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# The molecular dynamics simulation of self-diffusion in gases and liquids

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**Abstract.** The molecular dynamics calculations of self-diffusion coefficients in 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 the jumping motion of molecules. A good agreement of our results and the experimental data for liquid argon has been obtained.

## 1. Introduction

The study of transport processes in gases, liquids and solids always attracted attention of scientists. The strict transport theory, based on the solution of Boltzmann's equation, exists for rarefied gases [1]. In this case, the mass, momentum and energy transport occurs via pair collisions of atoms or molecules. In particular according to the kinetic Boltzmann – Chapman – Enskog theory, the self-diffusion coefficient in rarefied gas is related by [1]

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

where  $\Omega^{(1,1)*}$  is the reduced collision integral.

The self-diffusion in solids occurs via jumping motion of atoms in crystal lattice (see for example [2]). Such diffusion mechanism results in the expression

$$D = D_m e^{-\frac{\Delta W}{kT}}, \quad (2)$$

where  $\Delta W$  is the activation energy of the 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 [3, 4]. Most of these theories invoke a combination of vibrational and jumping molecules motions and result in an expression like (2) for self-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 of the diffusion mechanisms in dense gases and in simple liquids.

In the present paper, the results of molecular dynamics calculations of the self-diffusion coefficients in the Lennard-Jones liquids over a wide range of temperature are presented. 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 diffusion coefficient to theoretical Chapman–Enskog values (1) on density for the homogeneous systems is found.

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

Large deviations of the diffusion coefficient for systems in the phase transition region from the universal function are observed. However, the ratio  $D_{md}/D_0$  for the liquid phase ( $\rho \geq 0.78$ ) depends on temperature. Obviously, the equation (3) is not correct for very dense systems.

## 2. 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 the number of the particles placed in it are chosen depending on the density. The interaction potential is

$$\begin{aligned} U(r) &= 4\varepsilon \left[ \left( \frac{\sigma_0}{r} \right)^{12} - \left( \frac{\sigma_0}{r} \right)^6 \right], \quad r \leq 4.5\sigma_0, \\ U(r) &= a(r - 5\sigma_0)^2 + b(r - 5\sigma_0)^3, \quad 4.5\sigma_0 \leq r \leq 5\sigma_0, \\ U(r) &= 0, \quad r \geq 5\sigma_0, \end{aligned} \quad (4)$$

where  $\sigma_0$  and  $\varepsilon$  are the diameter of atom or a molecule and the depth of the potential respectively. For optimization of the calculation algorithm, the potential has been cut off by the cubic spline on 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 considerably reduces an operating time of the computer program.

Reduced units are used in the calculations: the distance is  $r = r^*/\sigma_0$ , the temperature is  $T = kT^*/\varepsilon$ , the energy is  $U = U^*/\varepsilon$ , the density is  $\rho = \rho^*\sigma_0^3$  and time is  $t = t^*/\sigma_0(\varepsilon/m_0)^{1/2}$ . Here  $m_0$  is the mass of a molecule. The variables labeled by an asterisk are dimensional. 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 are 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 by formula  $T_{sr} = 2E_k/(3n)$ , where  $n$  is the quantity of particles,  $E_k$  is the kinetic energy of all particles

$$E_k = \sum_{i=1}^n m_0 v_i^2 / 2.$$

After several steps of the program, the velocity components of each particle  $v_x$ ,  $v_y$

and  $v_z$  are multiplied by factor  $\sqrt{T/T_{sr}}$ , where  $T$  is the set temperature of the system.

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

$$F(t) = \langle \vec{v}(0) \cdot \vec{v}(t) \rangle = \frac{1}{n} \sum_{i=1}^n \vec{v}_i(0) \cdot \vec{v}_i(t). \quad (5)$$

Here  $\vec{v}_i(t)$  is the velocity of a particle at the time moment  $t$ . The procedure of the calculation of  $F(t)$  is repeated many times. Then the received results are averaged. The number of averaging for one point  $F(t)$  reaches the values from 1350000 to 13500000.

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

$$D = \frac{1}{3} \int_0^{\infty} F(t) dt . \quad (6)$$

### 3. Results and discussion

The self-diffusion coefficients of all investigated systems are given in table 1. The simulations show that the ratio  $D_{md}/D_0$  increases with increasing temperature. In figure 1 these results together with the data for less density systems from [16] are presented. One can see that the ratio  $D_{md}/D_0$  doesn't depend on temperature up to  $\rho=0.61$  at high temperature ( $T > 1$ ). However, the uniform temperature dependence is observed for the systems of the present paper.

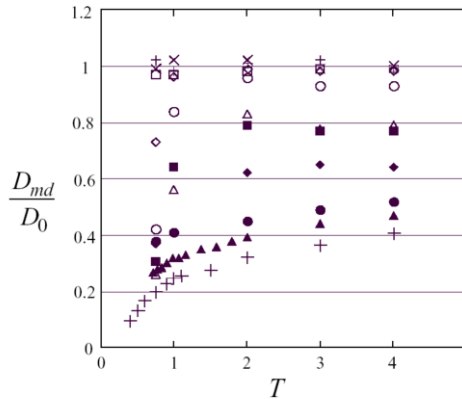
**Table 1.** Data of the self-diffusion coefficient calculation.

