

Molecular alignment under thermal gradients: A non-equilibrium molecular dynamics study

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1. Introduction

A fundamental understanding of heat transport is needed to design high performance fluids with applications in heat management problems. Thermal gradients are responsible for a number of interesting coupling effects, such as thermoelectricity or mass separation in electrolyte solutions and binary mixtures, where two species migrate to hot and cold regions respectively. A full microscopic explanation of this phenomenon, known as the Ludwig-Soret effect [1, 2] is nonetheless still outstanding. Very recently we have uncovered novel physical effects associated to thermal gradients. We have shown that temperature gradients can induce molecular orientation or alignment in anisotropic molecules. This alignment, in the case of polar fluids, results in strong ‘thermo-polarization’ effects, and sizable electrostatic fields [3].

Computer simulations offer the opportunity to study such processes at a molecular level and enable the computation of properties that are experimentally hard to obtain or not directly accessible. Non-equilibrium molecular dynamics (NEMD) simulations, where an energy or mass flux is applied to the system, provides a route to determine transport properties directly. The signal to noise ratio in these computations is larger as compared with equilibrium simulations [4, 5, 6], furnishing a route to investigate the response of molecular fluids to thermal gradients.

In this work we use boundary driven NEMD to investigate the heat transport mechanism and molecular alignment of diatomic molecules in thermal gradients. Thermal gradients induce alignment in non-polar fluids, showing that the concept of thermo-molecular orientation is general and dependent on molecular anisotropy.

2. Computational Details

We have performed simulations of a two centre Lennard-Jones (2CLJ) model where the interaction sites are bonded by a harmonic spring potential. The starting model is a symmetric molecule with Lennard-Jones (LJ) parameters corresponding to the carbon monoxide model reported by M. Bohn *et al.* [7]. The force constant for the harmonic bond was fitted to *ab initio* computations of CO at the MP2/6-31G(dp) level using Gaussian g09 [8].

In order to study the influence of the molecular asymmetry of the dumbbell molecules on the response to the thermal gradient, we systematically varied the different parameters of the model; site diameter, interaction strength and mass. The liquid-vapour phase coexistence lines were obtained performing simulations of the explicit interface [9], in order to fully characterize the different models and choose appropriate supercritical thermodynamic conditions. The temperature gradient was set up using the boundary driven NEMD method [3,10].

4. Main Conclusions

We find that thermal gradients can induce molecular alignment in simple molecular fluids, as it is shown in Figure 1 for diatomic molecules which are asymmetric in terms of the site diameter. This observation shows that the thermo-molecular alignment effect is driven by molecular anisotropy and completely general. The magnitude of the gradients needed to induce the effect is achievable with current nanomaterials, e.g., heating of metallic nanoparticles with light. This opens exciting possibilities to manipulate molecular fluids with temperature gradients.

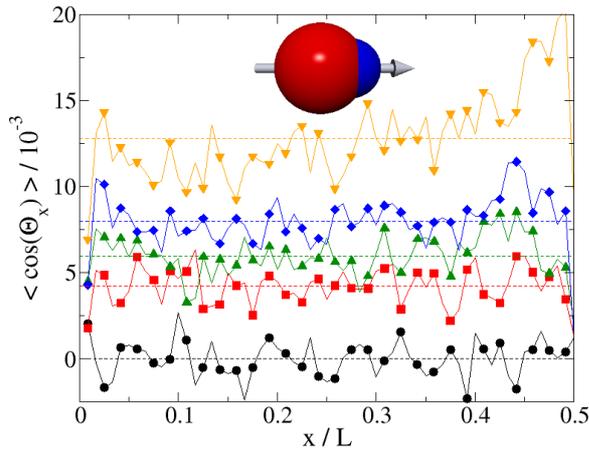


Figure 1. Alignment of molecules shown by the cosine of the angle between the vector of the heat flux and the molecule vector: symmetric (●), $\sigma_2/\sigma_1 = 5/6$ (■), $3/4$ (▲), $2/3$ (◆) and $1/2$ (▼).

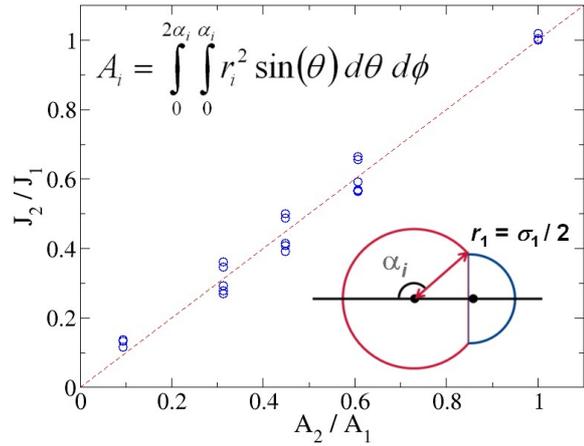


Figure 2. Ratio of the contribution of the different sites to the heat flux as a function of the ratio of the exposed surface area of the sites: NEMD results (O) and quadrant bisection $J_2/J_1 = A_2/A_1$ (---)

Moreover we find that the heat transport is anisotropic with regards to the relative size of the molecular sites, with the larger sites transporting more heat. We have developed a phenomenological model that quantitatively explains this trend in terms of the surface area accessible to each site (see Figure 2).

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