About diffusion mechanisms in gases and liquids from data of molecular dynamics simulation

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Abstract. The molecular dynamics calculations of diffusion coefficients in binary Lennard-Jones liquids have been carried out. The change of diffusion mechanism has been observed with transition from dense gas to liquid. The diffusion mechanism in liquids isn’t connected with jumping motion of molecules. A good agreement between our results and the experimental data for krypton diffusion in liquid argon has been obtained.

1. Introduction

The study of diffusion mechanisms in gases, liquids and solids always attracted attention of scientists. The strict transport theory, based on the solution of the Boltzmann equation, exists for rarefied gases \cite{1}. In this case, the mass transport occurs via pair collisions of atoms or molecules. According to the kinetic Boltzmann – Chapman – Enskog theory, the diffusion coefficient in rarefied gas is related by \cite{1}

$$D_{12} = \frac{3\sqrt{2\pi m_{12} kT}}{16 m_{12} \rho \sigma_{12}^2 \Omega^{112}},$$

where $\Omega^{112}$ is the reduced collision integral, $m_{12}$ is the reduced mass of molecules.

The diffusion in solids occurs via jumping motion of atoms in crystal lattice (see for example \cite{2}). Such diffusion mechanism results in the expression

$$D_{12} = D_m e^{-\Delta W / kT},$$

where $\Delta W$ is the activation energy of jumping motion and $D_m$ is the weak temperature dependent coefficient.

The diffusion mechanism in liquids is more complicated and not investigated completely. There are specific models of diffusion in liquids, although less strict \cite{3, 4}. Most of these theories invoke a combination of vibrational and jumping molecules motions and result in an expression like (2) for the diffusion coefficient. It is doubtful for simple liquids at any rate because the molecules jumps are not found for liquids. Thus, there is the problem of investigating the diffusion mechanisms in dense gases and in simple liquids.

The molecular dynamics simulation method is very good for this purpose. It has long been used for the calculations of the diffusion coefficients in dense gases and liquids. Many studies are carried out...
with the use of the Lennard-Jones 12-6 potential [5 - 14]. In our papers [15, 16], the universal dependence of the relation of self-diffusion coefficient to theoretical Chapman – Enskog value $D_0$ on density for the homogeneous systems is found.

$$f_{sd} = \frac{D_{ud}}{D_0} = 1 - 0.547 \rho + 0.3 \rho^2 - 0.574 \rho^3. \quad (3)$$

Large deviations of the diffusion coefficient from the universal function are observed for systems in the phase transition region. However, the ratio $D_{ud}/D_0$ for the liquid phase $(\rho \geq 0.78)$ depends on temperature. Obviously, the equation (3) is not correct for very dense systems. In paper [17], the change of self-diffusion mechanism has been observed with transition from dense gas to liquid. The self-diffusion mechanism in liquids isn’t connected with the jumping motion of molecules, as the self-diffusion temperature dependence is linear one.

In paper [18], the universal dependence of the relation of diffusion coefficient to $D_{12}$ (1) on density is found for the diffusion of krypton in argon.

$$f_d = \frac{D_{ud}}{D_{12}} = 1 - 0.432 \rho + 0.975 \rho^2 - 1.717 \rho^3. \quad (4)$$

In present paper, the results of molecular dynamics calculations of the diffusion coefficients of krypton in the Lennard-Jones liquid of argon over a wide range of temperature are presented. The diffusion mechanism is discussed.

2. The calculation procedure

A calculation cell of cubic shape with periodic boundary conditions is used. The binary system consists of 9900 first kind particles and 100 second kind particles. The sizes of the cell are chosen depending on the density. The interaction potential is

$$U(r) = 4 \varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - 2 \left( \frac{\sigma_{ij}}{r} \right)^6 \right], \quad r \leq 4.5 \sigma_0,$$

$$U(r) = a(r - 5\sigma_0)^2 + b(r - 5\sigma_0)^3, \quad 4.5 \sigma_0 \leq r \leq 5 \sigma_0,$$

$$U(r) = 0, \quad r \geq 5 \sigma_0,$$ \quad (5)

where $i, j = 1, 2$. $\sigma_{11}, \sigma_{22}, \sigma_{12}$ and $\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{12}$ are the potential parameters of the first kind particles, the second kind particles and the first kind and the second kind particles interaction respectively. $\sigma_0$ is maximum of $\sigma_{11}$ and $\sigma_{22}$. For optimization of the calculation algorithm, the potential has been cut off by the cubic spline on the distance $r = 4.5 \sigma_0$. It is obvious that the particles do not interact, if the distance between them exceeds $5 \sigma_0$. For this reason, the calculation cell is divided into zones which are identical cubic cells of the size $5 \sigma_0$. The interaction is considered only between particles of adjacent zones. Such procedure reduces operating time of the computer program considerably.

Reduced units are used in the calculations: the distance is $r = r \sigma_{ij} / \sigma_{11}$, the temperature is $T = k T^*/\varepsilon_{11}$, the energy is $U = U^*/\varepsilon_{11}$, the density is $\rho = \rho^* \sigma_{11}^3$ and the time is $t = t^*/\sigma_{11} (\varepsilon_{11}/m_1)^{1/2}$. Here $m_1$ is the mass of the first kind molecule. The variables labeled by an asterisk are dimensional. The reduced parameters of the interaction potentials for the second kind particles $\sigma_{22} = 1.056$ and $\varepsilon_{22} = 1.532$ are used. The mass of the second kind particle $m_2$ is 2.098. The Lennard-Jones parameters for the interaction potential between the particles of the first and the second kinds were calculated using the combination rules [1]
\[ \sigma_{12} = \frac{\sigma_{11} + \sigma_{22}}{2}, \quad \varepsilon_{12} = \sqrt{\varepsilon_{11} \varepsilon_{22}}. \]

This choice of parameters is good for argon – krypton mixture [19].

