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# Self-diffusion coefficients of the metastable Lennard-Jones vapor

Chu Nie<sup>1</sup>, Youhua Zhou<sup>1</sup>, W H Marlow<sup>2</sup> and Y A Hassan<sup>2</sup>

<sup>1</sup> School of Physics and Information Engineering, Jiangnan University, Wuhan 430056, People's Republic of China

<sup>2</sup> Department of Nuclear Engineering, Texas A&M University, College Station, TX 77843, USA

E-mail: [yhzhou@jhun.edu.cn](mailto:yhzhou@jhun.edu.cn)

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## Abstract

Self-diffusion coefficients of a metastable Lennard-Jones vapor were obtained using the memory function formalism and the frequency moments of the velocity autocorrelation function at reduced temperatures from 0.75 to 1.0. The radial density distribution functions used to evaluate the second, fourth and sixth frequency moments of the velocity autocorrelation function were obtained from the restricted canonical ensemble Monte Carlo simulation (Corti and Debenedetti 1994 *Chem. Eng. Sci.* **49** 2717). The self-diffusion coefficients at reduced temperature 0.75 do not vary monotonically as the density increases, and for the other three temperatures the self-diffusion coefficients vary normally.

## 1. Introduction

Numerous efforts have investigated static properties of the metastable Lennard-Jones (LJ) fluid such as the free energy barrier to the formation of liquid-like clusters [1–7] and thermal properties such as pressure [8], free energy and chemical potential [9], heat capacity [10] and so on. However, dynamic properties such as self-diffusion constant, shear viscosity and thermal conductivity are seldom treated. Because the atoms or molecules form clusters in the metastable fluid and these clusters may form or disappear instantaneously, the dynamic properties are expected to be different from the uniform fluid. Moreover, the inhomogeneity property of the metastable fluid provides a good prototype of the hotspot nanofluid, where the densely populated phase and dilute populated phase exist. It is still hotly debated why and how the atoms or molecules diffuse and transfer heat in the inhomogeneous surroundings from either experimental or theoretical sides [11–15]. Therefore, exploring the dynamical properties of the metastable fluid may shed some light on this debate.

Currently, the most widely used method to evaluate the self-diffusion coefficients of fluids is molecular dynamic simulations [16–19], in which the velocity autocorrelation function is recorded and averaged. After integrating the velocity autocorrelation function, the self-diffusion coefficients are obtained. However, it is hard to perform molecular dynamic simulations in a metastable fluid, in which density fluctuations

may lead to phase separation. If the density fluctuation is large enough the system will go to phase separation, but prevention of phase separation may destroy the trajectory evolution; thus, it is not that easy to perform molecular dynamic simulations in such systems. In [8], the authors developed an MD simulation method to study the thermal properties of the supersaturated vapor up to spinodal density at different temperatures. They averaged the thermal properties before the system goes to phase separation and used the instantaneous pressure, the numbers of atoms in the largest cluster, and the number of atoms not belonging to any cluster as the indication of phase separation. Their work shows that a reasonably long time interval is required to avoid phase separation. However, they did not use the method they developed to explore the dynamic properties of the metastable fluid and the robustness of their method to measure the dynamic properties of the metastable fluids remains to be validated. For these purposes, a large number of particles is required to perform the molecular dynamic simulations and we are not aware of any other similar work that has been used to investigate the dynamic properties of metastable fluids.

Besides the molecular dynamic simulation method, it is interesting to note that the dynamic thermal properties can also be approximated via static properties, the radial density distribution functions. Rah and Eu [20] proposed an algorithm to evaluate the self-diffusion constant via the free volume theory, where the free volume may be derived from the so

called generic van der Waals equation [21]. The advantage of the method is that after obtaining the self-diffusion coefficients the other dynamic quantities may also be evaluated by some manipulations of the self-diffusion constant itself and radial density distribution functions. Tankeshwar *et al* [22] developed a method to calculate the diffusion coefficients of LJ fluid over a wide range of densities and temperatures by applying a new phenomenological form of the memory function of the velocity autocorrelation function and its frequency moments. The results of this work were reported to correspond well to existing molecular dynamic simulation results [18, 19]. In this work we directly adopt the formula developed by this group to compute the self-diffusion coefficients of the metastable LJ fluid.

