THE SELF-DIFFUSION COEFFICIENT OF A LAGRANGE PARTICLE IN A SPATIALLY CONFINED LIQUID

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Thermally induced hydrodynamic fluctuations in a liquid subjected to nonhomogeneous conditions (spatial confinement within a plane-parallel layer) have been studied. In particular, the self-diffusion coefficient of a liquid Lagrange particle has been analyzed. The solution of the boundary-value problem for the hydrodynamic equations, which describe the components of the velocity field and include terms responsible for an external fluctuation field, has been obtained in the form of a series of harmonic functions. The spectral density of the correlation function (CF) for velocity field fluctuations, which depends only on a single coordinate normal to the bounding surfaces, has been calculated making use of the fluctuation-dissipation theorem. The spectral density obtained served as the basis for the analysis of the relative difference between the transversal and longitudinal components of the self-diffusion coefficient of a Lagrange particle in the liquid.

Nowadays, the dynamics of nonhomogeneous hydrodynamic systems constitutes one of the most challenging objects for studying [1—9]. Among the factors which are responsible for heterogeneity, the geometric confinement of a system is the most widespread one. The difference between the dynamical properties of the spatially confined systems and those of the bulk ones grows as the characteristic dimensions of the system decrease. The relevant theoretical analysis, if any, is rough in many cases and requires further amendments [7—12].

The self-diffusion coefficient is one of the major dynamical characteristics of the system. The geometric confinement of the system results in the relaxation of long-wave collective hydrodynamic modes which govern the behavior of the bulk self-diffusion coefficient. The corresponding reduction of the self-diffusion coefficient in finite-size systems has been studied in works [7, 8], where the system heterogeneity was simulated by a plane-parallel layer of liquid with thickness d. Making use of the theory of coupled modes and basing on intuitive ideas, the relative reduction of the component of the liquid self-diffusion coefficient, which is parallel to the interfaces, has been roughly estimated. The main contribution, obtained in the approximation $d \to \infty$, behaves as $(\sigma/d) \log (\sigma/d)$, where σ is the characteristic molecular size.

In this work, we propose a consecutive theoretical calculation of the self-diffusion coefficient for a Lagrange particle suspended in a plane-parallel liquid layer. This solution is known to be the exact long-time asymptote of the molecular self-diffusion coefficient [13]. The spectral density of the CF for velocity field fluctuations, in terms of which the self-diffusion coefficient is determined, has been obtained from the Euler hydrodynamic equations supplemented with the corresponding boundary conditions for the velocity field components, and using the fluctuation-dissipation theorem. The transition from the Euler CF to the Lagrange one has been carried out on the basis of the approach proposed by M.P. Malomuzh [14, 15]. The result has been expressed as the relative difference between the self-diffusion coefficient components parallel and normal to the bounding surfaces. The form of the components, as well as their relative contributions within the liquid layer and near the bounding surfaces, has been analyzed.

Spectral Density of the CF for the Thermally Induced Fluctuations of the Velocity Field

Consider a liquid layer between two parallel surfaces separated by distance d. The z-axis of the rectangular Cartesian coordinate system is directed perpendicularly to the bounding surfaces, and the z-coordinate is reckoned from one of the surfaces. The x- and y-axes can be directed arbitrarily, since the liquid properties are homogeneous in these directions. If the liquid is considered incompressible, the equations of motion for the velocity fluctuation field look like

$$\frac{\partial}{\partial t}v_\alpha = -\frac{1}{\rho_0}\nabla_\alpha p + \nu \Delta v_\alpha + \sigma_\alpha, \qquad (1)$$

$$\text{div } \vec{v} = 0$$

where ρ_0 is the equilibrium density, ν the coefficient of kinematic viscosity, p the pressure, and σ the source of

spontaneous fluctuations. The velocity components are equal to zero on the bounding surfaces:

$$\vec{v}\left(t, x, y, z=0\right) = 0,$$

$$\vec{v}\left(t, x, y, z=d\right) = 0. \tag{2}$$

Consider now the Fourier transformations of Eqs. (1) and boundary conditions (2) with respect to time and the transverse component of the spatial radius-vector:

$$\Phi\left(t, \vec{r}_{\parallel}, z\right) = \int d\omega \int d\vec{k}_{\parallel} e^{-i\left(\omega t - \vec{k}_{\parallel} \vec{r}_{\parallel}\right)} \Phi_{\omega k}\left(z\right). \tag{3}$$

