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Static Properties of Liquid Neon from Molecular Dynamics Simulation

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Abstract

The surface tension, mean square force and cordination number of liquid Neon are calculated from Molecular Dynamics simulation using the Lennard-Jones pair potential in this work. The surface tension, the mean square force and the packing fraction decreases as temperature increases and density decreases. The cordination number at all investigated densities and temperatures fluctuate about a mean value. The calculated diffusion coefficients compared well with the diffusion coefficient obtained from Levesque and Verlet interpolation formula.

Keywords. Molecular dynamics simulations; Surface tension; Cordination number; Packing fraction; Neon

1. Introduction

Molecular dynamics(MD) and Monte Carlo(MC) methods have become important tools for the study of fluids[1,2]. They have been used to study equilibrum and transport properties of hard sphere fluids[3], Lennard-Jones fluids[4] and molecular liquids[5].

In Molecular Dynamics method, the Newtonian equations of motion of a set of N particles in volume V are solved numerically. The total energy E of the system is conserved as the system moves along its trajectory. The average of any property over the trajectory is an approximation to the measured value of that property for the thermodynamic state with the specified values of N, V and E. Such an average is equivalent to an average over a microcanonical ensemble if thetrajectory passes through all parts of phase space that have the specified energy.

For liquid neon, several simulations involving different approaches were performed: Path-Integral Monte-Carlo (PIMC) [6,7], Path-Integral Brownian Dynamics(PIBD) [7], Monte-Carlo simulations using two effective pair potentials arising from Path-Integral formalism, the quadratic Feynmann-Hibbs(QFH), the Gaussian Feynmann-Hibbs (GFH) and the perturbation theory [8]. A number of researchers studied the thermodynamical, structural and transport properties of Neon using Molecular Dynamics simulation [9-12]. Gautam et al calculated the thermodynamic properties of Neon from sound velocity and density data[13].

In this work, the surface tension, mean square force and cordination number of Liquid Neon are investigated from Molecular Dynamics simulation using the Lennard-Jones potential at different state points. The diffusion coefficients are obtained from the MD simulation to calculate surface tension and mean square force on atoms in liquid Neon. The cordination numbers for the different densities and temperatures are calculated from the pair distribution function. The effects of temperature and density on surface tension, mean square force, packing fraction and the first minimum in the pair distribution function of liquid Neon are also studied.

2. Simulation Method

Molecular Dynamics calculations were performed on a sample of size N = 864 molecules of mass m. The molecules interact by Lennard-Jones pair potential specified by the parameters σ and ϵ.

$$V(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \qquad (1)$$

Where ε is the well depth, σ is the atomic diameter and r is the interatomic seperation between atom i and j. Diffusion coefficients can be calculated by EMD simulation through the Green-Kubo formalism[14,15]. In this formalism, transport coefficients are related to integrals of time-correlation functions. There are various methods to relate transport coefficients to time correlation functions; a good review can be found in [16].

$$D = \int_0^\infty < v(\tau)v(0) > d\tau \qquad (2)$$

Where τ = t - t′ and <(τ)v(0)> is a measure of the correlation between the velocity of an atom at time t – t′ and t = 0 and it is known as the velocity autocorrelation function. This function helps to determine the state of a system.
The expression for the diffusion coefficient given by Levesque and Verlet[17] in reduced units is

$$D^*(\rho^*, T^*) = \frac{AT^*}{\rho^{*2}} + B + C\rho^* \qquad (3)$$

where A = 0.0444998, B = 0.1538061 and C = −0.1939896. The mean square force $<F^2>$ on an atom gives information about the shape of the repulsive part of the intermolecular pair potential. It is both the zero-time limit of the force autocorrelation function and the second frequency moment of the Fourier transform of the velocity autocorrelation function[18]. The self diffusion coefficient is related to the mean square force by[19];

$$D = K_B T \sqrt{\frac{3nK_B T}{2m<F2>}} \ , \qquad (4)$$

where the terms have their usual meaning.

Both the liquid-vapour surface tension and diffusion coefficient are related by the equation [20]

$$\beta_{lv} = \frac{5K_B T}{32nrD(T)} \sqrt{\frac{N_A K_B T}{M}} \ , \qquad (5)$$

where N_A, M and K_B are respectively, the Avogadro's number, atomic mass and Boltzmann's constant.

