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Diffusion in Liquids: Results of Calculations by Molecular Dynamics Method

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Abstract

In the present paper the dependence of the self-diffusion coefficient in liquids on temperature and density is discussed. Our calculations using the molecular dynamics method show that the diffusion coefficient has a linear dependence on the temperature at the constant density of the liquid. Strong temperature dependence of the diffusion coefficient appears as a result of the strong dependence of the liquid density on the temperature. The acquired results are compared with the experimental data on the diffusion in liquid argon.

Keywords

Diffusion in Liquids, Molecular Dynamics Method, Liquid Argon

1. Introduction

The molecular diffusion in liquid has been long studied both experimentally and theoretically. However, up to now there has been no satisfactory theory of this process. It is connected with the complexity of the mathematic description of the molecules movement and interaction in such dense media as liquids. Difficulties occur in understanding of the diffusion physical mechanisms even for simple liquids.

At present, there is a good kinetic theory of diffusion in rarefied gases [1]. It is based on the Boltzmann equation solution by the Chapman-Enskog method. This theory results in the expression of the self-diffusion coefficient of molecules D_0 in the form

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

where m_0 is the molecule mass, k is the Boltzmann constant, T is the gas temperature, ρ is the gas molecular density, σ_0 is the molecular diameter, $\Omega^{(1,1)*}$ is the reduced collision integral. In this case, the diffusion mechanism is

connected with pair collisions of molecules with one another, which results in the molecule's velocity relaxation. This diffusion mechanism is called a "collisionning" one.

Attempts of this theory generalization have been made for the description of the diffusion in dense gases and liquids. They are based on the Enskog theory for the system consisting of hard absolutely elastic spheres [1]-[3]. Though this theory can be considered successful for the diffusion description in dense gases, the molecular dynamics simulation shows that it is not applicable for the diffusion coefficients calculations in liquids [4]-[6].

Another approach to the description of the diffusion in liquids is based on the idea of the jumping mechanism of the molecules movement, alike to that which takes place in a solid. Here, a liquid molecule spends most of its time in a certain cell of neighboring molecules and makes vibrations around the equilibrium position. From time to time such molecule makes jumps from one equilibrium position to another one, which is situated in a neighboring cell. At this time, the molecule must pass through the potential barrier, consisting of the neighboring molecules. The development of such model results in the following expression for the diffusion coefficient in liquids [7]:

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

where D_m is a weak temperature dependent coefficient, ΔW is the activation energy of the jumping motion. Very often such model is used for the interpretation of the experimental data on the diffusion in liquids.

These two mechanisms of the diffusion in liquid result in the different temperature dependences of the diffusion coefficient. The "collisionning" diffusion mechanism is characterized by the power temperature law with the exponent less than unity. The jumping mechanism is connected with a strong exponential dependence of the diffusion coefficient on the temperature. In our papers [8]-[17] it has been shown by the molecular dynamics method, that the "collisionning" diffusion mechanism occurs in rarified and dense gases. Here, the universal dependence of the diffusion coefficient on density is observed, and the temperature dependence of the diffusion coefficient is the same as that of rarified gas and is defined by Equation (1). In dense systems, *i.e.* liquids the temperature dependence of the diffusion coefficient is linear

$$D = \alpha + \beta T, \tag{3}$$

where the coefficients α and β depend on density. It testifies that the diffusion mechanism in liquids is neither the "collisionning" one, nor the jumping one. We suppose that a new collective diffusion mechanism occurs in this case, when a molecule moves together with its surrounding in viscous liquid media. The molecule velocity relaxation is determined by the relaxation of the average velocity in the group of the surrounding molecules.

Here the question arises: why the experimental data on the diffusion in liquids are often described well by Equation (2)? The present paper is devoted to the study

of this problem.

2. The Calculations Methods

For the calculations of the diffusion coefficients we used the molecular dynamics method with the Lennard-Jones modified potential. The calculation method was described in our previous papers [8] [10]-[12]. We used dimensionless values for physical variables. These dimensionless variables were

$$\text{distance} \quad r = r_d / \sigma_0 \ ;$$

$$\text{time} \quad t = t_d / \sigma_0 (\varepsilon / m_0)^{1/2} ;$$

$$\text{density} \quad \rho = \rho_d \sigma_0^3 ;$$

$$\text{temperature} \quad T = k T_d / \varepsilon ;$$

$$\text{energy} \quad U = U_d / \varepsilon ;$$

$$\text{diffusion coefficient} \quad D = D_d / [\sigma_0 (\varepsilon / m_0)^{1/2}] .$$

σ_0, ε were the Lennard-Jones potential. Index d marked the dimensional variables.

