm³ isochores and a temperature range of 250–700 K. The lines in panels (a) and (b) serve as a guide to the eye. Numerical values are reported in Table II.

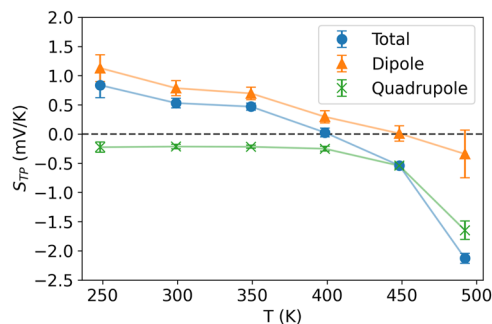


FIG. 4. The thermal polarization coefficient and its dipolar and quadrupolar contributions computed along the saturation line of liquid ethanol. The black horizontal dashed lines indicate $S_{TP} = 0$ V/K. The calculations for the quadrupole and dipole terms were conducted using the center of mass of the molecule as a reference point. The solid lines serve as a guide to the eye.

experiments at temperatures of $\sim 300 - 350$ K.^{57,62} While the Bridgman equation may not always provide quantitative conductivity values, it offers meaningful physical insight. In particular, the correlation between the speed of sound and thermal conductivity helps to explain the consistent underestimation of the thermal conductivity reported here.

In Fig. 3(b), we present the thermal conductivity of ethanol for different high-density isochores. We also examine temperatures up to 700 K, which result in high pressures of 4500 atm. The simulated thermal conductivity increases with density. The molecular packing increases with density, facilitating a more efficient intermolecular energy transfer, as indicated by Eq. (10). Within the high-density isochores ranging from 0.732 to 0.825 g/cm³, the thermal conductivity increases linearly with temperature at a uniform slope (~ 0.23 mWK⁻² m⁻¹). A similar rate of increase in thermal conductivity with temperature (~ 0.3 mWK⁻² m⁻¹) can be observed in the experimental data,⁵⁸ which supports the consistency between simulated and experimental results.

Figure 4 illustrates the thermal polarization coefficient, S_{TP} , along the liquid saturation line of ethanol. Our results show that thermal gradients induce the polarization of ethanol. The strength of this thermal polarization is comparable to that reported in previous studies of water¹¹ and acetonitrile.¹⁷ Notably, we observe an inversion of the polarization field at ~ 400 K (see Fig. 10 in Appendix C) for the electrostatic potential as a function of temperature near the inversion point. Above this temperature, the total polarization coefficient becomes negative. A similar inversion in the sign of the thermal polarization field is present in water. While the specific inversion temperature varies depending on the water force field used, we concluded that the expected inversion in experimental observations of water is likely to occur above 400–500 K.¹¹ This estimate is based on the results from two accurate water models, TIP4P/2005 and OPC, which successfully reproduced the thermal expansion of water, a key quantity in the phenomenological theory developed in Ref. 11.

The observation of an inversion temperature in water can be explained by considering the balance of different contributions to the total electrostatic field. Following earlier works,^{50,63} the charge

density can be expanded in a series of terms, including dipolar P and quadrupolar Q , contributions for systems that do not contain free charges.

The calculation of the electrostatic moments requires the choice of a molecular reference point. Following Ref. 50, the center of mass is the usual choice for this molecular reference, but others are possible. The dependence of the dipolar contribution on the molecular reference has been discussed recently.^{28,51} In our calculations, the total electrostatic potential derived from the sum of dipolar and quadrupolar terms for different choices is approximately equal (with average deviations on the order of 4%–6%) to that obtained from the integral of the charge density. This is illustrated in Fig. 1, which shows good agreement between the electrostatic potentials calculated from the integral of the charge density and those obtained through the molecular approach, incorporating both dipolar and quadrupolar contributions and using the molecular center of mass to calculate these contributions.

We analyzed how our results depend on the chosen origin. Figure 13 and Table III in Appendix G present the dipolar, quadrupolar, and total thermal polarization coefficients for various reference points: the molecular center of mass of ethanol, which is commonly chosen as the center of mass,⁵⁰ as well as the locations of CH₃, CH₂, O, and H.

When we bin the dipolar and quadrupolar contributions along the heat flux vector, we observe that different molecular reference points yield different values for the P and Q contributions to S_{TP} due to different assignments of the multipole to each bin. However, their sum gives consistent S_{TP} , and notably, the P and Q contributions have always opposite signs, regardless of the reference point used. This finding is significant as it allows us to understand the emergence of an inversion temperature as a balance between the contributions of P and Q . This balance is preserved for all the reference points sampled in our study. Hence, from now on, we will discuss our results using the center of mass as a reference point.

As the temperature increases along the saturation line, we observe a weakening of the dipole contribution due to a reduction in the structural organization of molecular dipoles and a loss of their alignment in a predominant direction. This diminishing trend has been observed in water near its critical point.²³

The structural differences between water and ethanol, particularly the presence of a nonpolar ethyl group and a weaker hydrogen-bonding network in ethanol, make the dipole orientation more susceptible to disruption, even under subcritical conditions. Additionally, these differences cause the contributions from the quadrupolar term to the thermal polarization to be less sensitive to temperature changes up to 400 K. The inversion we observe at ~ 400 K can be interpreted as a balance of different molecular multipole moments, which contribute with opposite signs to the total thermal polarization coefficient. Following the discussion in well-recognized texts on the subject,⁵⁰ examining the various molecular contributions provides a valuable approach to understanding the electrostatics of molecular fluids.

Our results indicate a significant increase in thermal polarization as the liquid approaches its critical point. This enhancement in polarization reaches values comparable to those observed near the primary liquid–vapor critical point of water, with $S_{TP} \sim -4$ mV/K.²³ A similar increase has recently been observed in simulations of

supercooled water, where this enhancement occurs within a thermodynamic region associated with the proposed liquid–liquid critical point.¹⁸ In ethanol, we observe an enhancement in one of the molecular moments near the critical point, which corresponds to a notable increase in the isobaric thermal expansion coefficient (see Table I).

Figure 5 illustrates the thermal polarization coefficient along various isochores. In all high-density isochores [Figs. 5(a)–5(c)], an inversion in thermal polarization is observed. This inversion is attributed to the balance of molecular multipoles. The inversion temperatures of 451, 481, and 505 K increase with the ethanol densities of 0.732, 0.781, and 0.825 g/cm³, respectively. However, compared to the strong enhancement observed along the coexistence line as the system approaches the critical point, these liquid isochores exhibit a weaker thermal polarization effect above the inversion temperature, with S_{TP} strength being less than 2 mV/K. Additionally, we observe that S_{TP} along the critical isochore shows a rapid increase with decreasing temperature [see Fig. 5(d)]. These results support the enhancement of the thermal polarization effect under critical conditions.

