

COLLECTIVE EFFECTS IN THE SELF-DIFFUSION PROCESS IN LIQUIDS

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The collective contributions to the self-diffusion process in liquids are estimated with the help of the Lagrange theory of thermal hydrodynamic fluctuations. It is shown that the relative value of the collective part of the self-diffusion coefficient changes approximately from 20% for simple liquids up to 50% for strongly associated ones. The low-frequency behavior of the spectral densities for the velocity autocorrelation function in liquid argon and water is successfully reproduced.

data on the self-diffusion in large temperature intervals.

The model of continuous self-diffusion, developed by Ma and Swalin in [12], was the reaction on the difficulties of the activation theories. In it, the local structure in liquids is completely ignored. Unfortunately, this model is weakly elaborated to get the reliable quantitative information.

Some features of the self-diffusion process in liquid can be understood due to the representations created to describe the thermal drift of Brownian particles [13–15]. This possibility seems to be quite evident for enough large molecules. But even for small molecules, these representations can be used to determine the effective size of a particle and its changes with temperature.

One of the main peculiarities of the thermal motion in liquids is the combination of the collective drift and the motion of a molecule relative to its nearest surrounding. The first attempt to take into account this fact in connection with neutron scattering problems was undertaken in [16]. In the approaches noted above, this circumstance was, as a rule, ignored. The methods based on kinetic equations allows us to estimate only the contributions to the self-diffusion coefficient, caused by the relative motion of molecules. Unlike, modeling the molecular motion as a Brownian drift, we obtain the approximate estimate for the collective part of the self-diffusion coefficient for a molecule. It is evident since the motion of a Brownian particle is caused by hydrodynamic flows collective by their nature. Unfortunately, these estimates for liquid with small molecules appear to be too overrated.

Introduction

The self-diffusion problem in liquids has a long history. Many rigorous results (see [1–3]) were obtained, and numerous heuristic propositions were made [4, 5]. However, the complete qualitative understanding and quantitative description of the self-diffusion process in liquids were not achieved. It is explained by the standard cause for liquids: the absence of the quite satisfactory ground state and the suitable small parameter for perturbation theory. Considering this problem, we would like to note the following.

The most successful solution of the self-diffusion problem takes place for rare gases. It is based on the rigorous kinetic equations [6–9], whose solution can be got with the help of perturbation theory with respect to dimensionless density η playing the role of small parameter. The attempts to extend the applicability region of these results demand the special assumptions [1, 2, 5]. In particular, the Rice and Alnatt kinetic equation [10] is the very known example of this.

From another point of view, the self-diffusion problem is studied in the so-called activation theories [4, 11]. In them, the motivations are based on the main assumption about the local crystal-like structure of liquids. However, the applications of similar representations are connected with numerous contradictions, which testifies about overestimating the crystal-like ordering in liquids. This fact becomes especially evident at the processing of the experimental

An approach allowing to estimate the collective part of the self-diffusion coefficient in liquids was proposed by I. Fisher in [17]. The central idea of [17] is the establishment of a clear interrelation between the collective drift of a molecule and the thermal motion of the Lagrange particle containing it. Supposing that the collective motion of a molecule is the slowest one,

I. Fisher gave one of the first original explanations for the long-time tails of the velocity autocorrelation function [18, 19]. Unfortunately, the Lagrange theory of thermal hydrodynamic fluctuations developed in [17] and in [20] had essential drawbacks.

A new variant of the Lagrange theory of thermal hydrodynamic fluctuations, surmounting all the difficulties of [17, 20], was developed in [21–24].

In the present work, we get the estimates for the collective parts of the self-diffusion coefficients for several liquids with very different intermolecular interactions. To confirm the correctness of these estimates, we apply our approach to reproduce the low-frequency behavior of the spectral function for the velocity autocorrelation function in liquid argon and water, for which numerical computer simulation data exist.