We calculated the diffusion coefficients for three different densities of liquid: ρ = 0.7816, ρ = 0.8448 and ρ = 0.888.

In order to calculate the liquid density in the equilibrium system liquid-vapor, we chose a cell in the form of rectangular parallelepiped and made a thick layer of liquid surrounding by the vapor in the middle of the cell (**Figure 1**). The temperature of the cell volume was uniform. Therefore, the liquid layer and vapor were in the thermodynamic equilibrium state.

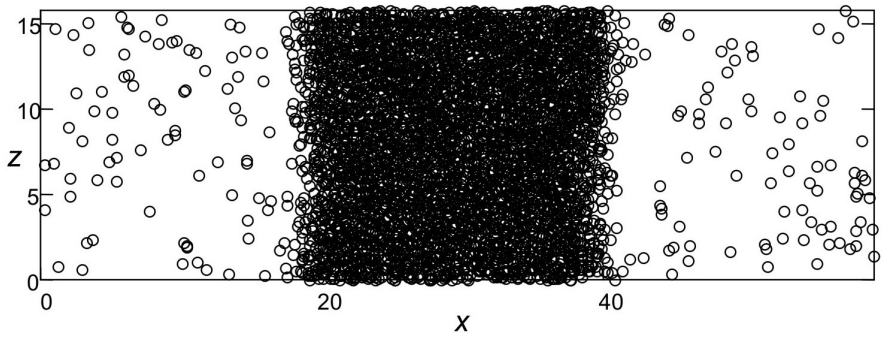

Figure 1. A liquid layer in vapor, which was in equilibrium in the cell of the molecular dynamics method.

Then we calculated the profile of the liquid and vapor density depending on the coordinate x. Using this profile, we calculated the average densities of the liquid and vapor at different system temperatures. The system temperature varied from 0.659 to 1.168. Correspondingly the liquid density changed from 0.853 to 0.566, and the vapor density changed from 1.35409×10^{-3} to 0.0932. Then, the plots of the liquid and vapor densities against the temperature of the equilibrium system were constructed and compared with the experimental data for argon [18].

3. Results and Discussion

In **Figure 2** the results of the calculations of the diffusion coefficients in the liquids at different densities depending on the temperature are presented [12]. It can be seen from the exposed plots that the temperature dependence of the diffusion coefficients is a linear one in accordance with Equation (3). The coefficients α and β are the linear functions on the density (**Figure 3**).

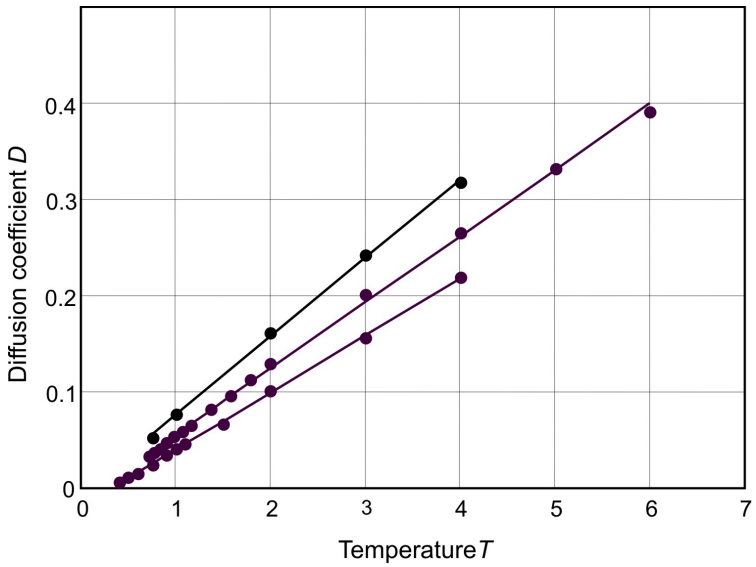

Figure 2. The temperature dependence of the self-diffusion coefficient in the liquid at different density: $\rho = 0.7816$, $\rho = 0.8448$, $\rho = 0.888$ (from the top to the bottom).