## 2. Methods and simulations

The radial density distribution functions are obtained from the restricted canonical ensemble Monte Carlo simulation [9]. In this work, the vapor is modeled by simulations with Lennard-Jones model interactions for atoms,

$$u(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]. \quad (1)$$

First, divide the system into subcells based on the number of atoms and density of the system studied. The length of the cubic subcell is taken with the following relations.

$$l = \frac{L}{N^{(1/3)}} \quad (2)$$

where  $L$  is the length of an edge of the simulation box and  $N$  is the total number of particles during simulation. Therefore, the ideal homogeneous case should correspond to one atom per cell. However, density fluctuations exist, and limiting the maximum number of atoms in each subcell may help to maintain the one phase state for the system studied. For a given density, a series run starts from the maximum density  $d_{\max}$ , when no number limitation is imposed on the subcell, to  $d_2$ , when only two atoms in one subcell are allowed; otherwise, the trial movement of a selected atom will be rejected. With all constraints applied to the system studied, the one with the local minimum free energy is chosen to be the approximated equilibrium state of the metastable fluid and the radial density distribution function is recorded and averaged. For each run, the excess chemical potential and pressure are averaged and recorded. With the obtained excess chemical potential and pressure, the excess free energy can be computed with the following formula:

$$f^{\text{ex}} = \mu^{\text{ex}} - P^{\text{ex}}/\rho \quad (3)$$

where  $f^{\text{ex}}$  is the excess free energy per particle,  $\mu^{\text{ex}}$  is the excess chemical potential and  $P^{\text{ex}}$  is the excess pressure of the system with respect to the ideal case. In this work, initially, all the atoms were placed on a simple cubic lattice. For all simulations, the system was set to at least  $40\sigma$ . The number of steps to reach equilibrium is  $10 \times 10^6$  moves, and another  $200 \times 10^6$  moves were used to sample the phase space. The

cut-off distance is set to be  $8.0\sigma$ , and beyond the cut-off distance standard long range corrections were employed. The simulations are carried out at  $T^* = 0.75, 0.8, 0.9$  and  $1.0$ , where  $T^* = kT/\varepsilon$ . For  $T^* = 0.75$  and  $0.8$  the number of particles involved in the simulation is 3375, and for  $T^* = 0.9$  and  $1.0$  the number of particles involved in the simulation is 5832 and 6859 respectively. The excess chemical potential is measured by performing brute force sampling of  $\exp(-\beta u)$ , the energy increase brought by the insertion of a test atom. To see the original idea of the atom insertion method, the reader may go to [23]; our program is based on classical textbooks on molecular simulation [16, 17].

After obtaining the radial density distribution function, the frequency moments of the velocity autocorrelation function were evaluated according to equation (4) in [22] and the self-diffusion coefficient is expressed as follows:

$$D = \frac{\pi k_B T}{2 M} \frac{(V_4 - V_2^2)^{3/2}}{V_2^{3/2}(V_6 V_2 - V_4^2)^{1/2}} \quad (4)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $V_2$ ,  $V_4$  and  $V_6$  are the second, fourth and sixth frequency moments respectively and  $M$  is the mass of the LJ atom.

$$V_2 = \frac{4\pi\rho}{3} \int_0^\infty dr g(r) r^2 (3B + Ar^2). \quad (5)$$

The second frequency moment consists of only the integration of the two-body radial density distribution, but the fourth and sixth frequency moments consist of not only the integration of the two-body radial density distribution function but also the triplet correlation function. In this work, we call the parts involving only the two-body radial density distribution function of the fourth and sixth frequency moments  $V_{41}$  and  $V_{61}$  respectively and the parts involving more than the two-body radial density distribution function of the fourth and sixth frequency moments  $V_{42}$  and  $V_{62}$  respectively.

