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Liquid Argon: Molecular Dynamics Calculations for the Van Hove Self-correlation Function

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Abstract

Molecular dynamics calculations for liquid argon were made using the Lennard-Jones potential and the Barker-Fisher-Watts pair potential with the Axilrod-Teller three-body interactions, which is known to be a more realistic potential for argon. Van Hove self-correlation function $G_s(r, t)$ was obtained at the intermediate time region, 0.32~4.6 ps. The present $G_s(r, t)$ curves for both potential functions are in essential agreement with each other. It was revealed that the differences between the potential functions have hardly any effect on the present $G_s(r, t)$.

1. Introduction

In this paper, we shall report the van Hove self-correlation function $G_s(r, t)$ of liquid argon by means of molecular dynamics (MD) calculations with the conventional Lennard-Jones (LJ) 6:12 potential and the Barker-Fisher-Watts (BFW) pair potential accompanied with the Axilrod-Teller (AT) three-body interactions, the latter potential being well known as a more realistic potential for argon.¹⁾

Starting from the very successful machine calculation of Rahman's in 1964,²⁾ the researches on liquid argon which is typical of classical fluids have been performed by means of MD method. The calculations were carried out conventionally using the LJ potential function for convenience of testing various theoretical models.³⁾ Until comparatively lately, only the static quantities such as internal energy U , pressure p , second virial coefficient B , radial distribution function $g(r)$ etc., have been compared with experimental values because of lack of dynamical data and the agreement between the MD values and the experimental ones is known to be satisfactory.^{4,5)}

In the preceding papers,^{6,7)} we performed the MD calculations of liquid argon over wide density and temperature range using the LJ 6:12 potential and the BFW pair potential with the AT three-body interactions. The results were compared with the experimental values of dynamical quantities such as coherent structure factor $S(Q, \omega)$, which was obtained by

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recent neutron inelastic scattering,^{8,9)} as well as those of static quantities (U , p , B , $g(r)$, etc.). Therein, with respect to reproducing the experimental values, the MD results for both potential functions agreed with each other and reproduced the experimental values including $S(Q, \omega)$. On the other hand, at higher densities (number density $\rho \gtrsim 0.02 \text{ \AA}^{-3}$), it was revealed that there is a marked difference in the behavior of the dynamic quantities, diffusion coefficient D , velocity auto-correlation function $f(t)$ and its frequency spectrum $\phi(\omega)$: unfortunately, there is no experimental data in the density region.

The quantities D , $f(t)$ and $\phi(\omega)$ are all associated with diffusional motions of single particles. Because the van Hove self-correlation function $G_s(r, t)$ is considered to be the most basic quantity in the study of particle diffusion in fluids, from the standpoint of elucidating the actual potential functions of liquid argon, it is required to elucidate the behavior of the $G_s(r, t)$ for the potential functions in the higher density region where a significant difference was seen between the LJ results and the BFW-AT results. For this sake we performed the MD calculations using the LJ and BFW-AT potential functions and obtained the $G_s(r, t)$ for both potential functions.

The framework of the present article is as follows. In chapter 2, we give an explicit description of potential functions used in the study, namely the LJ and BFW-AT potential functions. In chapter 3, the procedures of the MD calculations are briefly described, which are quite identical with those used in the preceding papers^{6,7)} as well as by various authors.³⁻⁵⁾ In chapter 4, the present $G_s(r, t)$ results are shown in an intermediate time region where the collisional effects are considered to be important. The behaviors of the $G_s(r, t)$ are compared with those of two idealized systems; a free particle system and a hydrodynamic system. Concluding remarks are also given in this chapter.