The pair distribution function measures how atoms organize themselves around one another. It is proportional to the probability of finding two atoms separated by distance r+_r. The g(r) can be simply evaluated from simulation data using:

$$g(r) = \frac{<N(r,\Delta r)>}{\frac{1}{2}N\rho T(r,\Delta r)} \ , \qquad (6)$$

N(r,_Δr) is the number of atoms found in a spherical shell of radius r and thickness Δr with the shell centered on another atom. V (r,_Δr) is the volume of the spherical shell. N is the total number of atoms. From the pair distribution function g(r), it is possible to calculate the coordination number Cn in the first shell [21,22]. The first shell can be defined in several ways, but the position of first minimum r_{min} is used to define the first shell in this calculations [23].

$$C_n = 4\pi\rho \int_0^{rmin} r^2 g(r)dr \qquad (7)$$

In many homogenous dense liquids, the packing fraction _liq can be calculated via the relation;

$$\eta_{liq} = \frac{\pi\rho\sigma^3}{6} \ , \qquad (8)$$

The reduced number density and temperature are given as; $\rho^* = \rho\sigma^3$ and T^* =kBT/϶. ϵ = 36.83K and σ = 2.789Å are used for Neon [24]. The thermodynamics state points are taken from the literature[25].

3. Results and Discussion

Table 1 shows the calculated diffusion coefficients of liquid Neon in this work and the theoretical results. Dsim is the diffusion coefficient obtained from the simulation and Dlv is the diffusion coefficient obtained from Levesque and Verlet interpolation formula[17]. The two values are comparable.

In table 2, the surface tension decreases as temperature increases and density decreases. This is due to the attraction of the molecules in the liquid surface which produces a resistance to penetration and decreases with temperature. Table 3 presents the cordination number and packing fraction of Neon. There is no appreciable difference in the cordination number at all investigated temperatures and densities. This is probably due to the fact that simulations are performed with values of densities that are close together. The cordination number fluctuate about a mean value at all investigated state points. The packing fraction is directly proportional to the density as can be seen in equation(8). And so, as density decreases, the packing of atoms reduces.

Figure 1 shows the variation of g(rmin) with temperature. As T increases, the first minimum in the pair distribution function increases. Figure 2 shows the variation of the mean square force with temperature. The mean square force decreases with temperature and tends to zero. As emperature increases, the distance between pairs of atoms increases. Since the attractive part of the intermolecular pair potential dominates at large distance, the repulsive part decreases.

Table 1: Diffusion Coefficients of Liquid Neon

T(K)	T^*	$\rho(g/cm^3)$	ρ^*	D^*_{md}	D^*_{lv}
25	0.679	1.236	0.800	0.04845	0.04635
26	0.706	1.224	0.792	0.05186	0.05081
27	0.733	1.209	0.783	0.05760	0.05571
28	0.760	1.192	0.772	0.06502	0.06143
29	0.787	1.177	0.762	0.07122	0.06698
30	0.815	1.152	0.746	0.07849	0.07499
31	0.842	1.134	0.734	0.08499	0.08174
32	0.869	1.110	0.719	0.09519	0.08997
33	0.896	1.089	0.705	0.10358	0.09816
34	0.923	1.066	0.690	0.11375	0.10719
35	0.950	1.043	0.675	0.12384	0.11669
36	0.977	1.018	0.659	0.14118	0.12720
37	1,005	0.991	0.642	0.14769	0.13899