1. Collective Contribution to the Self-diffusion Coefficient

In accordance with [1, 2], the self-diffusion coefficient D of a molecule is connected with the velocity autocorrelation function $\varphi_{\vec{v}}(t) = \langle \vec{v}(t)\vec{v}(0) \rangle$ of a molecule by the formula

$$D = \frac{1}{3} \int_0^{\infty} \varphi_{\vec{v}}(t) dt. \quad (1)$$

In general case, the velocity \vec{v} of a molecule can be considered as a sum $\vec{v} = \vec{v}_c(t) + \vec{v}_1(t)$, where $\vec{v}_c(t)$ is the velocity of a liquid (Lagrange) particle, including a given molecule, and $\vec{v}_1(t)$ is the velocity of relative motion. Since these types of molecular motion are independent, we can write

$$D = D_c + D_1, \quad (2)$$

where

$$D_c = \frac{1}{3} \int_0^{\infty} \varphi_c(t) dt, \quad \varphi_c(t) = \langle \vec{v}_c(t)\vec{v}_c(0) \rangle \quad (3)$$

takes meaning of the collective contribution to the self-diffusion coefficient of a molecule. To exclude the arbitrariness in the choice of the Lagrange particle size r_L , the following procedure is proposed:

1) among the roots of the equation

$$\varphi_m(t) = 0, \quad (4)$$

where $\varphi_m(t)$ is the velocity autocorrelation function for a molecule, we chose the least one t_h from the

hydrodynamic interval of times ($t_h \geq r_0/v_T$, r_0 and v_T are the average values of the interparticle spacing and thermal velocity of a molecule, respectively);

2) from the roots of the equation

$$\varphi_c(t) = 0, \quad (5)$$

where $\varphi_c(t)$ is determined with the help of the Lagrange theory of thermal hydrodynamic fluctuations [21–24], we take that one t_L , which corresponds to t_h ;

3) we determine the suitable radius r_* of a Lagrange particle from the equation

$$t_L(r_*) = t_h. \quad (6)$$

According to [25] for argon,

$$t_h = 1.6 \cdot 10^{-12} \text{ s}$$

at $T = 100 \text{ K}$.

In [23], it had been shown that, for incompressible liquids with relaxing shear viscosity

$$\eta(\omega) = \frac{\eta(0)}{1 + i\omega\tau_M},$$

the autocorrelation function $\varphi_c^{(\text{inc})}(t)$ of a Lagrange particle with good accuracy is approximated by the expression:

$$\varphi_c^{(\text{inc})}(t) = \frac{12 k_B T}{\pi m_L} F(x),$$

$$F(x) = e^{-x} \int_0^{\infty} \frac{du}{u^2} \left(\cos u - \frac{\sin u}{u} \right)^2 \left[\text{ch}x\sqrt{p} + \frac{\text{sh}x\sqrt{p}}{\sqrt{p}} \right]. \quad (7)$$

Here, $x = t/2\tau_M$, $p = 1 - \kappa^2 u^2$, where $\kappa = 2\sqrt{\nu\tau_M}/r_L$ is the dimensionless inverse radius of a Lagrange particle, $m_L = \frac{4\pi}{3} r_L^3 \rho$ is its mass. For Ar at $r_L = 5 \text{ \AA}$ and temperatures $T_1 = 88 \text{ K}$ and $T_2 = 133.5 \text{ K}$, the behavior of $\tilde{\varphi}_c(x) = \varphi_c^{(\text{inc})}(x)/\frac{2k_B T}{m_L}$ is presented in Fig. 1.

As seen, the roots t_L of Eq. (5), corresponding to t_h , are close at different κ to $1.5 \cdot 10^{-12} \text{ s}$. At $T = 100 \text{ K}$, Eq. (6) is satisfied at $r_* = 3.3 \cdot 10^{-8} \text{ cm}$. This size is close to the radius of the first coordination sphere (3.39 \AA) and has the same order of magnitude as the minimal permissible hydrodynamic size $\sqrt{\nu\tau_M}$. We note that the heat and sound modes do not practically influence the position of t_L , which follows immediately from [23].

It is essential that the ratio $\sqrt{\nu\tau_M}/r_*$ is less than unity for simple liquids and more than unity for water and other strongly associated liquids.

