

# Molecular Dynamics Simulation of the Molecular Diffusion in Gases and Liquids

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**Abstract**—The diffusion coefficients in molecular one-component and two-component systems of Lennard-Jones particles have been calculated by the molecular dynamics method in a wide range of density and temperature of the systems. Special attention was given to simulations of systems in the region of the vapor - liquid phase transition. In homogeneous systems a universal dependence of the reduced diffusion coefficients (in relation to the Chapman-Enskog diffusion coefficients) on density was found. Deviations from this dependence were observed in the phase transition region with liquid droplets in the vapor or vapor bubbles in the liquid. The calculation results were compared with experimental data on diffusion in gaseous and liquid argon.

**Index Terms**—molecular dynamics method, diffusion coefficient, vapor - liquid phase transition.

## I. INTRODUCTION

THE study of diffusion in gases and liquids always attracted attention of scientists. A strict theory of diffusion, based on the solution of Boltzmann's equation, exists for rarefied gases [1]. There are specific models of diffusion in liquids, although less strict [2], [3]. Data on the diffusion in the vapor - liquid phase transition region are lacking. This is due to the great difficulties both in theoretical and experimental studies of such processes. The results of many molecular dynamics simulations from different papers were presented in [4]. However, there are only two papers [5], [6], in which the self-diffusion coefficients in the vapor-liquid transition region were calculated. Unfortunately, the simulations were carried out with small numbers of particles (512 or less). It is difficult to obtain the two-phase systems at these conditions. The appearance of small liquid drops in vapor and vapor bubbles in the liquid is possible in a large system with a big number of particles [7], [8], [9], [10]. At the same time such studies have great practical value for harmful impurities propagation control in gases and liquids [11], [12]. In this context the methods of direct numerical simulation of diffusion in vapor - liquid phase transition conditions acquire special importance.

In the present paper results of molecular dynamics calculations of the diffusion coefficients in the Lennard-Jones system over a wide range of density and temperature are presented. The molecular dynamics method has long been used for the calculations of the diffusion coefficients in dense gases and liquids. Many studies are executed with the use of the Lennard-Jones 12-6 potential [4], [5], [6], [13], [14], [15], [16], [17]. However, in these papers not much attention is paid to the region of the vapor - liquid phase transitions. In

this region the formation of small liquid drops in the vapor and vapor bubbles in the liquid is possible. These phenomena influence the diffusion coefficient of molecules in the system.

## II. THE CALCULATION PROCEDURE

A calculation cell in the shape of a parallelepiped or a cube with periodic boundary conditions is used. The sizes of the cell and number of the particles placed in it (from 3000 to 40 000) is chosen depending on density. The self-diffusion coefficients in single component system and the diffusion coefficients in binary system have been calculated. The interaction potential is

$$U(r) = 4\epsilon_i \left( \frac{\sigma_i^{12}}{r^{12}} - \frac{\sigma_i^6}{r^6} \right), \quad r \leq 4.5\sigma_i,$$

$$U(r) = a(r - 5\sigma_i)^2 + b(r - 5\sigma_i)^3, \quad 4.5\sigma_i \leq r \leq 5\sigma_i. \quad (1)$$

Where  $\sigma_i$  and  $\epsilon_i$  are the particle diameter and the depth of the potential respectively. The subscript  $i$  is 0 for first kind of the particles and 1 for second kind of the particles or 2 for the interaction potential between the particles of the first and the second kinds. For optimization of the calculation algorithm the potential has been cut off by the cubic spline at  $r = 4.5\sigma_i$ . It is obvious that the particles do not interact, if the distance between them exceeds  $5\sigma_i$ . For this reason the calculation cell is divided into zones which are identical cubic cells of the size  $5\sigma_{max}$  (here  $\sigma_{max}$  is the maximum value of  $\sigma_i$ ). The interaction is considered only between particles of adjacent zones. This procedure reduces the operating time of the computer program considerably.

