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NEW RESULTS IN THE THEORY OF COLLECTIVE SELF-DIFFUSION IN LIQUIDS

Results of new researches concerning the collective nature of transfer phenomena in liquids are reported. Attention is concentrated on the consistent analysis of a nontrivial time dependence of the root-mean-square displacement (RMSD) of molecules. The account of the contribution associated with the collective component of the molecular motion is shown to result in a more adequate description of the RMSD of molecules at short time intervals. A new method for the determination of the Maxwell relaxation time, which is one of the most important dynamic parameters of molecular systems, is expounded. Mechanisms of one-particle diffusion in water and argon are proposed. The correlation between the results obtained and the results of molecular dynamics studies in computer experiments by G.G. Malenkov, Yu.I. Naberukhin, and V.P. Voloshin aimed at determining the dimensions of Lagrange particles are discussed. A brief historical review of the problem of self-diffusion in liquids is made.

K e y w o r d s: self-diffusion coefficient, collective and one-particle components of self-diffusion coefficient, Maxwell relaxation time, Lagrange particle.

1. Introduction

The concept of collective component in the self-diffusion coefficient for liquids was introduced for the first time in Oskotskii's work [1] in 1961. According to work [2], the self-diffusion coefficient of molecules in liquids has to be approximated by a sum of one-particle and collective components,

$$D_s = D_1 + D_c. \tag{1}$$

This separation was made owing to the problems that arise while describing the results of the incoherent scattering of thermal neutrons. The well-known paper by Singwi and Sjölander [3] dealing with the incoherent scattering of slow neutrons was published at the same time. The case in point was the self-diffusion coefficient that coincides by its attributes with the one-particle self-diffusion coefficient. The origin of the latter is closely related to the theory of quasicrystalline liquid structure proposed by Frenkel [4, 5], Andrade [6], and Eyring [7, 8] in the 1930s. In the framework

of this theory, every molecule is supposed to oscillate around a fixed equilibrium position during a certain residence time τ_0; then, within the time interval τ_1 ($\tau_1 \ll \tau_0$), it transits to a new transient equilibrium position. The corresponding self-diffusion coefficient of molecules is defined by the equation

$$D_1 = \frac{\langle (\Delta \mathbf{r})_1^2 \rangle}{\tau_0 + \tau_1} \approx \frac{\langle (\Delta \mathbf{r})_1^2 \rangle}{\tau_0}, \tag{2}$$

where $(\Delta \mathbf{r})_1$ is the displacement of the molecule during the lifetime of a certain molecular configuration; this displacement is close to the average distance between the molecules. In the framework of this approach, the main attention is concentrated on the sequence of displacements for a single molecule; for this reason, this approach is called one-particle. Accordingly, the temperature dependence of self-diffusion coefficient is governed by the residence time behavior,

$$\tau_0 = \tau_v \exp(-E/k_{\mathrm{B}}T), \tag{3}$$

where τ_v is identified as the oscillation period, and E corresponds to the activation energy of the process;

Fig. 1. I.Z. Fisher, the creator of the Lagrange theory of thermal hydrodynamic fluctuations

Fig. 2. Prof. L.A. Bulavin who experimentally proved the existence of the collective transfer in liquids

as usual, k_{B} stands for the Boltzmann constant, and T for the temperature.

At the same time, the temperature dependence of the self-diffusion coefficient described by formulas (2) and (3) contradicts modern experimental data [9–11]. The contradiction is the most pronounced for liquid metals, which were studied in detail at the Kyiv University in the 1960s–1970s [12, 13]. This fact stimulated the search for new approaches to the problem of self-diffusion in various liquids, which are classed, according to L.A. Bulavin's classification [14, 15], into atomic, molecular, ionic, and ion-electron (liquid metals) ones. However, the results obtained in the majority of theoretical researches carried out in the 1960s [16, 17], on the one hand, partially resolved some problems but, on the other hand, created new ones.

An essentially new approach to the problem of the self-diffusion in liquids was proposed in Fisher's (Fig. 1) work [2]. Namely, the thermal motion of molecules should be regarded as that consisting of their motion with respect to the nearest environment and their motion together with the nearest environment. Those two motions substantially differ from each other by their characteristic times and, as a consequence, are independent. This scenario agrees with formula (1) for the self-diffusion coefficient and, in addition, demonstrates a way to calculate the collective component D_c. The author of work [2] emphasized that the mutual motion of a certain molecule together with its nearest environment is not anything else but the thermal motion of a Lagrange particle. Accordingly, he associated D_c with the self-diffusion coefficient D_L for this particle characterized by the corresponding radius. The coefficient D_L was calculated in the framework of the Lagrange theory of thermal hydrodynamic fluctuations, the basis of which was laid in the same cited work. It was shown that D_c is formed by vortex modes in the liquid and equals

$$D_c = \frac{k_{\mathrm{B}}T}{16\pi\eta\sqrt{\nu\tau_M}}, \tag{4}$$

where η and ν are the dynamic and kinematic shear viscosities of the liquid, respectively; and τ_M is the Maxwell relaxation time for shear stresses in the liquid. The first estimations of expression (4) showed that the fraction D_c/D_s of the collective component reaches 10–20% for argon in a vicinity of its ternary point and grows with the temperature. Analogous estimations for water revealed a considerably smaller fraction of the collective contribution: $D_c/D_s \approx 0.05$. However, in both cases, the estimation error depended on the specific values of physical quantities and the temperature dependence of the Maxwell relaxation time. Since the calculations were rare [18] and their reliability was unverified, the further analysis of the role of collective diffusion in liquids was suspended.

