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TEMPERATURE DEPENDENCE OF TRANSPORT COEFFICIENTS OF 'SIMPLE LIQUID' BELOW 1 K

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ABSTRACT

Temperature variation of transport coefficients of liquid argon below temperature of 1 K (in reduced unit) for system of 500 atoms interacting through a Lennard-Jones 6-12 potential using classical molecular-dynamics (MD) simulations has been investigated. The study carried out at two densities, $\rho^* = 0.60$ and $\rho^* = 0.95$. Result shows erratic variations of the shear viscosity in the two lattices structures.

Key Words: Temperature effect, face centred, simple cubic, transport properties, simple liquid.

INTRODUCTION

In recent years, computer experiments have come to play a major part in liquid-state Physics. Their importance from the theoretician viewpoint rests majority on the fact that they provide essentially exact, quasi-experimental data on well-defined models. As there is no uncertainty about the form of the inter particle potential, theoretical results can be tested unambiguously in a way which is not possible with data obtained in experiments on real liquids, Hansen and Donald (1986). Moreover it is possible to obtain information on quantities of theoretical important which cannot easily be measured in the laboratory.

However, special interest has been paid to simple liquid: liquids composed of spherical molecules, which are chemically inert; by both chemists and physicists. These kinds of rare-gas systems are well described with simple pair additive energy functions such as the Lennard –Jones (LJ) potential, Calvo and Spiegelmann (1996). Levesque and Verlet (1973) have carried out a more systematic investigation of the properties of the Lennard-Jones fluid. in this work, recent data have been used to investigate in details temperature dependent of diffusion coefficient and shear viscosity using classical molecular-dynamics computer simulations.

This paper is organized as follows. In section 2 the method is presented, and briefly described the numerical technique, which was used to integrate the equation of motion. Section 3 is devoted to the description of the numerical results on transport coefficients conclusion is given in section 4.

METHOD OF COMPUTATION

Consider a particle with mass, $m = 6.630\text{x}10^{-26}$ kg (the mass of an argon atom) and were assumed to interact in pair according to a simple, truncated classical Lennard-Jones potential with parameters $\sigma = 3.4$A and $\varepsilon/k_B = 119.8$K:

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

where $V(r)$ is the sum of interatomic potentials, r_{ij} is the distance between atoms i and j,

ε is energy parameter, σ is length parameter.

Five hundred of such spheres were enclosed in arbitrary positions in cube of side L (with periodic boundary conditions, to minimize surface effects and to simulate more closely the properties of an infinite system). The simulation box length L= 9.8σ and 8.6σ thus providing a density of 2.28 g/cm^3 and 1.44 g/cm^3 respectively. A time step of 3750 (15 / 0.004) was used after which the transport coefficients were analyzed. Such a time step leads to the conservation of the total energy.

The simulation of Lennard-Jones system was started from a face centred cubic lattice at reduced densities $\rho^* = 0.60$ and 0.95 for increasing temperature in reduced units (0.60, 0.65, 0.70. 0.75, 0.80, 0.85,

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0.90, 0.95). At the same state condition a series of runs was performed from a simple cubic crystalline lattice.

The problem is to integrate the equation of motion:

$$m\frac{d^2\vec{r}_i}{dt^2} = -\nabla V(r). \qquad (2)$$

To integrate (2), the very simple Verlet algorithm was used, Allen and Tildesley (1987).

$$\vec{r}_i(t+h) = -\vec{r}_i(t-h) + 2\vec{r}_i(t) + \sum_{j\neq i} f(\vec{r}_{ij}(t))h^2 \qquad (3)$$

where h is the time increment, which we take equal to 0.004, $f(\vec{r}_{ij}(t))$ is the force exerted by particle j on particle i at time t.

2.1 Transport Coefficients

Transport coefficients are equilibrium properties of a substance and can be obtained from equilibrium molecular dynamics. There are several expressions of transport properties in literatures. Diffusion coefficient is computed using the expression given as:

$$D = \frac{1}{6N}\lim_{t\to\infty}\frac{d}{dt}\left\langle \sum_i^N [\vec{r}_i(t) - \vec{r}_i(0)]^2 \right\rangle, \qquad (4)$$

where $r_i(0)$, i = 1, 2,, ...N are initial positions of the atoms. $\vec{r}_i(t)$ the particles positions at time t. $[\vec{r}_i(t) - \vec{r}_i(0)]^2$ are the mean-square displacement of atoms in the simulation. N is the number of particles

Shear viscosity is calculated using the expression given as:

$$\eta = \frac{1}{Vk_BT}\int_0^\infty dt\langle J^{xy}(0).J^{xy}(t)\rangle, \qquad (5)$$

with

$$J^{xy} = \sum_i^N\left(m_i v^x{}_i v^y{}_i + \frac{1}{2}\sum_{j\neq i} x_{ij} f_y(r_{ij})\right), \qquad (6)$$

where J^{xy} is the microscopic stress autocorrelation function. V is the volume, k_B is the Boltzmann constant, and T is the temperature. The numerical results on shear viscosity for both face centred and simple cubic crystalline lattices are shown in Table 1 and 2.

