Simulating diffusion in the conditions of vapor-liquid phase transition by the molecular dynamics method

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Abstract. The molecular dynamics calculations of diffusion coefficients in binary Lennard-Jones systems have been carried out. The parameters of Lennard-Jones potentials correspond to argon and krypton atoms. The universal dependence of the reduced diffusion coefficient of krypton atoms on density for the homogeneous systems of low and middle densities is found. The deviations of the diffusion coefficients from the universal function are observed for the systems in the vapor – liquid phase transition region. The simulations have shown that almost all krypton atoms have situated inside the liquid phase of argon. Special numerical experiments have shown that the nanodroplets of argon are formed as a result of homogeneous nucleation and then the krypton atoms are captured by these droplets. This phenomenon decreases the diffusion coefficient of krypton atoms greatly.

1. Introduction

The study of transport processes in gases and liquids has always attracted attention of researchers both from practical and theoretical viewpoints. The mechanisms of the molecular diffusion in rarified gases have been studied well enough. We have the strict theory, based on the solution of Boltzmann’s equation to calculate the diffusion coefficients in rarefied gases [1]. Mechanisms of the diffusion in dense gases and liquids are not well understood. Though there are some theoretical models for calculating the diffusion coefficients in dense molecular systems, they have not yet given the results that well agree with the experimental data. In this case direct numerical simulation methods, such as Monte-Carlo and molecular dynamics methods acquire special importance.

The molecular dynamics method provides important information about the transport processes both in liquids and gases. Particularly it helps to understand diffusion mechanisms and their difference in gases and in liquids. The study of the diffusion in the two-phase vapor – liquid system from both practical and theoretical point of view is of special interest.

In our papers [2–5], the diffusion coefficients in the one-component and binary Lennard-Jones’s systems are calculated. It is found that the dependence of the reduced diffusion coefficient on the density is universal for the homogeneous systems of low and middle density. The reduced diffusion coefficient is the ratio of the diffusion coefficient to the theoretical Boltzmann – Chapman – Enskog...
value. The universal dependence shows that the reduced coefficient does not depend on the system temperature. Evidently, in such systems, this is defined by the same molecular velocity relaxation mechanism related to the collisions of the molecules with each other.

Deviations from this dependence are observed in the region of the second phase formation – the formation of liquid droplets in vapor or vapor bubbles in liquid. In papers [4, 5], it is shown, that the dependence of the diffusion coefficient in the dense systems (in liquids) on the temperature is linear, this is related with other collective diffusion mechanism, different both from mechanism via pair collisions of atoms and via jumping motion mechanism.

In the present paper, the diffusion coefficients in the binary molecular system of the Lennard-Jones particles, corresponding to the argon and krypton atoms by their parameters, are calculated. The special attention is given to the two-phase systems.

2. The calculation procedure
The molecular dynamics calculations procedure is represented in our previous papers [4, 5]. A calculation cell of cubic shape contains the system with two kinds of particles. The number of the first kind particles changes from 2230 to 9900 and the number of the second kind particles changes from 70 to 100. We use the Lennard-Jones interaction potential with the cutting by the cubic spline [5]

\[ U(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right], \quad r \leq 4.5\sigma_{22}, \]
\[ U(r) = a(r - 5\sigma_{ij})^2 + b(r - 5\sigma_{ij})^3, \quad 4.5\sigma_{22} \leq r \leq 5\sigma_{22}, \]
\[ U(r) = 0, \quad r \geq 5\sigma_{22}, \] (1)

where \( \sigma_{ij} \) and \( \varepsilon_{ij} \) are the potential parameters of the particles. The lower indices \( i, j = 1, 2 \) mark the first and second kinds of the particles.