Figure 6 compares the thermal polarization coefficients of ethanol, acetonitrile,¹⁷ and water,^{18,23} expressed in reduced units based on their critical temperature and density. Under subcritical conditions, water and ethanol show an inversion in their thermal polarization coefficients S_{TP} , changing from positive to negative values as the temperature approaches the critical point. In contrast, acetonitrile maintains consistently negative values of S_{TP} throughout the entire temperature range.

The inversion of S_{TP} in ethanol should correlate with the weakening of hydrogen bonding networks as the temperature increases. This loss of molecular order modifies the individual contributions

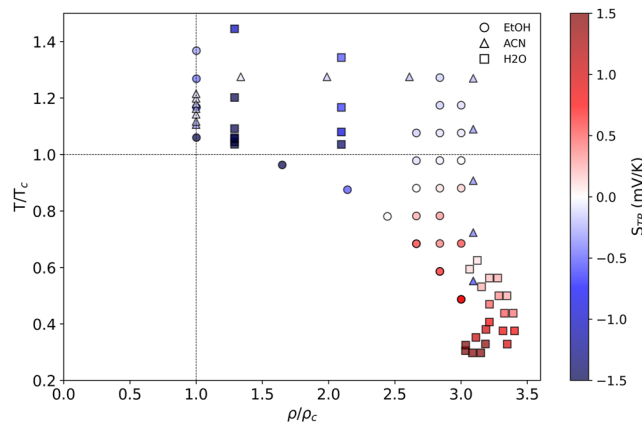


FIG. 6. The thermal polarization coefficient of ethanol (this study, represented as circles), acetonitrile (Ref. 17, represented as triangles), and TIP4P/2005 water (Refs. 18 and 23, represented as squares). The data are plotted in the temperature–density plane using reduced units based on the critical properties of each fluid. The critical temperature and density are taken from Refs. 39, 64, and 65 for TraPPE ethanol, TraPPE acetonitrile, and TIP4P/2005 water, respectively. The color mapping indicates both the magnitude and sign of the thermopolarization coefficient.

of the molecular moments to the thermal polarization coefficient of the fluid. The contributions balance each other, resulting in the inversion and sign change in the thermal polarization coefficient.

In a previous study, we examined how the liquid–vapor interfacial surface potential changes with temperature.¹¹ Earlier research

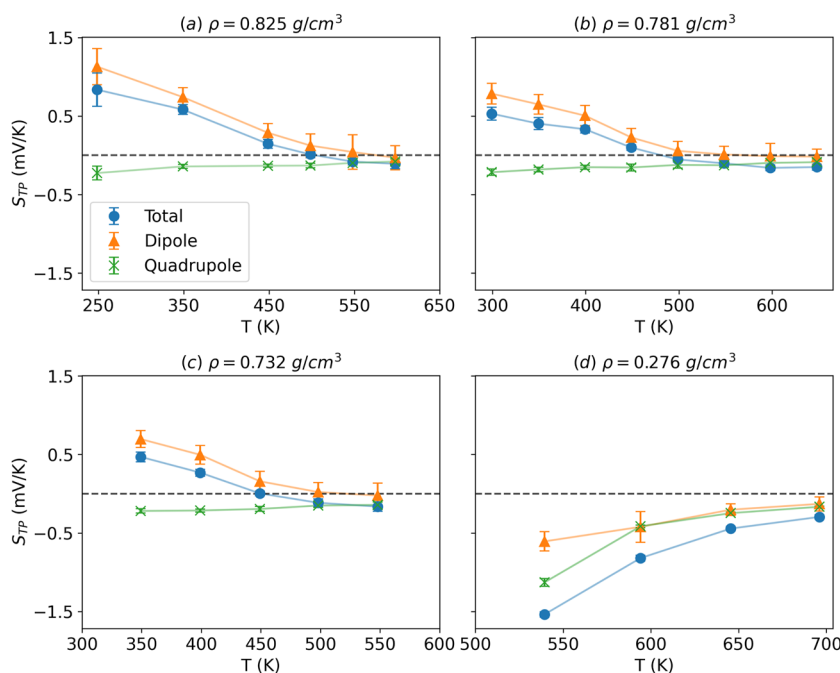


FIG. 5. Thermal polarization coefficient and dipolar and quadrupolar contributions obtained from NEMD simulations along different isochores. The horizontal dashed line indicates $S_{TP} = 0$ V/K. The dipolar and quadrupolar contributions were computed using the molecular center of mass as the reference point.

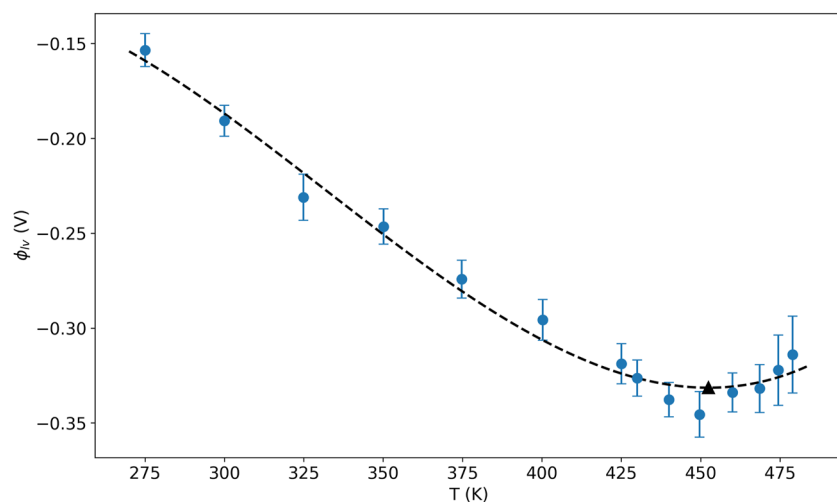


FIG. 7. The dependence of the surface potential of the ethanol liquid–vapor interface on temperature obtained through equilibrium simulations in the NVT ensemble. The black dashed line represents a third-order polynomial that fits the surface potential data, described by the following equation: $\phi_v = 3 \times 10^{-8} T^3 - 3 \times 10^{-5} T^2 + 9 \times 10^{-3} T - 0.9$. The black triangle marks the local minimum of the surface potential, where the derivative of the surface potential with respect to temperature changes sign, $T = 452.5$ K.

using the SPC/E water model⁶⁶ reported a surface potential gradient of -1 mV/K, which aligns with earlier experiments conducted by Randles and Schiffrin in aqueous solutions.⁶⁷ The surface potential of water displays a minimum between 350 and 425 K. Additionally, we found a linear correlation between the inversion temperature of the thermal polarization effect and the minimum of the surface potential across different water models.