The next crucial step was made by L.A. Bulavin (Fig. 2) in the mid-1980s. In work [19, 20], he and his coauthors carefully examined the incoherent scattering of slow neutrons in water and aqueous solutions of electrolytes and analyzed the obtained results with the help of the modified Singwi–Sjölander theory. The modification consisted in the introduction of contributions from the collective diffusion into the

model. The results obtained gained a wide response and confirmed the existence of the collective transfer in liquids. Moreover, it was demonstrated that the relative magnitude of D_c contribution in the objects studied by L.A. Bulavin reached 40%.

The same conclusion was drawn by S.O. Mykhailenko (the Institute for Low Temperature Physics and Engineering, Kharkiv) [21, 22]. However, his conclusion was based on the results of computer simulation and therefore was disputable.

The results obtained by L.A. Bulavin and S.O. Mykhailenko stimulated the further development in the theory of collective transfer [21–30], as well as researches of collective transfer features with the help of computer simulation methods for the thermal motion of molecules in liquids [31–35]. In this work, the results of detailed molecular dynamics (MD) analysis of the root-mean-square displacement (RMSD) of molecules in atomic liquids of the argon type are reported, a new method is applied to calculate the Maxwell relaxation time for viscous stresses, the relative and absolute magnitudes of the collective component in the self-diffusion coefficient are determined, and a new approach to the determination of one-particle contributions to the self-diffusion coefficient is proposed.

2. Nontrivial Properties of the Root-Mean-Square Displacement of Molecules

In this section, we consider the properties of the RMSD of molecules in liquids. The special attention is concentrated on the contribution, which is proportional to the square root of time and which is the measure of a deviation from the Markovian process, with any diffusion process being always associated with the latter. The results of the theoretical analysis and molecular dynamic calculations are presented. The latter include the RMSD of an argon molecule, the Maxwell relaxation time, and the relative magnitude of collective component in the self-diffusion coefficient.

2.1. Structure of the root-mean-square displacement of molecules in liquids

In works [23, 24], it was shown that the expression for the RMSD of a molecule has the following structure:

$$\Gamma(t) = \Gamma_r(t) + \Gamma_c(t), \tag{5}$$

where

$$\Gamma_r(t) = C + 6D_r t \tag{6}$$

is the contribution associated with the motion of the molecule with respect to its nearest environment, D_r the corresponding component of the self-diffusion coefficient, t the time, C a constant determining a shift of the linear asymptotics of the RMSD of a molecule from the coordinate origin,

$$\Gamma_c(t) = 6D_c t - \frac{k_{\mathrm{B}}T}{\rho(\pi\nu)^{3/2}}\sqrt{t} + ... \tag{7}$$

is the component of the RMSD (it is formed by the collective motion of molecules and can be described, by using the methods of Lagrange hydrodynamics [23, 26]), ρ the liquid density, and D_c the collective component of the self-diffusion coefficient.

The term proportional to $\sqrt{t}$ in expression (7) is very important. It testifies that the collective motion of Lagrange particles, as well as molecules, does not obey the regularities of the Markovian process, which are typical of standard models describing the diffusion motion of molecules [36]. In other words, the discovery of the root contribution in molecular dynamic experiments would become an important argument in favor of the collective transfer mechanism in liquids.

But in essence, formula (7) is much more important. Really, proceeding from the formula

$$D_c = \frac{k_{\mathrm{B}}T}{10\pi\eta\sqrt{\nu\tau_M}}, \tag{8}$$

which was derived in work [4] on the basis of the consistent Lagrange theory for thermal hydrodynamic fluctuations, formulas (5)–(8) give the following result:

$$\Gamma(t) = C + 6D_s t \left[1 - \frac{10}{3\pi^{1/2}}\frac{D_c}{D_s}\left(\frac{\tau_M}{t}\right)^{1/2} + ...\right], \tag{9}$$

where

$$D_s = D_r + D_c \tag{10}$$

is the total self-diffusion coefficient of molecules in the liquid. From whence, it follows that, by analyzing the asymptotic behavior of the function

$$G(t) = \frac{\Gamma(t) - C}{6D_s t} \Rightarrow 1 - \frac{10}{3\pi^{1/2}}\frac{D_c}{D_s}\left(\frac{\tau_M}{t}\right)^{1/2} + ..., \tag{11}$$
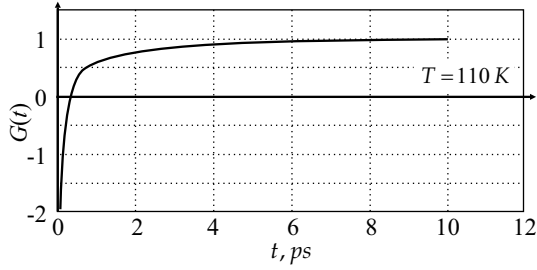
Fig. 3. Time dependence $G(t)$ for argon at $T = 110$ K. At short times, the deviation from the asymptotic series (11) is substantial

as $t \to \infty$, we can determine the ratio D_c/D_s, i.e. the relative contribution of the collective component to the self-diffusion coefficient. A typical behavior of the function $G(t)$ is shown in Fig. 3.

However, the calculation is possible only provided that the Maxwell relaxation time has a known value. Unfortunately, the available methods of calculation of τ_M [18, 37, 38] do not allow one to obtain a sufficiently complete picture of the dependence of this parameter on the temperature and the density, in particular, at the liquid–vapor coexistence curve. However, on the basis of the Lagrange theory of thermal hydrodynamic fluctuations, it is possible to propose rather a simple method to find τ_M, which is closely related to the calculation methods applied to the RMSD of molecules.

