# Hydrodynamic asymptotic form of the rotational-motion correlation function of a molecule in a liquid

## I. Z. Fisher, A. V. Zatovskiǐ, and N. P. Malomuzh

*Odessa State University*
(Submitted February 3, 1973)
Zh. Eksp. Teor. Fiz. **65**, 297–306 (July 1973)

Random rotational motion of a molecule together with its environment in a thermal hydrodynamic fluctuation field is studied for a classical liquid. A long-time asymptotic behavior of the angular velocity and angular momentum correlation functions of the molecule is obtained which is the same for various liquids. The rotational-motion correlation functions and mean-square displacements of molecules in a liquid with relaxing shear stresses are obtained which are valid for all hydrodynamic times. A more exact value of the Lagrange diffusion coefficient is presented. The low-frequency asymptotic form of the Fourier transform of the rotational-motion correlation functions of a molecule is considered.

## 1. INTRODUCTION

Rotational thermal motion of molecules becomes significantly manifest in the spectra of many processes and liquids, namely, dielectric relaxation, electron and nuclear magnetic resonances, infrared absorption, Raman and Rayleigh scattering of light, and other processes. In all cases, the theory calls for knowledge of the time-dependent correlation functions of quantities that describe the rotational and turning motion of liquid particles. The simplest of them are the correlation functions of the components of the angular velocity $\omega(t)$ and the angular momentum $m(t)$ of a certain selected molecule

$$\langle\!\langle \omega_\alpha(0)\omega_\beta(t)\rangle\!\rangle = \tfrac{1}{3}\langle\!\langle\omega(0)\omega(t)\rangle\!\rangle\delta_{\alpha\beta} \equiv \tfrac{1}{3}\varphi(t)\delta_{\alpha\beta}, \quad (1)$$

$$\langle\!\langle m_\alpha(0)m_\beta(t)\rangle\!\rangle = \tfrac{1}{3}\langle\!\langle m(0)m(t)\rangle\!\rangle\delta_{\alpha\beta} \equiv \tfrac{1}{3}\varphi_1(t)\delta_{\alpha\beta}, \quad (2)$$

where the double angle brackets denote averaging over the equilibrium distribution of the molecular variables. In the case of magnetic resonance, the functions $\varphi(t)$ and $\varphi_1(t)$ suffice to describe the spin-lattice relaxation. In more complicated cases, the correlation functions of the functions of the turning angles of the molecules can be frequently expressed exactly or approximately in terms of $\varphi(t)$ or $\varphi_1(t)$[1,2]. Irrespectively, knowledge of the functions $\varphi(t)$ and $\varphi_1(t)$ is quite important for the analysis and understanding of the mechanism of turning and rotational thermal motions of molecules and liquids. Certain information concerning the exact course of these functions are known from computer experiments[3,4].

The detailed course of the functions $\varphi(t)$ and $\varphi_1(t)$ is quite complicated and differs for different liquids. Their asymptotic behavior at long times, however, as will be shown below, is universal and can be described exactly. If we are interested not only in the limiting asymptotic forms of the functions $\varphi(t)$ and $\varphi_1(t)$ as $t \to \infty$, but also in their behavior at shorter times that are nevertheless long in comparison with the characteristic proper molecular times, then the universal asymptotic form gives way to certain simple types of behavior, depending on the type of liquid, which again can be accurately described. In the present paper we study the limiting asymptotic forms of the functions $\varphi(t)$ and $\varphi_1(t)$ at very long times and their behavior at moderately long times for liquids with mechanically isotropic or weakly anisotropic molecules.

The "long" times of interest to us are those falling in the hydrodynamic time interval for a given type of liquid. Accordingly, the estimates we need can be obtained by the methods of the theory of thermal hydrodynamic fluctuations. Analogous estimates for the correlation functions of the translational motion of a molecule in a liquid were investigated in detail by one of the authors[5,6]. It was shown that for simple and nearly simple liquids, the region of applicability of such a theory extends quite far in the direction of short times, and it is always possible to enhance this property by choosing more refined hydrodynamic models.