We investigate now the correlation between the temperature inversion of thermal polarization and the minimum in the liquid–vapor surface potential of ethanol. We calculated the temperature dependence of the surface potential of the ethanol liquid–vapor interface using equilibrium simulations in the NVT ensemble (see Fig. 11 in Appendix D). Figure 7 displays the surface potential obtained from our equilibrium NVT simulations. Initially, the potential decreases as the temperature increases, with a gradient of ~ 1 mV/K. This behavior resembles the thermal polarization coefficients shown in Figs. 4 and 5.

The surface potential exhibits a local minimum around 450 K, which causes an inversion in its temperature derivative, as shown in Fig. 7. The inversion temperature for the thermal polarization coefficient, ~ 400 K, is roughly 50 K lower than the temperature at which the surface potential reaches its minimum. A similar phenomenon was reported in water, where the inversion temperature for polarization was also lower than the temperature corresponding to the minimum surface potential.¹¹ The results obtained for ethanol further strengthen the correlation between these two properties: the change in sign of the thermal polarization coefficient and the presence of a minimum in the surface potential at the liquid–vapor interface.

Non-equilibrium thermodynamic theory suggests that effects such as thermal polarization can decrease the thermal conductivity of a fluid.¹² These effects are not present at the inversion temperatures mentioned earlier as there is no thermal polarization in those conditions. To quantify the impact of thermal polarization on the thermal conductivity of ethanol, we can use Eq. (9),¹⁷ which involves calculating the dielectric permittivity and the Debye relaxation time.

Table I presents our results for the static dielectric permittivity and the Debye relaxation times at various thermodynamic states along the coexistence line, covering temperatures from 300 to 495 K. Additional simulation details and results that clarify the calculation of these properties from our equilibrium simulations can be found in Appendix E.

At 300 K, the simulated dielectric permittivity is lower than the experimental values reported at the same temperature.^{68,69} However, it is similar to the results obtained by Saiz *et al.*,⁷⁰ who used the OPLS potential. The approximate 25% deviation from the experimental data can be partly attributed to the approximations made in representing non-polarizable united atoms. As noted in Ref. 70, adding the high-frequency dielectric permittivity (~ 1.85) would improve the agreement between the simulated and experimental results.

The decrease in the dielectric constant with increasing temperature occurs due to the disruption of dipole alignment caused by enhanced thermal agitation. The Debye relaxation time, which is obtained from fitting the total dipole moment time correlation function to an exponential function, shows a significant decrease as the temperature rises. This trend has been previously observed in water, where relaxation times decrease exponentially with temperature, following the Arrhenius equation due to reduced viscosity.^{71,72} Moreover, the fitted relaxation time at ambient temperature aligns reasonably well with experimental results corresponding to the bulk reorientation modes.^{68,69}

The reduction in thermal conductivity caused by the coupling effect of thermal polarization is shown in Table I. The reduction was calculated using Eq. (9). The reduction remains relatively small at ambient temperatures, reaching zero at the inversion temperature $S_{TP} = 0$. In other fluids that exhibit rapid rotation, such as acetonitrile, the effects of thermal polarization are more pronounced, resulting in a reduction of $\sim 4\%$ at 300 K due to these effects.¹⁷ However, as the system approaches the critical point, the significantly shorter Debye relaxation time and increased S_{TP} lead to a noticeable impact on the thermal conductivity of the liquid. Consequently, as the critical point is approached, the reduction caused by thermal polarization is significantly amplified.

IV. SUMMARY AND CONCLUSIONS

Using non-equilibrium molecular dynamics and accurate empirical force fields, we have investigated the thermal transport properties and thermal polarization effect of ethanol across various thermodynamic states in both its liquid and supercritical phases. The TraPPE force field accurately reproduces the general temperature dependence of the thermal conductivity of ethanol. In agreement with experimental results, the thermal conductivity decreases along the coexistence line as the temperature increases, but it exhibits a linear increase when heated at a constant density.

Similarly, ethanol has much lower thermal conductivity than water. This difference suggests that the non-polar alkyl group in ethanol hinders heat conduction without affecting the fundamental transport process. However, the TraPPE force field systematically underestimates the thermal conductivity of ethanol by $\sim 15\%$. We conclude that this underestimation is linked to a reduced speed of sound or an overestimation of isothermal compressibility. Our work, therefore, provides insights that could help refine ethanol force fields by targeting specific thermophysical properties that can be analyzed through fluctuations in equilibrium simulations.

Additionally, we have demonstrated that applying thermal gradients to ethanol leads to the phenomenon of thermal polarization. The inversion of the thermal polarization electric field occurs both along the liquid saturation curve and across various liquid isochores. This effect results from the balance between molecular multipole moments, namely, dipolar and quadrupolar components, which contribute with opposite signs to the total thermal polarization coefficients. While we have calculated the molecular moments using (the most common choice) the center of mass as the reference, we acknowledge the dependence of these molecular moments on the location of the reference point. However, for ethanol, different reference points for calculating the electrostatic moments predict consistent results, showing that the thermal polarization inversion can be interpreted as the balance of two opposing electrostatic moment contributions.

The existence of the thermal polarization coupling effect in ethanol indicates that ethanol becomes a worse heat conductor when this effect is significant. Large polarization responses are expected as the fluid approaches the critical point; therefore, this coupling effect must be included to calculate the thermal conductivity of molecular fluids accurately.