For instance, in accordance with works [23, 27, 39], the contribution of vortex modes in the fluctuation hydrodynamic field of velocities to the autocorrelation function of molecule's velocity (ACFMV) equals

$$\varphi_{\mathbf{V}}(t) = \frac{k_{\mathrm{B}}T}{16\pi\rho(\nu\tau_M)^{3/2}} \, e^{-x} \frac{I_1(x) + I_2(x)}{x},$$
$$x = \frac{t}{2\tau_M}, \quad x > 1, \tag{12}$$

where $I_n(x)$, $n = 1$ and 2, are the modified Bessel functions of imaginary argument. At $x \gg 1$, the ACFMV $\varphi_{\mathbf{V}}(t)$ has the following asymptotics:

$$\varphi_{\mathbf{V}}(t) \underset{t \to \infty}{\to} \frac{A}{t^{3/2}} \left(1 - \frac{9}{4} \frac{\tau_M}{t} + ... \right),$$
$$A = k_{\mathrm{B}}T/4\pi\rho\nu^{3/2}. \tag{13}$$

From whence, it follows that the Maxwell relaxation time for viscous stresses equals

$$\tau_M = \frac{4}{9} \lim_{t \to \infty} t \left(1 - \frac{\varphi_{\mathbf{V}}(t)t^{3/2}}{A} \right), \tag{14}$$

or

$$\tau_M = \frac{4}{9} \lim_{t \to \infty} t \left(1 - \frac{\Gamma''_{MD}(t)t^{3/2}}{2A} \right). \tag{15}$$

In the latter case, the known equation [36],

$$\varphi_{\mathbf{V}}(t) = \frac{1}{2}\Gamma''(t),$$

which expresses the ACFMV in terms of the RMSD of a molecule, was used. It is essential that the method proposed for the calculation of τ_M is independent of those used in works [18, 37, 38], being at the same time much easier.

Really, in work [18], the Maxwell relaxation time for shear stresses was calculated using the formula $\tau_M = \eta/G_\infty$, in which the high-frequency modulus of shear stresses G_∞ has to be determined. For this purpose, the methods of molecular dynamics were used. It was supposed that, at the initial time moment, the molecules in the model system undergo a shift of the type $x \to x + y \tan\theta$, where θ is the angle of a shear deformation. The value of high-frequency shear modulus was determined by averaging the quantity $G_\infty = \frac{1}{V} \frac{\partial^2 U}{\partial(\tan\theta)^2}$, where U is the potential energy of the system, and V its volume. The averaging was carried out over a time interval several tens of integration steps in length.

In work [37], the Maxwell relaxation time τ_M was also determined with the use of molecular dynamics methods. Its value was calculated by the formula $\tau_M = \frac{1}{F(0)} \int_0^\infty F(t)\,dt$, where $F(t)$ is the autocorrelation function for shear stresses. In comparison with work [18], the contributions of the kinetic origin were also taken into consideration in the cited work.

An attempt was made to determine the Maxwell relaxation time experimentally [38]. In the framework of this approach, τ_M was considered as the proportionality coefficient in the relation $\eta = \tau_M p_{\mathrm{th}}$, where p_{th} stands for the so-called thermal pressure, which is a sum of the external and internal pressures in the system. In work [38], it was identified, with no explanations, with the shear stress modulus. The method is applicable only for high pressures.

Unlike the cited works, no additional assumptions are used in this work. Here, the asymptotics of the autocorrelation function for the velocity of a molecule is calculated, which is the simplest of all functions of this kind.

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2.2. Determination of the autocorrelation function for the velocity of a molecule and the Maxwell relaxation time

To simulate the motion of a molecule, a system consisting of $25^3 = 15625$ argon atoms was used. The atoms were supposed to be contained in a cubic cell. The software package GROMACS [40] was used for the simulation. Argon atoms were supposed to interact with one another following the law [41]

$$U\left(r\right) = \frac{C_i^{(12)}}{r^{12}} - \frac{C_i^{(6)}}{r^6}, \qquad (16)$$

where

$$C_i^{(12)} = 0.9847 \times 10^{-5}\ \frac{\text{kJ} \cdot \text{nm}^{12}}{\text{mol}},$$
$$C_i^{(6)} = 0.6265 \times 10^{-2}\ \frac{\text{kJ} \cdot \text{nm}^6}{\text{mol}}.$$

This potential is equivalent to the standard Lennard-Jones potential

$$U\left(r\right) = 4\varepsilon\left(\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^6\right), \qquad (17)$$

with the following parameter values: $\varepsilon/k_{\mathrm{B}} = 120.06$ K and $\sigma = 3.409$ Å. The Nose–Hoover thermostat was used [42, 43]. The step of integration was selected to equal 0.1 fs.

A typical behavior of the ACFMV during long enough time intervals is depicted in Figs. 4 and 5. The values obtained for the Maxwell relaxation time at the argon liquid-vapor coexistence curve are collected in the third column of Table 1. In what follows, however, we use the values obtained with the use of a simpler and more reliable method in comparison with those applied in the works indicated in Table 1.

The values of the parameters governing the RMSD of molecules – the time interval t_a separating the initial, quasidynamic stage of the motion of a molecule from the next, mainly stochastic one; the shift C of the linear asymptotics for the RMSD of a molecule from the coordinate origin; and the self-diffusion coefficients D_s at various temperatures are listed in Table 2. All of them agree well with the values obtained in molecular dynamics experiments [44, 45] dealing with the analysis of the RMSD of a molecule, as well as with experimental data. One should expect that a similar error will also characterize the values of
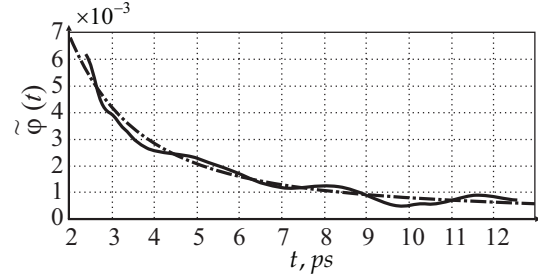