The system volume, the temperature and the quantity of particles are constant during the calculation (NVT ensemble). The standard method of molecular dynamics is used. The system of \( n \) Newton's equations is solved. For integration of the movement equations, the Verlet method of numerical integration with step \( t = 0.001 \) is used. The average temperature of the system is calculated using the formula \( T_{\rho} = 2E_k/(3n) \), where \( n \) is the quantity of particles, \( E_k \) is the kinetic energy of all particles \( E_k = \sum_{i=1}^{n} m_i v_i^2 / 2 \). After several steps of the program, the velocity components of each particle \( v_x, v_y \) and \( v_z \) are multiplied by factor \( \sqrt{T/T_{\rho}} \), where \( T \) is the set temperature of the system.

The velocity autocorrelation function (VACF) of the second kind particles \( F_v(t) \) is calculated by formula

\[ F_v(t) = \frac{\langle \bar{v}(0) \cdot \bar{v}(t) \rangle}{\langle \bar{v}(0) \rangle} = \frac{1}{n_v} \sum_{i=1}^{n_v} \bar{v}_i(0) \cdot \bar{v}_i(t). \]  

Here \( \bar{v}_i(t) \) is the velocity of a particle at the time moment \( t \). The procedure of the calculation of \( F_v(t) \) is repeated many times. Then the received results are averaged. The number of averaging for one point \( F_v(t) \) reaches up to the values from 2000000 to 3000000.

The self-diffusion coefficient \( D \) is calculated using the Green–Kubo formula:

\[ D = \frac{1}{3} \int_0^\infty F_v(t) \, dt. \]

3. Results and discussion

The diffusion coefficients of investigated systems are presented in table 1. The simulations show that the ratio \( D_{md}/D_{12} \) increases with temperature increasing. In figure 1 these results together with the data for less density systems from [18] are presented. One can see that the ratio \( D_{md}/D_{12} \) doesn’t depend on temperature up to \( \rho = 0.61 \) at high temperature \( (T > 1) \). Significant deviations are observed for the systems at low temperature \( (T \leq 1) \). It is connected with the formation of the second phase in the system [18]. However, the uniform temperature dependence isn’t observed for the systems of the present paper (table 1).

In figure 2 the temperature dependence of diffusion coefficients is shown. It is linear dependence with high accuracy

\[ D_{md} = \alpha + \beta T. \]

The analytic fit parameters are \( \alpha = -0.01181 \) and \( \beta = 0.05907 \).

| Density \( \rho \) | Temperature \( T \) | Number of particles | Diffusion coefficient \( D_{md} \) | \( D_{md}/D_{12} \) |
|-----------------|-----------------|---------------------|-------------------------------|-------------------|
| 0.84 | 4 | 10000 | 0.22 | 0.50 |
| 3 | | | 0.17 | 0.48 |
| 2 | | | 0.11 | 0.44 |
| 1 | | | 0.046 | 0.36 |
| 0.75 | | | 0.003 | 0.32 |
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Figure 1. Density dependence of the reduced diffusion coefficients $D_{md}/D_{12}$ at different system temperatures: $T = 0.75$ ($\times$), $T = 1$ (+), $T = 2$ (□), $T = 3$ (◊), $T = 4$ (○).

Figure 2. Temperature dependence of the diffusion coefficients $D_{md}$ for liquid systems (□) with experimental data from [20] (●) and [21] (♦).

Thus, we can conclude that the diffusion mechanism is changed with transition from dense gas to liquid. In dense gases, the diffusion mechanism is the same as in rarefied gases and the temperature dependences of diffusion coefficient are alike (see (1)). A new diffusion mechanism appears in liquids. One can expect that the new mechanism is related to jumping motion of molecules in liquids. Then the temperature dependence of the diffusion coefficient must follow the formula (2). To test this assumption, the dependence of $\ln(D_{md})$ on $1/T$ is presented in figure 3. One can see that the molecular dynamics calculations results don’t agree with the dependence (2). Consequently, this diffusion mechanism isn’t connected with jumping motion of molecules. Probably, it is connected with the motion of the molecules group surrounding a molecule. Then the velocity of the molecule is relaxed with increasing the average velocity of the molecules group. In other words, this diffusion mechanism is related to relaxation of momentum fluctuations in liquids. The time dependence of VACF supports this assumption (see figure 4). An initial velocity of the particle is decreased quickly and the initial momentum is transmitted to surrounding molecules. Then the particle is reflected and moves back. But it turns to the initial direction again as the surrounding molecules return a part of the momentum to it. This mechanism results in many little displacements of the particle in liquid without jumps.

Our molecular dynamics simulations allow us to compare the results with experimental diffusion coefficient of krypton in liquid argon [20, 21]. The parameters $\varepsilon/k = 124$ K and $\sigma_0 = 3.418$ Å are used for argon to scale the experimental data. These parameters are obtained from experimental data.
on viscosity of gaseous argon [19]. According to figure 2b we have a good agreement of our results with the experimental data.

4. Conclusions

In this paper, the molecular dynamics calculations of diffusion coefficients in binary Lennard-Jones liquid have been carried out. The diffusion mechanism change has been observed with transition from dense gas to liquid. The diffusion mechanism in liquid isn’t related with jumping motion of molecules. A good agreement between our results and the experimental data for krypton diffusion in liquid argon has been obtained.

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