THE NATURE OF MOLECULAR SELF-DIFFUSION IN ARGON AND WATER

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Dedicated to the 65-th anniversary of Prof. Leonid Bulavin

The nature of the self-diffusion of argon and water molecules, which are typical representatives of simple liquids and liquids with developed hydrogen bonds, respectively, has been examined. The self-diffusion coefficient of liquids is assumed to be a sum of collective and one-particle contributions. The estimation of the collective contribution is made on the basis of the Lagrange theory of thermal hydrodynamic fluctuations and has been demonstrated to completely agree with the data of neutron experiments. The proposed estimate of the one-particle contribution to the self-diffusion coefficient has correctly reproduced experimental data.

1. Introduction

Prof. L.A. Bulavin made an outstanding contribution to the solution of the problem formulated in the title of this paper [1, 2] (see also works [3, 4]). He was a pioneer in the experimental determination of the collective contribution to the self-diffusion coefficient of molecules in water and aqueous electrolyte solutions [3, 4]. In two decades, he together with his coauthors returned to this issue, using more adequate and modern methods [5, 6]. A certain summary of the results obtained was presented in review [7].

In accordance with ideas formulated in work [8] and in the works cited above, the self-diffusion coefficient of molecules of a liquid is a sum of collective and one-particle components. The magnitude and the temperature dependence of the collective component are successfully described in the framework of the Lagrange theory of thermal hydrodynamic fluctuations [7–9]. On the contrary, a well-developed theory of the one-particle contribution is absent today. Only work [10] can be marked in this connection.

In this work, we report the results of our researches dealing with the contribution of the collective component to the molecular self-diffusion coefficient in water and argon within the whole interval of their existence in the liquid state. We also discuss the magnitude and the temperature dependence of the one-particle contribution to the self-diffusion coefficient.

2. Collective Component of Self-Diffusion Coefficient

The collective component D_c of the self-diffusion coefficient is defined as the self-diffusion coefficient of a Lagrange particle with a suitable radius r_* [7]:

$$D_c = D_{\mathrm{L}}|_{r_{\mathrm{L}}=r_*}. \tag{1}$$

In work [7], it was also shown that the self-diffusion coefficient of a Lagrange particle is determined by the expression

$$D_{\mathrm{L}} = \frac{k_{\mathrm{B}}T}{5\pi\eta r_{\mathrm{L}}}, \tag{2}$$

and the suitable radius of a Lagrange particle equals

$$r_* = 2\sqrt{\nu\tau_{\mathrm{M}}}, \tag{3}$$

where τ_{M} is the Maxwellian time of the elastic strain relaxation in a liquid. Hence, the temperature dependence of the collective component of the molecular self-diffusion coefficient in a liquid is described by the formula

$$D_c = \frac{k_{\mathrm{B}}T}{10\pi\eta\sqrt{\nu\tau_{\mathrm{M}}}}. \tag{4}$$

As is seen, in order to calculate the collective component of the self-diffusion coefficient, it is necessary to know the magnitude and the character of the temperature dependence of the Maxwellian relaxation time.
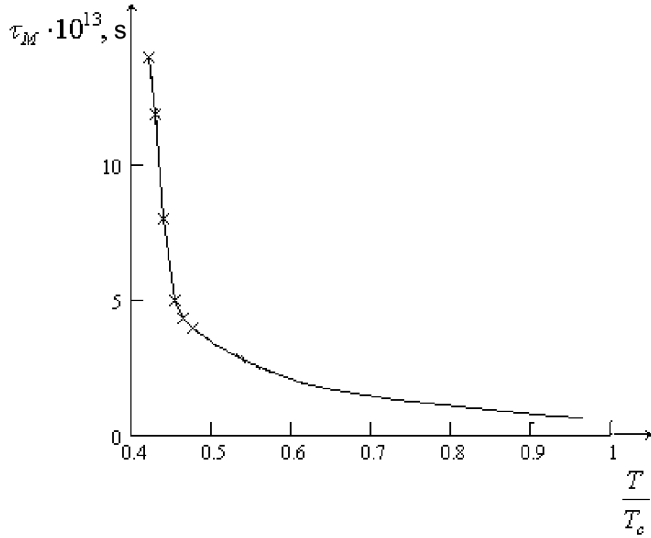
Fig. 1. Temperature dependence of the Maxwellian water relaxation time (see formula (5), where $T_H = 315$ K [12])