The thermal polarization effect has been reported in theoretical studies of hydrogen-bonded solvents, such as water, and aprotic solvents, such as acetonitrile. We have demonstrated here that this phenomenon is also present in ethanol. It will be interesting to expand these studies to include other solvents and obtain a complete picture of the molecular mechanisms behind thermally induced electrostatic fields and their impact on the thermal transport properties of liquids.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Guansen Zhao: Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Supervision (equal); Validation (equal); Writing – original draft (lead); Writing – review & editing (equal). **Yaxuan Xiao:** Data curation (equal); Formal analysis (supporting); Investigation (supporting); Methodology (supporting); Validation (equal); Writing – review & editing (equal). **Angad Deshmukh:** Data curation (supporting); Formal analysis (supporting); Investigation (supporting); Validation (supporting); Writing – review & editing (equal). **Aidan Chapman:** Data curation (equal); Formal analysis (lead); Investigation (equal); Methodology (lead); Software (lead); Supervision (equal); Validation (equal); Writing – review & editing (equal). **Fernando Bresme:** Conceptualization (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Project administration (lead); Resources (lead); Supervision (lead); Validation (equal); Writing – original draft (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

APPENDIX A: ENERGY CONSERVATION CHECK

Figure 8 shows the energy exchanged between the cold and hot thermostat regions during a typical NEMD simulation. The

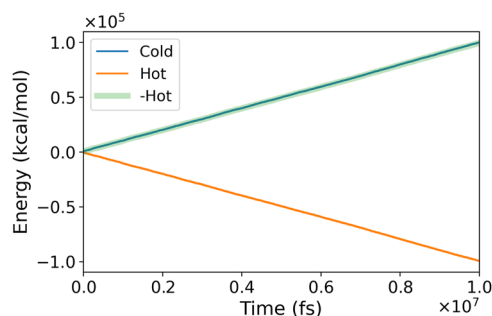


FIG. 8. Energy conservation check for a representative NEMD run at an average temperature of 397 K and a density of 0.672 g/cm^3 . The temperatures of the cold and hot thermostats were set to 350 and 400 K, respectively. The blue and orange lines denote the cumulative energy exchange vs simulation time at the cold and hot thermostats, respectively. The green line represents the negative of the energy exchange in the hot region for a clearer assessment of energy conservation. The total heat rate, $\dot{Q}$, can be obtained from the time derivative of the energy.

agreement between the energy exchanged at the hot and cold thermostats indicates that our approach demonstrates excellent energy conservation.

APPENDIX B: COMPARISON OF CONTINUITY AND MICROSCOPIC CALCULATIONS OF THE HEAT FLUX

In Fig. 9, we show the microscopic heat flux vector computed using the Irving–Kirkwood formula truncated to first order,^{48,49} with the implementation to perform calculation in K-space.^{73,74}

The virial stress tensor includes contributions from both short- and long-range interactions. The short-range terms, which consist of pairwise, bond, angle, and dihedral interactions, were computed using the centroid-based atomic stress formulation.^{75,76} The agreement between the microscopic heat flux and the flux calculated with the continuity equation [Eq. (2)] demonstrates that the IK1 method yields accurate results for the heat flux when considering a slowly varying density field.

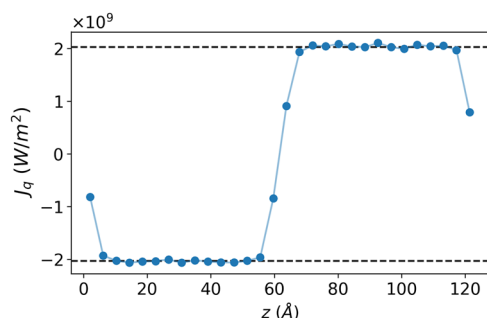


FIG. 9. Comparison of the microscopic heat flux profile (blue dots), calculated using the IK1 method, and the heat flux (dashed black line), calculated with Eq. (2). The results are from a representative NEMD simulation, with T_{hot} and T_{cold} set at 400 and 300 K, respectively. The system was simulated at an average density of 0.732 g/cm³, under the same conditions as Fig. 1.

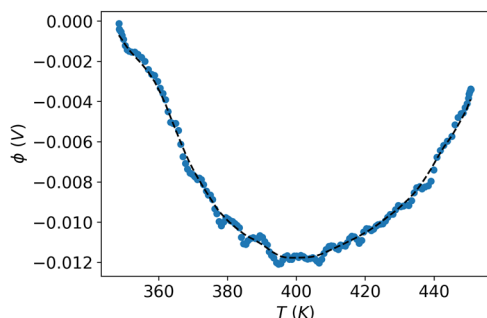


FIG. 10. The electrostatic potential as a function of temperature from a sample NEMD run with hot and cold thermostats set at 450 and 350 K, respectively. This simulation was conducted at 397 K average temperature and 0.672 g/cm³ density. The dashed black line shows a smoothed fit for clarity.

APPENDIX C: POTENTIAL PROFILE NEAR THE INVERSION TEMPERATURE

Figure 10 illustrates the relationship between the electrostatic potential and temperature. For this plot, the local temperature and corresponding electrostatic potential values from each bin were extracted and rearranged in the order of increasing temperature, allowing for a clearer visualization of the overall trend. The local electrostatic potential was obtained by double integration of the local charge density profile. The local electrostatic potential was obtained by integrating the charge density to compute the electric field [see Eq. (4)], followed by integration of the electric field. The negative first derivative of this relationship gives the thermal polarization coefficient (S_{TP}), as defined in Eq. (5). The figure shows a clear trend with S_{TP} changing sign at around 400 K.

APPENDIX D: LIQUID-VAPOR INTERFACE SIMULATIONS

Figure 11 illustrates a sample configuration used in the equilibrium simulations of the ethanol liquid–vapor interface. To prevent drift of the liquid phase, the center-of-mass momentum of the entire system was reset at every timestep. The average density of the liquid and vapor phases was obtained from the density profiles shown in the middle panel. These densities are represented by magenta triangle markers in Fig. 2. The surface potentials are calculated by determining the potential difference between the average electrostatic potentials of the liquid and vapor phases ($\phi_{\text{liq}} - \phi_{\text{vap}}$). This difference is visually represented in the bottom panel by the gap between the blue and orange dashed lines.