## 2. FUNDAMENTAL EQUATIONS

Let $\tau_1$ be the longest of the characteristic times of the translational and rotational motions of the selected molecule with respect to its surrounding (without allowance for the nuclear-spin motions). For low-viscosity and nonpolar liquids, $\tau_1 \sim 10^{-12}$ sec. The molecule together with its environment as a unit execute slower motions, which can be described in hydrodynamic terms. If the molecule together with its environment is identified with the "liquid particle" of the Lagrangian formulation of the hydrodynamic equations, and if $\Phi(t)$ and $\Phi_1(t)$ are the Lagrangian correlation functions of the thermal fluctuations of the hydrodynamically-determined angular velocity $\Omega$ and density of the angular momentum $M$, then we have asymptotically for the functions of (1) and (2)

$$\varphi(t) \to \Phi(t), \quad \varphi_1(t) \to \Phi_1(t), \quad t \gg \tau_1. \quad (3)$$

Let $u(r, t)$ be the Euler field of the fluctuational hydrodynamic velocities and let $u_\perp(r, t)$ be its solenoidal part. Then $\Omega(r, t)$ equals $(1/2)\mathrm{curl}\, u_\perp(r, t)$. If $a_0 = a(0)$ and $a(t)$ are the Lagrangian coordinates of the liquid particle at two instants of time, then we get for $\Phi(t)$ from (3)

$$\Phi(t) = \tfrac{1}{4}\langle\mathrm{rot}\, u_\perp(a_0, 0)\mathrm{rot}\, u_\perp(a(t), t)\rangle = -\tfrac{1}{4}\langle u(a_0, 0)\Delta u(a(t), t)\rangle_\perp, \quad (4)$$

where $\Delta$ is the Laplace operator and the angle brackets denote averaging over the distribution of the thermal fluctuations. Let furthermore $\alpha(r, t)$ be the average density of the moment of inertia of a liquid consisting of spherically-symmetrical or nearly symmetrical molecules[7,8]. Then $M(r, t) = \alpha(r, t)\Omega(r, t)$, and in the linear theory of fluctuations we must put $\alpha = \langle\alpha(r, t)\rangle = $ const. For the function $\Phi_1(t)$ it follows from (3) that

$$\Phi_1(t) = -\tfrac{1}{4}\alpha^2\langle u(a_0, 0)\Delta u(a(t), t)\rangle_\perp = \alpha^2\Phi(t), \quad (5)$$

so that the functions $\varphi(t)$ and $\varphi_1(t)$ of (1) and (2) have the same asymptotic form as $t \to \infty$. If the molecules have a mechanical angular momentum of their own or are noticeably anisotropic, then the definition of the function $\Phi_1(t)$ must be replaced in accordance with the known expanded hydrodynamic models for these cases[7-10]. We are not interested in this situation in the present

paper. It can be noted, however, that the relaxation time of the angular momentum or the anisotropy in ordinary liquids is quite small. For all longer times, the definitions (4) and (5) remain in force. The presence of a proper angular momentum or of anisotropy of the molecules leads only to a redefinition of the kinetic coefficients (and of the coefficient $\alpha$ in (5))[8,10].

If we neglect the displacement of the liquid particle during the time t and replace approximately in the right-hand side of (4) the Lagrangian correlation function by the Euler function, putting $\mathbf{a}(t) \approx \mathbf{a}_0 = \mathbf{r}$, then the result

$$\Phi(t) \approx -\tfrac{1}{4}\langle \mathbf{u}(\mathbf{r}, 0)\Delta\mathbf{u}(\mathbf{r}, t)\rangle_{\perp} \qquad (6)$$

can be easily calculated with the aid of the known formulas of the theory of thermal hydrodynamic fluctuations[11,12]. Such estimates were made at $t \to \infty$ in[13,14]. It is clear from the foregoing that such an approximation cannot serve as an exact asymptotic estimate for the molecular correlation functions (1) and (2), in which the multipliers under the averaging sign pertain to different points on the trajectory of the molecule center.

For an explicit calculation of the right-hand side of (4) and (5), the latter must be expressed in terms of known Euler correlation functions. We use for this purpose the method and the approximation of[5]. We expand the function $\mathbf{u}(\mathbf{a}(t), t)$ in a Taylor series in powers of the displacement $\delta\mathbf{a}(t) = \mathbf{a}(t) - \mathbf{a}_0$, and assume that the time t is long enough that the correlations between the displacement at the instant t and the gradients of the velocity field at the initial point $\mathbf{u}(\mathbf{a}_0, t)$ can be neglected. Simultaneously, the distribution of the displacement approaches a normal distribution with increasing t. If $\Gamma(t)$ is the mean-squared particle displacement, $\Gamma(t) = \langle[\delta\mathbf{a}(t)]^2\rangle$, then, taking into account the isotropy of the liquid in the absence of fluctuations, and repeating the simple procedure of[5], we obtain

$$\Phi(t) = -\frac{1}{4}\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{1}{6}\Gamma(t)\right)^n \langle\mathbf{u}(\mathbf{r}, 0)\Delta^{n+1}\mathbf{u}(\mathbf{r}, t)\rangle_{\perp}. \qquad (7)$$