Fig. 4. Time dependence $\tilde{\varphi}\left(t\right) = \varphi_{\mathbf{V}}\left(t\right)/\varphi_{\mathbf{V}}\left(0\right)$ obtained by the molecular dynamics (MD) simulation of argon molecules in liquid (solid curve) and its fitting by expression (13) (dash-dotted curve). $T = 120$ K
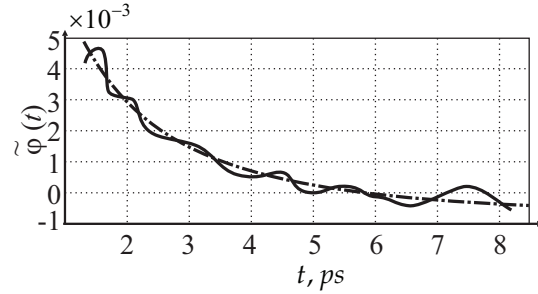

Fig. 5. The same as in Fig. 2, but for $T = 130$ K

Table 1. **Maxwell relaxation times at the coexistence curve of argon and their comparison with literature data**

T, K	A, ps$^{3/2}$	$\tau_M \times 10^{13}$, s	$\tau_M \times 10^{13}$, s [18]	$\tau_M \times 10^{13}$, s [37]	$\tau \times 10^{12}$, s [38]
80	–	–	–	1.84	–
83.815	–	–	2.36	1.79	–
90	0.011	2.53	≈2.28	1.68	–
95	0.013	2.46	≈2.23	1.6	2.2
110	0.021	2.31	–	1.58	2.2
120	0.0269	2.23	–	1.57	2.1
130	0.0336	2.407	–	1.66	–
140	0.038	2.474	–	1.73	–

Maxwell relaxation time for shear stresses in liquids determined within our method.

Moreover, the parameters of the RMSD of a molecule quoted in Table 2 were calculated at the coexistence curve (i.e. for normal argon states) and at its continuation into the supercooled-liquid region. Here, as one can see, the self-diffusion coefficient has a substantial jump between temperatures of 50 K and 60 K,
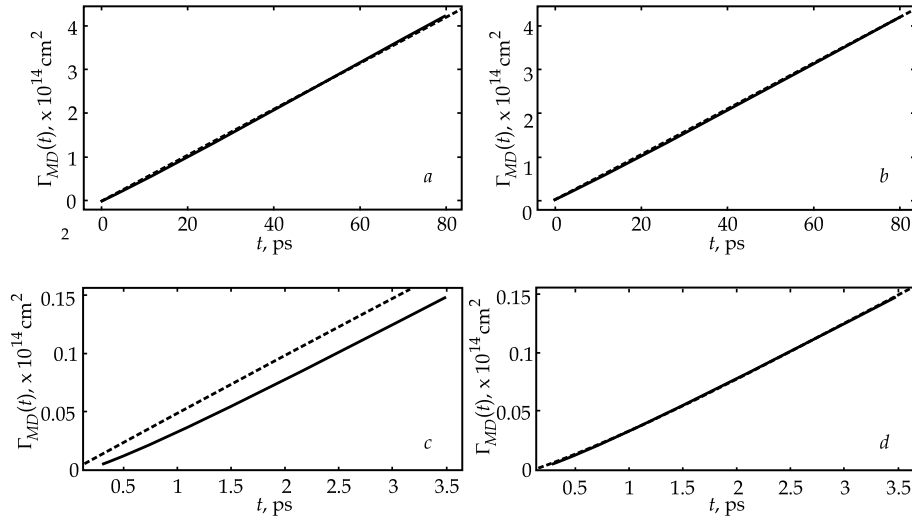
Fig. 6. Fitting of the calculated RMSDs of a molecule $\Gamma_{MD}(t)$ by the simplified expression $\Gamma_{MD}(t) = C + 6D_s t$ (panels *a* and *c*) and formula (9) (panels *b* and *d*)

Table 2. **Parameters D_s, $D_{\exp}$ [44], C, and t_a at various temperatures**

T, K	$t_a \times 10^{13}$, s	$C \times 10^{18}$, cm^2	$D_s \times 10^{-5}$, cm^2	$D_{\exp} \times 10^{-5}$, cm^2
40	4	0.0039	0.0424	–
50	4	0.0052	0.0695	–
60	4.3	0.0054	0.4679	–
70	4.3	0.0054	0.8007	–
80	4.3	0.0043	1.4116	–
83.8	4.3	0.005	1.6825	1.8
95	4.3	0.00096	2.79	2.73
110	4.3	−0.0084	4.43	4.717
120	4.3	−0.0164	5.91	6.179
130	4.6	−0.0227	7.73	7.769

Table 3. **Ratio D_c/D_s determined from Eq. (11), Table 2, and Eq. (8)**

T, K	D_c/D_s, (11)	D_c/D_s
40	0.043	
50	0.068	
60	0.128	
70	0.184	
80	0.19	
83.815	0.227	
90	0.242	0.232
95	0.253	0.242
110	0.280	0.273
120	0.33	0.318
130	0.39	0.374

which can be interpreted as the approach to the argon spinodal. This conclusion completely agrees with the results of work [46], where the stability limits for the liquid and crystalline phases of argon were studied in the framework of the molecular dynamics method. The density–pressure ($\rho-P$) phase diagrams obtained in the cited work were used to determine the position of a spinodal as the locus of points, where $(dP/d\rho)_T = 0$.

However, the following result substantially differs from the standard one. The matter concerns the existence of a contribution proportional to $\sqrt{t}$ in the RMSD of a molecule, which is predicted by the La-

grange theory of thermal hydrodynamic fluctuations (see Eq. (9)). This conclusion is completely confirmed by the time dependence of the RMSD of a molecule exhibited in Fig. 6. It is evident that the adequacy of the fitting depends not only on the applied formula, but also on the used scale.