We adopt that the Maxwellian time of the shear stress relaxation is described by the formula

$$\tau_{\mathrm{M}}\left(T\right) = \begin{cases} \tau_0\left(T\right), & T < T_H, \\ \tau_0(T_H)\left(\frac{\nu(T)}{\nu(T_H)}\right)^{2/3}, & T > T_H, \end{cases} \quad (5)$$

where τ_0 is the residence time of water molecules which was determined in works [5, 6, 11], and T_H is a characteristic temperature of water that corresponds to the transition of the motion of water molecules from quasicrystal- to argon-like [12, 13]. The character of the temperature dependence of τ_{M} at $T > T_H$ was determined in work [14]. The behavior of τ_{M} in the whole temperature range, where a liquid water exists, is depicted in Fig. 1. Concerning argon, the most expedient is a constant value $\tau_{\mathrm{M}}(T) = \tau_{\mathrm{M}}(T_m)$ for it.

The dependences $D_c(T)$ calculated in such a way for argon and water are shown in Figs. 2 and 3, respectively. For water, they agree well with the corresponding values determined in works [5, 6] on the basis of experimental data on the noncoherent scattering of slow neutrons (see Fig. 3).
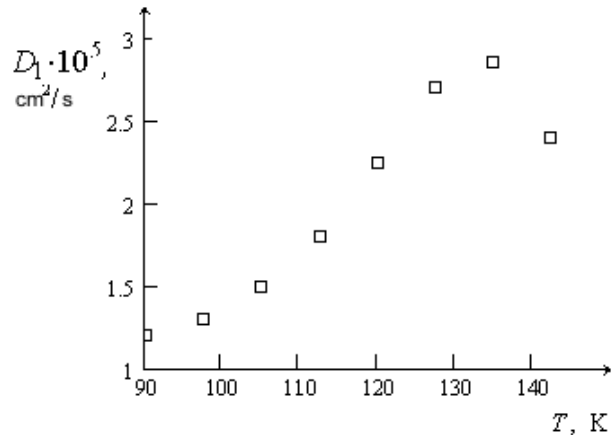
Unfortunately, the independent experimental or calculation results concerning the values of D_c in argon and other atomic liquids are absent at present.

3. One-Particle Contribution to the Self-Diffusion Coefficient of Liquid Molecules

To find the one-particle component of the self-diffusion coefficient, let us first discuss common and different
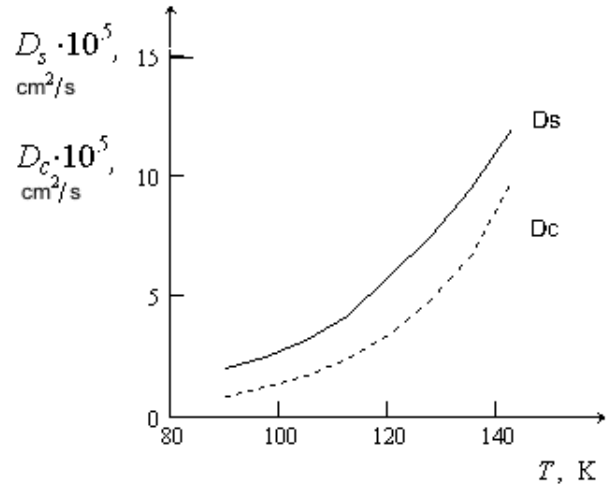
Fig. 2. Temperature dependences of (*a*) the total self-diffusion coefficient D_s of argon atoms (solid curve) and its collective component D_c (dashed curve) and (*b*) its one-particle component $D_1 = D_s - D_c$

points between this parameter and D_c. The contributions to the collective component D_c (4) are mainly made by vortex modes of the velocity field. In this connection, this quantity has to depend essentially on the kinematic viscosity and the Maxwellian time of the viscous stress relaxation. In addition, the important characteristics of the liquid state are the temperature T and the density ρ. As a result, D_c must increase with the temperature and decrease with the growth of the shear viscosity and the liquid density.