Equation (7) contains the total mean-squared displacement $\Gamma(t)$ of the liquid particle, which depends both on the solenoidal and on the potential parts of the field $\mathbf{u}(\mathbf{r}, t)$. Let

$$\Psi(t) = \langle\mathbf{u}(\mathbf{a}_0, 0)\mathbf{u}(\mathbf{a}(t), t)\rangle \qquad (8)$$

be the Lagrangian correlation function of the total velocity of the liquid particle investigated in[5]. In analogy with (7), we can obtain for it an expansion in the Euler correlation functions[5]

$$\Psi(t) = \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{1}{6}\Gamma(t)\right)^n\langle\mathbf{u}(\mathbf{r}, 0)\Delta^n\mathbf{u}(\mathbf{r}, t)\rangle. \qquad (9)$$

We separate in each Euler correlator its solenoidal and potential parts and take into account the identity $2\Psi(t) = d^2\Gamma/dt^2$. This leads to a closed equation for $\Gamma(t)$, in the form

$$\frac{d^2\Gamma(t)}{dt^2} = 2\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{1}{6}\Gamma(t)\right)^n[\langle\mathbf{u}(\mathbf{r}, 0)\Delta^n\mathbf{u}(\mathbf{r}, t)\rangle_{\perp} + \langle\mathbf{u}(\mathbf{r}, 0)\Delta^n\mathbf{u}(\mathbf{r}, t)\rangle_{\parallel}], \qquad (10)$$

with the natural initial conditions

$$\Gamma(0) = (d\Gamma/dt)_{t=0} = 0. \qquad (11)$$

If the Euler correlation functions of the fluctuation field $\mathbf{u}(\mathbf{r}, t)$ are known, Eqs. (7) and (10) constitute a closed system of equations for the functions $\Gamma(t)$ and $\Phi(t)$, from which the functions $\Phi_1(t)$ and $\Psi(t)$ can be easily reconstructed. The explicit form of these equations and the character of the solutions depend on the employed

hydrodynamic model. We shall show below that the series in (7) and (10) can be summed in several important cases.

Equations (7) and (10) correspond to the Gaussian approximation for the distribution law of the random displacements of a liquid particle, which is automatically valid at large values of t. They turn out to be exact also at very short times, as is seen directly from (4) and (8). Assuming that they are acceptably accurate also at intermediate values of t, we use them as the fundamental equations for the conversion of the Euler correlation functions into Lagrangian ones.

## 3. THE NAVIER-STOKES APPROXIMATION

To obtain the universal limiting asymptotic form, mentioned in the Introduction, for the molecular correlation functions (1) and (2) as $t \to \infty$, it suffices to use in (7) and (10) an incompressible-liquid model obeying the Navier-Stokes equation, which is valid for slow flow in any "Newtonian" liquid. In such a case we have

$$\mathbf{u}_{\parallel}(\mathbf{r}, t) = 0, \quad \Delta\mathbf{u}_{\perp}(\mathbf{r}, t) = \frac{1}{\nu}\frac{\partial}{\partial t}\mathbf{u}_{\perp}(\mathbf{r}, t), \qquad (12)$$

where $\nu = \eta/\rho$ is the kinematic viscosity coefficient, and Eqs. (7) and (10) take the form

$$\Phi(t) = -\frac{1}{4\nu}\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{1}{6\nu}\Gamma(t)\right)^n\frac{\partial^{n+1}}{\partial t^{n+1}}\psi(t) \qquad (13)$$

$$\frac{d^2\Gamma(t)}{dt^2} = 2\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{1}{6\nu}\Gamma(t)\right)^n\frac{\partial^n}{\partial t^n}\psi(t), \qquad (14)$$

where $\psi(t)$ is the correlator of the solenoidal part of the field $\mathbf{u}(\mathbf{r}, t)$ in the Navier-Stokes approximation with equal spatial arguments. This correlator is equal to[5]

$$\psi(t) = 2kT/\rho(4\pi\nu t)^{3/2} \qquad (15)$$

($\rho$ is the density and kT is the product of the Boltzmann constant by the absolute temperature). The series (13) and (14) can be easily summed, and we obtain

$$\Phi(t) = -\frac{1}{4\nu}\psi'\left(t + \frac{1}{6\nu}\Gamma(t)\right), \quad \Gamma''(t) = 2\psi\left(t + \frac{1}{6\nu}\Gamma(t)\right), \qquad (16)$$

where the primes denote differentiation with respect to the argument.