APPENDIX E: EQUILIBRIUM SIMULATIONS OF ETHANOL WITH GROMACS

For the calculation of the thermophysical properties of ethanol, we performed equilibrium molecular dynamics simulations with GROMACS (vs January 2024).⁵² We first ran 20 ns simulations in the isothermal–isobaric (NPT) ensemble to test the force field implementation and compute the equation of state. The isobaric thermal expansion coefficient (α) was calculated with $\langle \delta V \delta H \rangle_{NPT} = k_B T^2 V \alpha$, and the isothermal compressibility (κ_T) was calculated with $\langle \delta V^2 \rangle_{NPT} = V k_B T \kappa_T$.⁷⁷ In the fluctuation relations, V denotes the volume, H represents the enthalpy, and k_B is the Boltzmann constant. Additionally, $\delta \mathcal{P} = \mathcal{P} - \mathcal{P}_{\text{ens}}$, where “ens” represents the ensemble average of property $\mathcal{P}$. The isentropic (adiabatic) speed of sound in ethanol was determined using mass density ρ , the isobaric ($C_P = \langle \delta H^2 \rangle / k_B T^2$) and isochoric ($C_V = C_P - V T \alpha^2 / \kappa_T$) heat capacities, and the isothermal compressibility,

$$c_s = \sqrt{\frac{C_P}{C_V} \frac{1}{\rho \kappa_T}}. \quad (\text{E1})$$

NVT simulations were conducted at the target density and temperature equal to the average of T_{hot} and T_{cold} in NEMD to obtain the dielectric properties. Additionally, we ran long simulations (at least 100 ns) to ensure convergence in the static dielectric

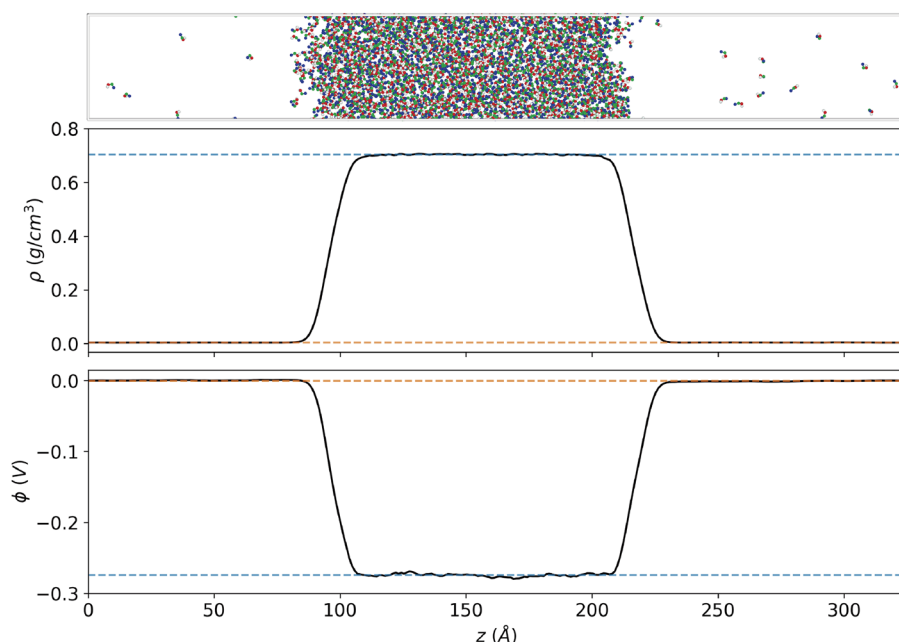


FIG. 11. (Top panel) Setup for the sample equilibrium simulation of the ethanol liquid–vapor interface at an average temperature of 375 K. The spheres represent different united atom groups or atoms: blue for CH₃, green for CH₂, red for oxygen, and white for hydrogen. (Bottom panels) Density and electrostatic potential profiles obtained from the simulations. The dashed blue and orange lines indicate the average values calculated for the liquid and vapor phases, respectively.

permittivity [see Fig. 12(a)]. The dielectric permittivity (ϵ_r) values were calculated using the average from the last 20 ns of the production run with⁷⁸

$$\epsilon_r - 1 = \frac{\langle \mathbf{P}^2 \rangle - \langle \mathbf{P} \rangle^2}{3Vk_B T \epsilon_0}, \quad (\text{E2})$$

where the angle brackets $\langle \cdot \rangle$ denote a time average and $\mathbf{P} = \sum_i q_i \mathbf{r}_i$ represents the total dipole moment of the simulation box, which was obtained by calculating a sum of the atomic charges (q_i) multiplied

by their position vector ($\mathbf{r}_i$) in the simulation box. To determine the Debye relaxation time (τ_D), we first calculated the time correlation function of the total dipole moment,

$$C_P(t) = \frac{\langle \mathbf{P}(t) \cdot \mathbf{P}(0) \rangle}{\langle \mathbf{P}(0) \cdot \mathbf{P}(0) \rangle}. \quad (\text{E3})$$

τ_D was then obtained by fitting the long time part of the correlation function to a single exponential, $C_P(t) = A \exp(-t/\tau_D)$, as shown in Fig. 12(b).

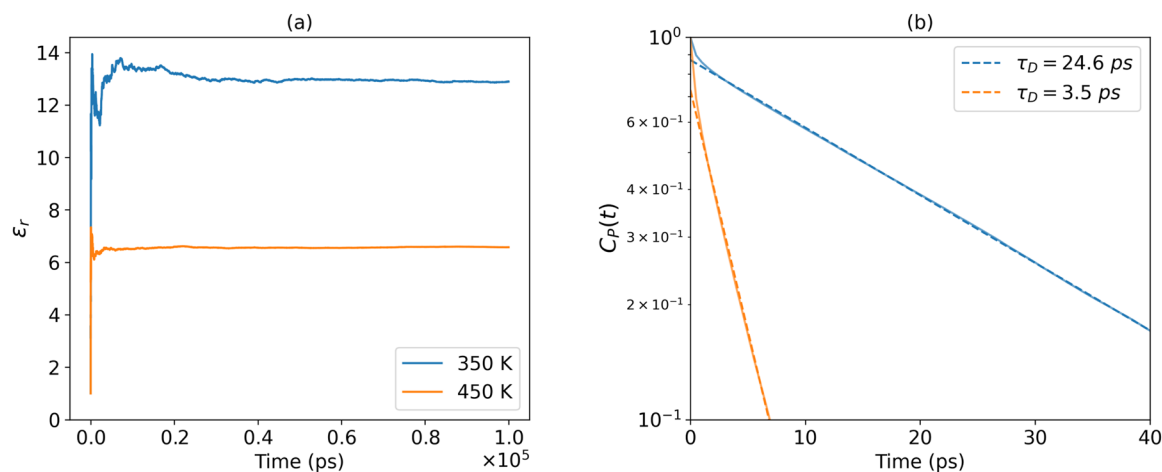


FIG. 12. (a) Time evolution of the dielectric constant from 0 to 100 ns at 350 and 450 K temperatures, along the saturation line. (b) The total dipole correlation functions, $C_P(t)$, are shown for the same thermodynamic conditions. The dashed lines indicate the fit to the exponential function.