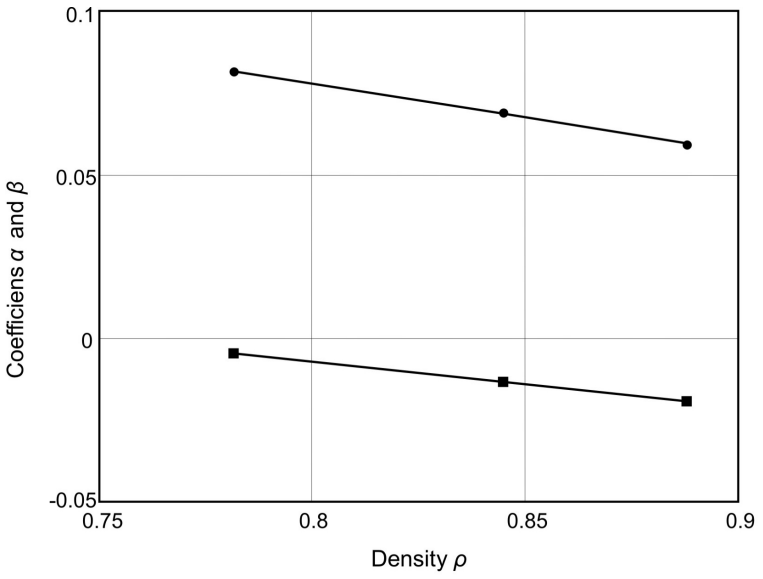

Figure 3. The dependence of the coefficients α (▪) and β (●) from Equation (3) on the system density.

The dependences of the coefficients α and β on the density are expressed by the equations

$$\alpha = 0.101 - 0.135\,\rho\,,$$

$$\beta = 0.244 - 0.208\,\rho. \tag{4}$$

In order to determine the dependence of the diffusion coefficient in the liquid on the temperature at the conditions of the thermodynamic equilibrium in the system liquid-vapor one should find the dependence of the liquid density on the temperature and substitute it in Equation (4). For this purpose, we make special calculations as it has been described in part 2 (**Figure 4**).

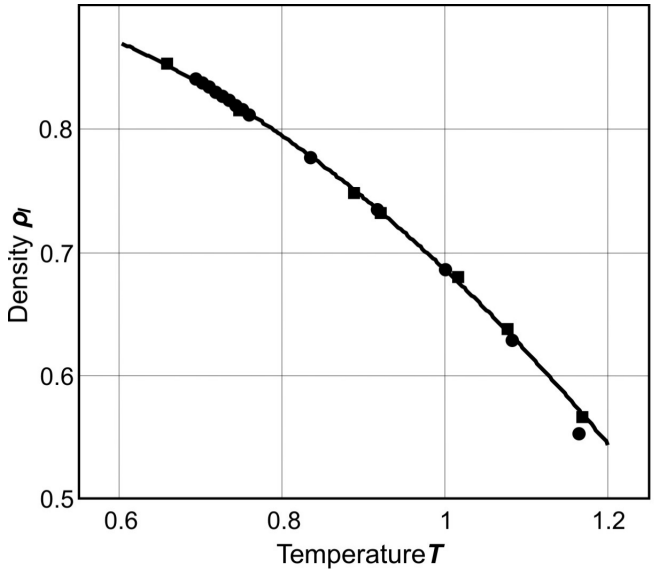

Figure 4. The dependence of the liquid density on the temperature at the conditions of the thermodynamic equilibrium vapor-liquid. ▪ our results of the molecular dynamics simulation, ● the experimental data for the liquid argon [18].

The dependence of the liquid density on the temperature is approximated by the fit

$$\rho_l = 0.901149 + 0.192782 \cdot T - 0.408842 \cdot T^2. \tag{5}$$

The comparison of the results of our calculations with the experimental data [18] shows good accordance, if the values $\sigma_0 = 3.402$ Å, $\varepsilon/k = 121$ K are chosen as the Lennard-Jones potential parameters. These parameters differ from those obtained with the help of the experimental self-diffusion coefficients in rarified argon in accordance with Equation (1) [1]: $\sigma_0 = 3.418$ Å, $\varepsilon/k = 124$ K.