We put

$$t + \frac{1}{6\nu}\Gamma(t) = z(t), \quad \frac{kT}{3\eta(\pi\nu)^{3/2}} = b. \qquad (17)$$

Equations (16) and (9) are rewritten as follows:

$$z''(t) = \frac{b}{4}z^{-5/2}(t), \quad \Phi(t) = \frac{9b}{32}z^{-5/2}(t), \quad \Psi(t) = 3\nu bz^{-3/2}(t). \qquad (18)$$

The first of these equations can be integrated once directly, and we have

$$z'^2(t) = (1 + D/\nu)^2 - b/\sqrt{z(t)}, \qquad (19)$$

where $(1 + D/\nu)^2$ is the integration constant. One more integration leads to

$$t = (z + \tfrac{3}{2}\sqrt{z_0 z})(1 - \sqrt{z_0/z})^{1/2} + \tfrac{3}{8}z_0\ln(z/z_0) + \tfrac{3}{2}z_0\ln[1 + (1 - \sqrt{z_0/z})^{1/2}] + c, \qquad (20)$$

where c is a new constant and

$$b = (1 + D/\nu)^2\sqrt{z_0}. \qquad (21)$$

The Navier-Stokes approximation is not satisfactory at very short times, so that the correlation function (14) does not exist at $t \to 0$. Consequently no choice of the constants c and D can satisfy the initial condition $z(0) = 0$ (see (11)). The second initial condition in (11), in conjunction with (17), yields $z'(0) = 1$, and from (17),

(19), and (20) we obtain the values of c, z(0), and $\Gamma(0)$. It follows then from (18) that the Lagrangian correlation functions $\Phi(t)$ and $\Psi(t)$, in contrast to the Euler function $\psi(t)$, remain finite as $t \to 0$.

In the opposite case of large values of t we obtain from (20) an expansion

$$z(t) = (1 + D / v)t - [(1 + D / v)z_0 t]^{\frac{1}{2}} - \frac{3}{4}z_0 \ln (4t / z_0)$$
$$+ [\frac{11}{8}z_0 - \frac{3}{4}z_0 \ln (1 + D / v) - (1 + D / v)c] + \ldots, \quad (22)$$

the first three terms of which do not depend on the constant c and on the incorrect initial conditions at t = 0. After simple substitutions, these terms determine, with the aid of the formulas given above, the sought limiting asymptotic form of the functions $\Gamma(t)$, $\Psi(t)$, and $\Phi(t)$, and in accordance with (3) also of the functions $\varphi(t)$ and $\varphi_1(t)$. For example, for $\Gamma(t)$ and $\Phi(t)$ we obtain

$$\Gamma(t) = 6Dt - \frac{2kT}{\rho [\pi(v+D)]^{\frac{1}{2}}}\sqrt{t} - \frac{(kT)^2}{12\pi^3\rho^2 v(v+D)^4} \ln \frac{\rho^2 v^5 t}{(kT)^2} + \ldots,$$

$$\Phi(t) = \frac{3\pi\, kT}{32\rho[\pi(v+D)t]^{\frac{1}{2}}}\Big[1 + \frac{5\pi\, kT}{6\rho[\pi(v+D)]^{\frac{1}{2}}}\frac{1}{\sqrt{t}} \quad (23)$$

$$+ \frac{5(kT)^2}{72\pi^3\rho^2(v+D)^5 t}\ln\frac{\rho^2 v^5 t}{(kT)^2} + \ldots\Big]. \quad (24)$$

According to (3), as $t \to \infty$, we obtain for the molecular correlation functions $\varphi(t)$ and $\Phi_1(t)$, asymptotically, $\varphi(t) = \Phi(t)$ and $\varphi_1(t) = \alpha^2\Phi(t)$, so that expression (24) does indeed determine the universal asymptotic limiting form of these functions. The first term of (24) with an inaccurate coefficient was indicated in[13,14].