We use the reduced units: the reduced distance is \( r = r^d/\sigma_{11} \), the reduced time is \( t = t^d/\sigma_{11}(\varepsilon/\rho_1)^{1/2} \), the reduced density is \( \rho = \rho^d/\sigma_{11}^3 \), the reduced temperature is \( T = kT^d/\varepsilon_{11} \) and the reduced energy is \( U = U^d/\varepsilon_{11} \). \( m_1 \) is the first kind molecule mass. The superscript \( d \) marks the dimensional variables. We use \( \sigma_{22} = 1.056\sigma_{11}, \varepsilon_{22} = 1.532\varepsilon_{11} \) and \( m_2 = 2.098m_1 \) for the second kind particles. We use the combination rules [1]

\[ \sigma_{12} = \frac{\sigma_{11} + \sigma_{22}}{2}, \varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}} \]

for the Lennard-Jones parameters of the interaction potential between the particles of the first and second kinds. We simulate the argon – krypton mixture using this choice of the Lennard-Jones parameters [1]. We use parameters \( \varepsilon_{11}/k = 124 \) K and \( \sigma_{11} = 3.418 \) Å for the argon atoms to compare the calculation results with the experimental data [1].

At first, we calculate the velocity autocorrelation function (VACF) of the second kind particles \( F(t) \)

\[ F(t) = \langle \vec{v}(0) \cdot \vec{v}(t) \rangle = \frac{1}{n_2} \sum_{i=1}^{n_2} \vec{v}_i(0) \cdot \vec{v}_i(t). \] (2)

Here \( \vec{v}_i(t) \) is the velocity of a second kind particle at the time moment \( t \). Then, we calculate the diffusion coefficients \( D_{nd} \) using the Green–Kubo formula:
\[ D_{md} = \frac{1}{3} \int_{0}^{\infty} F(t) \, dt. \]  

The reduced diffusion coefficients \( D_{md}/D_{12} \) are calculated. Here

\[ D_{12} = \frac{3\sqrt{2\pi m_{a}kT}}{16m_{a}\rho \sigma_{12}^{2}\Omega^{1/3}}, \]

is Chapman – Enskog diffusion coefficient from the kinetic theory of rarified gases [1]. The calculations are carried out for the systems with reduced densities \( \rho = 0.00349, 0.0348, 0.1, 0.4, 0.61 \) and 0.84.

3. Results and discussion

In figure 1a, the calculation results for the dependence of reduced diffusion coefficients of the second kind particles on the density at different temperatures are presented. For comparison in figure 1b, the calculations results of the reduced self-diffusion coefficients \( D_{md}/D_{0} \) are presented. Here

\[ D_{0} = \frac{3\sqrt{2\pi m_{a}kT}}{8m_{a}\rho \sigma_{0}^{2}\Omega(1.1)^{3/2}}, \]

is Chapman – Enskog diffusion coefficient [1].

In figure 1, the universal dependences are shown by the solid lines

\[ f_{d} = \frac{D_{md}}{D_{12}} = 1 - 0.210 \rho - 0.257 \rho^{2} - 0.244 \rho^{3}, \]  

(6)

\[ f_{sd} = \frac{D_{md}}{D_{0}} = 1 - 0.547 \rho + 0.3 \rho^{2} - 0.574 \rho^{3}. \]  

(7)

Figure 1. Density dependences of the reduced diffusion coefficients \( D_{md}/D_{12} \) (a) and reduced self-diffusion coefficients \( D_{md}/D_{0} \) (b) at different system temperatures: \( T = 0.75 \) (×), \( T = 1(+) \).
It can be seen, that great deviations of reduced diffusion coefficients from the universal dependence are observed at system densities $\rho = 0.0348; 0.1; 0.4; 0.61$ and at low temperatures $T = 0.75$ and $T = 1$. This is related to the fact, that under these conditions there are two phases in the system – vapor and liquid. For example, in figure 2 the positions of the first and second kind particles in the system with the density $\rho = 0.1$ at two different temperatures $T = 0.75$ (a) and $T = 1$ (b) are presented. It can be seen, that at the temperature $T = 0.75$ all second kind atoms are situated inside the first kind particles liquid nanodrops, while at $T = 1$ some second kind particles are situated outside the liquid drop, that is in the vapor of the first kind particles.