The values of the ratio D_c/D_s at the coexistence curve, which were calculated for various temperatures by analyzing the time-dependent function $G(t)$ in accordance with Eq. (11), are quoted in Table 3. One can see a good agreement between the values determined by the MD simulation and those calculated directly. The fraction of the collective component in

the self-diffusion coefficient varies from 24% near the water ternary point to 40% at 130 K. The results obtained testify that the collective transfer in liquids plays an important role, so that it has to be studied in detail.

3. Simulation of One-Particle Contributions to the Self-Diffusion Coefficient

In this section, we will shortly dwell on the methods used to estimate the D_1 contributions to the self-diffusion coefficient. In works [2, 19, 20, 26], they were called one-particle. In effect, those contributions are not one-particle, because they result from the relative displacements of molecules that form a Lagrange particle. This means that this component should also be interpreted as collective. The choice of method to calculate D_1 considerably depends on whether a characteristic local structure of the liquid exists or not. This statement becomes especially clear, if comparing the relative motions of molecules in water and in argon.

Really, as was shown in work [4], the structure of supercooled water and water in the temperature interval 273 K $< T <$ 315 K is crystal-like. This means that every molecule oscillates around its equilibrium position during the residence time interval τ_0. In other words, the local formation of crystal-like structure in water can exist only during the time τ_0. Afterward, the structure of the formation, or the crystal-like cluster, becomes destroyed, which is accompanied by relative displacements of neighbor molecules by a characteristic distance equivalent to that between the nearest neighbor molecules in ice, i.e. by $l \approx 2.8$ Å. In the framework of this model, the coefficient of relative self-diffusion can be estimated using the formula

$$D_1 \approx \frac{l^2}{6\tau_0}. \tag{18}$$

The residence time τ_0 can be estimated on the basis of experimental data on the incoherent scattering of slow neutrons [3, 4, 15, 47, 48]. However, their accuracy, especially for supercooled states, is low. Therefore, the application of the dipole relaxation time τ_D seems to be more reasonable. It is clear that the parameters of the translational and rotational motion modes have to be mutually correlated. This means that the oscillatory character of the motion should be

expected for both degrees of freedom in the crystal-like state of water. In principle, water is characterized by strong angular correlations, although this is not a key point. Therefore, appreciable variations in the orientation of the dipole moment of a water molecule should be expected only after the destruction of the crystal-like cluster. In work [49], it was shown that the temperature dependence of τ_D experiences drastic changes precisely at $T_H \approx 315$ K, which testifies that the crystal-like character of the molecular thermal motion manifests itself self-consistently both in the translational and rotational degrees of freedom. From whence, it follows that

$$D_1 \approx \frac{\langle l^2 \rangle}{6\tau_D}, \quad T < T_H$$

or

$$\langle l^2 \rangle = 6\tau_D D_1 \Rightarrow 6\tau_D(D_s - D_c), \quad T < T_H. \tag{19}$$

In Eq. (19), formula (10) was taken into account.

The quantity $\langle l^2 \rangle$ calculated using this method is tabulated in Table 4. From the analysis of calculation results, it follows that the values within the interval $3.25 < \tilde{l} < 3.35$ are in satisfactory agreement with the requirement to the magnitude of molecular displacement resulting from the destruction of crystal-like clusters, which was formulated above. A similar concept concerning the character of the thermal motion of molecules in the computer model of supercooled water was also considered in work [56].

In contrast to water, no crystal-like states arise in argon [57]. Note that they are also absent in water at temperatures when the character of the thermal motion is similar to that in argon. In the latter, a simple stirring of atoms is impossible in a wide temperature interval, because the average gap between argon

Table 4. **Root-mean-square displacements of water molecules determined using D_s from works [50–53], D_c from work [4], and τ_D from works [54] (second column) and [55] (third column). $\tilde{l} = l \times 10^8$ cm^{-1}**

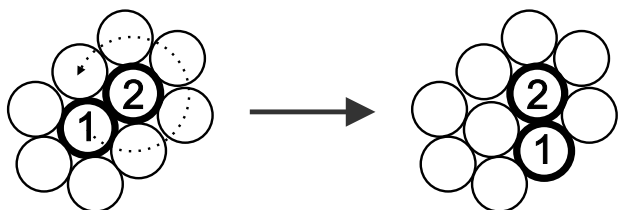| T, K	$\langle \tilde{l}_1^2 \rangle$	$\langle \tilde{l}_2^2 \rangle$	T, K	$\langle \tilde{l}_1^2 \rangle$	$\langle \tilde{l}_2^2 \rangle$
253	11.4		299		10.4
263	11.3		303	11.4	
273	11.3		304		10.2
283	11.4	10.7	308		10.3
293	11.3	10.5	313	11.5	

Fig. 7. Rotational motion of a group of molecules around molecule 2 in liquid. As a result, molecule 1 becomes shifted into a new position
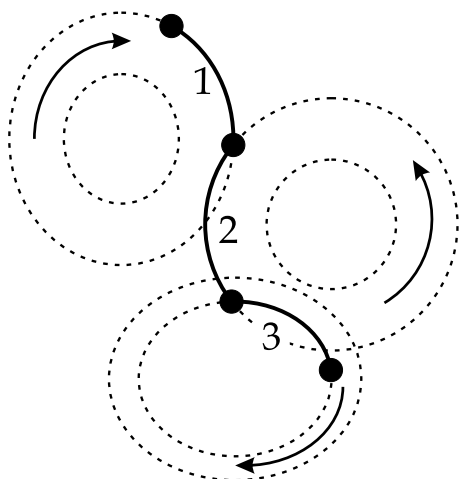

Fig. 8. Schematic illustration of the mechanism of collective transfer of a Lagrange particle by fluctuation vortices

atoms is about 0.1 Å, which is an order of magnitude smaller than their diameter. This circumstance makes the argon liquid essentially different from the vapor, even if the latter is saturated. However, the stirring does take place in the liquid, and it should be considered as a result of rotational motions of molecular groups (see Fig. 7). In this case, the corresponding velocity of rotational motion is determined by the formula

$$v_{cl} \approx \sqrt{k_{\mathrm{B}}T/mn},$$

where m is the mass of an argon atom, and $n \approx 6 \div 7$ is the number of nearest neighbors. By magnitude, $v_{cl} \approx (6 \div 7) \times 10^3$ cm/s.