Only the nondivergent part of the velocity is important for the diffusion coefficient. Therefore, preserving the previous notations for the Fourier-transforms of the nondivergent parts of hydrodynamic fields and carrying out simple transformations, we obtain

$$\left(-i\omega - \nu\left(k_{\parallel}^2 - \frac{\partial^2}{\partial z^2}\right)\right) v_{\alpha} = \sigma_{\alpha}. \tag{4}$$

The solution is sought by expanding the velocity field and the source components in a series of harmonic functions. Taking Eq. (2) into account, those expansions look as

$$v_{\alpha}\left(z\right) = \sum_m A_{\alpha m} \sin \mu_m z,$$

$$\sigma_{\alpha}\left(z\right) = \sum_m A_{\alpha m}^0 \sin \mu_m z, \tag{5}$$

where the eigenvalues $\mu_m = \pi m / d$. Making use of expansions (5) and applying the fluctuation-dissipation theorem, one can easily find the spectral density components for the amplitudes of the thermally induced fluctuations of the hydrodynamic field of velocities:

$$\langle A_{\alpha m}^* A_{\alpha' m}\rangle_{\omega} = \mathrm{Re}\, \frac{\Theta \Gamma_{\alpha\alpha'} \delta_{mm'}}{\left[-i\omega + \nu\left(k_{\parallel}^2 + \mu_m^2\right)\right]}, \tag{6}$$

where

$$\Theta = \frac{k_{\mathrm{B}} T}{2\pi^2}, \tag{7}$$

and $\Gamma_{\alpha\alpha'}$ is the tensor constructed of the δ-functions and the direction cosines in the k-space, $\cos\gamma_{\alpha} = k_{\alpha}/k$, which makes allowance for the non-homogeneity of liquid properties towards the longitudinal and transverse directions for the given confining geometry. The components of the tensor $\Gamma_{\alpha\alpha'}$ are

$$\Gamma_{\alpha\alpha'} = \delta_{\alpha\alpha'} - \frac{k_{\alpha} k_{\alpha'}}{k^2}, \tag{8}$$

where

$$k_x = k_{\parallel}, \quad k_y = 0, \quad k_z = k_{\perp}, \quad k^2 = k_{\parallel}^2 + k_{\perp}^2. \tag{9}$$

The corresponding spectrum of the CF between thermal fluctuations of the Euler hydrodynamic field of velocities is

$$\left\langle v_{\alpha}^*\left(\vec{r}_{\parallel}, z, t\right) v_{\alpha'}\left(\vec{r}_{\parallel}', z', t'\right)\right\rangle_{E,\omega} =$$

$$= \frac{1}{(2\pi)^2} \int d\vec{k}_{\parallel} e^{i\vec{k}_{\parallel}\left(\vec{r}_{\parallel} - \vec{r}_{\parallel}'\right)} \times$$

$$\times \sum_m \sum_{m'} \langle A_{\alpha m}^* A_{\alpha' m'}\rangle_{\omega} \, \sin\mu_m z \sin\mu_{m'} z'. \tag{10}$$

In order to obtain the self-diffusion coefficient for a Lagrange particle, it is necessary to change over from the Euler to Lagrange CF. (The latter is of separate interest, because it is the hydrodynamic approximation for the CF between molecular variables.) To tackle the problem, we used the approach proposed in work [14]. It is based on a non-local connection between the Euler and Lagrange hydrodynamic variables; if the displacement of the Lagrange particle is neglected, as it was done in work [13], the method is reduced to the averaging of the CF between the Euler variables over the Lagrange particle's volume. As a result of the averaging procedure (6) and taking the $\delta_{mm'}$-function into account, we obtain that

$$\left\langle v_{\alpha}^*\left(\vec{r}_{\parallel}, z, t\right) v_{\alpha'}\left(\vec{r}_{\parallel}', z', t'\right)\right\rangle_{L,\omega} = \frac{R_{\mathrm{L}}^2}{V_{\mathrm{L}}^2} \sum_m \int_0^{\infty} \frac{J_1^2\left(k_{\parallel} R_{\mathrm{L}}\right)}{k_{\parallel}} \times$$

$$\times \frac{\langle A_{\alpha m}^* A_{\alpha' m'}\rangle_{\omega}}{\mu_m^2} \left(\cos\mu_m z - \cos\mu_m\left(z + R_{\mathrm{L}}\right)\right)^2 dk_{\parallel}, \tag{11}$$

where $J_1(y)$ is the Bessel function, and $R_{\mathrm{L}} = \left(\frac{3}{4\pi} V_{\mathrm{L}}\right)^{4/3}$. Therefore, on the basis of Eq. (11) and knowing the specific expression for the Euler spectral density, one can find the spectrum of the Lagrange CF between the velocity field fluctuations. The value of this spectrum at $\omega = 0$ is just the self-diffusion coefficient of the Lagrange particle in the liquid

$$D_{\mathrm{L}}\left(z\right) = \frac{1}{3}\left\langle v_{\alpha}^*\left(\vec{r}_{\parallel}, z, t\right) v_{\alpha}\left(\vec{r}_{\parallel}, 0, t'\right)\right\rangle_{L,\,\omega=0}, \tag{12}$$

which is the ultimate goal of our research.