Density $\rho$	Temperature $T$	Number of particles	Self-diffusion coefficient $D_{md}$	$D_{md}/D_0$
0.7816	4	6347	0.318	0.516
	3		0.242	0.49
	2		0.162	0.45
	1		0.077	0.41
	0.75		0.053	0.376
0.8448	6	6861	0.391	0.518
	5		0.332	0.499
	4		0.266	0.469
	3		0.201	0.44
	2		0.129	0.392
	1.792		0.113	0.377
	1.582		0.096	0.357
	1.372		0.082	0.348
	1.162		0.066	0.328
	1.07		0.059	0.318
	0.983		0.054	0.316
	0.905		0.047	0.299
	0.831		0.041	0.284
	0.77		0.037	0.277
	0.72		0.033	0.265
0.888	4	3000	0.219	0.407
	3		0.157	0.363
	2		0.101	0.321
	1.5		0.067	0.274
	1.1		0.046	0.253
	1		0.041	0.247
	0.9		0.034	0.225
	0.75		0.024	0.196
	0.6		0.016	0.165
	0.5		0.011	0.131
	0.4		0.00614	0.094

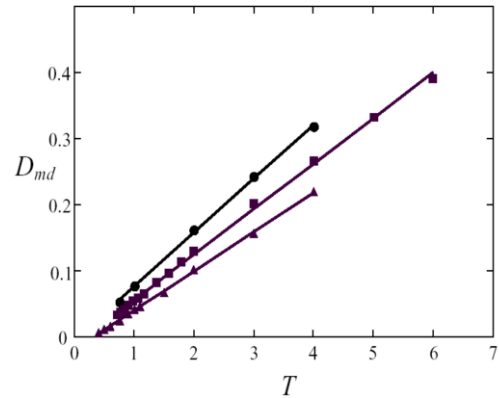
In figure 2 the temperature dependences of self-diffusion coefficients are shown. They are linear dependences with a high accuracy

$$D_{md} = \alpha + \beta T. \quad (7)$$

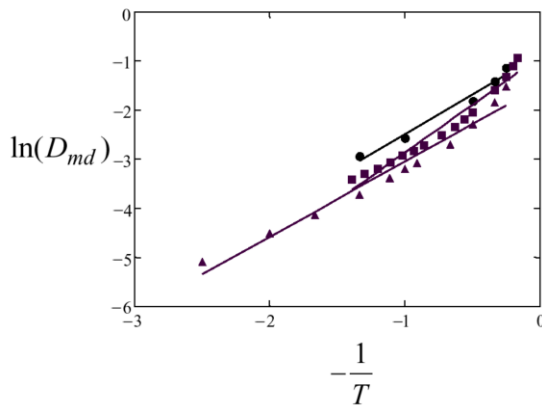
The analytic fit parameters  $\alpha$  and  $\beta$  depend on system density:  $\alpha = -4.76 \cdot 10^{-3}$  and  $\beta = 0.081$  for  $\rho = 0.7816$ ;  $\alpha = -0.013$  and  $\beta = 0.069$  for  $\rho = 0.8448$ ;  $\alpha = -0.019$  and  $\beta = 0.059$  for  $\rho = 0.888$ .



**Figure 1.** Temperature dependences of the reduced self-diffusion coefficients  $D_{md}/D_0$  at different system densities:  $\rho = 3.42 \cdot 10^{-5}$  ( $\times$ ),  $\rho = 3.43 \cdot 10^{-4}$  ( $+$ ),  $\rho = 3.47 \cdot 10^{-3}$  ( $\square$ ),  $\rho = 3.48 \cdot 10^{-2}$  ( $\diamond$ ),  $\rho = 0.1$  ( $\circ$ ),  $\rho = 0.4$  ( $\Delta$ ),  $\rho = 0.437$  ( $\blacksquare$ ),  $\rho = 0.61$  ( $\blacklozenge$ ),  $\rho = 0.7816$  ( $\bullet$ ),  $\rho = 0.8448$  ( $\blacktriangle$ ),  $\rho = 0.888$  ( $+$ ).



**Figure 2.** Temperature dependences of the self-diffusion coefficients  $D_{md}$  for liquid systems at different densities:  $\rho = 0.7816$  ( $\bullet$ ),  $\rho = 0.8448$  ( $\blacksquare$ ),  $\rho = 0.888$  ( $\blacktriangle$ ).



**Figure 3.** Dependence of  $\ln(D_{md})$  on  $1/T$  for the liquid systems at different densities:  $\rho = 0.7816$  ( $\bullet$ ),  $\rho = 0.8448$  ( $\blacksquare$ ),  $\rho = 0.888$  ( $\blacktriangle$ ).

the molecule is relaxed with increasing the average velocity of the molecules group. In other words, this diffusion mechanism is connected with relaxation of momentum fluctuations in liquids.

Our molecular dynamics simulations allow us to compare the results with experimental data in liquid argon [17]. The parameters  $\varepsilon/k = 124$  K and  $\sigma_0 = 3.418$  Å are used to scale the experimental

Thus, we can understand 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 self-diffusion coefficient are alike (see (1)). A new diffusion mechanism appears in the liquids. One can expect that the new mechanism is connected with jumping motion of molecules in liquids. Then the temperature dependence of self-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 motion of molecules group surrounding a molecule. Then the velocity of

data. These parameters are obtained from experimental data on viscosity of gaseous argon [18]. The experimental self-diffusion coefficient at 84.56 K is  $(1.53 \pm 0.03) 10^{-5} \text{ cm}^2/\text{sec}$ . We have obtained the value  $1.75 10^{-5} \text{ cm}^2/\text{sec}$ .

#### 4. Conclusions

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

To understand the nature of the diffusion mechanism, it is necessary to study fluctuation of density and momentum in liquids. Clusters and nanodrops can appear in dense gases [15, 16]. These structures have unusual properties [19, 20]. They strongly affect self-diffusion coefficient in dense gases. Perhaps, similar structures can appear in liquids. They must influence the diffusion greatly. The molecular dynamics study of such fluctuations is a very important and interesting problem.

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