![Snapshot of particle distribution in the cell at $\rho = 0.1$ and $T = 0.75$ (a) and $T = 1$ (b).](image)

**Figure 2.** Snapshot of particle distribution in the cell at $\rho = 0.1$ and $T = 0.75$ (a) and $T = 1$ (b).

The small points are the positions of first kind particles, bold points are the positions of second kind particles.

In figure 3, the velocity autocorrelation functions of particles of the second kind in the system with density $\rho = 0.1$ are presented. The autocorrelation function at $T = 0.75$ (the lower curve) has a negative region, which is typical for liquid phase. The autocorrelation function at $T = 1$ (the second curve from the bottom) has two relaxation regions: the initial sharp region and long exponential region (see figure 4). Such effect is observed for one component systems [2]. Evidently, it is related with the second kind particles velocity relaxation in the liquid drop and in the vapor.

A special numerical experiment is carried out to ascertain how the second kind particles get to the droplets of the first kind particles. In the system with density $\rho = 0.0348$ at temperature $T = 1$ the first kind particles clusters presence is detected. For this purpose, particles situated at the distance $r < 1.5 \sigma_1$ from one another are detected. If there are more than four of such particles, they are considered to belong to the same cluster.

In figure 5, the positions of the first kind particles belonging to clusters and the positions of the second kind particles are shown. It may be seen, that the second kind particles are not the nucleation centers. Thus, as a result of homogeneous nucleation the formation of the clusters and then of the first kind particles droplets takes place, and only after that the second kind particles are captured by these droplets.

In our papers [4, 5], it is shown, that the diffusion coefficient dependence on temperature is approximately linear in dense systems (in liquids). It is related with the appearance of a new collective diffusion mechanism, different from both the mechanism via pair collisions of atoms and via jumping
motion mechanism. Approximation of the calculation results of the second kind particles diffusion coefficients at the system density $\rho = 0.84$ leads to the equation

$$D_{md} = -0.01181 + 0.05907 \cdot T.$$  

(8)

**Figure 3.** Velocity autocorrelation functions of the second kind particles in the system with density $\rho = 0.1$ at different temperatures (from bottom to top): $T = 0.75$, $T = 1$, $T = 2$, $T = 3$, $T = 4$.

**Figure 4.** Velocity autocorrelation function of the second kind particles in the system with density $\rho = 0.1$ at temperature $T = 1$ in semi-logarithmic scale. The straight line is the function approximation by the exponential dependence.

The calculations with the help of equation (8) show good agreement with the experimental data [6, 7] on the krypton atoms diffusion in liquid argon. Thus, at $T = 87.6$ K the experimental diffusion coefficient equals $D_{exp} = (1.57 \pm 0.04) \times 10^{-5}$ cm$^2$/sec [6], and our calculations give $D_{md} = 1.64 \times 10^{-5}$ cm$^2$/sec. The experimental diffusion coefficient of the krypton atoms in liquid argon $D_{exp}$ at $T = 90.2$ K is from $1.62 \times 10^{-5}$ to $1.72 \times 10^{-5}$ cm$^2$/sec [7], whereas our calculations by formula (8) give $D_{md} = 1.71 \times 10^{-5}$ cm$^2$/sec.

**Conclusions**

In this paper, the molecular dynamics calculations of diffusion coefficients in binary Lennard-Jones systems have been carried out. It is shown that the formation of clusters and liquid nanodroplets in vapor as a result of homogeneous nucleation occurs in the region of vapor – liquid phase transition of the basic component. Then the impurity atoms are captured by these droplets, so that almost all of them are situated inside the droplets. It leads to a great decrease of the impurity diffusion coefficient. Nanodrops similar to nanoparticles [8, 9] can diffuse in surrounding vapor and transport impurities. Nanodroplets forming as a result of nucleation also possess unusual properties from the thermodynamics viewpoint [10, 11].
Figure 5. Snapshot of particle distribution in the cell at $\rho = 0.0348$ and $T = 1$.

The calculations of impurity diffusion coefficients for the liquid phase show good agreement with the experimental data on the krypton impurity diffusion in liquid argon.

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