Reduced units are used in the calculations: the distance is  $r = r^*/\sigma_0$ , the temperature is  $T = kT^*/\epsilon_0$ , the energy is  $U = U^*/\epsilon_0$ , the density is  $\rho = \rho^*\sigma_0^3$ , and time is  $t = t^*/\sigma_0(\epsilon_0 m_0)^{1/2}$ . Here  $m_0$  is the mass of the first kind particle. The variables labeled by an asterisk are dimensional. The reduced parameters of the interaction potentials for the second kind particles  $\sigma_1 = 1.056$  and  $\epsilon_1 = 1.532$  are used. The mass of the second kind particle is 2.098. The Lennard-Jones parameters for the interaction potential between the particles of the first and the second kinds were calculated by the combination rules[1]

$$\sigma_2 = \frac{\sigma_0 + \sigma_1}{2}, \epsilon_2 = \sqrt{\epsilon_0 \epsilon_1}$$

This choice of the parameters is good for argon - krypton mixture [21]. The system volume, the temperature and the number of particles were constant during a calculation (NVT ensemble). The binary system consists of 9900 the first kind particles and 100 the second kind particles.

The standard method of molecular dynamics was used. The system of  $N$  Newton's equations was solved. For integration of the equations of motion the Verlet method of

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numerical integration with step bite  $\Delta t = 0.001$  was used. The average temperature of the system was calculated by formula  $T_{sr} = 2E_k/(3N)$ , where  $N$  is the number of particles,  $E_k$  is the kinetic energy of all particles  $E_k = \sum_{i=1}^N m_0 v_i^2/2$ . After several steps (20 ÷ 100) of the program the velocity components of each particle  $v_x$ ,  $v_y$  and  $v_z$  are multiplied by factor  $\sqrt{T/T_{sr}}$ , where  $T$  is the set temperature of the system.

The velocity autocorrelation function (VACF) of particles  $F(t)$  is calculated by the formula

$$F(t) = \langle \vec{v}(0) \cdot \vec{v}(t) \rangle = \frac{1}{N} \sum_{i=1}^N \vec{v}_i(0) \cdot \vec{v}_i(t) \quad (2)$$

Here  $\vec{v}(t)$  is the velocity of a particle at the time moment  $t$ . The procedure of the calculation of  $F(t)$  is repeated about 1350000 - 13500000 times. Then the results are averaged.

The diffusion coefficient  $D$  is calculated by Green-Kubo formula

$$D = \frac{1}{3} \int_0^\infty F(t) dt \quad (3)$$

### III. RESULTS AND DISCUSSION

#### A. The one-component system

In the region of low density ( $\rho = 3.42 \cdot 10^{-5} \div 3.48 \cdot 10^{-2}$ ) and high temperatures ( $T = 1 \div 4$ ) the system consist of homogeneous gas. The VACF of such a gas shows an exponential decay, and the self-diffusion coefficients are close to the theoretical coefficients calculated by the formula

$$D_0 = \frac{3\sqrt{\pi m_0 k T}}{8m_0 \rho \pi \sigma_0^2 \Omega^{(1,1)*}} \quad (4)$$

according to the kinetic theory of Boltzmann - Chapman - Enskog. Here  $\Omega^{(1,1)*}$  the reduced collision-integral, for which numerical values are reported in the book of Hirschfelder et al. [1]

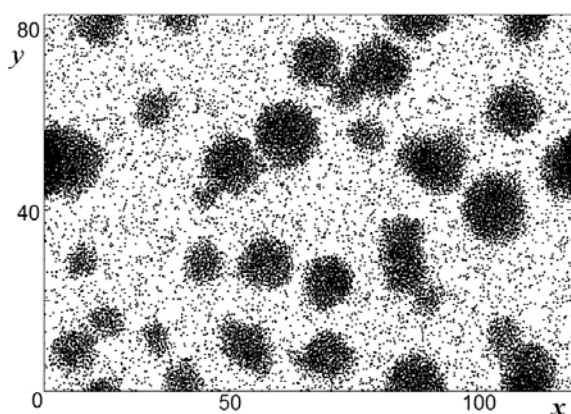


Fig. 1. Snapshot of particle distribution in the cell at  $\rho = 3.48 \cdot 10^{-2}$  and  $T = 0.75$ .