## 4. IMPROVED ESTIMATE OF THE FUNCTION $\Gamma(t)$

To obtain not only an asymptotic estimate for $\Phi(t)$, but also an expression suitable for all hydrodynamic times, it is necessary to resort to more exact hydrodynamic models and to know the function $\Gamma(t)$ for them. The latter problem was discussed in[5,6]. We present below some significant additions to the results of[5,6].

We consider first an incompressible liquid with a dynamic viscosity coefficient $\eta(\omega) = \eta_0/(1 - i\omega\tau)$, where $\tau$ is the Maxwellian relaxation time of the viscous stresses. The equation of motion for the velocity field is

$$\Delta u(r,t) = \frac{1}{v}\Big(\frac{\partial}{\partial t} + \tau\frac{\partial^2}{\partial t^2}\Big)u(r,t), \quad (25)$$

where $v = \eta_0/\rho$ and $u(r, t) \equiv u_\perp(r, t)$. The Euler correlation function for $u(r, t)$, for equal spatial arguments, was obtained for this case in[5] and is equal to

$$\psi(t) = \frac{kT}{8\pi\rho v\sqrt{\tau v}\, t}e^{-t/2\tau}\Big[I_1\Big(\frac{t}{2\tau}\Big) + I_2\Big(\frac{t}{2\tau}\Big)\Big], \quad t > 0. \quad (26)$$

Here $I_n(x)$ is the modified Bessel function and we have left out the singular term concentrated at the point t = 0, so that expression (26) has a finite limit as $t \to +0$. Substitution of (25) in (10) leads to the equation

$$\frac{d^2\Gamma(t)}{dt^2} = 2\sum_{n=0}^{\infty}\frac{1}{n!}\Big(\frac{1}{6v}\Gamma(t)\Big)^n\Big(\frac{\partial}{\partial t} + \tau\frac{\partial^2}{\partial t^2}\Big)^n\psi(t), \quad (27)$$

in which the right-hand side can be summed. It is easy to verify that the result of the summation is[6]

$$\Gamma''(t) = \frac{2}{\sqrt{\pi}}\int_{-\infty}^{\infty}\psi\Big(t + \frac{1}{6v}\Gamma(t) + s\Big[\frac{2\tau}{3v}\Gamma(t)\Big]^{\frac{1}{2}}\Big)e^{-s^2}ds, \quad (28)$$

where the function $\psi(t)$ from (26) is assumed to be continued in even fashion in to the region $t < 0$. It is necessary to add to (28) the initial conditions (11).

We introduce the dimensionless quantities

$$\frac{kT}{24\pi\rho v^2\sqrt{\tau v}} = a, \quad \frac{t}{2\tau} = x, \quad \frac{1}{2\tau}\Big(t + \frac{1}{6v}\Gamma(t)\Big) = Z(x).$$

Equation (28) can now be written in the form

$$Z''(x) = \frac{a}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\psi_0(|Z(x) + s[Z(x) - x]^{\frac{1}{2}}|)\exp\Big\{-\frac{1}{2}s^2\Big\}ds, \quad (30)$$

with initial conditions

$$Z(0) = 0. \quad Z'(0) = 1. \quad (31)$$

and with a function $\psi_0(x)$ equal to

$$\psi_0(x) = e^{-x}[I_1(x) + I_2(x)] / x. \quad (32)$$

At $x < 0$, Eq. (30) can be solved directly in the form of a series in powers of x, and after changing over to $\Gamma(t)$ we obtain

$$\Gamma(t) = \frac{3}{4}av\tau\Big\{\frac{t^2}{\tau^2} - \frac{t^3}{8\tau^3} + \frac{t^4}{64\tau^4}\Big(1 - \frac{a}{4}\Big) - \frac{t^5}{3840\tau^5}\Big(7 + \frac{3a}{4}\Big) + \ldots\Big\}. \quad (33)$$

At $x \gg 1$, we can obtain from (30) an asymptotic expansion for $Z(x)$, in which the first three terms lead exactly to expression (23) for $\Gamma(t)$. The only difference is that in (23) the diffusion coefficient D appeared as an integration constant and remained undetermined. Now the coefficient D can be determined by solving (30). An approximate estimate can be obtained immediately by neglecting in (30) the second term in the argument of the integrand. The first integral of the resultant differential equation, taking (31) into account, leads to

$$Z'^2(\infty) = 1 + 2a\int_0^{\infty}\psi_0(x)dx = 1 + 3a, \quad (34)$$

whence

$$D \equiv \frac{1}{6}\Gamma'(\infty) = v(\sqrt{1 + 3a} - 1). \quad (35)$$

At small values of $D \approx 3va/2$, which coincides with the estimate of[5]. A more accurate value of D will be given later on.