2. Intermolecular Forces

2.1 LJ 6:12 potential energy functions

For the LJ potential, the total potential energy U^{LJ} of a set of interacting atoms in a system is assumed to be represented as a sum of pair interactions:

$$U^{\text{LJ}} = \sum_{\mathbf{k} < \mathbf{l}} \sum_{\mathbf{l}} u^{\text{LJ}}(\mathbf{k}\mathbf{l}), \quad (1)$$

and,

$$u^{\text{LJ}}(\mathbf{k}\mathbf{l}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{\mathbf{k}\mathbf{l}}} \right)^{12} - \left(\frac{\sigma}{r_{\mathbf{k}\mathbf{l}}} \right)^6 \right], \quad (2)$$

where \mathbf{k} and \mathbf{l} denote the \mathbf{k} -th and \mathbf{l} -th atoms in the system, $r_{\mathbf{k}\mathbf{l}}$ is the distance between the atoms, ε the depth of the pair potential function $u^{\text{LJ}}(\mathbf{k}\mathbf{l})$, and σ the separation at the zero of the pair potential. The values of potential parameters ε and σ are taken to be,^{10,11)}

$$\varepsilon/k_B = 119.8 \text{ K and } \sigma = 3.405 \text{ \AA (LJ)},$$

where k_B is the Boltzmann constant. These values have been conventionally used for Monte Carlo (MC) and MD calculations of liquid and gaseous argon.^{3-5,12)}

2.2 BFW-AT potential energy functions

Another type of the potential energy function used in the present study is the BFW two-body potential function accompanied with the AT three-body interaction.¹⁾ The total BFW-AT potential energy of the system $U^{\text{BFW-AT}}$ is assumed to be represented as a sum of the BFW pair potential energy U_2^{BFW} and the AT triplet potential energy U_3^{BFW} ,

$$\begin{aligned} U^{\text{BFW-AT}} &= U_2^{\text{BFW}} + U_3^{\text{AT}} \\ &= \sum_{\mathbf{k}<\mathbf{l}} u_2^{\text{BFW}}(\mathbf{k}\mathbf{l}) + \sum_{\mathbf{k}<\mathbf{l}<\mathbf{m}} u_3^{\text{AT}}(\mathbf{k}\mathbf{l}\mathbf{m}). \end{aligned} \quad (3)$$

According to Barker et al.,¹⁾ the $u_2^{\text{BFW}}(\mathbf{k}\mathbf{l})$ is represented as a linear combination of the function of Barker and Pompe ($u_2^{\text{BP}}(\mathbf{k}\mathbf{l})$)¹³⁾ and the function of Bobetic and Barker ($u_2^{\text{BB}}(\mathbf{k}\mathbf{l})$),¹⁴⁾

$$u_2^{\text{BFW}}(\mathbf{k}\mathbf{l}) = (1-x)u_2^{\text{BP}}(\mathbf{k}\mathbf{l}) + xu_2^{\text{BB}}(\mathbf{k}\mathbf{l}) \quad \text{with } x=0.25, \quad (4)$$

where both functions $u_2^{\text{BP}}(\mathbf{k}\mathbf{l})$ and $u_2^{\text{BB}}(\mathbf{k}\mathbf{l})$ have an analytical form,

$$\begin{aligned} u_2^{\text{BP, BB}}(\mathbf{k}\mathbf{l}) &= \varepsilon \left\{ \sum_{i=0}^5 A_i (r-1)^i \exp[\alpha(1-r)] \right. \\ &\quad \left. - \sum_{j=0}^2 C_{2j+6} / (\delta + r^{2j+6}) \right\}, \end{aligned} \quad (5)$$

with $r = r_{\mathbf{k}\mathbf{l}}/r_m$ (r_m is the separation at the minimum of the potential function). The potential parameters of the two-body functions, $u_2^{\text{BFW}}(\mathbf{k}\mathbf{l})$, $u_2^{\text{BP}}(\mathbf{k}\mathbf{l})$ and $u_2^{\text{BB}}(\mathbf{k}\mathbf{l})$, are shown in Table 1 of ref. 1. The minimum value ε of the BFW pair function and the distance σ at the zero of the pair potential (4) are,

$$\varepsilon/k_B = 142.095 \text{ K and } \sigma = 3.3605 \text{ \AA (BFW)},$$

respectively. It is noted that the BFW pair potential function becomes increasingly deepened compared with the LJ potential function in the vicinity of σ^{BFW} and damps faster than the $u^{\text{LJ}}(r)$ at higher r region beyond ca. 5 \AA (Fig. 1 in ref. 6).