The phase transition is observed for the density  $\rho = 3.48 \cdot 10^{-2}$  at the temperature  $T = 0.75$ . At this state point the system consists of a set of clusters and nanodrops, moving in the gas (see Fig. 1). The VACF of the system consists of a sharp decrease of the initial relaxation and a long exponential decay [7]. Such complicated form of the VACF is related to

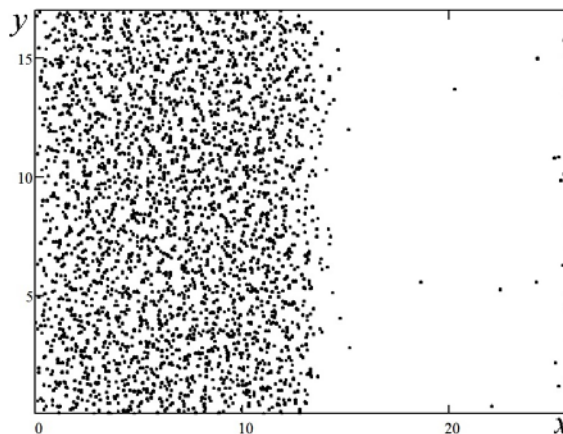


Fig. 2. Snapshot of particle distribution in a cell at  $\rho = 0.4$  and  $T = 0.75$ .

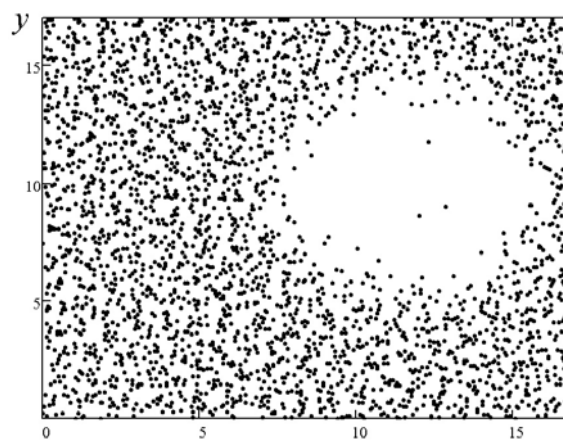


Fig. 3. Snapshot of particle distribution in a cell at  $\rho = 0.437$  and  $T = 0.75$ .

the relaxation of the velocity of the particles moving in the liquid droplets and in the vapor correspondingly.

In the region of average density ( $\rho = 0.1 \div 0.61$ ) the stratification of the system into vapor and liquid layers has been observed, as well as the formation of a vapor bubble surrounded with the liquid. Fig. 2 shows that the system is stratified into two layers, and the flat interphase boundary is formed. Thus the temperature decrease leads only to decrease of the number of particles in the vapor phase. In Fig. 3 the vapor bubble in the liquid is shown. In this case the temperature decrease also leads to a decrease of the number of particles in the vapor. Further density increase leads to the decrease of the vapor bubble up to its total disappearance. In this case the all content's homogeneous liquid. The VACF of such systems is well-known as it was investigated earlier [4]. On the basis of our data we conclude that the Lennard - Jones system can be in four different states depending on density and temperature:

- i The homogeneous system is observed at a low and high density of the system or at high temperatures ( $T \geq 2$ );
- ii Clusters and nanodrops surrounded with vapor (Fig. 1);
- iii Stratification of the system and formation of the flat interphase boundary (Fig. 2);
- iv Formation of vapor bubbles in the liquid (Fig. 3).