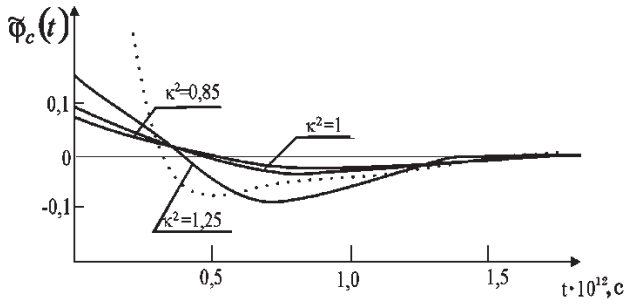


Fig. 1. Time dependence of the normalized velocity autocorrelation function $\varphi_c(x)$ for Ar at different temperatures. The dotted curve corresponds to $T = 88$ K and the smooth curve — to $T = 133.5$ K. The values of the radius for the first coordination sphere and G, ρ, ν are taken from [1, 26, 27], respectively

The typical life time t_l of such a liquid particle can be estimated according to

$$t_l \sim \frac{r_*^2}{6D} \simeq 10^{-11} \text{ s}, \quad (8)$$

that corresponds to $r_* \sim (3 - 5) \cdot 10^{-8}$ cm and $D \sim 5 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}}$ [1]. Definition (3) of the self-diffusion coefficient will be correct if

$$\int_0^\infty \varphi_c(t) dt \simeq \int_0^{t_l} \varphi_c(t) dt. \quad (9)$$

The detailed analysis of $\varphi_c(t)$ performed in [23] shows that condition (9) is reliably satisfied.

In [21] and [17, 20], it was shown that the contribution of the compressibility effects is negligibly small and can be ignored. In accordance with (3) and (10), the collective contribution into the self-diffusion coefficient takes the value

$$D_c = D_0 [f_s(\kappa) + f_r(\kappa)], \quad (10)$$

where

$$D_0 = \frac{k_B T}{16\pi\eta\sqrt{\nu\tau_M}}, \quad (11)$$

and $f_s(\kappa)$ and $f_r(\kappa)$ are the functions described in [23].

2. Spectral Function of the Velocity Autocorrelation Function

Let us discuss peculiarities of the spectral function

$$D_c(\omega) = \frac{1}{3} \int_0^\infty \varphi_c^{(\text{inc})}(t) e^{i\omega t} dt. \quad (12)$$

For arbitrary $z = 2\tau_M\omega$,

$$D_c(z) = \frac{1}{3} \int_0^\infty \frac{du}{u^2} \left(\cos u - \frac{\sin u}{u} \right)^2 \frac{1}{\sqrt{p}} \times \left[\frac{1 + \sqrt{p}}{1 - \sqrt{p} - iz} - \frac{1 - \sqrt{p}}{1 + \sqrt{p} - iz} \right]. \quad (13)$$

To establish the asymptotics of $D_c(z)$ at $z \rightarrow \infty$, it is more expedient to pass to the representation

$$\varphi_c^{(\text{inc})}(t) = \varphi_s(t) + \varphi_r(t), \quad (14)$$

in which $\varphi_s(t)$ and $\varphi_r(t)$ describe the contributions of the elastic and more slow transversal diffusion modes. The analysis performed in [23] shows that $\varphi_c^{(\text{inc})}(t)$ is characterized by the following details: 1) in the initial stage, it decays exponentially: $\sim \exp(-t/2\tau_M)$; 2) for long times, it decays proportionally to $1/t^{3/2}$; 3) at intermediate times ($t \sim 2\tau_M$), it reveals a smooth nonmonotonic polynomial behavior. The high frequency asymptotics of $D_c(z)$ should be determined by the most rapidly changing part of $\varphi_c^{(\text{inc})}(t)$, i.e. by the initial exponential one:

$$D_c(z) = -\frac{2\kappa^3 D_0}{iz} \left\{ 1 + \frac{1}{iz} + \dots \right\}. \quad (15)$$

In the opposite case where $z \rightarrow 0$, the asymptotics of $D(z)$ is determined by the behavior of $\varphi_c(t)$ for long times. The approximation

$$\varphi_a(t) \simeq \frac{k_B T}{8\pi\rho(\nu\tau_M)^{3/2}} \frac{e^{-x}}{x} (I_1(x) + I_2(x)), \quad (16)$$

where $I_n, n = 1, 2$, are the Bessel functions of imaginary argument [28], describes correctly $\varphi_c^{(\text{inc})}(t)$ at $t \geq \frac{2r_*}{c_t}$, $c_t = \sqrt{\frac{\nu}{\tau_M}}$, and remains finite at all times. Due to that, we obtain

$$D_c(z) \simeq D_c - 2D_0 + \frac{4}{3}D_0 \left(\frac{3}{2} - 3iz + 2(1-i) \times \times z^{1/2} - (1+i)z^{3/2} \right). \quad (17)$$

Note that the fraction power terms in $D_c(z)$ at $z \rightarrow 0$ reflect the long-time tails for $\varphi_c^{(\text{inc})}(t)$.