TABLE II. Results of the NEMD simulations. The temperatures are in K, densities (ρ) in g/cm³, pressures in atmosphere, thermal conductivities (λ) in W/(Km), and thermal polarization coefficients (S_{TP}) in the units of mV/K. $\sigma\lambda$ and σS_{TP} are the standard deviations obtained from replicas.

T	ρ	P	σ_P	λ	σ_λ	S_{TP}	$\sigma_{S_{TP}}$
247.8	0.83	-4.2	3.1	0.146	0.006	0.836	0.21
298.1	0.78	-1.0	1.8	0.134	0.004	0.530	0.08
348.1	0.73	-2.9	1.9	0.128	0.004	0.469	0.06
397.3	0.67	1.2	2.4	0.119	0.003	0.026	0.08
445.4	0.59	14.2	1.2	0.111	0.003	-0.539	0.03
490.1	0.45	48.2	0.6	0.098	0.007	-2.129	0.08
348.5	0.83	1097.0	2.1	0.166	0.006	0.582	0.06
448.2	0.83	2332.5	3.5	0.191	0.005	0.147	0.06
498.0	0.83	2993.6	4.8	0.204	0.007	0.011	0.04
547.8	0.83	3659.8	3.4	0.216	0.008	-0.081	0.04
597.7	0.83	4320.2	3.7	0.224	0.009	-0.108	0.06
348.5	0.78	429.0	2.3	0.146	0.004	0.403	0.08
398.4	0.78	921.3	2.7	0.158	0.005	0.332	0.05
448.2	0.78	1455.3	2.0	0.172	0.005	0.099	0.04
498.0	0.78	2015.5	3.3	0.182	0.007	-0.053	0.03
547.7	0.78	2581.6	3.5	0.194	0.008	-0.102	0.04
597.6	0.78	3150.0	2.7	0.203	0.008	-0.160	0.04
647.5	0.78	3702.8	4.6	0.209	0.008	-0.150	0.04
398.1	0.73	356.2	2.6	0.139	0.004	0.269	0.04
448.2	0.73	788.2	2.9	0.152	0.004	0.004	0.03
497.8	0.73	1246.4	2.8	0.161	0.005	-0.115	0.05
547.8	0.73	1719.4	3.7	0.172	0.006	-0.163	0.06
539.4	0.28	68.0	0.7	0.073	0.006	-1.536	0.03
594.1	0.28	132.9	0.6	0.075	0.003	-0.820	0.04
645.5	0.28	192.7	0.9	0.073	0.003	-0.444	0.03
696.0	0.28	248.8	0.8	0.075	0.003	-0.295	0.03

APPENDIX F: NEMD SIMULATION RESULTS

The results of the NEMD simulations are given in [Table II](#).

APPENDIX G: DIPOLAR AND QUADRUPOLAR CONTRIBUTIONS TO THE THERMAL POLARIZATION FROM DIFFERENT REFERENCE POINTS

In [Fig. 13](#), we present the total electric potential and the contributions from both the dipolar and quadrupolar terms as a function of temperature. This figure was plotted using the same procedure described in [Appendix C](#). These values were computed based on different reference molecular points in the temperature range 250–350 and 350–450 K. Additionally, [Table III](#) provides a summary of the corresponding thermal polarization coefficients, which were calculated from various reference points.

Although the dipolar and quadrupolar terms exhibit some variation depending on the chosen reference point, the combined contribution of these two terms remains nearly constant and closely aligns with the total S_{TP} calculated from the total electrostatic charge density, falling well within the range of the associated error bars. The small variations observed can be attributed to fluctuations in the raw data, which affect the slope determined through linear fitting around the target temperature, and show that the multipole expansion, including the dipolar and quadrupolar terms, does not reproduce exactly the electrostatic potential obtained from the double integration of the atomic charge density.

Calculations of the octupole moment density according to⁵⁰

$$O_{zzz}(z) = \frac{1}{A} \left(\sum_m^{N_m} \delta(z - z_m) \frac{1}{6} \sum_{i \in m}^{N_{charges}} q_{i,m} z_{i,m}^3 \right) \quad (G1)$$

did not yield a potential contribution that accounted for the small discrepancy between the sum of the dipolar and quadrupolar

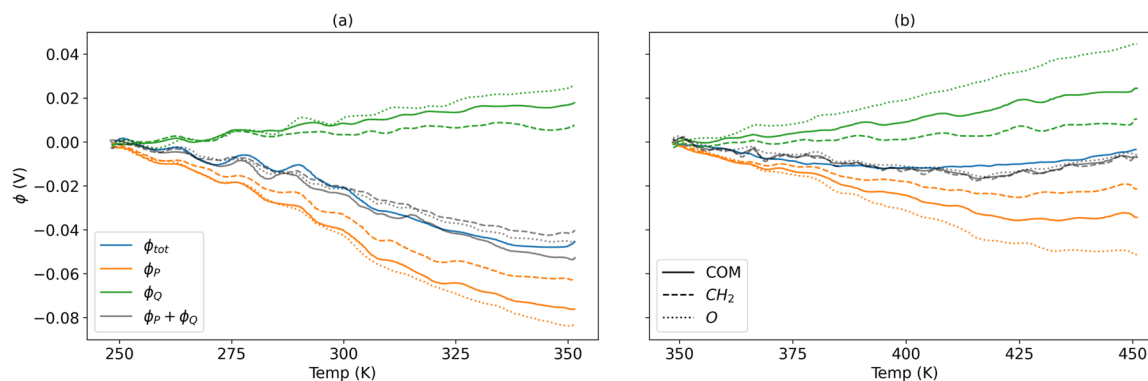


FIG. 13. Total electrostatic potential together with its dipolar and quadrupolar contributions as a function of temperature from sample NEMD simulations over the temperature ranges of (a) 250–350 and (b) 350–450 K. The average temperature and density for these two runs are 298 K and 0.781 g/cm³ for (a) and 397 K and 0.672 g/cm³ for (b). The combined dipolar and quadrupolar contributions are shown in black and compared to the total potential. Different line styles represent results calculated from distinct reference points: the ethanol molecular center of mass (solid lines), the CH₂ group (dashed lines), and the oxygen atom (dotted lines).

TABLE III. Dipolar and quadrupolar contributions to the thermal polarization coefficient, computed from different reference points, including the molecular center of mass, the CH₃, CH₂ groups, and the oxygen and hydrogen atoms. The sum of the dipolar and quadrupolar terms is compared with the total S_{TP} , calculated from the atomic charge density. All values are reported in units of mV/K. The results are obtained from two sample NEMD simulation runs over the 250–350 and 350–450 K temperature ranges. Standard deviations across replicas are indicated by the $\pm$ symbol.