In Table 1 the self-diffusion coefficients of all investigated systems are reported. The simulations show that diffusion

is faster in a system of type iv ( $\rho = 0.437$  with a vapor bubble) than in type iii system ( $\rho = 0.4$  with a flat interphase boundary), although the density in system iii is lower, than in system iv. It is related to the change of effective density of that system part in which the diffusion mainly takes place, i.e. the effective liquid density in system iii is greater than that in system iv, despite of the inverse relationship of the average systems densities. All results of self-diffusion coefficients calculations ( $\circ - T = 4$ ,  $\diamond - T = 3$ ,  $\square - T = 2$ ,  $+ - T = 1$ ,  $\times - T = 0.75$ ) are presented in Fig. 4. The experimental data for argon from [18] ( $\blacksquare$ ), from [19] ( $\bullet$ ) and from [20] ( $\blacktriangle$ ) are presented in Fig. 5. The parameters  $\epsilon/k = 124K$  and  $\sigma = 3.418 \text{ \AA}$  were used to scale the experimental data. These parameters were obtained from experimental data on viscosity of gaseous argon [21].

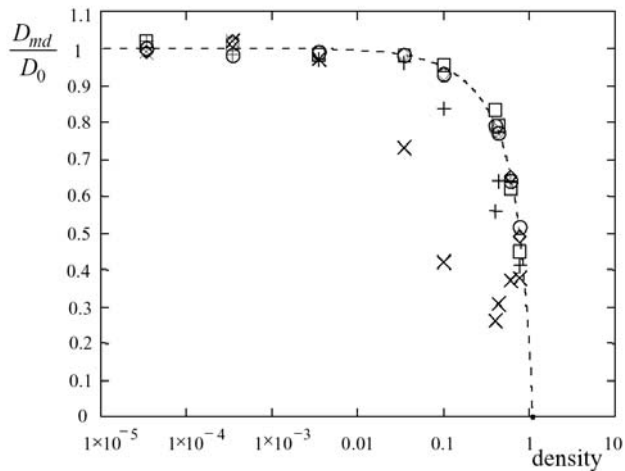


Fig. 4. The results of molecular dynamics calculations (see Table 1). The universal dependence of ratio  $D_{md}/D_0$  on density (5).

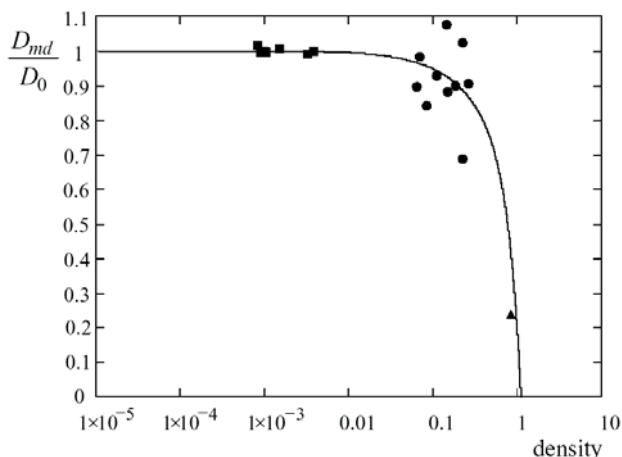


Fig. 5. The experimental data for argon. The universal dependence of ratio  $D_{md}/D_0$  on density (5).

The data of molecular dynamics calculations denoted as  $D_{md}$  were reduced to the Chapman - Enskog value  $D_0$  calculated by equation (4). As a result it was revealed that the dependence of  $D_{md}/D_0$  on density for all homogeneous systems can be approximated by the same density dependent

function at any temperature (deviation from the curve does not exceed 3 %):

$$f_{sd}(\rho) = 1 - 0.547\rho + 0.3\rho^2 - 0.574\rho^3 \quad (5)$$

This function is also shown in Fig. 4. If the system is not homogeneous ( $T \leq 1$ ), its points deviate strongly from this universal function. However, if we calculate the effective density ( $\rho_{eff}$ ) of the system part in which the diffusion takes mainly place and plot the ratio  $D_{md}/D_0$  over  $\rho_{eff}$ , the points come closer to the universal curve. It is necessary to stress that the ratio  $D_{md}/D_0$  for the liquid phase ( $\rho = 0.782$ ) depends weakly on temperature (see Table I). Obviously equation (5) is not correct for very dense systems.