The parameter a, defined in (29), is small. For low-viscosity liquids at ordinary temperatures we have $a \sim 10^{-13}$. This can be used to obtain for (30) and approximate solution that is uniformly suitable for all values of x. We put

$$Z(x) = x + aZ_1(x) + a^2Z_2(x) + \ldots, \quad (36)$$

Substitute this in (30) and (31), and after expanding the right-hand side of (30) we equate terms with light powers of a. As a result we obtain the following system of equations:

$$Z_1''(x) = \psi_0(x), \quad Z_1(0) = Z_1'(0) = 0; \quad (37)$$
$$Z_2''(x) = [\psi_0'(x) + \frac{1}{2}\psi_0''(x)]Z_1(x),$$
$$Z_2(0) = Z_2'(0) = 0, \quad (37')$$

etc. We consider the function

$$\omega(x) = 3 + \frac{3}{2}x - e^{-x}[(3 + 4x)I_0(x) + (1 + 4x)I_1(x)]. \quad (38)$$

It is easy to verify that $\omega''(x) = \psi_0(x)$ and $\omega(0) = \omega'(0) = 0$. We therefore obtain from (37)

$$Z_1(x) = \omega(x), \quad (39)$$

and after substituting in (37') and integrating, we get

$$Z_2(x) = \frac{1}{2}\Big[2\omega(x)\omega'(x) + \omega(x)\omega''(x) - \omega'^2(x)$$
$$- 3\int_0^x \omega'^2(y)dy + \int_0^x (x - y)\psi_0^2(y)dy\Big]. \quad (40)$$

We can analogously reduce to quadratures the next approximation of (36). Substituting (39) and (40) in (36), we

I. Z. Fisher et al.

get

$$\Gamma(t) = 12a\nu\tau[\omega(t/2\tau) + aZ_2(t/2\tau) + \ldots], \qquad (41)$$

with $Z_2(x)$ from (40). Differentiating this once with respect to $t$ and then putting $t \to \infty$, and taking into account the explicit form of $\omega(x)$ in (38), we obtain

$$D \equiv \tfrac{1}{6}\Gamma'(\infty) = \tfrac{3}{2}a\nu[1 - 32a/15\pi + O(a^2)]. \qquad (42)$$

It is necessary to substitute here the value of $a$ from (29). The first term in (29) coincides with the first term of the expansion (35) and with the result of[5]. We see also that the approximation (35) is very good.

We have so far disregarded the effects of the compressibility of a real liquid. A complete calculation of $\Gamma(t)$ for a compressible liquid with relaxing kinetic coefficients and with allowance for the dispersion of the speed of sound the thermal conductivity is an exceedingly complicated manner. The problem was discussed and partially solved in[5]. A qualitative picture of the phenomenon can be obtained by putting $c_p \approx c_V$. Neglecting by the same token the influence of the thermal conductivity on the longitudinal motions of the liquid and assuming the damping decrement and the speed of sound to be constant, we find that the Euler correlation function of the longitudinal component of the field $u(r, t)$ with equal spatial arguments is then a particular case of the more general function obtained in[5], and is equal to

$$\psi^{3s}(t) = \langle u(r,0) u(r,t) \rangle_{\parallel} = \frac{4kTc^3}{\pi^2\rho\gamma^3}\sigma''\left(\frac{c^2t}{\gamma}\right), \qquad (43)$$

$$\sigma(x) = 1 - e^{-2x} - 2\sqrt{x}\,e^{-x}\int_0^{\sqrt{x}} e^{y^2}dy, \qquad (43')$$

where $c$ is the speed of sound, $\gamma = 4\nu/3 + \zeta/\rho$, and $\zeta$ is the second viscosity coefficient. In addition, we neglect the difference between the Euler and Lagrangian correlation functions for the acoustic branch of the fluctuations of the field $u(r, t)$. In this case, according to (10), it is necessary to add to the right-hand side of (28) the value of $\psi^S(t)$ multiplied by 2, and by changing over to the dimensionless quantities (29) we obtain the inhomogeneous equations

$$Z''(x) = \frac{a}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\psi_0(|Z(x) + s[Z(x) - x]^{1/2}|)\exp\left\{-\frac{1}{2}s^2\right\}ds$$
$$+ \frac{4a}{\pi}\left(\frac{4c^2}{\gamma^2}\tau\nu\right)^{3/2}\sigma''\left(\frac{2c^2\tau}{\gamma}x\right), \qquad (44)$$

with initial conditions (31).