The displacement of a group of molecules by a distance equal to the diameter of an argon atom is, in effect, an elementary event of the self-diffusion, i.e.

$$D_1 \approx \frac{1}{6}\sigma v_{\mathrm{cl}}. \tag{20}$$

At $T = 100$ K, the corresponding value $D_1 \approx 3 \times \times 10^{-5}$ cm^2/s satisfactorily correlates with the results presented in Table 2. Moreover, the sum $D_1 + D_c$ is almost exactly equal to the experimental value (see Table 2).

The temperature dependence of D_1 is approximately described by the expression

$$D_1 \approx D_1(T_m)\sqrt{Tn_m/n(T)T_m}. \tag{21}$$

4. Discussion of the Results

In a dense medium, all molecular motions are collective. This means that both the contribution D_c to the self-diffusion coefficient and the contribution D_1, which is conventionally referred to as one-particle [2, 19], have a collective origin. Concerning the component D_c, it stems from fluctuation vortex motions in liquid. The character of the transfer of a definite Lagrange particle, as well as the molecules in it, is illustrated by a sequence of vortices depicted in Fig. 8. The Lagrange particle on the periphery of a fluctuation vortex is transferred by the latter at a short distance. The displacement terminates, when the vortex fades. After a certain time interval, the particle turns out on the periphery of another vortex, which transfers it further. Then the process repeats again. Note that, unlike Fig. 7, which illustrates the rotational motion of molecular groups, Fig. 8 schematically exhibits the motion of a Lagrange particle in the field of thermal hydrodynamic fluctuations.

The vortex-assisted transfer of molecules in liquids is adequately described by the Lagrange theory of thermal hydrodynamic fluctuations [25]. At the same time, collective motions corresponding to the component D_1 are more complicated, and their consideration requires finer model concepts, similar to those used above for water and argon.

The concept of Lagrange particle that shifts in the field of thermal hydrodynamic fluctuations is one of the key concepts in the Lagrange theory of thermal hydrodynamic fluctuations, which forms a basis of our approach. The conceptional works [31–35] were aimed at revealing such particles and researching the character of their motion. The cited authors – G.G. Malenkov, Yu.I. Naberukhin, and V.P. Voloshin – applied the MD methods to study correlations in the mutual motion of two particles. They analyzed the time dependence of the root-mean-square distance between

two particles,

$$\Gamma_{12}(t|r_{12}(0)) = \langle (\mathbf{r}_{12}(t) - \mathbf{r}_{12}(0))^2 \rangle,$$

where $\mathbf{r}_{12}(t) = \mathbf{r}_2(t) - \mathbf{r}_1(t)$, as a function of the distance $r_{12}(0)$ between them at the initial time moment. In the absence of correlations between the motions of particles 1 and 2, the function $\Gamma_{12}(t|r_{12}(0))$ grows linearly in time, irrespective of the initial distance $r_{12}(0)$, i.e. $\Gamma_{12}(t|r_{12}(0)) \Rightarrow 12D_s t$. Actually, this correlation is substantial, and it has to manifest itself both in the dependence of $\Gamma_{12}(t|r_{12}(0))$ on $r_{12}(0)$ (Fig. 9) and in the existence of a correlation between the directions of molecular motions. This correlation is described by the correlation function

$$C_{12}(t|r_{12}(0)) = \langle \Delta\mathbf{r}_1(t)\Delta\mathbf{r}_2(t)\rangle / \langle (\Delta\mathbf{r}_1(t))^2 \rangle,$$

which is a cosine of the angle between the displacement vectors of the molecules.

Let us dwell in brief on the behavior of the correlation functions $\Gamma_{12}(t|r_{12}(0))$ and $C_{12}(t|r_{12}(0))$, which were calculated in work [35] and are plotted in Fig. 9. The rectilinear character of the time dependence of the function $\Gamma_{12}(t|r_{12}(0))$ really indicates the asymptotic behavior, when $\Gamma_{12}(t|r_{12}(0)) \Rightarrow 12D_s t$. This conclusion is confirmed by the result of direct calculations of the molecular self-diffusion coefficient,

$$D_s = \frac{\Delta\Gamma_{12}(t|r_{12}(0))}{12\Delta t} \approx 1.9 \ \text{cm}^2/\text{s}.$$

With a satisfactory error, this value is identical to the experimental value obtained at room temperature. Actually, this means that, in order to observe the dependence of $\Gamma_{12}(t|r_{12}(0))$ on $r_{12}(0)$, one has to use a much smaller time scale in measurements, as was done in works [31, 32], or to search for this correlation dependence within the time interval $0 < t < 200$ ps.