RESULTS AND DISCUSSION

Figure 1 shows temperature variation of diffusion coefficient for the Lennard-Jones fluid for face cenred cubic lattice at density of 0.60. There is a steady, slow and continuous increase in self-diffusion as temperature increases. The variation is of course almost linear. The simple least-square line used to fit the simulation data indicates the linear relationship. The vertical lines are the standard errors. Diffusion coefficient versus temperature at density of 0.95 is plotted in Figure 2. The data do not fit a straight line. Similarly, there is continuous increase in self-diffusion with increasing temperature. Uncertainty in diffusion coefficient increases as the density is increased from 0.60 to 0.95. Though there is a variation in values of diffusion coefficient at the same temperature from one density to the other. It should be noted that self-diffusion is weakly dependent on temperature but strongly dependent on density.

When the simulation started with simple cubic crystalline system at the same temperature range and the same run parameters, there is no significant change in temperature variation with diffusion-coefficient. Figures 3 and 4 display the changes. The data are fitted well with a regression equation in simple cubic lattice than in face-centred crystalline lattice.

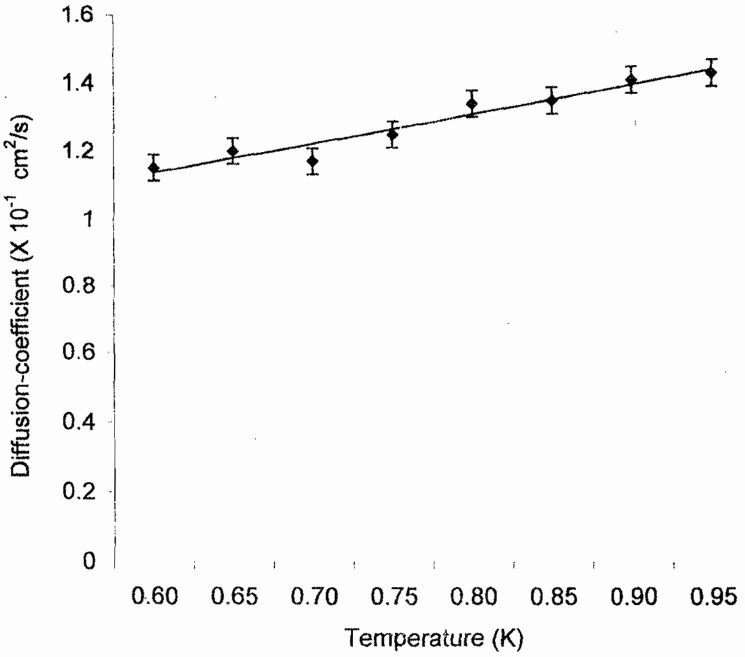

Figure 1: Effect of temperature on the self-diffusion coefficient for the Lennard-Jones fluid at density 0.60 for face centred lattice.

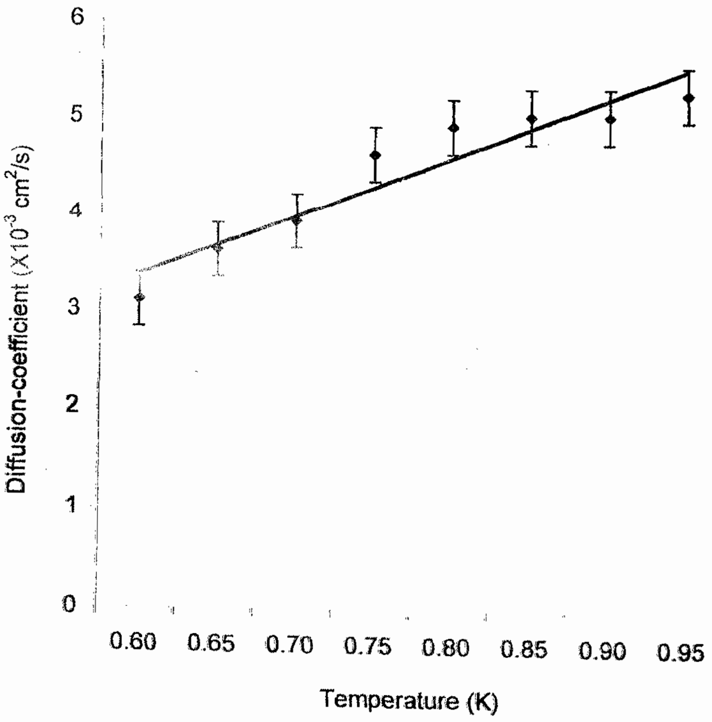

Figure 2: Effect of temperature on the self-diffusion coefficient for the Lennard-Jones fluid at density 0.95 for face centred lattice.

Molecular dynamics data on shear viscosity for face centred crystalline lattice are provided in Table 1. The results indicated that there is a very pronounced erratic variation in shear viscosity as temperature is steadily increased. The changes are the same for both densities of interest. The results of shear viscosity

Table 1: Molecular dynamics data on shear viscosity for face centred lattice. (T* is the temperature, η* the shear viscosity, ρ* the density. An asterisk denotes reduced units.)