1. Transverse and Longitudinal Components of the Lagrange Self-diffusion Coefficient

The confinement of a medium changes its dynamic properties. We are interested in the variation character of the self-diffusion coefficient of a Lagrange particle in the liquid. From the viewpoint of the selected confinement geometry, it is expedient to study the difference between the transverse and longitudinal components of the self-diffusion coefficient. In view of Eqs. (6) and (12), we take the explicit form of the Γ_{zz} component of tensor (8) into account and obtain the following expression for the transverse component:

$$D_{\mathrm{L}}^{\perp}(z) = \frac{\Theta R_{\mathrm{L}}^2}{3V_{\mathrm{L}}^2} \sum_m \int_0^\infty \left(1 - \frac{\mu_m^2}{(k_\parallel^2 + \mu_m^2)}\right) \times$$

$$\times \frac{\mu_m^{-2} J_1^2(k_\parallel R_{\mathrm{L}})}{k_\parallel (k_\parallel^2 + \mu_m^2)} \times$$

$$\times \left(\cos\mu_m\left(z - \frac{R_{\mathrm{L}}}{2}\right) - \cos\mu_m\left(z + \frac{R_{\mathrm{L}}}{2}\right)\right)^2 dk_\parallel. \quad (13)$$

The longitudinal one is determined in terms of the Γ_{xx} component of tensor (8) as follows:

$$D_{\mathrm{L}}^{\parallel}(z) = \frac{\Theta R_{\mathrm{L}}^2}{3V_{\mathrm{L}}^2} \sum_m \int_0^\infty \left(1 - \frac{k_\parallel^2}{\left(k_\parallel^2 + \mu_m^2\right)}\right) \times$$

$$\times \frac{\mu_m^{-2} J_1^2\left(k_\parallel R_L\right)}{k_\parallel \left(k_\parallel^2 + \mu_m^2\right)} \times$$

$$\times \left(\cos\mu_m\left(z - \frac{R_{\mathrm{L}}}{2}\right) - \cos\mu_m\left(z + \frac{R_{\mathrm{L}}}{2}\right)\right)^2 dk_\parallel. \quad (14)$$

The total self-diffusion coefficient of a Lagrange particle in the liquid is

$$D_{\mathrm{L}}(z) = D_{\mathrm{L}}^{\parallel}(z) + D_{\mathrm{L}}^{\perp}(z). \quad (15)$$

Therefore, while considering the relative variation of the self-diffusion coefficient in the longitudinal and transverse directions, stimulated by the finite-size effects, we obtain

$$\frac{D_{\mathrm{L}}^{\perp}(z) - D_{\mathrm{L}}^{\parallel}(z)}{D_{\mathrm{L}}(z)} = 1 - 2\frac{D_{\mathrm{L}}^{\parallel}(z)}{D_{\mathrm{L}}(z)}. \quad (16)$$

Provided that $D_{\mathrm{L}}(z)$, according to Eqs. (13) and (15), is expressed in the form

$$D_{\mathrm{L}}(z) = \frac{\Theta R_{\mathrm{L}}^2}{3V_{\mathrm{L}}^2} \sum_m \int_0^\infty \frac{J_1^2\left(k_\parallel R_{\mathrm{L}}\right)\mu_m^{-2}}{k_\parallel \left(k_\parallel^2 + \sigma\mu_m^2\right)_{\sigma=1}} \times$$

$$\times \left(\cos\mu_m\left(z - \frac{R_{\mathrm{L}}}{2}\right) - \cos\mu_m\left(z + \frac{R_{\mathrm{L}}}{2}\right)\right)^2 dk_\parallel, \quad (17)$$

its longitudinal component $D_{\mathrm{L}}^{\parallel}(z)$ is

$$D_{\mathrm{L}}^{\parallel}(z) = -\left[\frac{\partial}{\partial\sigma} D_{\mathrm{L}}(z)\right]_{\sigma=1}. \quad (18)$$