In contrast to D_c, the one-particle component of the molecular self-diffusion coefficient, D_1, must be independent of macroscopic liquid characteristics such as the shear viscosity ν and the Maxwellian time of the viscous
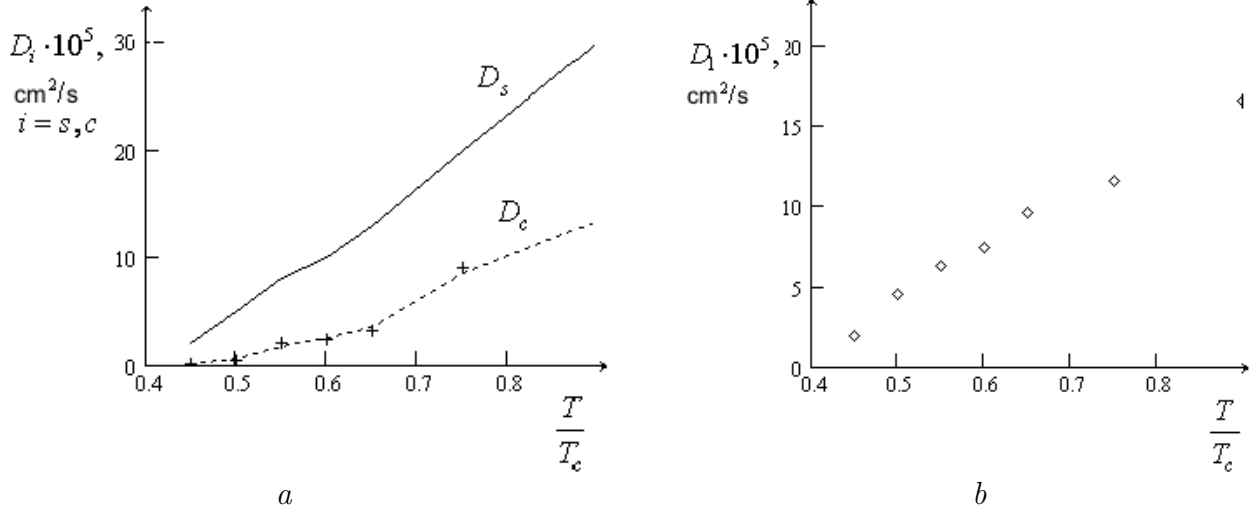
a

b

Fig. 3. The same as in Fig. 2, but for water molecules

stress relaxation. Those stresses govern the space-time evolution of collective modes. Accordingly, the dependence of D_1 on liquid parameters has to look like

$$D_1 = D_1 (T, n, r_{\rm eff}) , \qquad (6)$$

where n is the concentration of molecules of a liquid, and $r_{\rm eff}$ is the effective radius of a molecule which is to be determined with the use of intermolecular interaction parameters.

From the dimensional reasoning, we can construct the following combination of molecular parameters:

$$D_1 \sim \left(\frac{k_{\rm B} T}{m} \right)^{1/2} \frac{1}{n r_{\rm eff}^2}. \qquad (7)$$

It has the dimensionality of the self-diffusion coefficient and depends properly on the temperature and density. For the determination of the proportionality factor in expression (7), let us analyze the behavior of the autocorrelation function of a molecule velocity (ACFMV) $\phi(t) = \langle \mathbf{v}(t) \mathbf{v}(0) \rangle$. Its time dependence is very different in the intervals $0 \leq t < \tau_h$ and $\tau_s < t \leq \infty$, where τ_h and τ_s are the characteristic times of hard and soft, respectively, pair contacts of molecules in a liquid [15].