The experimental data agree with the universal dependence for rarefied argon [18] and for liquid argon [20] very well. Some experimental data in the medium region ( $\rho = 0.05 \div 0.2$ ) of density deviate from the curve (see Fig. 5). Probably it is due to errors of experimental procedure as the authors supposed [19]. However, it may also be evidence of the formation of clusters and nanodroplets in nonequilibrium conditions of the experiments.

### B. The two-component system

Let's turn to the calculation results of the diffusion coefficients in the binary systems.

In Fig. 6 the dependence of the ratio  $D_{2md}/D_{12}$  on the system density is shown (see Table II).  $D_{12}$  is the Chapman - Enskog diffusion coefficient

$$D_{12} = \frac{3\sqrt{2\pi m_{12}kT}}{16m_{12}\rho\pi\sigma^2\Omega^{(1,1)*}} \quad (6)$$

Here  $m_{12}$  is the reduced mass of particles.

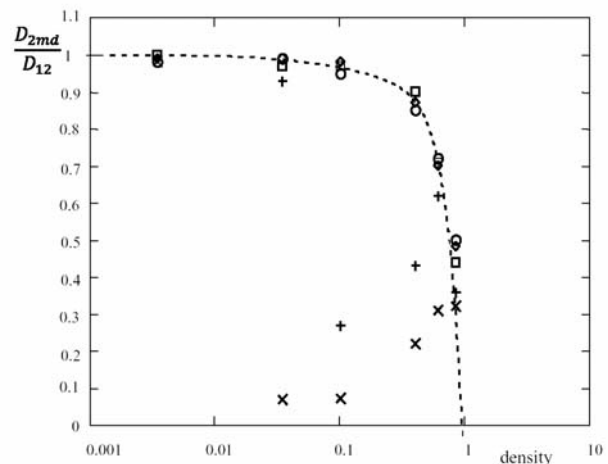


Fig. 6. The results of molecular dynamics calculations of the diffusion coefficients in the binary system. The universal dependence of ratio  $D_{2md}/D_{12}$  on density (7).

The dependence of  $D_{2md}/D_{12}$  on density for homogeneous systems can be approximated by the universal density dependent function at any temperature like  $D_{md}/D_0$  (5)

$$f_d(\rho) = 1 - 0.432\rho + 0.975\rho^2 - 1.717\rho^3 \quad (7)$$

Deviations from this dependence are connected with heterogeneity and formation of clusters and nanodroplets in

TABLE I  
DATA OF THE SELF-DIFFUSION COEFFICIENT CALCULATIONS

Density $\rho$	Temperature $T$	Number of the particles	Self-diffusion coefficient $D_{md}$	$D_{md}/D_0$
$3.42 \cdot 10^{-5}$	4	40000	$1.40 \cdot 10^4$	1.00
	3		$1.12 \cdot 10^4$	0.99
	2		$8.34 \cdot 10^3$	1.02
	1		$4.4 \cdot 10^3$	1.02
	0.75		$3.17 \cdot 10^3$	0.99
$3.43 \cdot 10^{-4}$	4	10000	$1.37 \cdot 10^3$	0.98
	3		$1.15 \cdot 10^3$	1.02
	2		818	1.01
	1		422	0.98
	0.75		327	1.02
$3.47 \cdot 10^{-3}$	4	10000	137.0	0.99
	3		110	0.99
	2		79	0.98
	1		41.1	0.97
	0.75		30.8	0.97
$3.48 \cdot 10^{-2}$	4	30000	13.5	0.98
	3		10.9	0.98
	2		7.87	0.98
	1		4.07	0.96
	0.75		2.308	0.73
0.1	4	10000	4.44	0.93
	3		3.59	0.93
	2		2.66	0.96
	1		1.23	0.84
	0.75		0.463	0.42
0.4	4	3000	0.947	0.79
	3		0.748	0.78
	2		0.580	0.83
	1		0.206	0.56
	0.75		0.0715	0.26
0.437	4	3000	0.842	0.77
	3		0.682	0.77
	2		0.503	0.79
	1		0.216	0.64
	0.75		0.0774	0.31
0.61	4	3000	0.505	0.64
	3		0.409	0.65
	2		0.281	0.62
	1		0.155	0.64
	0.75		0.0669	0.37
0.782	4	6347	0.318	0.52
	3		0.242	0.49
	2		0.162	0.45
	1		0.077	0.41
	0.75		0.053	0.38