Thus, we get

$$\frac{D_{\mathrm{L}}^{\perp}(z) - D_{\mathrm{L}}^{\parallel}(z)}{D_{\mathrm{L}}(z)} = 1 + 2\left[\frac{\partial\ln D_{\mathrm{L}}(z)}{\partial\sigma}\right]_{\sigma=1}. \quad (19)$$

Calculating the integral on the right-hand side of Eq. (17), we obtain the following expression for the Lagrange self-diffusion coefficient:

$$D_{\mathrm{L}}(z) = \frac{9\Theta}{16\pi^2\nu R_{\mathrm{L}}} \sum_m \frac{I_1\left(R_{\mathrm{L}}\mu_m\sqrt{\sigma}\right) K_1\left(R_{\mathrm{L}}\mu_m\sqrt{\sigma}\right)}{\left(R_{\mathrm{L}}\mu_m\sqrt{\sigma}\right)^2} \times$$

$$\times \mu_m^{-2}\left(\cos\mu_m\left(z - \frac{R_{\mathrm{L}}}{2}\right) - \cos\mu_m\left(z + \frac{R_{\mathrm{L}}}{2}\right)\right)^2, \quad (20)$$

where $K_1(y)$ is the Macdonald function. Since $R_L \ll d$, expression (20) can be simplified:

$$D_{\mathrm{L}}(z) \sim \sum_m \frac{\left(\cos\mu_m\left(z - \frac{R_{\mathrm{L}}}{2}\right) - \cos\mu_m\left(z + \frac{R_{\mathrm{L}}}{2}\right)\right)^2}{\mu_m^2} \times$$

$$\times \left(\frac{1}{2}\ln\frac{R_{\mathrm{L}}\mu_m\sqrt{\sigma}}{2} + \left(R_{\mathrm{L}}\mu_m\sqrt{\sigma}\right)^{-2} + \frac{1}{2}\left(C_{\mathrm{L}} - \frac{1}{4}\right)\right),$$

$$\quad (21)$$

where C_L is the Euler constant. The main contributions to the relative difference between the components of the self-diffusion coefficient, in accordance with Eqs. (19) and (20), are

$$\frac{D_{\mathrm{L}}^{\perp}(z) - D_{\mathrm{L}}^{\parallel}(z)}{D_{\mathrm{L}}(z)} = 1 - 2f^{-1}(z) \times$$

$$\times \left(\frac{z}{d} - \left(\frac{z}{d}\right)^2 - \frac{5R_{\mathrm{L}}}{12d} + o\left(\frac{R_{\mathrm{L}}}{d}\right)^2\right), \quad (22)$$

where

$$f(z) = \frac{z}{d}\left(1 + o\left(\frac{R_{\mathrm{L}}}{d}\right)^2\right) - \left(\frac{z}{d}\right)^2\left(1 + o\left(\frac{R_{\mathrm{L}}}{d}\right)^2\right) +$$

$$+\frac{R_{\mathrm{L}}}{d}\left(\frac{37}{12}-\frac{1}{2}\ln\frac{8\pi d}{R_{\mathrm{L}}}\right)+o\left(\frac{R_{\mathrm{L}}}{d}\right)^2. \qquad (23)$$

is the dimensionless Lagrange self-diffusion coefficient in the same approximation.

Equations (22) and (23) demonstrate that the difference between the longitudinal and transverse components is very large with respect to the value of the total self-diffusion coefficient in the middle of the liquid layer and near its bounding surfaces.

Near the bounding surfaces (at $z = 0$ and $z = d$), this difference is determined, according to Eq. (22), by the expression

$$\frac{D_{\mathrm{L}}^{\perp}(z)-D_{\mathrm{L}}^{\parallel}(z)}{D_{\mathrm{L}}(z)}\approx 1-2\left(-\frac{5R_{\mathrm{L}}}{12d}+o\left(\frac{R_{\mathrm{L}}}{d}\right)^2\right)\times$$

$$\times\left(\frac{R_{\mathrm{L}}}{d}\left(\frac{37}{12}-\frac{1}{2}\ln\frac{8\pi d}{R_{\mathrm{L}}}\right)+o\left(\frac{R_{\mathrm{L}}}{d}\right)^2\right)^{-1}. \qquad (24)$$

Here, it is positive and amounts to almost 80% of the total self-diffusion coefficient amplitude. Therefore, the contribution of the transverse component to the Lagrange self-diffusion coefficient dominates, while only a share of 20% belongs to the longitudinal one.