$$V_4 = V_{41} + V_{42} \quad (6)$$

$$V_6 = V_{61} + V_{62}. \quad (7)$$

They are defined as follows:

$$V_{41} = \frac{8\pi\rho}{3M} \int_0^\infty dr g(r) r^2 (3B^2 + A^2 r^4 + AB r^2) \quad (8)$$

$$V_{42} = \frac{8\pi^2\rho^2}{3M} \int_0^\infty \int_0^\infty dr dr_1 r^2 r_1^2 \int_{-1}^1 d\beta_1 g_3(\vec{r}, \vec{r}_1) \times (3BB_1 + AB_1 r^2 + A_1 B r_1^2 + AA_1 r^2 r_1^2 \beta_1^2) \quad (9)$$

$$V_{61} = \frac{16\pi\rho}{3M^3} \int_0^\infty dr g(r) r^2 [2B^3 + (B + Ar^2)^3 + 3k_B T (C^2 r^6 + 15A^2 r^2 + 6ACr^4)] \quad (10)$$

$$V_{62} = \frac{8\pi^2\rho^2}{M^3} \int_0^\infty \int_0^\infty dr dr_1 r^2 r_1^2 \int_{-1}^1 d\beta_1 g_3(\vec{r}, \vec{r}_1) \times \{3k_B T (5AA_1 r r_1 + 2CC_1 r^3 r_1^3 \beta_1^3 / 3) - (AA_1 A_2 r^2 r_1^2 r_2^2 \beta_1 \beta_2 \beta_3 + AA_1 B_2 r^2 r_1^2 \beta_1^2 + AB_1 A_2 r^2 r_2^2 \beta_2^2 + BA_1 B_2 r_1^2 + AB_1 B_2 r^2 + A_2 B B_1 r_2^2 + A_1 B A_2 r_1^2 r_2^2 \beta_3^2 + 3B B_1 B_2) / 3 + 2[B^2 (A_1 r_1^2 + 3B_1) + Ar^2 (Ar^2 + 2B) \times (B_1 + A_1 r_1^2 \beta_1^2)]\} + V_2^3. \quad (11)$$

**Table 1.** Frequency moments of the velocity autocorrelation function for various temperatures and densities.

$T^*$	$\rho^*$	$V_2$	$V_{41}$ ( $\times 10^3$ )	$V_{42}$ ( $\times 10^3$ )	$V_{61}$ ( $\times 10^6$ )	$V_{62}$ ( $\times 10^6$ )	$d_{\max}$
0.75	0.030	12.807	7.723	0.030	16.049	0.522	9
0.75	0.035	20.159	12.347	0.096	25.753	1.713	8
0.75	0.040	17.480	10.547	0.057	21.912	0.992	6
0.75	0.045	23.170	14.110	0.116	29.402	2.037	6
0.75	0.050	31.498	19.351	0.255	40.407	4.558	6
0.80	0.030	10.520	6.619	0.015	14.531	0.285	10
0.80	0.035	13.159	8.311	0.026	18.277	0.476	9
0.80	0.040	17.072	10.890	0.049	24.025	0.903	8
0.80	0.045	19.073	12.560	0.067	27.713	1.233	7
0.80	0.050	20.753	13.202	0.071	29.099	1.298	6
0.80	0.055	21.244	13.484	0.069	29.688	1.267	5
0.80	0.060	24.829	15.833	0.101	34.911	1.846	5
0.90	0.030	9.202	6.349	0.009	15.512	0.182	9
0.90	0.040	12.642	8.748	0.018	21.398	0.354	9
0.90	0.050	16.533	11.476	0.032	28.089	0.631	8
0.90	0.060	20.291	14.143	0.049	34.675	0.970	6
0.90	0.070	23.457	16.350	0.064	40.082	1.282	5
0.90	0.080	25.180	17.559	0.069	43.047	1.385	4
0.90	0.085	27.256	19.012	0.082	46.587	1.651	4
1.00	0.040	11.553	8.705	0.012	23.439	0.258	7
1.00	0.050	14.644	11.064	0.019	29.835	0.420	7
1.00	0.060	17.937	13.588	0.030	36.543	0.642	7
1.00	0.070	21.624	16.410	0.044	44.294	0.962	7
1.00	0.080	25.209	19.180	0.061	51.819	1.332	6
1.00	0.090	28.148	21.437	0.075	57.916	1.644	5
1.00	0.100	29.651	22.571	0.079	60.988	1.726	4

