Molecular diffusion in gases and liquids

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Abstract. The diffusion coefficients in gases and liquids calculated by the molecular dynamics method with the use of the hard absolutely rough elastic spheres model are compared with those calculated using the Lennard-Jones potential. It is shown that dependences of reduced diffusion coefficients on density are similar, but differ numerically for different intermolecular interaction models. The simulation results have been compared with the experimental data on the diffusion in gaseous and liquid argon and in liquid benzene.

1. Introduction

Transport processes in gases and liquids are of great practical importance because of their wide use in engineering. They are studied actively both by experimental and theoretical methods. The transport coefficients used in engineering mathematical models are usually taken from experiments. Nevertheless the problem of calculating such coefficients theoretically often arises. There is the exact kinetic theory of transport processes in rarified gases based on the Boltzmann equation \cite{1}. The theory of transport processes in dense gases and liquids is unsatisfactory. The existing models of such processes do not permit to calculate transport coefficients (diffusivity, viscosity, heat conductivity coefficient and others) with the experimental precision. In this case the molecular dynamics method is actively used. The method is based on the direct numerical simulation of the motion and interaction of molecules. Determining the potential of the molecule interaction this method permits to calculate transport coefficients in dense gases and liquids. The method also permits to check the kinetic transport process models, as the molecular dynamics calculations are numerical experiments.

The diffusion coefficient calculations by molecular dynamics method with the use of different intermolecular potentials are being made for a long time \cite{2–21}. The hard absolutely smooth elastic spheres model \cite{2–5, 18, 19} and the Lennard-Jones potential \cite{6–11} are used very often. Earlier we made calculations of diffusion and self-diffusion coefficients using the hard absolutely rough elastic spheres model \cite{12} and the Lennard-Jones potential \cite{13–17}. The calculations showed that the universal dependence of the reduced diffusion coefficient (the ratio of the diffusion coefficient to the theoretical Boltzmann–Chapman–Enskog value) on the density for the systems of low and medium densities is detected. This dependence is expressed in the fact that the reduced coefficient is independent of the system temperature. Deviations from this dependence are observed in the region of coexistence of vapor and liquid phases and in the region of dense systems (liquids). The formation of clusters and liquid nanodroplets in vapor as a result of homogeneous nucleation occurs in the region of...
vapor–liquid phase coexistence. These nanodroplets also have unusual thermodynamic properties [20, 21].

This paper analyzes the dependence of the diffusion coefficient on density in various models of intermolecular interaction.

2. The calculation procedure

The procedure of molecular dynamics calculations is represented in our previous papers [12, 15]. First we calculate the velocity autocorrelation functions

\[ F(t) = \langle \vec{v}(0) \cdot \vec{v}(t) \rangle = \frac{1}{n^2} \sum_{i=1}^{n} \vec{v}_{i}(0) \cdot \vec{v}_{i}(t), \]  

(1)

and then the diffusion coefficients by the Green–Kubo formula

\[ D_{md} = \frac{1}{3} \int_{0}^{\infty} F(t) \, dt. \]  

(2)

The calculation cell contains 1000–10000 particles. The reduced units are used in the calculations: the distance is \( r = r^*/\sigma_0 \), the temperature is \( T = k T^*/\varepsilon_0 \), the energy is \( U = U^*/\varepsilon_0 \), the density is \( \rho = \rho^*/\sigma_0^3 \), and the time is \( t = t^*/\sigma_0^2 (\varepsilon_0/m_0)^{\nu/2} \). Here \( m_0 \) is the mass of the molecule. The variables labeled by an asterisk are dimensional. The self-diffusion coefficients are calculated using the hard absolutely rough elastic spheres model and the Lennard-Jones potential. The diffusion coefficients are calculated for the binary system of the Lennard-Jones particles with potential parameters \( \sigma_2 = 1.056 \sigma_0 \) and \( \varepsilon_2 = 1.532 \varepsilon_0 \) [15]. The Lennard-Jones parameters for the interaction potential between the particles of different kinds are calculated by the combination rules [1]

\[ \sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}, \quad \varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2}. \]

This choice of parameters is good for argon–krypton mixture [1]. The parameters \( \varepsilon_0/k = 124 \) K and \( \sigma_0 = 3.418 \) Å are used for argon to scale the experimental data [1].