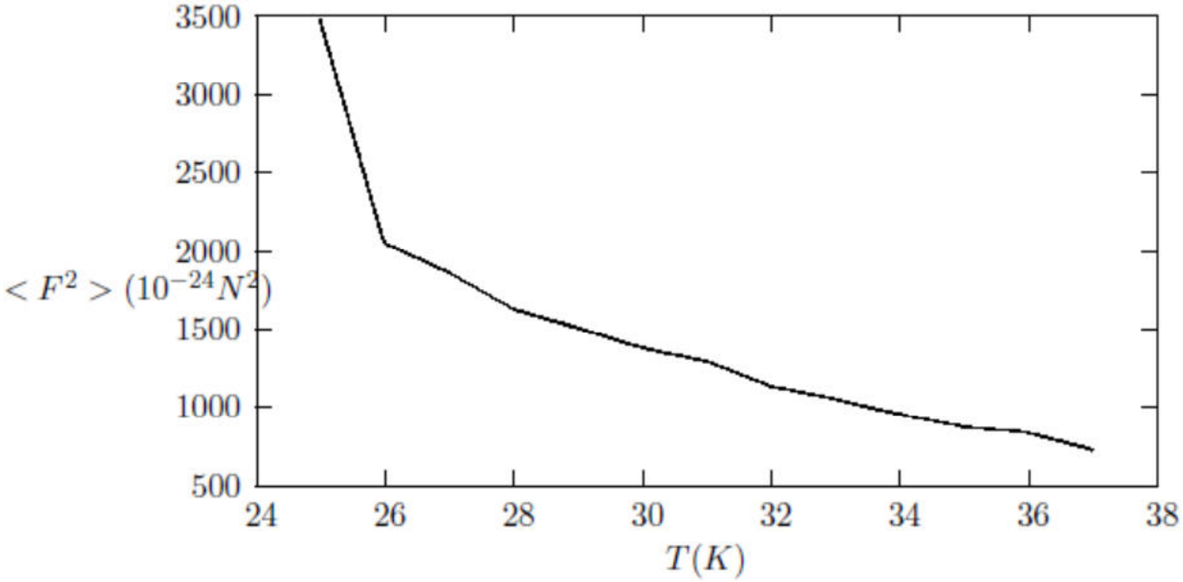

Figure 1: Mean Square Force on Atoms in Liquid Neon

Table 2: Calculated Liquid-vapour Surface Tension in Liquid Neon

T(K)	$\rho(g/cm^3)$	$\beta_{lv}(mNm^{-1})$
25	1.236	0.237
26	1.224	0.235
27	1.209	0.224
28	1.192	0.210
29	1.177	0.202
30	1.152	0.193
31	1.134	0.187
32	1.110	0.175
33	1.089	0.168
34	1.066	0.160
35	1.043	0.154
36	1.018	0.141
37	0.991	0.140

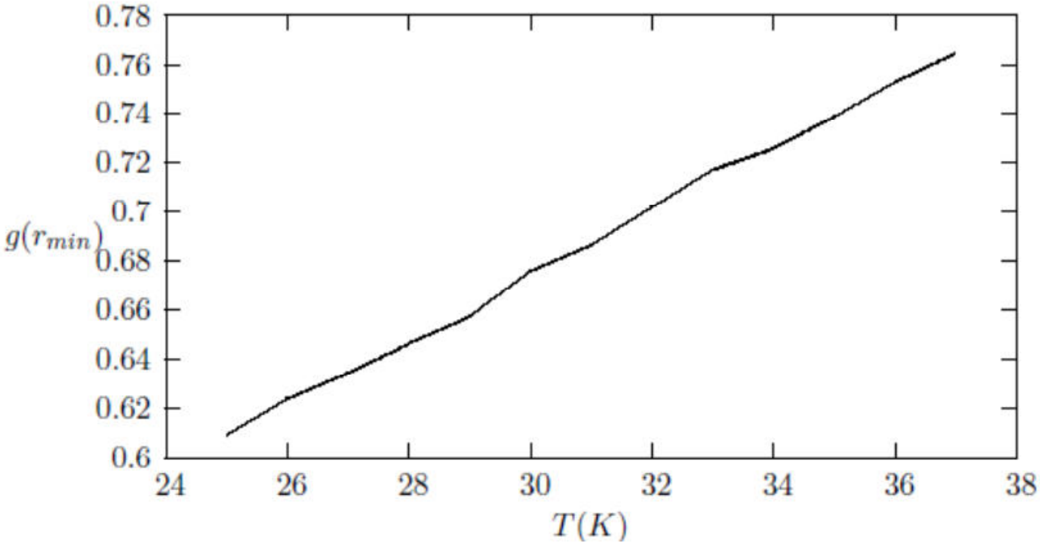

Figure 2: The First Minimum in the Pair Distribution Function of Liquid Neon

Table 3: Calculated Structural Properties of Liquid Neon

T(K)	T^*	$\rho(g/cm^3)$	ρ^*	C_n	η_{liq}
25	0.679	1.236	0.800	7.895	0.419
26	0.706	1.224	0.792	8.086	0.415
27	0.733	1.209	0.783	7.904	0.410
28	0.760	1.192	0.772	8.379	0.404
29	0.787	1.177	0.762	8.522	0.399
30	0.815	1.152	0.746	8.427	0.391
31	0.842	1.134	0.734	8.220	0.384
32	0.869	1.110	0.719	8.407	0.377
33	0.896	1.089	0.705	8.589	0.369
34	0.923	1.066	0.690	8.695	0.361
35	0.950	1.043	0.675	8.851	0.354
36	0.977	1.018	0.659	8.658	0.345
37	1,005	0.991	0.642	8.795	0.336

4. Conclusion

When the density of liquid Neon reduces, the pressure on the molecules also reduces. The molecules which then reach the surface are speed up due to breakage in bonds with neighbouring molecules. So the average translational kinetic energy of all the liquid molecules is increased. On this account, the liquid warms while the density is reduced. Hence the attractive force between the surfaces of two atoms of Neon reduces. The mean square force explains the dynamical response of pairs of atoms to temperature. At low temperature, interatomic distance is small and the motion of atoms is dominated by the repulsive part of the intermolecular pair potential but at large temperature, the atoms are well spaced out so that the motion of atoms is dominated by the attractive part and so the mean square force reduces with temperature. The calculated diffusion coefficients compared well with the theoretical results and so the Lennard-Jones pair potential models liquid Neon well.

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