In this respect, the information content of Fig. 9, *b* is much larger, because the corresponding time scale is by an order of magnitude smaller than that used in Fig. 9, *a*. In the former, the dependence of $\Gamma_{12}(t|r_{12}(0))$ on $r_{12}(0)$ is evident. From Fig. 9, *b*, it follows that the correlation function $C_{12}(t|r_{12}(0))$ decreases rather quickly as $r_{12}(0)$ grows, so that we may define the radius of a Lagrange particle as the distance $r_{12}(0)$, where $C_{12}(t \to 0|r_{12}(0)) \approx 1/e$. In particular, the so determined radius of the Lagrange particle amounts to about 5 Å, which is close to the Lagrange particle radius $r_* = 2\sqrt{\nu\tau_M}$ [4, 27].
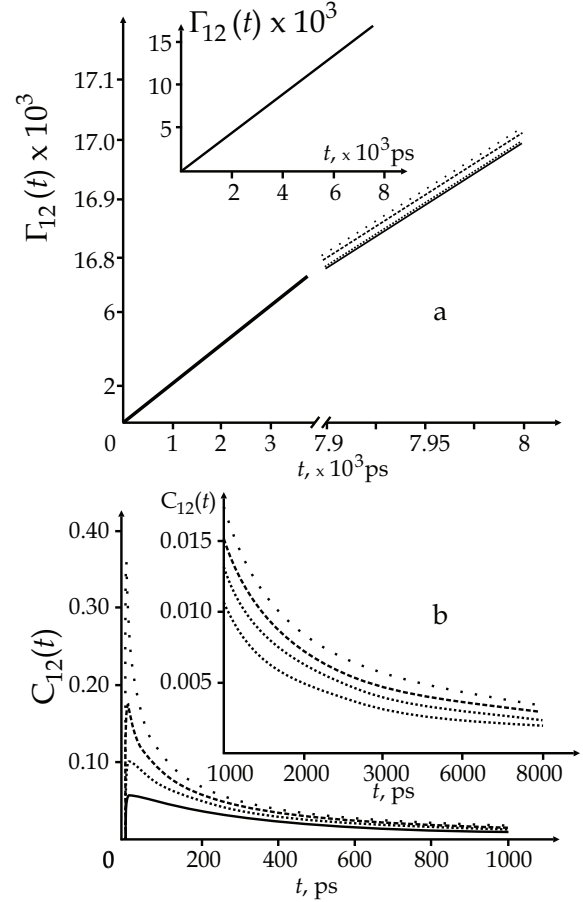

Fig. 9. Time dependences $\Gamma_{12}(t|r_{12}(0))$ and $C_{12}(t|r_{12}(0))$ for various initial distances $r_{12}(0)$ (from top to bottom): $r_{12}(0) = 2-4$, $6-8$, $10-12$, and $15-20$ Å (*a*); $r_{12}(0) = 2-3$, $4-5$, $6-7$, and $9-10$ Å (*b*)

Note that the displacements of two molecules remain correlated during several thousands of picoseconds. This fact testifies that every time interval is associated with vortices of the corresponding radius. For instance, in a vicinity of 5000 ps, correlations are connected with vortices 140 AA in diameter.

fer in liquids. Actually, it was Prof. Leonid Bulavin who stimulated a new wave of development in the Lagrange theory of thermal hydrodynamic fluctuations at the beginning of the 1990s. All our works were reported at the seminars and conferences chaired by Leonid Anatoliyovych, and they were always supported by him. Many works were performed by his initiative and/or in cooperation with him. A certain summary of the results of our cooperation was made in a review published in the Journal of Molecular Liquids in 2008 [27].