At the midpoint of the liquid layer ($z = d/2$), the main contributions to the difference concerned are

$$\frac{D_{\mathrm{L}}^{\perp}(z)-D_{\mathrm{L}}^{\parallel}(z)}{D_{\mathrm{L}}(z)}\approx 1-2\left(\frac{z}{d}-\left(\frac{z}{d}\right)^2+o\left(\frac{R_{\mathrm{L}}}{d}\right)\right)\times$$

$$\times\left(\frac{z}{d}-\left(\frac{z}{d}\right)^2+o\left(\frac{R_{\mathrm{L}}}{d}\right)\right)^{-1}, \qquad (25)$$

Now, the difference becomes negative and amounts to approximately 100% of the value of the total self-diffusion coefficient. his means that the longitudinal component dominates in the middle of the liquid layer, while the transverse one can be neglected there.

The studies how the confinement effects influence the behavior of the self-diffusion coefficient have already been attempted in works [7, 8]. In these works, the relative difference between the longitudinal component of the Euler self-diffusion coefficient in the spatially confined liquid and the self-diffusion coefficient D_{bulk} in the bulk (the unconfined case) was evaluated in the framework of the theory of coupled modes and using the $d \to \infty$ approximation. In the course of calculations, the parameter of the wave number k cutoff was introduced. Its physical interpretation was intuitively identified with the inverse molecular size σ^{-1}. As a result, the main

contribution to the relative difference was written down in the form

$$\frac{D_{E}^{\parallel}(d)-D_{\mathrm{bulk}}}{D_{\mathrm{bulk}}}=-\frac{\sigma}{d}\left(A\log\left(\frac{d}{\sigma}\right)+B\right)+o\left(\frac{1}{d}\right)^2, (26)$$

where A and B are constants.

Our result is more rigorous. According to it, the relative difference between the longitudinal component and the total Lagrange self-diffusion coefficient demonstrates a logarithmic behavior in the case of a spatially confined liquid. In accordance with the relations given above,

$$\frac{D_{\mathrm{L}}^{\parallel}(z)-D_{\mathrm{L}}(z)}{D_{\mathrm{L}}(z)}=-\frac{D_{\mathrm{L}}^{\perp}(z)}{D_{\mathrm{L}}(z)}=2f^{-1}(z)\times$$

$$\times\left(\frac{R_{\mathrm{L}}}{d}\left(\frac{7}{2}-\frac{1}{2}\ln\frac{8\pi d}{R_{\mathrm{L}}}\right)+o\left(\frac{R_{\mathrm{L}}}{d}\right)^2\left(1+\frac{z}{d}-\left(\frac{z}{d}\right)^2\right)\right).$$

$$(27)$$

In fact, the role of our cutoff parameter is played by the quantity R_{L}^{-1}. Expressions (22) and (27), which are valid for small $d \sim 10R_{\mathrm{L}}$, contain the dependence on the z-coordinate (the z-axis is directed perpendicularly to the bounding surfaces) and the information concerning the competition between the longitudinal and transverse components of the Lagrange self-diffusion coefficient at an arbitrary distance from the surfaces. The longitudinal component $D_{\mathrm{L}}^{\parallel}(z)$ includes, according to Eqs. (16), (22), and (23), the main dependence of the Lagrange self-diffusion coefficient on the z-coordinate. The component $D_{\mathrm{L}}^{\perp}(z)$, according to Eq. (27), is considerably smaller and depends on z very weakly; its behavior is determined by the contribution $\sim (R_{\mathrm{L}}/d)\ln(R_{\mathrm{L}}/d)$. While moving normally to the liquid layer, the self-diffusion coefficient of the Lagrange particle in the liquid changes essentially, and, at $d \to \infty$, approaches the value of that in the unconfined liquid.

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КОЕФІЦІЄНТ САМОДИФУЗІЇ ЛАГРАНЖЕВОЇ
ЧАСТИНКИ ОБМЕЖЕНОЇ РІДИНИ

О.І. Сахненко

Р е з ю м е

На основі аналізу коефіцієнта самодифузії лагранжевої частинки рідини розглянуто теплові гідродинамічні флуктуації рідини в неоднорідних умовах, змодельованих плоскопаралельним шаром. Знайдено розв'язок крайової задачі за наявності стороннього флуктуаційного поля для гідродинамічних рівнянь компонент поля швидкості у вигляді розкладу за гармонічними функціями. Спектральну густину кореляційної функції флуктуацій поля швидкості, яка залежить лише від однієї координати, нормальної до обмежуючих поверхонь, отримано з використанням флуктуаційно-дисипативної теореми. На її основі проаналізовано відносну різницю поперечної та поздовжньої складових коефіцієнта самодифузії лагранжевої частинки рідини.