Through equations (8)–(11),

$$r_2 = |\vec{r} - \vec{r}_1| \quad (12)$$

$$B = \frac{1}{r} \frac{\partial U}{\partial r} \quad (13)$$

$$A = \frac{1}{r} \frac{\partial B}{\partial r} \quad (14)$$

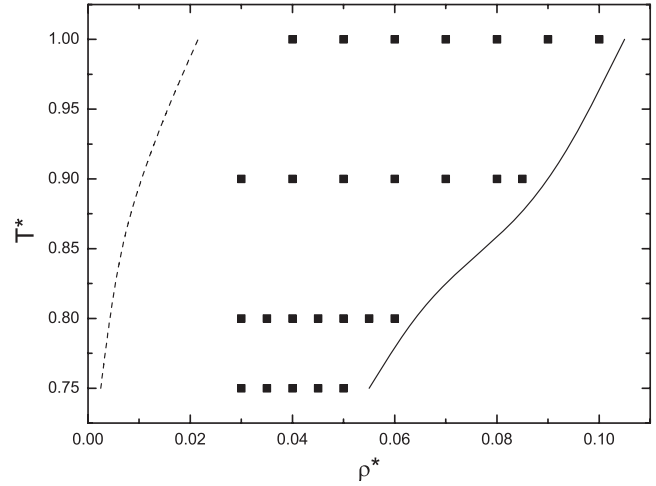
$$C = \frac{1}{r} \frac{\partial A}{\partial r} \quad (15)$$

and  $\beta_1$ ,  $\beta_2$  and  $\beta_3$  are the cosines of the angles between  $\vec{r}$  and  $\vec{r}_1$ ,  $\vec{r}$  and  $\vec{r}_2$  and  $\vec{r}_1$  and  $\vec{r}_2$  respectively. The subscripts 1 and 2 on  $A$ ,  $B$  and  $C$  imply that the argument of the potential  $U$  is changed to  $r_1$  and  $r_2$  respectively.

The superposition approximation is used for the triplet correlation function,

$$g_3(\vec{r}_1, \vec{r}_2) = g(r_1)g(r_2)g(|\vec{r}_1 - \vec{r}_2|). \quad (16)$$

In this work we took the reduced unit of both the frequency moments and the diffusion coefficients and the frequency moments in units of  $\varepsilon M \sigma^{-2}$  for  $V_2$ ,  $\varepsilon^2 M^2 \sigma^{-4}$  for  $V_4$  and  $\varepsilon^3 M^3 \sigma^{-6}$  for  $V_6$ , and the self-diffusion coefficient is in units of  $(\varepsilon M \sigma^{-2})^{1/2}$ , where  $M$  is the mass of the LJ atom. The accuracy of the above method relies on the model for the relaxation kernel. In [22] and [24], extensive works have been done to test the phenomenological form of the memory function proposed by the group, including the comparisons of dynamic properties and correlation functions of LJ fluid by their method and MD simulations [18, 19] for a wide



**Figure 1.** State points investigated on the phase diagram. The dashed line stands for the binodal line, the solid line is the spinodal line [8] and the square points are the state points investigated.

**Table 2.** Frequency moments of the velocity autocorrelation function evaluated with two-body correlation functions ( $D_1$ ) and full correlation functions ( $D_2$ ) for  $T^* = 0.75$ .

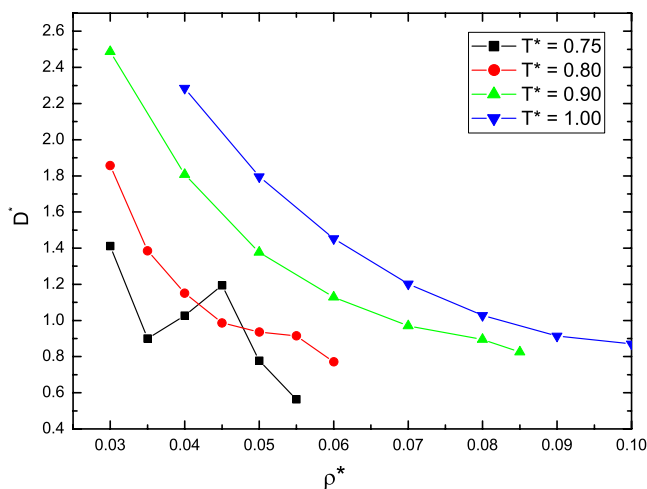
$T^*$	$\rho^*$	$D_1$	$D_2$
0.75	0.030	1.3985	1.4058
0.75	0.035	0.8869	0.8962
0.75	0.040	1.0134	1.0209
0.75	0.045	0.7607	0.7691
0.75	0.050	0.5532	0.5630