3. Numerical Estimates

To obtain the numerical estimates for the collective part D_c of the self-diffusion coefficient and to try to reproduce the low-frequency behavior of the spectral function $D_c(\omega)$, we approximate the relaxation time τ_M by using the Maxwell relation,

$$\tau_M = \frac{\eta}{G}, \quad (18)$$

between the shear viscosity and the shear elastic modulus G . In particular, such an approximation was also used in [26].

The temperature dependences of the collective contributions D_c into the self-diffusion coefficients of liquid Ar, Hg, and H₂O are presented in Fig. 2.

We see that the relative value of D_c essentially depends on the deep of the intermolecular potential: increasing from approximately 20% for argon with relatively weak interaction between molecules up to 50% for water, in which the strong H-bonds form. In other words, the magnitudes and the temperature dependences of the ratio $\frac{D_c}{D_e}$ for water and liquid Ar, Hg are dependent on the relative values of κ : $\kappa < 1$ for Ar, Hg and $\kappa > 1$ for H₂O. The value $r_m = 4 \text{ \AA}$ for water needs the additional explanations, since water is strongly clusterized [32,33]. While analyzing this problem in [34], it was shown that 1) the fraction volume of the crystal-like clusters in normal states of water does not exceed 0.1; 2) the typical size of that clusters near the melting point has the order of magnitude of 10 \AA and quickly diminishes when temperature grows. These facts allow us to identify the sizes of a Lagrange particle and the first coordination shell, similarly to that for simple liquids.

To demonstrate the adequacy of the developed representations to the picture of thermal motion in liquids, we consider the possibility to reproduce the real part of the spectral function

$$D^{(r)}(\omega) = \frac{1}{3} \int_0^\infty \varphi_{\vec{v}}(t) \cos \omega t dt \quad (19)$$

for the velocity autocorrelation function of a molecule. This important characteristics of thermal motion was investigated in the computer experiments for argon in [25] and for water in [35]. Here, unlike the self-diffusion problem, the account of compressibility effects is very important. As was shown in [21], from two additional contributions generated by the heat and sound modes, only the last is essential. Therefore, we suppose that

$$\varphi_c(t) \simeq \varphi_c^{(\text{inc})}(t) + \varphi_c^{(s)}(t), \quad (20)$$

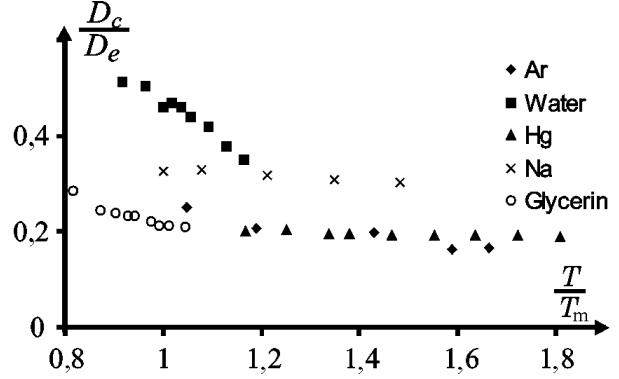


Fig. 2. The temperature dependences of the ratio $\frac{D_c}{D_e}$ for liquid Ar, Hg, and H₂O. The experiment values of the self-diffusion coefficient D_e for them are taken from [29,31] respectively. The values of ν for Ag, H₂O and Hg — in [27,31]. The values of G for Ar, Hg and H₂O are given in [26,30,31], respectively

