Note: How does the treatment of electrostatic interactions influence the magnitude of thermal polarization of water? The SPC/E model

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Non-equilibrium phenomena feature fascinating effects arising from the coupling of two or more fluxes. The Soret and the Seebeck effects are two well known examples, with the Seebeck effect being of particular interest for energy conversion applications. Recently, we used non-equilibrium thermodynamics (NET) and non-equilibrium molecular dynamics (NEMD) simulations to investigate the response of polar fluids to thermal gradients. We proposed that thermal gradients can induce the thermal polarization (TP) of water, a physical phenomenon that resembles the Seebeck effect. We also showed that thermal gradients induce a preferred orientation, thermomolecular orientation (TMO), in non-polar fluids. The underlying NET framework of TMO and TP is very similar, but TMO resembles the Soret effect.

Most works to date have ignored the TP and TMO effects and their importance when pure fluids or solutions are exposed to thermal gradients. A good understanding of the magnitude of these effects is therefore desirable. This note focuses on the TP effect and the impact that the treatment of the electrostatic interactions has on its magnitude.

Using NET, we showed that a polar fluid polarizes under a thermal gradient according to

\[ E = \left( 1 - \frac{1}{\varepsilon} \right) \frac{L_{pq}}{L_{pp}} \nabla T \frac{T}{T}, \]

where \( E \) is the TP field, \( \varepsilon \) the fluid dielectric constant, and \( \nabla T \) and \( T \) the thermal gradient and the temperature, respectively. For polar fluids of interest to us, \( \varepsilon \gtrsim 10 \) and \( 1 - 1/\varepsilon \approx 1 \); hence, the strength of the TP is determined by the thermal gradient, the temperature, and the ratio of the phenomenological coefficients \( L_{pq}/L_{pp} \), where \( L_{pq} \) measures the coupling of the heat and polarization fluxes. We found in previous computer simulations of the Modified Central Force Model (MCFM) and Extended simple point charge model (SPC/E) that water does indeed polarize under a thermal gradient. We concluded that at high temperatures, \( L_{pq}/L_{pp} \sim -2 \) V in SPC/E water. These computations were performed using Boundary Driven-NEMD (BD-NEMD) in explicit thermal gradients. The molecules were thermostatted to predefined (different) temperatures in two regions, at the edges and the middle of the simulation cell, hence generating two heat fluxes in opposite directions. The treatment of electrostatic interactions in polar fluids has to be considered carefully. In our earlier work, we employed the Wolf method, which provides an efficient route to compute the electrostatic interactions. This method has been employed to compute interfacial properties and heat transport. However, recent work on the water liquid-vapor interface reported discrepancies between the Wolf and Ewald approaches, showing that the Wolf method predicts erroneous interfacial electrostatic potentials.

We have undertaken a simulation study to assess the impact of the electrostatic approach on the magnitude of the TP effect. In addition to the Wolf and Ewald methods, we employed the Coulombic potential, which provides an exact reference system. The Coulombic simulations consisted of a droplet with 5240 SPC/E water molecules. The droplet was confined by an external harmonic wall, \( k(r - r_0)^2 \), with \( k = 70 \) kcal/mol and \( r_0 = 40 \) Å, with a cutoff of 3 Å from \( r_0 \). The thermal gradient was set up by defining spherical shells in the center and at the edge of the droplet. The molecules inside the shells were thermostatted at predefined temperatures every time step, using simple velocity rescaling and conserving the linear and angular momenta. We used a very long cutoff for the electrostatic interactions, 90 Å, which encompasses all the molecules inside the droplet, and a cutoff of 9 Å for the Lennard-Jones potential. Several trajectories of 1 \times 10^6 steps with a time step of 2 fs were integrated with LAMMPS.

We show in Figure 1 typical temperature and density profiles for the spherical droplet, as well as the electrostatic field induced by the thermal gradient for a thermodynamic state where water features a significant TP response. The sign of the TP field agrees with Ref. 4, however, the field is weaker, \(-10^7 \) V/m vs. \(-10^8 \) V/m, for thermal gradients of \(-1 \) K/Å. We have estimated the ratio of the phenomenological coefficients at \( r = 20 \) Å and \( T = 857 \) K (see Fig. 1). Using Eq. (1), and neglecting the dielectric constant contribution, we get \( L_{pq}/L_{qq} \sim -0.3 \) V. The strength of the TP effect is one order of magnitude lower than previously estimated.

We performed additional BD-NEMD simulations using the Wolf or Ewald (3D PPPM-tin foil) methods. The simulation cell consisted of a rectangular prism with dimensions \( L_x = L_y = 27.23 \) Å and \( L_z = 81.69 \) Å. We computed the TP field at 550 K and \( P = 310 \) bars and different thermal gradients, \( \nabla T = 3.67 \) K/Å for Ewald and \( \nabla T = 2.45 \) K/Å for the Wolf method.
and 1.22 K/Å for Ewald only. The Wolf method predicts a field (using the parameters in Ref. 4) that is one order of magnitude higher than the Ewald result (see Figure 2). The ratio of coefficients $L_{pq}/L_{pp} \sim -0.5$ V for Ewald is similar to that obtained with the Coulombic approach. Further, the Ewald TP field is linear with $\nabla T$ and hence compatible with Eq. (1) (see Fig. 2). We conclude that the standard implementation of the Wolf method overestimates the strength of the TP field. Simulations of the droplet system using 3D-Ewald (tin foil) produced a field in agreement with the Coulombic results.

In summary, the Wolf method might be problematic in NEMD simulations involving thermal and/or density inhomogeneities. Our simulations show that the standard implementation of this method overestimates the magnitude of the TP effect in SPC/E water, although it predicts correctly the sign of the TP field. The Ewald TP field agrees with the Coulombic one. The TP field of water may be relevant to understand the thermoelectric response of aqueous solutions. This topic will be analysed in future works.

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