The AT triplet function $u_3^{\text{AT}}(\mathbf{k}\mathbf{l}\mathbf{m})$ is expressed as the Axilrod-Teller form,^{1,15)}

$$u_3^{\text{AT}}(\mathbf{k}\mathbf{l}\mathbf{m}) = \nu \frac{1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3}{r_1^3 r_2^3 r_3^3}, \quad (6)$$

in which r_1 , r_2 , r_3 and θ_1 , θ_2 , θ_3 are the sides and angles formed by the three atoms \mathbf{k} , \mathbf{l} and \mathbf{m} . The coefficient ν of the AT triplet potential function, eq. (6), was taken to be $73.2 \times 10^{-107} \text{ Jm}^9$.¹⁾

3. Molecular Dynamics Calculations

The procedures and initial conditions (number density and temperature of the simulated system) of the present MD calculations are quite identical with those in the preceding paper⁶⁾ and only a brief review needs to be given here.

We considered a system of 864 particles with mass of $0.03995 \times 1.6606 \times 10^{-24} \text{ kg}$ (the mass of an argon atom) enclosed in a cube with periodic boundary conditions. The value of number density ρ of the simulated system is 0.02011 \AA^{-3} : thus, the side of the cube becomes 35.024 \AA .

With respect to the pair potential functions used in our calculation, it was assumed that the interactions extend up to a range $r \lesssim 2.5\sigma = 8.5125 \text{ \AA}$ for the LJ potential³⁻⁷⁾ and $r \lesssim r_c =$

8.50 Å for the BFW-AT potential.¹⁾ It was also assumed that the three-body interactions due to the AT potential function $u_3^{\text{AT}}(\text{klm})$ extend up to a range r_1 , r_2 and $r_3 \lesssim r_c = 8.50 \text{ Å}$.¹⁾

For the initial configuration and velocities, the particles were placed at the nodes of a face-centered-cubic lattice, and the velocities were chosen at random with a Gaussian probability law with the value of $T = 120 \text{ K}$ as the temperature of the system. Then, the motions of the particles were calculated using a set of difference equations with a time increment of 10^{-14} sec .³⁻⁷⁾ The computation was carried out for 250 time steps with correcting temperatures at each fifth step, and the total momentum of the system at each twentieth step, and was continued for 250 time steps with correcting the total momentum. After these initial stages of the calculation, the computation was continued for 1000 time steps with correcting the total momentum at each twentieth step, and positions and velocities of the particles were recorded at each second step for later analysis.

4. Results and Discussion

The quantities resulting in the present MD calculations, T , p , U , B , D , etc., agreed with those reported in the preceding paper⁶⁾ within $\pm 0.1 \sim \pm 0.5\%$ and in this paper, we focus our interest on the van Hove self-correlation function $G_s(r, t)$ of the simulated systems.

4.1 The effect of the potential on $G_s(r, t)$

Self-correlation function $G_s(r, t)$ at $t = 0.32 \text{ ps}$, 1.80 ps and 4.60 ps are shown in Fig. 1 for the LJ and the BFW-AT potential functions. The time points are chosen as follows: velocity auto-correlation $f(t)$ becomes negative at $t = 0.34 \text{ ps}$ for the BFW-AT result and at $t = 0.32 \text{ ps}$ for the LJ result, and almost vanishes up to $t = 1.80 \text{ ps}$.⁶⁾ $G_s(r, t)$ is normalized to satisfy the condition,

$$\int d^3r G_s(r, t) = 1. \quad (7)$$

As seen in the figure, the curves $G_s^{\text{BFW-AT}}(r, t)$ and $G_s^{\text{LJ}}(r, t)$ are coincident with each other in this time region and both are damped and spread rapidly with the passage of time. It is noted that the effect of the potential hardly appears in $G_s(r, t)$, as well as in the case of $S(Q, \omega)$,^{6,7)} although that appears markedly in D , $f(t)$ and $\phi(\omega)$.^{6,7)}