The reduced diffusion coefficients \( D_{md}/D_0 \) and \( D_{md}/D_{12} \) are calculated. Here

\[ D_0 = \frac{3\sqrt{2\pi m_0 kT}}{8m_0 \rho \sigma_0^3} \left( 1 + k \right), \]  

(3)

(hard absolutely rough elastic spheres),

\[ D_0 = \frac{3\sqrt{2\pi m_0 kT}}{8m_0 \rho \sigma_0^3 \Omega^{1/12}} \]  

(Lennard-Jones system),

\[ D_{12} = \frac{3\sqrt{2\pi m_1 kT}}{16m_{12} \rho \sigma_0^3 \Omega^{1/12}} \]  

(Lennard-Jones system) –

(4)

(5)

Chapman–Enskog self-diffusion and diffusion coefficients are taken from the kinetic theory of rarified gases [1]. Here, \( k = 4I/(m_0 \sigma_0^2) \), \( I \) is the moment of inertia of the sphere.

3. Results and discussion

Figure 1a presents calculated dependence of the reduced diffusion coefficients of hard absolutely rough elastic spheres on the density. The calculated reduced self-diffusion coefficients \( D_{md}/D_0 \) of the Lennard-Jones system are presented in Figure 1b for comparison.

In figure 1 the fitting curves are shown by the solid lines...
The diffusion coefficient in the hard absolutely rough elastic spheres depends on the temperature proportionally $\sqrt{T}$. Thus, $f_{HS}$ in (6) does not depend on the temperature. For the Lennard-Jones system a complex dependence of the diffusion coefficient on the temperature is observed. It is related, first, with the dependence of the omega integrals in (4) and (5) on the temperature and, second, with the complex phase transformations in the system depending on the density and temperature.

\[ f_{HS} = \frac{D_{md}}{D_0} = 1 - 0.574 \rho - 1.019 \rho^2 + 0.627 \rho^3 \quad \text{(Figure 1a),} \tag{6} \]

\[ f_{LJ} = \frac{D_{md}}{D_0} = 1 - 0.547 \rho + 0.3 \rho^2 - 0.574 \rho^3 \quad \text{(Figure 1b).} \tag{7} \]

**Figure 1.** Density dependences of the reduced self-diffusion coefficients $D_{md}/D_0$ for the system of the hard absolutely rough elastic spheres (a) and for the Lennard-Jones system (b) at different system temperatures: $T = 0.75, 1, 2, 3$ and $4$. The solid lines are the fitting curves (6) and (7).

**Figure 2.** The fitting curves (6) and (7) for the reduced self-diffusion coefficients $D_{md}/D_0$ for the system of the hard absolutely rough elastic spheres (dashed line) and for the Lennard-Jones system (solid line).
In figure 1b the dots show the values of the reduced self-diffusion coefficients at the density \( \rho = 0.00347, 0.0348, 0.1, 0.4, 0.437, 0.61, 0.782, 0.84 \) and 0.88 and at the temperatures \( T = 0.75, 1, 2, 3 \) and 4. The system remains homogeneous at low and middle density \( (\rho = 0.00347 - 0.61) \) and at high temperatures \( (T > 1) \). At the same time the reduced diffusion coefficients at each density do not depend on the temperature. The dots in figure 1b for these densities coincide. The approximation curve (7) passes just through these dots. Deviations from this curve are observed in the region of coexistence of two phases: vapor and liquid \( (T \leq 1) \). At the same time, formation of liquid nanodrops, stratification of the system in vapor and liquid layers or formation of vapor bubbles and cavities in liquid are possible [14, 15]. On the other hand, for the dense systems – liquids \( (\rho = 0.782, 0.84 \) and 0.88) – linear dependence of the self-diffusion coefficient on the temperature is observed [17]. At the same time the liquid remains homogeneous at any temperature. This is related with other collective diffusion mechanisms in such systems. In this case, the molecules move together with their environment in the process of diffusion movement.

In figure 2 the dependences (6) and (7) are represented for comparison. One can see that the reduced self-diffusion coefficients depend much on the molecule interaction potential. The hard absolutely rough elastic sphere model leads to a stronger relative reduction of the self-diffusion coefficient vs. the system density than the Lennard-Jones potential.