In **Figure 5** the results of our calculations of the saturated vapor density depending on the temperature are presented. Here, the experimental data from [18] are also shown. We use the same Lennard-Jones parameters as for liquid argon. The temperature dependence of the saturated vapor density is well fitted by the polynomial approximation

$$\rho_g = -0.223974 + 0.922578 \cdot T - 1.300931 \cdot T^2 + 0.636531 \cdot T^3. \tag{6}$$

It should be acknowledged that our calculations are in accordance with the experimental data as far as the region of low temperatures is concerned $T = 0.6$ –

0.9. Here, we have to choose other parameters of the Lennard-Jones potential. It is small wonder, because this potential is a pair one and can hardly describe the interaction of the argon molecules in dense gases and liquids. That is why the Lennard-Jones potential should be considered as some effective potential, parameters of which must be chosen for every specific system.

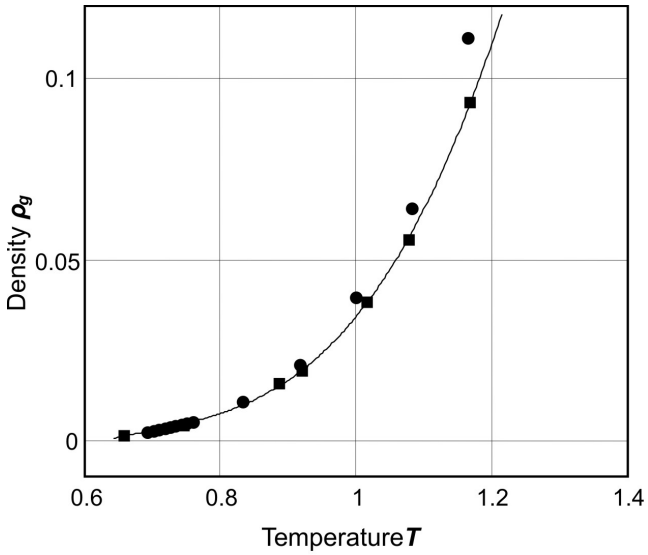

Figure 5. The dependence of the vapor density on the temperature under the conditions of the thermodynamics equilibrium vapor-liquid. ▪ the results of our calculations by the molecular dynamics method, ● the experimental data for argon [18].

Now we can consider the dependence of the self-diffusion coefficient in the liquid argon on the temperature under the conditions of the thermodynamic equilibrium vapor-liquid. For this purpose Equation (3), Equation (4) and Equation (5) should be used. The corresponding dependence is shown in **Figure 6**. The experimental data on the self-diffusion in liquid argon acquired in [19] [20] are presented in the same **Figure 6**. Here, we apply the Lennard-Jones parameters obtained in our calculations. We see that alongside with a certain accordance of our results with the experimental data, there is a systematic discrepancy. It may be connected with the fact, that the experiment [19] [20] has been held at a comparatively high pressure with respect to the equilibrium one. The rise of the pressure increases the liquid argon density, which influences greatly the diffusion coefficient. Unfortunately, the authors [19] [20] have not controlled the liquid argon density, that is why it is impossible now to estimate the influence of this factor on the results of the experiment.

In **Figure 7** our dependence of the self-diffusion coefficient on the temperature is shown as the plot of $\ln(D)$ against $1/T$ for the sake of comparison of it with Equation (2). In **Figure 7** one can see, that this dependence is close to the linear one, especially in a short temperature region. That's why Equation (2) is often in good accordance with experimental data on the diffusion in liquids, if the corresponding parameters D_m and ΔW are fitted. The Equation (2) is often