4.2 The collisional effect on $G_s(r, t)$

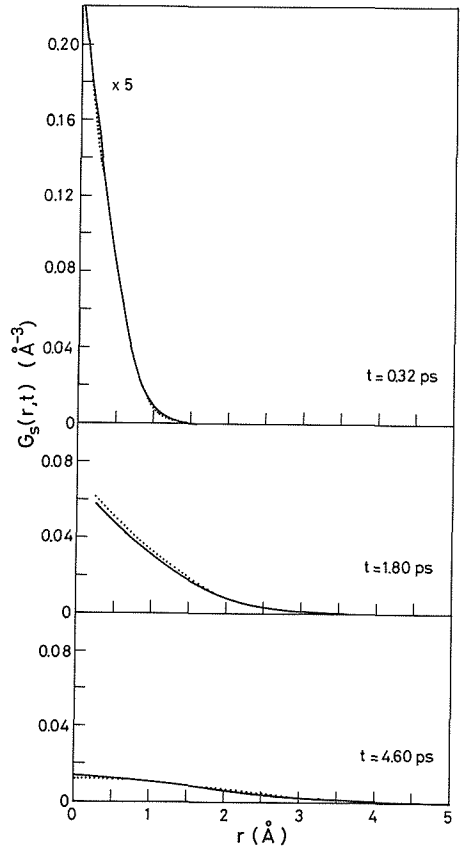


Fig. 1 Present $G_s(r, t)$. Solid curves are the BFW-AT results and dotted curves are the LJ results.

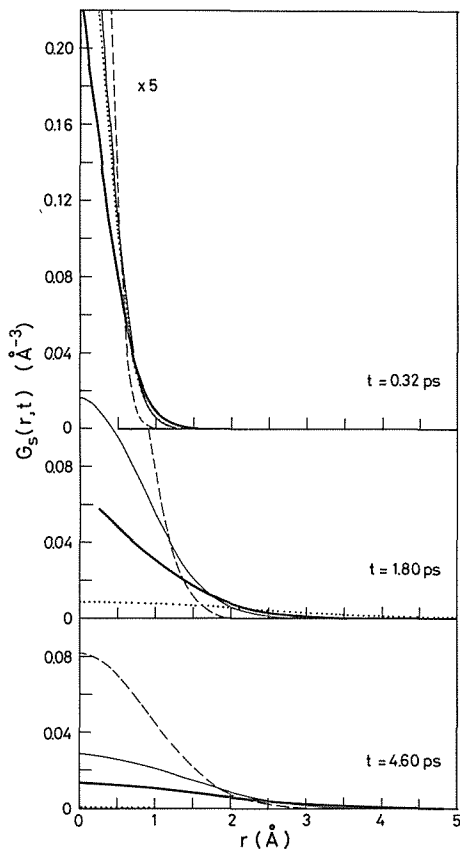


Fig. 2 Comparison between the $G_s(r, t)$ results for the BFW-AT potential and the theoretical values of two idealized systems. Solid curves are the BFW-AT results, thin solid curves are theoretical values of a hydrodynamic system with $D = 3.7 \times 10^{-5} \text{ cm}^2/\text{s}$, dashed curves are those with $D = 1.8 \times 10^{-5} \text{ cm}^2/\text{s}$ and dotted curves are theoretical values of a free-particle system with $T = 121 \text{ K}$.

discrepancies between the present $G_s(r, t)$ and $G_s^{\text{FP}}(r, t)$ are already seen at $t = 0.32 \text{ ps}$: the particles collide with each other and the effects are accumulated until $t = 0.32 \text{ ps}$. On the other hand, $G_s^{\text{HD}}(r, t)$ for the BFW-AT potential comes to agree with the present $G_s(r, t)$ with the passage of time, although $G_s^{\text{HD}}(r, t)$ is about two times as large as the $G_s(r, t)$ at $t = 4.6 \text{ ps}$. In contrast to this case, the $G_s(r, t)$ curves for the LJ potential disagree with the present $G_s^{\text{HD}}(r, t)$ over entire time range.