The characteristic time of the soft pair contact in simple liquids of the argon type is determined in the same way as in the limiting case of a rarefied gas:

$$\tau_s = \frac{1}{\pi n r_{\rm eff}^2 v_T}. \qquad (8)$$

In liquids with numerous hydrogen bonds, the quantity τ_s should be identified as the hydrogen bond lifetime τ_H.

As was shown in work [6], the behavior of ACFMV in the time interval $\tau_s \leq t \leq \infty$ is governed by hydrodynamic collective modes. On the contrary, in the ranges $0 \leq t < \tau_h$ for simple liquids and $0 \leq t < \tau_H$ for water, the details of a behavior of $\phi(t)$ are directly coupled with the relative molecular motion. Therefore, we obtain

$$D_1 \approx \frac{2}{9} \int\limits_0^{\tau_*} \phi(t) dt, \quad \tau_* = \tau_h, \tau_H , \qquad (9)$$

where the appearance of an additional factor 2/3 stems from the fact that the process of molecular self-diffusion is mainly connected only with the vortex modes of the velocity field [7, 8]. By the order of magnitude,

$$D_1 \approx \frac{2}{9} v_T^2 \tau_*. \qquad (10)$$

According to work [15] and formula (8), we obtain for simple liquids that $\tau_h \sim \frac{1}{q} \tau_s \sim \frac{1}{q} \frac{1}{\pi n r_{\rm eff}^2 v_T}$, where q is a power exponent in the repulsive part of the intermolecular interaction potential, and $U_r \sim \left(\frac{\sigma}{r} \right)^q$.

Therefore, (10) yields

$$D_1 \approx \frac{2}{9} \frac{r_{\rm eff}}{q \tilde{n}} \left(\frac{k_{\rm B} T}{m} \right)^{1/2} , \qquad (11)$$

where $\tilde{n} = n r_{\rm eff}^3$ is the dimensionless concentration. In accordance with Eq. (11), the required proportionality coefficient in formula (7) equals $\frac{2}{3q}$.

The value of $r_{\rm eff}$ can be identified, with a satisfactory accuracy, with the position of the minimum of the intermolecular potential, $U(r)$. For $U(r)$ taken in the
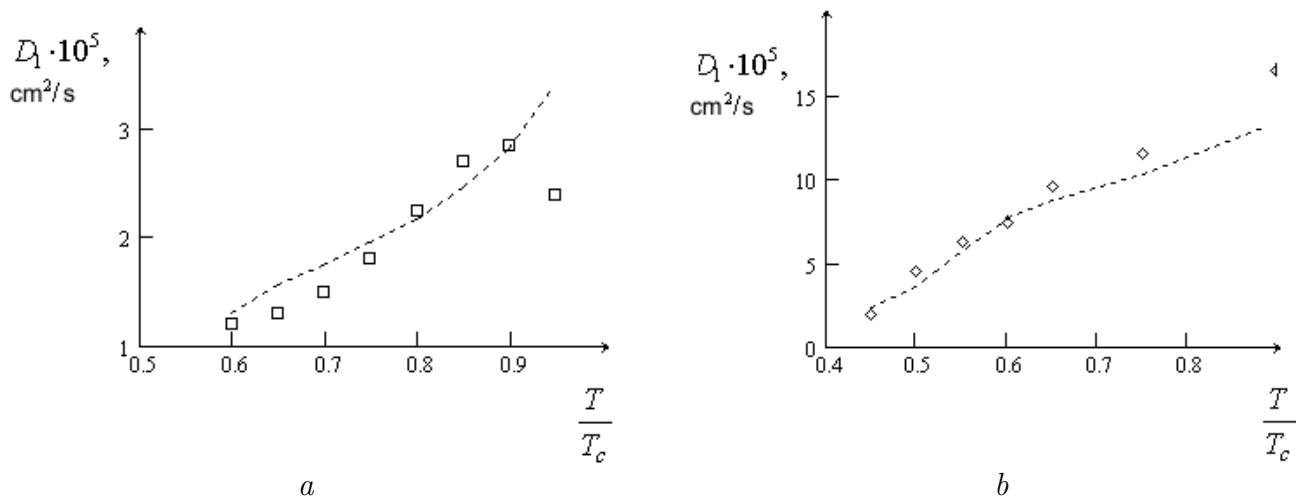
Fig. 4. Dependences of the one-particle component D_1 of the self-diffusion coefficient in argon (a) and pure water (b) on the temperature. The dashed curve corresponds to the values calculated by formula (12); squares and diamonds are the values taken from Figs. 2 and 3