298 K				
Ref	$S_{TP,P}$	$S_{TP,Q}$	$S_{TP,P} + S_{TP,Q}$	$S_{TP,tot}$
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	$S_{TP,P}$	$S_{TP,Q}$	$S_{TP,P} + S_{TP,Q}$	$S_{TP,tot}$
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

contributions seen in Fig. 13—this contribution was uniformly on the order of 1.2×10^{-5} V over 250–350 K, with the oxygen atom as the reference point.

REFERENCES

¹A. Habibi Khalaj and S. K. Halgamuge, *Appl. Energy* **205**, 1165 (2017).
²O. Kalaf, D. Solyali, M. Asmael, Q. Zeeshan, B. Safaei, and A. Askir, *Int. J. Energy Res.* **45**, 6495 (2021).
³A. L. Moore and L. Shi, *Mater. Today* **17**, 163 (2014).
⁴S. Kunkel, T. Teumer, P. Dörnhöfer, F. Wunder, J. U. Repke, and M. Rädle, *J. Energy Storage* **28**, 101178 (2020).
⁵S. B. Oskouei and Ö. Bayer, *J. Energy Storage* **62**, 106959 (2023).
⁶R. Saidur, K. Y. Leong, and H. A. Mohammed, *Renewable Sustainable Energy Rev.* **15**, 1646 (2011).
⁷*Measurement of the Transport Properties of Fluids*, edited by W. Wakeham, A. Nagashima and J. Sengers, *Experimental Thermodynamics* (Blackwell Scientific Publications, Oxford, 1991), Vol. 3.
⁸P. W. Bridgman, *Proc. Natl. Acad. Sci. U. S. A.* **9**, 341 (1923).
⁹R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, 2nd ed. (John Wiley & Sons, 2002).
¹⁰F. Bresme, A. Lervik, D. Bedeaux, and S. Kjelstrup, *Phys. Rev. Lett.* **101**, 020602 (2008).
¹¹A. Chapman and F. Bresme, *Phys. Chem. Chem. Phys.* **24**, 14924 (2022).
¹²S. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (Dover Publications, New York, 1984).
¹³C. Ludwig, “Diffusion zwischen ungleich erwärmten orten gleich zusammengesetzter lösungen,” in *Sitzungsberichte der Bayerischen Akademie der Wissenschaften* (Mathematisch-Naturwissenschaftliche Klasse, 1856), Vol. 539.
¹⁴C. Soret, “Sur l’état d’équilibre que prend, du point de vue de sa concentration, une dissolution saline primitivement homogène, dont deux parties sort portées à des températures différentes,” *C. R. Arch. Sci. Phys. Nat., Genève* **2**, 48–61 (1879).
¹⁵S. Wiegand, *J. Phys.: Condens. Matter* **16**, R357 (2004).
¹⁶N. A. T. Miller, P. J. Daivis, I. K. Snook, and B. D. Todd, *J. Chem. Phys.* **139**, 144504 (2013).

¹⁷O. R. Gittus, P. Albella, and F. Bresme, *J. Chem. Phys.* **153**, 204503 (2020).
¹⁸G. Zhao and F. Bresme, *J. Phys. Chem. Lett.* **15**, 9774–9779 (2024).
¹⁹F. Römer, F. Bresme, J. Muscatello, D. Bedeaux, and J. M. Rubí, *Phys. Rev. Lett.* **108**, 105901 (2012).
²⁰A. Gardin and A. Ferrarini, *Phys. Chem. Chem. Phys.* **21**, 104 (2019).
²¹T. Shen, Y. Hou, J. Yang, L. Yang, and R.-Y. Dong, *J. Chem. Phys.* **162**, 064904 (2025).
²²J. Armstrong and F. Bresme, *Phys. Rev. E* **92**, 060103 (2015).
²³I. Iriarte-Carretero, M. A. Gonzalez, J. Armstrong, F. Fernandez-Alonso, and F. Bresme, *Phys. Chem. Chem. Phys.* **18**, 19894 (2016).
²⁴J. L. F. Abascal and C. Vega, *Phys. Rev. Lett.* **98**, 237801 (2007).
²⁵H. Ding, Z. Chen, C. Ponce, and Y. Zheng, *Chem. Commun.* **59**, 2208 (2023).
²⁶W. Milestone, Q. Hu, A. M. Loveless, A. L. Garner, and R. P. Joshi, *J. Appl. Phys.* **132**, 094701 (2022).
²⁷S. Kjelstrup, K. R. Kristiansen, A. F. Gunnarshaug, and D. Bedeaux, *J. Chem. Phys.* **158**, 020901 (2023).
²⁸O. Nickel, L. J. V. Ahrens-Iwers, R. H. Meißner, and M. Janssen, *Phys. Rev. Lett.* **132**, 186201 (2024).
²⁹S. Alosious, S. R. Tee, and D. J. Searles, *J. Phys. Chem. C* **128**, 2190 (2024).
³⁰J. Wei, H. Huang, Q. Luo, N. Liu, X. Wang, X. Wang, M. Zhong, and X. Huang, *Catal. Lett.* **152**, 263 (2022).
³¹J. W. Kinart and Z. Kinart, *Current Organic Synthesis* (Bentham Science, 2017), Vol. 14, p. 477.
³²Z. Liu, B. Guo, L. Hong, and T. H. Lim, *Electrochem. Commun.* **8**, 83 (2006).
³³O. Neumann, A. D. Neumann, E. Silva, C. Ayala-Orozco, S. Tian, P. Nordlander, and N. J. Halas, *Nano Lett.* **15**, 7880 (2015).
³⁴L. Zhang, Y. Jing, P. Qu, W. Wang, X. Yao, and L. Tian, *Appl. Therm. Eng.* **215**, 119031 (2022).
³⁵R. D. Johnson III, *NIST Computational Chemistry Comparison and Benchmark Database* (NIST, 2020).
³⁶J. Chen, H. Xing, T. Zhan, L. Chen, M. He, and Y. Zhang, *Fluid Phase Equilib.* **552**, 113276 (2022).
³⁷W. Wagner and A. Pruß, *J. Phys. Chem. Ref. Data* **31**, 387 (2002).
³⁸B. Chen, J. J. Potoff, and J. I. Siepmann, *J. Phys. Chem. B* **105**, 3093 (2001).