where, in accordance with [23], the sound contribution $\varphi_c^{(s)}(t)$ is

$$\varphi_c^{(s)}(t) = \frac{k_B T}{m_L} \tilde{\varphi}_c^{(s)}(x),$$

$$\tilde{\varphi}_c^{(s)}(x) = \frac{3}{\pi} \int_0^\infty \frac{du}{u^2} \left(\cos u - \frac{\sin u}{u} \right)^2 \tilde{\psi}_c^{(s)}(u, x), \quad (21)$$

where $\tilde{\psi}_c^{(s)}(u, t) = \exp[-\frac{\sigma \kappa^2 u^2}{2\nu} \theta(u)x] \cos \kappa u x$, $\theta(u) = \frac{u^2}{\theta_0 + u^2}$ is the step function with $\theta_0 \simeq 10$, σ is the damping coefficient for sound waves [2].

Formulas (7), (12), (20), and (10) allow us to reproduce numerically the behavior of $D_c^{(r)} = \text{Re} D_c(\omega)$. The comparison of $D^{(r)}(\omega)$ and $D_c^{(r)}(\omega)$ for argon and water is given in Fig.3.

As seen, at the values of the hydrodynamic parameters and r_m used earlier for the description of D_c , the low-frequency behavior of $D^{(r)}(\omega)$ is reproduced with high accuracy. This result cannot be occasional and testifies to the correctness of our conclusions.

The considerable divergence of our and computer simulation data at $z > 1$ testifies to the important role of the relative motions of a molecule. The lasts are more rapid in comparison with the collective drift and should manifest themselves at higher frequencies.

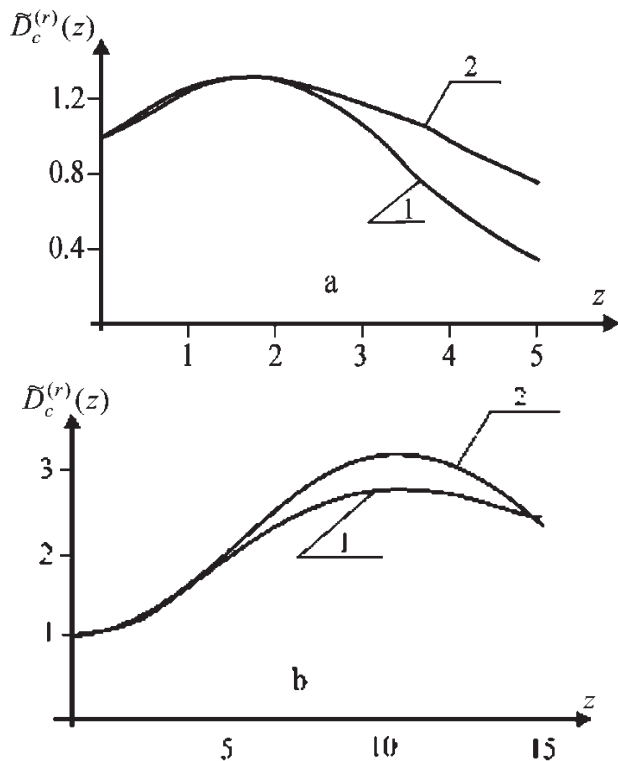


Fig. 3. The normalized spectral densities $\tilde{D}_c^{(r)}(z) = \frac{D_c^{(r)}(z)}{D_c^{(r)}(0)}$ for argon (a) and water (b) as the functions of the dimensionless frequency z . Curves (1) are calculated according to (19), (20), (7) and (21). The values of parameters are the same as in Fig. 2. The curves (2) for $\frac{D_c^{(r)}(z)}{D_c^{(r)}(0)}$ are borrowed from [25] and [35], respectively

Conclusion

To understand better the sense of the results obtained for the self-diffusion coefficient, let us consider the evident form of D_c for $\kappa \ll (<)1$. This situation takes place for high enough temperatures, at which the shear viscosity and the Maxwell relaxation time are small, and also for enough large Lagrange particles. From physical point of view, we expect that formula (10) for D_c should pass to a similar one for a Brownian particle:

$$D_c = \frac{k_B T}{6\pi\eta a(T)}, \tag{22}$$

where a is its radius. In fact, approximating the function $f(\kappa) = f_s(\kappa) + f_r(\kappa)$ at $0.1 < \kappa < 1$ by its leading asymptotic term $f(\kappa) \simeq 0.9\kappa$, we find that the collective part (10) of the self-diffusion coefficient takes the form (22) with

$$a \simeq 1.5r_*. \tag{23}$$

Because the boundary conditions for Lagrange and Brownian particles are different, the proportionality coefficient in (23) is not equal to unit. The temperature dependence of D_c is proportional to $\frac{T}{\eta}$, i.e. it has the same form as that for a Brownian particle and is close to that observed in experiments [29, 31]. Due to this fact, the ratio $\frac{D_c}{D_e}$ should be practically invariable until $\kappa \ll (<)1$.