Lennard-Jones form $U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$, we obtain $r_{\mathrm{eff}} = \frac{\sigma}{2^{1/6}}$. For argon, we adopt that $r_{\mathrm{eff}} \approx 2.4$ Å. Formula (11) can be rewritten in an alternative form

$$D_1 \approx \frac{2}{9q^*}\frac{10^{16}}{n}\left(\frac{k_{\mathrm{B}}T}{m}\right)^{1/2}, \qquad (12)$$

where $q^* = qr'^{2}_{\mathrm{eff}}$, and r'_{eff} should be considered as the effective radius of a molecule not taking its order of magnitude into account: $r_{\mathrm{eff}} = r'_{\mathrm{eff}} \times 10^{-8}$. A comparison between the D_1-values calculated by formula (12) with those exhibited in Fig. 2,b is depicted in Fig. 4,a.

A comparison between one-particle contributions to the self-diffusion coefficient of argon molecules calculated by formula (12) and the corresponding D_1-values from Fig. 2,b evidences their good agreement everywhere, but a vicinity of the critical point, where the reliable values for D_1 are absent. The numerical agreement between the indicated values was attained at the repulsion parameter $q^*(\mathrm{Ar}) = 135$. Since, $r^2_{\mathrm{eff}}(\mathrm{Ar}) = 5.76$, we obtain $q = 23.4$. This value is in good agreement with the corresponding value of the repulsion parameter that was found in work [15], when analyzing the asymptotic law for the fall revealed by the depolarized light scattering spectrum for simple liquids revealed at large frequency shifts.

In the case of water, the situation is more intricate. Here, one should bear in mind that the thermodynamic and kinetic properties of water are governed by the averaged intermolecular potential [16], which gives rise to a substantial temperature dependence of r_{eff}. This dependence originates from the growth of orientational corre-

lations induced by hydrogen bonds, as the temperature decreases. Formula (12) successfully agrees with the results of neutron experiments, provided that the following assumptions are made. 1) At temperatures close to the water crystallization one, $r_{\mathrm{eff}}(\mathrm{H_2O}) = 3$. This value practically coincides with the hydrogen bond length, the situation being quite natural. 2) At temperatures close to the critical point of water, hydrogen bonds become destroyed, and the effective radius of water molecules decreases to the value $r_{\mathrm{eff}}(\mathrm{H_2O}) = 1.6$ which corresponds to approximately half the hydrogen bond length, i.e. the geometrical radius of a water molecule. 3) At intermediate temperatures, the effective radius of water molecules linearly grows from one indicated value to the other. The value $q^*(\mathrm{H_2O}) = 105$ of the dimensionless repulsion parameter near the crystallization temperature corresponds to $q \approx 12$, which agrees with the repulsion parameter in the Lennard-Jones effective potential.

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ПРИРОДА САМОДИФУЗІЇ МОЛЕКУЛ В АРГОНІ ТА ВОДІ

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Р е з ю м е

Досліджено природу самодифузії молекул аргону і води, які є характерними для класів простих рідин і рідин з розвинутими водневими зв'язками. Прийнято, що коефіцієнт самодифузії рідин є сумою колективних і одночастинкових внесків. Показано, що оцінка колективного внеску, зроблена на основі лагранжевої теорії теплових гідродинамічних флуктуацій, повністю узгоджується з даними нейтронних експериментів. Запропоновано оцінку одночастинкового внеску в коефіцієнт самодифузії, яка також коректно відтворює експериментальні дані.