1. V.S. Oskotskii, Fiz. Tverd. Tela **5**, 1082 (1963).
2. I.Z. Fisher, Zh. Eksp. Teor. Fiz. **61**, 1647 (1971).
3. K.S. Singwi and A. Sjölander, Phys. Rev. **119**, 863 (1960).
4. T.V. Lokotosh, N.P. Malomuzh, and K.N. Pankratov, J. Chem. Eng. Data **55**, 2021 (2010).
5. J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955).
6. E.N. da C. Andrade, Proc. Phys. Soc. London **52**, 748 (1940).
7. H. Eyring, J. Chem. Phys. **4**, 283 (1936).
8. R.H. Ewell and H. Eyring, J. Chem. Phys. **5**, 726 (1937).
9. R.A. Swalin, Acta Metall. **7**, 736 (1959).
10. R.A. Swalin, Acta Metall. **9**, 379 (1961).
11. R.A. Swalin, Z. Naturforsh. **23a**, 805 (1968).
12. A.L. Zvyagintsev, Ph.D. thesis (Kyiv State University, Kyiv, 1971) (in Russian).
13. D.K. Belashchenko, *Transfer Phenomena in Liquid Metals and Semiconductors* (Atomizdat, Moscow, 1970) (in Russian).
14. L.A. Bulavin, D.A. Gavryushenko, and V.M. Sysoev, *Molecular Physics* (Znannya, Kyiv, 2006) (in Ukrainian).
15. L.A. Bulavin, *Neutron Diagnostics of Liquid Matter State* (Institute for Safety Problems of Nuclear Power Plants, Chornobyl, 2012) (in Ukrainian).
16. C.H. Ma and R.A. Swalin, J. Chem. Phys. **39**, 3014 (1962).
17. N. Nachtrieb, Adv. Phys. **16**, 62 (1967).
18. A.R. Dexter and A.J. Matheson, J. Chem. Phys. **54**, 203 (1971).
19. L.A. Bulavin, P.G. Ivanitskii, V.T. Krotenko, and V.N. Lyaskovskaya, Zh. Fiz. Khim. **61**, 3270 (1987).
20. L.A. Bulavin, A.A. Vasilkevich, A.K. Dorosh, P.G. Ivanitskii, V.T. Krotenko, and V.I. Slisenko, Ukr. Fiz. Zh. **31**, 1703 (1986).
21. S.A. Mikhailenko and V.V. Yakuba, Ukr. Fiz. Zh. **26**, 784 (1981).
22. S.A. Mikhailenko and V.V. Yakuba, Ukr. Fiz. Zh. **27**, 712 (1982).
23. T.V. Lokotosh and N.P. Malomuzh, Physica A **286**, 474 (2000).
24. T.V. Lokotosh and N.P. Malomuzh, J. Mol. Liq. **93**, 95 (2001).
25. T.V. Lokotosh, N.P. Malomuzh, and K.S. Shakun, J. Mol. Liq. **96-97**, 245, (2002).
26. T.V. Lokotosh, N.P. Malomuzh, and K.S. Shakun, J. Chem. Phys. **118**, 10382 (2003).
27. L.A. Bulavin, T.V. Lokotosh, and N.P. Malomuzh, J. Mol. Liq. **137**, 1 (2008).
28. L.A. Bulavin, A.I. Fisenko, and N.P. Malomuzh, Chem. Phys. Let. **453**, 183 (2008).
29. Yu.B. Mel'nichenko and L.A. Bulavin, Polymer **32**, 3295 (1991).
30. Y.B. Mel'nichenko, G.D. Wignalla, D.R. Cole, H. Frielinghaus, and L.A. Bulavin, J. Mol. Liq. **120**, 7 (2005).
31. G.G. Malenkov, Yu.I. Naberukhin, and V.P. Voloshin, Zh. Ross. Khim. Obshch. **53**, 25 (2009).
32. G.G. Malenkov, Yu I. Naberukhin, and V.P. Voloshin, Struct. Chem. **22**, 459 (2011).
33. Yu.I. Naberukhin and V.P. Voloshin, Zh. Strukt. Khim. **48**, 1066 (2007).
34. G.G. Malenkov, Yu.I. Naberukhin, and V.P.Voloshin, Zh. Fiz. Khim. **86**, 1485 (2012).
35. V.P. Voloshin, G.G. Malenkov, and Yu.I. Naberukhin, Zh. Strukt. Khim. **54**, S233 (2013).
36. P. Resibois and M. De Leener, *Classical Kinetic Theory of Fluids* (Wiley, New York, 1977).
37. R. Hartkamp, P.J. Daivis, and B.D. Todd, Phys. Rev. E **87**, 032155 (2013).
38. P.S. van der Gulik, Physica A **256**, 39 (1998).
39. P.M. Morse and H. Feshbach, *Methods of Theoretical Physics, Part I* (McGraw-Hill, New York, 1953).
40. D. van der Spoel, E. Lindahl, B. Hess, G. Groenhof, A.E. Mark, and H.J.C. Berendsen, J. Comput. Chem. **26**, 1701 (2005).
41. C. Oostenbrink, A. Villa, A.E. Mark, and W.F. van Gunsteren, J. Comput. Chem. **25**, 1656 (2004).
42. S. Nose, Mol. Phys. **52**, 255 (1984).
43. W.G. Hoover, Phys. Rev. A **31**, 1695 (1985).
44. J. Naghizadeh and S.A. Rice, J. Chem. Phys. **36**, 2710 (1962).
45. R. Laghaei, A.E. Nasrabad, and Byung Chan Eu, J. Phys. Chem. B **109**, 5873 2005.
46. A.Yu. Kuksin, G.E. Norman, and V.V. Stegailov, High Temp. **45**, 37 (2007).
47. L.A. Bulavin, N.P. Malomuzh, and K.N. Pankratov, Zh. Strukt. Khim. **47**, 52 (2006).
48. L.A. Bulavin, N.P. Malomuzh, and K.N. Pankratov, Zh. Strukt. Khim. **47**, S54 (2006).
49. N.P. Malomuzh, V.N. Makhlaichuk, P.V. Makhlaichuk, and K.N. Pankratov, Zh. Strukt. Khim. **54**, S210 (2013).
50. P. Blanckenhagen, Ber. Bunsenges. Phys. Chem. **76**, 891 (1972).
51. S.M. Iskenderov and A.G. Novikov, Preprint PEI-965 (Phys.-Energ. Inst., Obninsk, 1979) (in Russian).
52. J. Teixeira, M.-C. Bellisent-Funel, S.-H. Chen, and J. Dianoux, Phys. Rev. A **31**, 1913 (1985).
53. L.A. Bulavin, G.M. Verbinska, L.O. Komarova, and V.T. Krotenko, Ukr. Fiz. Zh. **50**, 938 (2005).
54. G. Pruppacher, J. Chem. Phys. **56**, 101 (1972).
55. U. Kaatze, J. Sol. Chem. **26**, 1049 (1997).

56. T.V. Lokotosh, S. Magazu, G. Maisano, and N.P. Malomuzh, Phys. Rev. E **62**, 3572 (2000).

57. A. Rahman, Phys. Rev. A **136**, 405 (1964).

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НОВІ РЕЗУЛЬТАТИ В ТЕОРІЇ
КОЛЕКТИВНОЇ САМОДИФУЗІЇ В РІДИНАХ

Р е з ю м е

В роботі викладені нові результати досліджень колективної природи явищ переносу у рідинах. Увага приділяється послідовному аналізу нетривіальної поведінки часової залежності середньоквадратичного зміщення молекули (СЗМ). Показано, що урахування внеску, пов'язаного з колективною складовою руху молекули, приводить до більш адекватного опису часової залежності СЗМ на малих проміжках часу. Викладено новий метод визначення максвелівського часу релаксації, що є одним з найважливіших динамічних параметрів молекулярних систем. Запропоновано механізми одночастинкової дифузії у воді та аргоні. Обговорюється сумісність отриманих результатів з результатами молекулярно-динамічних досліджень Г.Г. Маленкова, Ю.І. Наберухіна та В.П. Волошина, присвячених визначенню розмірів лагранжевих частинок у комп'ютерних експериментах. На початку роботи дано короткий історичний огляд проблеми самодифузії у рідинах.