the system (see Fig. 7). One can see that almost all the second kind particles are inside the nanodroplets. Special calculations have shown that at first the clusters of the first kind particles are formed as result of homogeneous nucleation and then they capture the second kind particles.

It is necessary to stress that the ratio  $D_{2md}/D_{12}$  for the liquid phase ( $\rho = 0.84$ ) depends on temperature also and equation (6) is not correct for the liquid systems.

#### IV. CONCLUSIONS

The diffusion coefficient calculations in Lennard-Jones systems in a wide range of density and temperatures have

been carried out. Various structures of systems within the vapor-liquid phase transition region have been found and were investigated. An abnormal increase of the self-diffusion coefficient is revealed with increasing density. It is related to the change of the vapor - liquid system structure. A universal dependence of the relation of diffusion coefficient to theoretical Chapman - Enskog values on density for the homogeneous systems is found. The large deviations of the diffusion coefficient for systems in the phase transition region from the universal function are observed. A comparison of the simulation results with experimental data on diffusion in gaseous and liquid argon yields good agreement.

TABLE II  
DATA OF THE DIFFUSION COEFFICIENT CALCULATIONS IN TWO-COMPONENT SYSTEM

Density $\rho$	Temperature $T$	Number of the particles	Diffusion coefficient $D_{2md}$	$D_{2md}/D_{12}$
$3.47 \cdot 10^{-3}$	4	10000	103.7	0.98
	3		83.4	0.99
	2		60.4	1.00
	1		30.5	0.99
	0.75		22.4	0.98
$3.48 \cdot 10^{-2}$	4	10000	10.6	0.99
	3		8.42	0.99
	2		5.81	0.97
	1		2.87	0.93
0.1	4	10000	3.42	0.95
	3		2.81	0.98
	2		1.98	0.97
	1		0.281	0.27
	0.75		0.057	0.073
0.4	4	10000	0.769	0.85
	3		0.629	0.87
	2		0.459	0.9
	1		0.112	0.43
	0.75		0.0425	0.22
0.61	4	10000	0.438	0.72
	3		0.341	0.70
	2		0.245	0.71
	1		0.109	0.62
	0.75		0.041	0.31
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

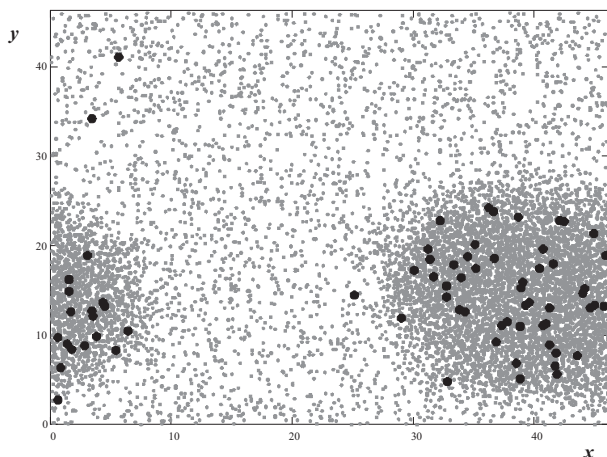


Fig. 7. Snapshot of particle distribution in a cell at  $\rho = 0.1$  and  $T = 1$ .

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