- ³⁹B. L. Eggimann, Y. Sun, R. F. DeJaco, R. Singh, M. Ahsan, T. R. Josephson, and J. I. Siepmann, *J. Chem. Eng. Data* **65**, 1330 (2020).
- ⁴⁰Y. Li, J. C. Liu, P. F. Lu, and X. D. Yang, *Acta Phys. Sin.* **59**, 4880 (2010).
- ⁴¹S. Plimpton, *J. Comput. Phys.* **117**, 1 (1995).
- ⁴²A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in 't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott, and S. J. Plimpton, *Comput. Phys. Commun.* **271**, 108171 (2022).
- ⁴³G. Bussi, D. Donadio, and M. Parrinello, *J. Chem. Phys.* **126**, 014101 (2007).
- ⁴⁴R. W. Hockney and J. W. Eastwood, *Computer Simulation Using Particles* (Adam Hilger, New York, 1989).
- ⁴⁵R. E. Isele-Holder, W. Mitchell, and A. E. Ismail, *J. Chem. Phys.* **137**, 174107 (2012).
- ⁴⁶R. E. Isele-Holder, W. Mitchell, J. R. Hammond, A. Kohlmeyer, and A. E. Ismail, *J. Chem. Theory Comput.* **9**, 5412 (2013).
- ⁴⁷A. Stukowski, *Modell. Simul. Mater. Sci. Eng.* **18**, 015012 (2010).
- ⁴⁸B. D. Todd, P. J. Daivis, and D. J. Evans, *Phys. Rev. E* **51**, 4362 (1995).
- ⁴⁹J. H. Irving and J. G. Kirkwood, *J. Chem. Phys.* **18**, 817 (1950).
- ⁵⁰J. D. Jackson, *Classical Electrodynamics*, 3rd ed. (Wiley, New York, 1999).
- ⁵¹L. J. V. Ahrens-Iwers, O. Nickel, and R. H. Meißner, *J. Phys. Commun.* **9**, 041001 (2025).
- ⁵²H. Bekker, H. Berendsen, E. Dijkstra, S. Achterop, R. Drunen, D. van der Spoel, A. Sijbers, H. Keegstra, B. Reitsma, and M. Renardus, *Phys. Comput.* **92**, 252 (1993).
- ⁵³M. Abraham, A. Alekseenko, V. Basov, C. Bergh, E. Briand, A. Brown, M. Doijade, G. Fiorin, S. Fleischmann, S. Gorelov, G. Gouaillardet, A. Gray, M. E. Irrgang, F. Jalalypour, J. Jordan, C. Kutzner, J. A. Lemkul, M. Lundborg, P. Merz, and E. Lindahl (2024). "GROMACS 2024.0 source code (2024.0)," Zenodo. <https://zenodo.org/records/10589643>
- ⁵⁴M. Gude and A. S. Teja, "Vapor-liquid critical properties of elements and compounds. 4. Aliphatic alkanols," *J. Chem. Eng. Data* **40**, 1025 (1995).
- ⁵⁵P. Ahmadi, B. N. Karim Nobakht, and A. Chapoy, *J. Chem. Eng. Data* **63**, 2486 (2018).
- ⁵⁶D. Pečar and V. Doleček, *Fluid Phase Equilib.* **230**, 36 (2005).
- ⁵⁷T. Zhan, J. Chen, X. Li, Q. Zhou, M. He, and Y. Zhang, *Fluid Phase Equilib.* **515**, 112585 (2020).
- ⁵⁸M. J. Assael, E. A. Sykioti, M. L. Huber, and R. A. Perkins, *J. Phys. Chem. Ref. Data* **42**, 023102 (2013).
- ⁵⁹J. Petrávic, *J. Chem. Phys.* **123**, 174503 (2005).
- ⁶⁰J. Fan, S. Liu, C. Gao, and F. Song, *Case Stud. Therm. Eng.* **32**, 101888 (2022).
- ⁶¹G. Guevara-Carrion, C. Nieto-Draghi, J. Vrabec, and H. Hasse, *J. Phys. Chem. B* **112**, 16664 (2008).
- ⁶²J. M. Brown, L. J. Slutsky, K. A. Nelson, and L.-T. Cheng, *Science* **241**, 65 (1988).
- ⁶³M. A. Wilson, A. Pohorille, and L. R. Pratt, *J. Chem. Phys.* **90**, 5211 (1989).
- ⁶⁴C. D. Wick, J. M. Stubbs, N. Rai, and J. I. Siepmann, *J. Phys. Chem. B* **109**, 18974 (2005).
- ⁶⁵C. Vega, J. L. F. Abascal, and I. Nezbeda, *J. Chem. Phys.* **125**, 034503 (2006).
- ⁶⁶V. P. Sokhan and D. J. Tildesley, *Mol. Phys.* **92**, 625 (1997).
- ⁶⁷J. E. B. Randles and D. J. Schiffrin, *J. Electroanal. Chem.* **10**, 480 (1965).
- ⁶⁸J. T. Kindt and C. A. Schmittenmaer, *J. Phys. Chem.* **100**, 10373 (1996).
- ⁶⁹U. Möller, D. G. Cooke, K. Tanaka, and P. U. Jepsen, *J. Opt. Soc. Am. B* **26**, A113 (2009).
- ⁷⁰L. Saiz, E. Guàrdia, and J.-À. Padró, *J. Chem. Phys.* **113**, 2814 (2000).
- ⁷¹C. Rønne, L. Thrane, P. O. Åstrand, A. Wallqvist, K. V. Mikkelsen, and S. R. Keiding, *J. Chem. Phys.* **107**, 5319 (1997).
- ⁷²P. Zarzycki and B. Gilbert, *Phys. Chem. Chem. Phys.* **22**, 1011 (2020).
- ⁷³F. Bresme, B. Hafskjold, and I. Wold, *J. Phys. Chem.* **100**, 1879 (1996).
- ⁷⁴T. W. Sirk, S. Moore, and E. F. Brown, *J. Chem. Phys.* **138**, 064505 (2013).
- ⁷⁵D. Surblys, H. Matsubara, G. Kikugawa, and T. Ohara, *Phys. Rev. E* **99**, 051301 (2019).
- ⁷⁶D. Surblys, H. Matsubara, G. Kikugawa, and T. Ohara, *J. Appl. Phys.* **130**, 215104 (2021).
- ⁷⁷M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, London, England, 1987).
- ⁷⁸S. W. de Leeuw, J. W. Perram, E. R. Smith, and J. S. Rowlinson, *Proc. R. Soc. London, Ser. A* **373**, 27 (1980).