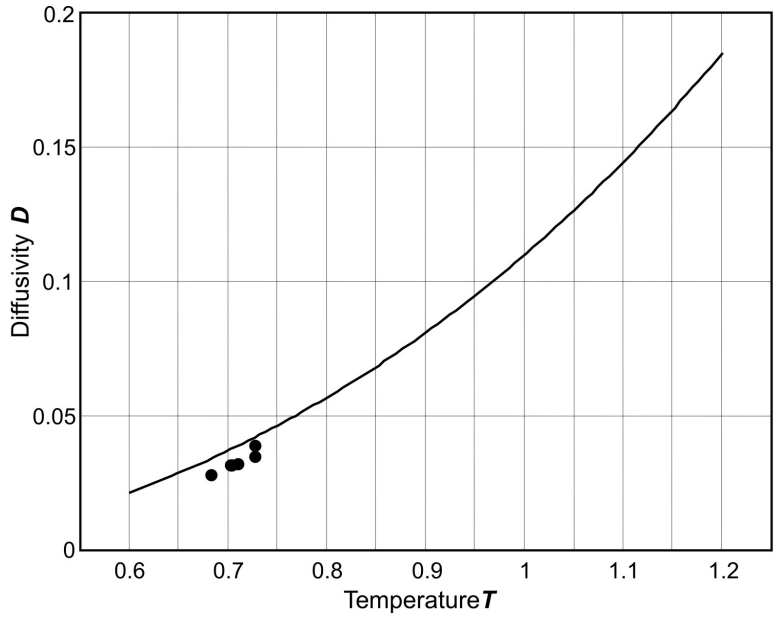

Figure 6. The temperature dependence of the self-diffusion coefficient in the liquid under the conditions of the thermodynamic equilibrium vapor-liquid. ● experimental data on the diffusion in the liquid argon [19] [20].

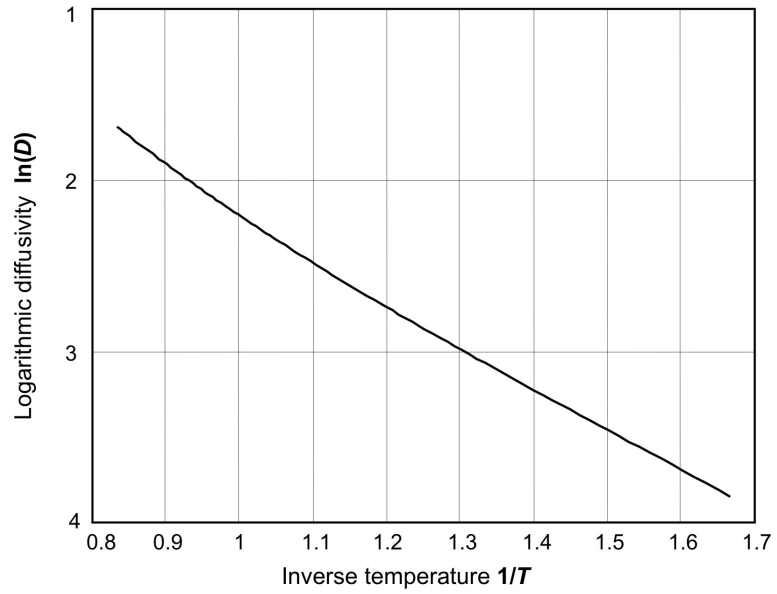

Figure 7. The dependence of the self-diffusion coefficient logarithm in the liquid under the conditions of the thermodynamic equilibrium vapor-liquid on the inverse temperature.

used for interpretation of experimental data, in particular in paper [20]. It is supposed, that the diffusion mechanism in liquids is a jumping one. However, it is not correct. The strong dependence of the diffusion coefficient in the liquids on the temperature is not connected with the jumping mechanism, but with its strong dependence on the liquid density, which in its turn depends on the temperature. And the dependence of the diffusion coefficient on the temperature at a constant density of the liquid is linear, which is related with the different collective diffusion

mechanism.

4. Conclusions

The molecular dynamic method used in the present paper made it possible not only to obtain the numeric values of the physical variables close to the experimental ones, but also to study the subtle details of the diffusion mechanisms in liquids, which was impossible to do experimentally. The diffusion of nanoparticles in dense gases and liquids [21]-[23], fluctuations of physical variables in small open systems [24] [25], surface tension of nanodrops [26]-[29] were studied earlier in our papers.

Further investigation of the diffusion in liquids and dense gases supposes the development of the kinetic theory of this process, taking into account all the dependences, which we have found by the molecular dynamics method.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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