In figure 3 the dependence of the reduced diffusion coefficient \( D_{md}/D_{12} \) on the density in the binary Lennard-Jones system is presented. The universal dependence of the reduced diffusion coefficient on the density for low and middle density of the system is observed here. The approximation curve of this dependence is expressed by the formula

\[
f_d = \frac{D_{md}}{D_{12}} = 1 - 0.210 \rho - 0.257 \rho^2 - 0.244 \rho^3.
\]  

\textbf{Figure 3.} Density dependences of the reduced diffusion coefficients \( D_{md}/D_{12} \) for the Lennard-Jones binary system at different system temperatures: \( T = 0.75, 1, 2, 3 \) and 4. The solid line is the fitting curve (8).

The deviations from this dependence are observed in the region of coexistence of two phases: vapor and liquid. The linear dependence of the diffusion coefficient on the temperature for the dense system – liquid \( (\rho = 0.84) \) – is also observed [17].

\textbf{Figure 4.} The fitting curves (7) and (8) for the reduced self-diffusion coefficients \( D_{md}/D_0 \) (solid line) (dashed line) and for the reduced diffusion coefficients \( D_{md}/D_{12} \) of the Lennard-Jones systems.
In figure 4, the dependences (7) and (8) are presented for comparison. One can see that the dependence of the reduced diffusion coefficient on the parameters of the intermolecular interaction potential is essential.

Simulation results [12] and the experimental data on the self-diffusion coefficients in liquid benzene are shown in figure 5 [22]. The model of the hard absolutely rough elastic spheres is used for the simulation. The radii of the spheres are found from the same experimental data [22] by comparison of the simulation result with one of the experimental values for each temperature. In this way the sphere radius depends on the temperature of benzene. The comparison shows a satisfactory agreement of the simulation results and the experimental data.

**Figure 5.** The dependence of the self-diffusion coefficient $D$ on the number density $n$ in benzene [12]. The experimental data [22]: □ $303$ K, × $348$ K, ◦ $393$ K, + $433$ K. The solid curves are the results of the molecular dynamic calculations.

In figure 6 the calculation results of the angular velocity autocorrelation function

$$F_r(t) = \left\langle \mathbf{\omega}(0) \cdot \mathbf{\omega}(t) \right\rangle / \left\langle \mathbf{\omega}^2(0) \right\rangle$$

are presented using the model of the hard absolutely rough elastic spheres. The experimental data are shown by the dots. The data are obtained at temperature of $23^\circ$C and pressure of 1 bar [23]. An essential discrepancy of the experimental data and the simulation results is observed. This fact shows that the model of the hard absolutely rough elastic spheres cannot be used for the calculations of the benzene molecule rotational relaxation.

In our papers [15 – 17] the comparison of the experimental data on self-diffusion in rarified, dense and liquid argon with the results of the simulation by molecular dynamics method using the Lennard-Jones potential is made. A good agreement is shown. The comparison of the experimental data on the krypton diffusion in liquid argon with the results of our simulations is also made and a good agreement of the calculations with the experimental data is also obtained.

**4. Conclusions**

In this paper the comparison of results of molecular dynamics simulation in gases and liquids with the use of different intermolecular interaction models is made. The temperature independence of the
reduced diffusion coefficient for the Lennard-Jones systems of low and medium densities shows that the diffusion mechanisms in rarified and dense gases are identical. In this case the molecular velocity relaxation is related with the pair collisions of the molecules. In the dense systems – liquids – the reduced diffusion coefficient begins to depend on the system temperature, and the temperature dependence of the diffusion coefficient in the liquids is close to the linear one. This means that a new collective diffusion mechanism arises in liquids. This mechanism is not related with the jumps of the molecules from a quasi-stationary state to another one, but is caused by the molecules motion together with their environment. From this point of view the hard absolutely elastic spheres model differs greatly from the continuous potential models like the Lennard-Jones potential. The collective correlations of the molecules motion also arise for the hard absolutely elastic (smooth or rough) spheres model, but they depend only on the density, and do not depend on the temperature. In this case the reduced diffusion coefficient does not depend on the temperature even for the dense systems (liquids).

The comparison of the calculations results with the experimental data shows that the continuous potential models lead to a better agreement, therefore the choice of a good intermolecular interaction potential is very important for successful molecular dynamics simulation.

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