In the opposite case where $\kappa \gg 1$ and $f(\kappa) \rightarrow \frac{8}{5}\kappa^2$, the effective radius of a "liquid particle" is

$$a(T) = \frac{5}{12} \frac{r_*^2}{\sqrt{\nu\tau_M}}. \tag{24}$$

Since the value r_* depends weakly on temperature similarly to the radius of the first coordination sphere, $a(T)$ grows according to $\frac{1}{\nu}$ and the combination $\eta a(T)$ will be close to constant: $\eta a(T) \sim \sqrt{\rho}$. As a result, in the temperature interval for which $\kappa > 1$, the values D_c should change weakly and the ratio $\frac{D_c}{D_e}$ will decrease with increase in temperature.

The behavior of $\frac{D_c}{D_e}$ presented in Fig. 2 is consistent with these conclusions. It is interesting to complete our picture by the consideration of the formal limit $r_L \rightarrow r_m$ where r_m is the molecular radius. In this case, κ appears to be more than unity at almost all temperatures, so the effective radius of a "liquid particle" satisfies the inequality

$$a(T) = \frac{5}{12} \frac{r_m^2}{\sqrt{\nu\tau_M}} < (<<) r_m. \tag{25}$$

It means that all results will be incorrect in this limit.

Of course, the multiplier D_0 in (10) could be written with the help of reasons, based on the analysis of dimensional representations. However, the lasts are not applicable to determine the function $f(\kappa)$. Its apparent form is essentially dependent on the type of a hydrodynamic model used in our calculations. So, the usage of the simplest diffusive model for the transversal modes in [21] leads to $f(\kappa) \simeq 1.95$ that gives noticeably overestimated values of D_c , especially at enough high temperatures. Unlike this, in work [36] devoted to the collective self-diffusion in water, the function $f(\kappa)$ is equal to unit and the corresponding estimates for D_c were considerably underrated. This value of $f(\kappa)$ was given by the old version of the Lagrange theory of thermal hydrodynamic fluctuations (see [17]), having numerous serious shortcomings.

The successful reproduction of the spectral function $D^{(r)}(\omega)$ for low frequencies ($z < 1$) is the weighty argument in the favor of our approach and the estimates obtained. Our approach can be immediately applied

to describe the broadening of a quasielastic peak in neutron scattering [37, 38]. It leads to essentially more successful results in comparison with simple diffusion models and those with a more complex picture of thermal motion. Here, it necessary to note that the spectral function contains the fraction power contributions and therefore the inelastic peak cannot be adequately approximated by several contours of the Lorentz-like type.

The Lagrange theory of thermal hydrodynamic fluctuations allows us to study the manifestations of the collective effects in the rotational motion of molecules as well. In particular, with the help of it, one can improve the theory of dielectric relaxation in polar liquids [39]. There are also other applications of the proposed approach.

The analysis of one-particle contributions D_1 to the self-diffusion coefficient, as well as the spectral density of the velocity autocorrelation function at high frequencies, demands new ideas and will be carried out later.

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КОЛЕКТИВНІ ВНЕСКИ В ПРОЦЕС
САМОДИФУЗІЇ В РІДИНАХ

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Резюме

На основі лагранжевої теорії теплових гідродинамічних флуктуацій зроблено оцінку колективних внесків в процес само-

дифузії молекул. Показано, що відносний внесок колективної складової в коефіцієнт самодифузії змінюється приблизно від 20% для простих рідин до 50% — для сильно асоційованих. Розраховані в роботі низькочастотні складові спектральної густини автокореляційних функцій швидкості молекули в рідкому аргоні та воді добре узгоджуються з отриманими в комп'ютерних експериментах.