Equation (44) can be investigated by the same methods as (30). At $x \lesssim 1$, a direct solution in the form of a series in powers of $x$ leads in place of (33) to the expression

$$\Gamma(t) = 2a\nu\tau\left[\left(\beta + \frac{3}{8}\right)\frac{t^2}{\tau^2} - \left(\frac{2}{5}\beta + \frac{3}{64}\right)\frac{t^3}{\tau^3} + \ldots\right], \quad \beta = \frac{8\nu}{c\gamma\pi}\sqrt{\frac{\nu}{\tau}}. \qquad (45)$$

For ordinary liquids we have $\beta \sim 10$, so that expressions (33) and (45) differ significantly. At $t > \gamma/c^2$, however, the free term in (44) attenuates rapidly, and the asymptotic solution as $t \to \infty$ again leads in the principal terms to the universal asymptotic form (23). In the region of intermediate values of $x$, the solution of (44) in the form of a series in powers of $a$ leads to the result

$$\Gamma(t) = \frac{kT}{2\pi\rho\nu}\sqrt{\frac{\tau}{\nu}}\left[\omega\left(\frac{t}{2\tau}\right) + \beta\sigma\left(\frac{c^2t}{\gamma}\right)\right] + O(a^2). \qquad (46)$$

The term with $\beta$ makes no contribution to the behavior of $\Gamma'(t)$ as $t \to \infty$, so that the definition of the diffusion coefficient (42) remains in force. It can be shown that the next higher approximations yield a small correction to $D$, of the order of $(\alpha\beta)^2$.

## 5. CORRELATION FUNCTIONS OF THE ROTATIONAL MOTION

We turn to the rotational motion of a liquid particle. We consider again the case of a liquid with relaxing viscosity. From (7) and (25) in analogy with (30), we get

$$\Phi(x) = \frac{9a}{32\tau^2\sqrt{2\pi}}\int_{-\infty}^{\infty}\chi_0(Z(x) + s[Z(x) - x]^{1/2})\exp\left\{-\frac{1}{2}s^2\right\}ds, \qquad (47)$$

where we have used the dimensionless notation of (29) and

$$\chi_0(x) = e^{-x}(I_2(x) + I_3(x))/x^2, \quad x > 0 \qquad (48)$$

is the dimensionless Euler correlation function of the angular velocity at equal spatial arguments, which must be continued in even fashion into the region $x < 0$. $Z(x)$ in (47) should be replaced by any one of the estimates obtained above. At $x < 1$, direct expansion in powers of $x$ leads to the result

$$\Phi(t) = \frac{9a}{256\tau^2}\left[1 - \frac{5t}{12\tau} + \frac{5}{48}\left(1 - \frac{a}{4} - \frac{2a}{3}\beta\right)\frac{t^2}{\tau^2} + \ldots\right]. \qquad (49)$$

For $\Phi(t)$, unlike $\Gamma(t)$, the effect of compressibility of the liquid is weak, namely, $\beta$ enters only in the combination $\alpha\beta$. Putting $t = 0$ in (49) and taking (5) and (29) into account, we obtain an estimate for the mean-squared hydrodynamic thermal fluctuations of the angular velocity and the density of the angular momentum

$$\langle M^2 \rangle = \alpha^2\langle\Omega^2\rangle = \frac{3\alpha^2kT}{2\pi\rho(16\tau\nu)^{3/2}}, \qquad (50)$$

which would be difficult to obtain by another method.

In the case $x \gg 1$, regardless of whether we take the compressibility of the liquid into account or not, we obtain from (48) again the limiting asymptotic form (24) with $\Phi(t) \propto t^{-5/2}$.

