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Evaluation of Lennard-Jones Potentials in Calculations of Transport Properties of Near Critical Argon

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INTRODUCTION

Supercritical fluids are an important class of fluids of great technological importance ranging from green chemistry to rocket fuel combustion. They are defined as the thermodynamic state that has temperature (T) and pressure (P) values above the critical point (T_c, P_c). Far from it, supercritical fluids behave quite similarly to a dense fluid or a gas depending on T and P values. However, the most notable behavior is in the neighborhood of the critical point. This region is characterized by critical anomalies due to long range interactions, which leaves several open questions.[1] Moreover, there are experimental difficulties to measure physical-chemical and thermodynamic properties for near critical fluids.

Molecular dynamics (MD) is a powerful technique that allows one to investigate in details the anomalous region. From suitablestatistics of trajectories, interactions and velocities, properties of these fluids can be determined. In this work, focused on two transport properties of engineering interest: shear viscosity (η) and thermal conductivity (κ). Both can be computed from the Green-Kubo relations that are time-autocorrelation functions of momentum J_{xy} and heat fluxes S:

$$\eta = \frac{1}{Vk_BT}\int_0^\infty \langle J_{xy}(0)J_{xy}(t)\rangle dt \qquad (1)$$

$$\kappa = \frac{1}{3Vk_BT^2}\int_0^\infty \langle S(0)S(t)\rangle dt \qquad (2)$$

J_{xy} and S strongly depend on the pair potential which models the interatomic/intermolecular energies. Although it is possible to find very complex and extremely precise models for these interactions, the Lennard-Jones 12-6 (eq. 3) potential is still in use mainly for noble gases for which a spherically symmetric potentials is appropriate.

$$U(r_{ij}) = 4\varepsilon\left[\left(\sigma / r_{ij}\right)^{12} - \left(\sigma / r_{ij}\right)^{6}\right] \qquad (3)$$

η and κ were computed for Ar near its critical point using the Lennard-Jones potential with different pairs of parameters.[2-5] Results were compared with NIST experimental data.

METHODS

We have used LAMMPS MD program to run systems with 10^4 atoms using the *NVT* ensemble and temperatures from 1.00 to 2.00 T_c. Each state was equilibrated for 2 ns and averaged for 1 ns. A time step of 1 fs was used.

RESULTS, DISCUSSION AND CONCLUSION

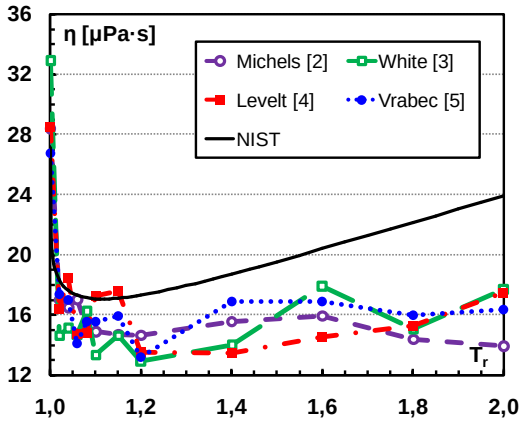

Figure 1. Shear viscosity of argon calculated via MD with different pairs of parameters for $P = P_c$.

The LJ potential presents errors of up 30% in predicting transport properties near the critical point. Although this agreement is quite good for these macroscopic properties, work is underway to improve this agreement including the use of other type of potentials.

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