	Shear viscosity, η*	
T*	ρ* = 0.60	ρ* = 0.95
0.60	1.737	1.540
0.65	2.860	-1.115
0.70	5.015	2.290
0.75	-1.134	11.509
0.80	3.615	0.297
0.85	0.090	2.431
0.90	-0.141	0.241
0.95	2.764	-0.838

Table 2: Molecular dynamics data on shear viscosity for simple cubic lattice. (T* is the temperature, η* the shear viscosity, ρ* the density. An asterisk denotes reduced units.)

	Shear viscosity, η*	
T*	ρ* = 0.60	ρ* = 0.95
0.60	0.983	-0.204
0.65	-0.489	-3.519
0.70	0.527	-1.768
0.75	1.867	3.273
0.80	0.730	12.467
0.85	1.612	5.038
0.90	0.383	1.121
0.95	0.081	1.987

for simple cubic lattice are provided in Table 2. The pattern of variation is the same as that of face centred lattice. It is interesting to note that a high value of shear viscosity observed at ρ* = 0.95, T* = 0.75 for face centred and at ρ* = 0.95, T* = 0.80 for simple cubic is in the neighborhood of the triple points of argon. It is also observed that shear viscosity is sensitive to the long-range part of the intermolecular potential, Haile (1992).

In general, temperature variation with shear viscosity is quite opposite to that of self-diffusion. This is expected because self-diffusion is a single-particle phenomenon, while a shear viscosity necessarily involves the entire system.

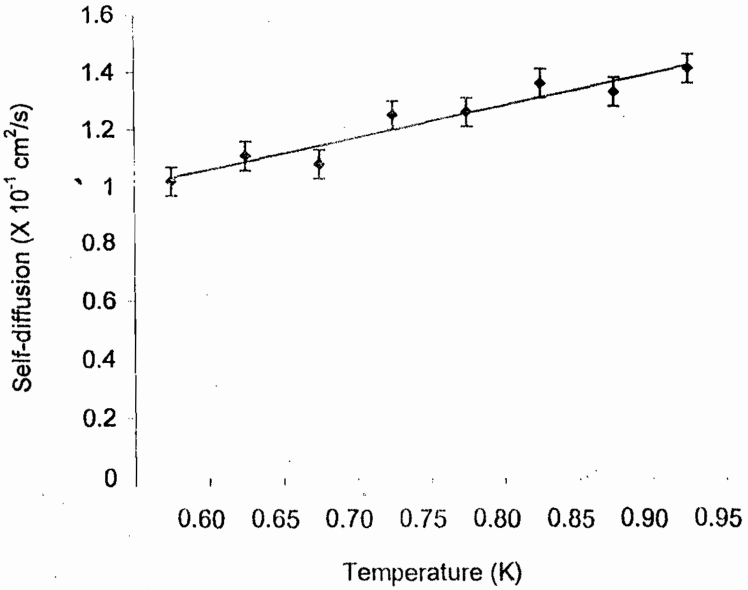

Figure 3: The variation of self-diffusion with temperature for Lennard-Jones fluid at density 0.60 for simple cubic lattice.

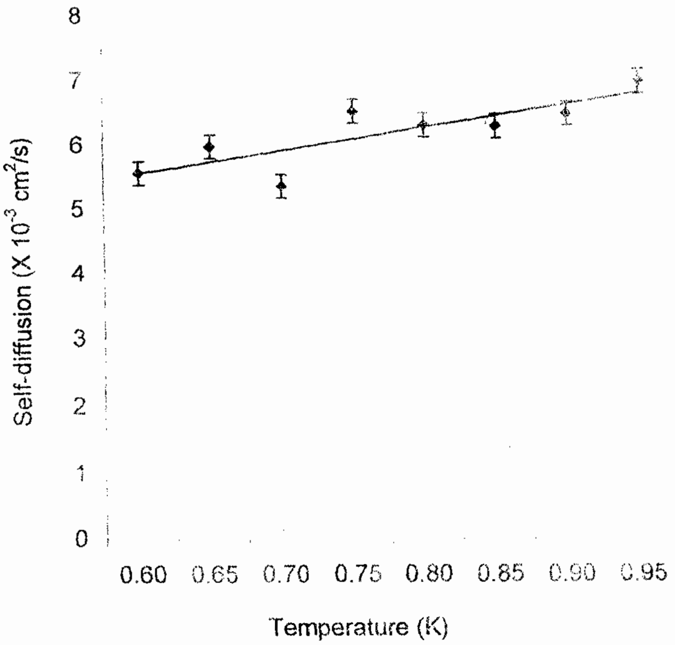

Figure 4: The variation of self-diffusion with temperature for the Lennard-Jones fluid at density 0.95 for simple cubic.

CONCLUSION

Systematic study of the effect of temperature on the self-diffusion and shear viscosity of Lennard-Jones fluid has been presented. Best fits through the simulation data points showed that diffusion coefficient could be explained by linear model. Changes in shear viscosity with temperature are completely erratic. The study can be viewed as contributions that incorporate the effects of initial configurations for the purpose of studying transport properties of Lennard-Jones systems.

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