The MD calculations of liquid argon were performed by using the LJ and BFW-AT potential functions, and the van Hove self-correlation functions $G_s(r, t)$ were obtained. It became apparent that the differences between the potential functions have hardly any effect

As well known, at very short times, the collisional effects have not yet built up and the spatial evolution of $G_s(r, t)$ can be described by the distribution in a free-particle system. On the other hand, at very long times, the fluid medium can be treated as a continuum and the particle motions are well described as those in a hydrodynamic system. At intermediate times, i. e., at present time region, the collisional effects can be expected to play a dominant role in determining the behavior of $G_s(r, t)$. A way of exhibiting these effects is to compare the present $G_s(r, t)$ with those of two idealized systems: one of them is a free-particle system and the other is a hydrodynamic system. In a free-particle system, $G_s(r, t)$ is represented as,³⁾

$$G_s^{\text{FP}}(r, t) = (\pi v_0^2 t^2)^{-3/2} \exp[-(r/v_0 t)^2], \quad (8)$$

where v_0 is the thermal velocity. On the other hand, in a hydrodynamic system, $G_s(r, t)$ is,³⁾

$$G_s^{\text{HD}}(r, t) = (2\pi D t)^{-3/2} \exp(-r^2/2Dt), \quad (9)$$

where D is self-diffusion coefficient of the system. Using the resulting temperature T and the coefficient D in the MD calculations, $G_s^{\text{FP}}(r, t)$ and $G_s^{\text{HD}}(r, t)$ can be calculated precisely: present T and D are 121 K and $3.7 \times 10^{-5} \text{ cm}^2/\text{s}$ for the BFW-AT potential, respectively, and 121 K and $1.8 \times 10^{-5} \text{ cm}^2/\text{s}$ for the LJ potential, respectively.⁶⁾

The theoretical curves of those extreme systems are shown in Fig. 2 together with the present BFW-AT results. As seen in Fig. 2, the

on the present $G_s(r, t)$.

References

- 1) J. A. Barker, R. A. Fisher and R. O. Watts: *Mol. Phys.* **21** (1971) 657.
- 2) A. Rahman: *Phys. Rev.* **136** (1964) A405.
- 3) J. P. Boon and S. Yip: *Molecular Hydrodynamics* (McGraw-Hill Inc., New York, 1980).
- 4) L. Verlet: *Phys. Rev.* **159** (1967) 98.
- 5) L. Verlet: *Phys. Rev.* **165** (1968) 201.
- 6) N. Ohtomo and Y. Tanaka: *J. Phys. Soc. Jpn.*, **56** (1987) No. 8 in press.
- 7) Y. Tanaka and N. Ohtomo: *J. Phys. Soc. Jpn.*, **56** (1987) No. 8 in press.
- 8) A. A. van Well, P. Verkerk, L. A. de Graaf, J. -B. Suck and J. R. D. Copley: *Phys. Rev.* **A31** (1985) 3391.
- 9) A. A. van Well and L. A. de Graaf: *Phys. Rev.* **A32** (1985) 2384.
- 10) A. Michels, Hub. Wijker and Hk. Wijker: *Physica* **15** (1949) 627.
- 11) A. Michels, J. M. Levelt and W. de Graaff: *Physica* **24** (1958) 659.
- 12) I. R. McDonald and K. Singer: *J. Chem. Phys.* **50** (1969) 2308.
- 13) J. A. Barker and A. Pompe: *Aust. J. Chem.* **21** (1968) 1683.
- 14) M. V. Bobetic and J. A. Barker: *Phys. Rev.* **B2** (1970) 4169.
- 15) B. M. Axilrod and E. Teller: *J. Chem. Phys.* **11** (1943) 299.