At intermediate values of $x$, an approximate expression for $\Phi(t)$ can be obtained by expanding $Z(x)$ and $\Phi(x)$ in powers of $a$. With the aid of (46) we thus obtain

$$\Phi(t) = \frac{9a}{32\tau^2}\left\{\chi_0\left(\frac{t}{2\tau}\right) + a\left[\chi_0'\left(\frac{t}{2\tau}\right) + \frac{1}{2}\chi_0''\left(\frac{t}{2\tau}\right)\right]\cdot\right.$$
$$\left.\cdot\left[\omega\left(\frac{t}{2\tau}\right) + \beta\sigma\left(\frac{c^2t}{\gamma}\right)\right] + O(a^2)\right\}. \qquad (51)$$

The function $\Phi(t)$ is integrable over the entire semiaxis $t \geq 0$. From (51) we obtain with the aid of (48) the estimate

$$\int_0^{\infty}\Phi(t)dt = \frac{5kT}{128\pi\eta(4\tau\nu)^{1/2}}(1 + O(a)). \qquad (52)$$

The quantity

$$D_r = \frac{1}{3}\int_0^{\infty}\Phi(t)dt$$

can be taken to be the "coefficient of rotational diffusion" of the liquid particle.

For spectral experiments it is necessary to know the Fourier representation of the function $\Phi(t)$. We put

$$\Phi_\omega = \int_0^{\infty}\Phi(t)\cos\omega t\,dt. \qquad (53)$$

Taking into account only the first term in (51), we get

$$\Phi_\omega = \tfrac{3}{2}D_r\{Re\,[6s + 2s^2 - 2s^3 - s^4] + O(a)\}, \qquad (54)$$
$$s = 1 - 2i\omega\tau - [(1 - 2i\omega\tau)^2 - 1]^{1/2}.$$

The power-law asymptotic form of $\Phi(t)$ as $t \to \infty$ makes $\Phi_\omega$ non-analytic as $\omega \to 0$. From (54) we obtain at small values of $\omega$ the expansion

$$\Phi_\omega = 3D_r \left[ 1 + \frac{128}{5\sqrt{2}} (\omega\tau)^{1/2} - 48(\omega\tau)^2 + \frac{64}{\sqrt{2}} (\omega\tau)^{1/2} + \dots \right]. \tag{55}$$

A similar result was obtained earlier for the correlation function of the angular velocity of a Brownian particle with allowance for the viscous aftereffect[13]. That a Brownian particle behaves like a "liquid" particle as $t \rightarrow \infty$ or $\omega \rightarrow 0$ is physically obvious. The presence of fractional-power terms in (55) can be verified in principle by means of suitable spectral measurements, for example in EPR.

In conclusion we recall once more that, in accordance with the ideas developed at the beginning of the article, the investigated function $\Phi(t)$ determines the behavior of the correlation function of the angular velocity and of the angular momentum of a singled-out molecule in the liquid at extremely long times, and their behavior at all hydrodynamics times, for a model of a liquid with relaxing shear stresses.

[1] T. Nee and R. Zwanzig, J. Chem. Phys. 52, 6353, 1970.

[2] A. V. Zatovskiĭ and G. I. Salistra, Ukr. Fiz. Zh. 18, 435 (1973).

[3] G. Harp and B. Berne, J. Chem. Phys. 49, 1249, 1968; Phys. Rev. A2, 975, 1970.

[4] A. Rahman and F. Stillinger, J. Chem. Phys. 55, 3336, 1970. F. Stillinger and A. Rahman, J. Chem. Phys. 57, 1281, 1972.

[5] I. Z. Fisher, Zh. Eksp. Teor. Fiz. 61, 1647 (1971) [Sov. Phys.-JETP 34, 878 (1972)].

[6] I. Z. Fisher, Materialy rabochego soveshchaniya po statisticheskoi fizike (Proc. of Working Conf. on Statistical Physics), Naukova dumka, 1972.

[7] S. R. de Groot and P. Mazur, Non-equilibrium Thermodynamics, Interscience, 1962.

[8] M. I. Shliomis, Zh. Eksp. Teor. Fiz. 51, 258 (1966) [Sov. Phys.-JETP 24, 173 (1967)].

[9] M. A. Leontovich, J. Phys. USSR 4, 499, 1941.

[10] T. Keyes and D. Kivelson, J. Chem. Phys. 54, 1786, 1971.

[11] S. M. Rytov, Zh. Eksp. Teor. Fiz. 33, 166 (1957) [Sov. Phys.-JETP 6, 130 (1958)].

[12] L. Kadanoff and P. Martin, Ann. Phys. 24, 419, 1963.

[13] A. V. Zatovskiĭ, Izv. Vuzov Fizika No. 10, 13 (1969).

[14] N. Ailawadi and B. Berne, J. Chem. Phys. 54, 3569, 1970. N. Ailawadi and S. Harris, J. Chem. Phys. 56, 5783, 1972.