range, and the two sets of data corresponded well to each other. Therefore, we conclude that the method proposed in [22] recovers the main feature of the memory function form of the LJ fluid, and it may be applied to the computation of the dynamic properties of metastable LJ fluid.

### 3. Results and discussion

Table 1 gives various frequency moments at different temperatures and densities. In order to show the region being explored clearly, the state points investigated are placed on a phase diagram in figure 1. Except for  $T^* = 0.75$ , for the same temperature, as density increases, the frequency moments increase. But for  $T^* = 0.75$  anomalous behavior appears; the frequency moments do not vary monotonically as density increases. Second, from table 1 we find that the contribution made by three- and four-body distribution functions to fourth and sixth frequency moments is not very significant, and for the purpose of evaluating the self-diffusion coefficients of a metastable vapor we may neglect them; that is to say, only considering  $V_2$ ,  $V_{41}$  and  $V_{61}$  is enough. In table 2 we list the comparison of two sets of self-diffusion constants with full correlations and two-body correlations only for the  $T^* = 0.75$  case. It is apparent that neglecting the high-order correlation does not affect the final result. The same conclusion also applies to the other three temperatures.

In figure 2 we plot the self-diffusion coefficients versus density at four different temperatures studied. For  $T^* = 0.75$



**Figure 2.** Self-diffusion coefficients for  $T^* = 0.75, 0.80, 0.90$  and  $1.00$ , respectively.

(This figure is in colour only in the electronic version)

the self-diffusion coefficient does not vary monotonically as density increases and this corresponds to what happens in table 1. For  $T^* = 0.80$  and  $0.90$  it is apparent that there exists a plateau of the self-diffusion coefficient between certain densities and then it drops to a small value, and for  $T^* = 1.00$  the plateau disappears and the curve acts like the stable vapor or liquid.

We believe that our findings are related to the existence of clusters formed by atoms in the metastable fluid, and the current method gives the average self-diffusion coefficients of atoms belonging to clusters and not belonging to clusters. Therefore, the number of atoms belonging to clusters and the density of the metastable fluid competes with each other; this may be the reason why the plateau appears. This may also be the reason why the anomalous trend appears for  $T^* = 0.75$ .

#### 4. Summary

In this work, we have used the memory function formalism and the frequency moments of the velocity autocorrelation function method to explore the self-diffusion coefficients of metastable Lennard-Jones vapor at the reduced temperature from  $0.75$  to  $1.0$ . We found that for  $T^* = 0.75$  the self-diffusion coefficient does not vary monotonically as density increases, and for  $T^* = 0.80$  and  $0.90$  it is apparent there exists a plateau of the self-diffusion coefficient between certain densities and it then drops to a small value, and for  $T^* = 1.00$  the plateau disappears. It is also very interesting to point out that no conclusion has been reached on the system size of metastable liquid simulation. For example, in [25] the authors found that the metastable phase can exist longer the smaller the box is. This is probably because small simulation systems suppress phase separation, in which large density fluctuations leading to phase separation

are difficult to create. Thus, small simulation systems allow us to reach the spinodal more closely. There is no doubt that a systematic study on the system size of simulation is necessary, but so far no work has been seen dedicated to this point. However, [8] reported a successful work on the simulation of the metastable LJ system; the particles involved in their simulation are of the order of several thousands, and in this work the same order of particle numbers is used in order to avoid suppression phase separation. This is our preliminary work and in the future the work will be extended to the liquid side of the metastable fluid as well as to the other two most visited dynamic properties, viscosity and thermal conductivity.

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