THEORY OF THE BROWNIAN MOTION AND POSSIBILITIES OF USING IT FOR THE STUDY OF THE CRITICAL STATE OF A PURE SUBSTANCE

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Through the fluctuation-dissipation theorem the characteristic features of the Brownian motion near the critical point of a pure substance are determined entirely by the features of the dependence of the mobility $b(\omega)$ of a particle on the frequency of the force acting on it. For a macroscopic particle finding the mobility is a hydrodynamical problem, and in solving it near the critical point one must take into account, first, the effect of the great compressibility of the liquid, and second, the possible influence of the large density-correlation radius. General formulas are derived for the mobility and the Brownian displacement, and the characteristic frequencies that are important for the critical region are calculated. It is found that for the displacements during times larger than the characteristic time $\tau_1 = |\omega_{01}|^{-1}$ [ω_{01} is the characteristic frequency, see (31)] the mean square displacement of a Brownian particle is given by the usual Einstein formula (33). For times smaller than τ_1 the formula involves an additional coefficient which depends on the ratio of the shear viscosity η and the volume viscosity ζ [cf. (38)]. The presence of a large correlation radius of the density fluctuations near the critical point also does not significantly affect the character of the Brownian motion, and reduces essentially to a renormalization of the radius of the Brownian particle. These conclusions are based on the assumption that there is no strong frequency dependence of the viscosity (for periods of vibration of the order of the times of displacement of the Brownian particle which are of interest to us).

1. STATEMENT OF THE PROBLEM

As is well known, the study of the Brownian motion which was made in the last century gave one of the first proofs of the existence of atoms and made possible a determination of Avogadro's number. Since that time physicists have very rarely engaged in experiments on the Brownian motion. However, as has been pointed out by Krichevskiĭ and others,[1] the study of the Brownian motion can be useful for the investigation of the critical state of matter.

The liquid-vapor critical point of a one-component liquid is fixed by the conditions[2]

$$(\partial p / \partial \rho)_T = (\partial^2 p / \partial \rho^2)_T = 0. \tag{1}$$

The infinite increase of the compressibility $\rho^{-1}(\partial\rho/\partial p)_T$ as the critical point is approached leads to a number of peculiarities in the behavior of a substance near its critical point, in particular to a large increase of the correlations between the positions of different particles [the correlation radius is proportional to $(\partial\rho/\partial p)_T$], which corresponds to an increase of characteristic relaxation times, and so on.

As has been shown by Leontovich,[3] the fluctuation-dissipation theorem reduces the problem of the Brownian motion to finding the dependence of the mobility of a Brownian particle on the frequency—that is, for a macroscopic particle, to a hydrodynamical problem. The hydrodynamics of the critical phase is of a very special kind, since here $(\partial\rho/\partial p)_T \to \infty$, whereas ordinarily the compressibility of a liquid is small. Besides this, the solution of the hydrodynamical problem depends strongly on the magnitude of the viscosity at the critical point and on its frequency dependence.

The fluctuation-dissipation theorem connects the susceptibility $\alpha = \alpha' + i\alpha''$ of a system to the action of a perturbing force f with the fluctuations of the quantity $x (x = \alpha f)$. In the classical region[2] we have

$$x(t) = \int_{-\infty}^{\infty} x_\omega e^{-i\omega t}\, d\omega, \quad \overline{x_\omega x_{\omega'}} = \frac{kT}{\pi}\frac{\alpha''(\omega)}{\omega}\delta(\omega + \omega'). \tag{2}$$

In our case the susceptibility $\alpha(\omega)$ is simply related to the frequency-dependent mobility $b(\omega)$, namely $b(\omega) = -i\omega\alpha(\omega)$.

In the problem of the Brownian motion of a single particle one studies the mean square displacement of this particle

$$X^2(\tau) = \overline{[x(t) - x(t+\tau)]^2},$$

and in the stationary case it is easy to get for it the following expression:

$$X^2(\tau) = \frac{2kT}{\pi}\int_{-\infty}^{\infty}\frac{\alpha''(\omega)}{\omega}(1-\cos\omega\tau)\,d\omega. \tag{3}$$

For this there are the obvious relations

$$X^2(0) = 0, \quad X^2(-\tau) = X^2(\tau).$$

Since $1 - \cos\omega\tau$ is an even function, (3) can be rewritten in the form

$$X^2(\tau) = \frac{2kT}{\pi i}\int_{-\infty}^{\infty}\frac{\alpha(\omega)}{\omega}(1-\cos\omega\tau)\,d\omega, \tag{4}$$

and because $\alpha(\omega)$ is analytic the integral (4) can be calculated as a contour integral. The relations (3) and (4) are valid for arbitrary generalized coordinates x, including cyclic coordinates, for example for the angle of rotation in rotatory Brownian motion. For cyclic coordinates it is necessary that $X^2 \ll 1$. For small τ we have: $1 - \cos\omega\tau \approx \omega^2\tau^2/2$, and therefore

$$X^2(\tau) \approx \frac{kT}{\pi}\tau^2\int_{-1/\tau}^{1/\tau}\omega\cdot\alpha''(\omega)\,d\omega = v_0^2\tau^2.$$

The motion occurs with constant velocity v_0. The function $X^2(\tau)$ is completely determined by the singularities of the analytic function $\alpha(\omega)$, and it is much easier to analyze these than to investigate the cumbersome formulas for $X^2(\tau)$. The features of the behavior of $X^2(\tau)$ which follow from the analyticity of $\alpha(\omega)$ are studied in Sec. 2. The form of the function $\alpha(\omega)$, which is determined in our case from hydrodynamics, will be derived in Sec. 3. The mean square displacement of a Brownian particle for certain types of motion of the liquid is examined in Sec. 4. Peculiarities of the Brownian motion near the critical point and some conclusions are discussed in Sec. 5.

2. CONSEQUENCES OF THE ANALYTICITY OF $\alpha(\omega)$

For any stable physical system it is easily verified[2] that the function $\alpha(\omega)$ has the following properties:

1. All poles and other singularities at which $\alpha = \infty$ lie in the lower half plane.

2. Since under the action of a constant force the motion is with constant velocity, we have

$$\lim_{\omega\to 0}(-i\omega\alpha) = A_0, \quad A_0 > 0, \tag{5}$$

where A_0 is a real positive constant.

3. The function $\alpha(\omega)$ can have branch points at $\omega = 0$ and $\omega = \infty$.

4. On the real axis

$$\alpha^*(-\omega) = \alpha(\omega). \tag{6}$$

As will be shown in Sec. 3, $\alpha(\omega)$ is a rational function of $\omega^{1/2}$, which can be expanded in terms of simple fractions:

$$\alpha = -\frac{A_0}{i\omega} + \sum_k \frac{A_k}{\omega - \sigma_k} + \sum_s \frac{B_s}{\sqrt{\omega} - \beta_s}. \tag{7}$$

We do not consider the case of multiple poles.

From the relations (6) it is easy to get a condition on the location of the singularities in the ω plane, and also on the coefficients of the expansion:

$$\sigma_k^* = -\sigma_k; \quad \beta_s^{2*} = -\beta_s^2, \quad A_k^* = -A_k, \quad B_s^* = -B_s. \tag{8}$$

As can be seen from (8) the singularities of the function $\alpha(\omega)$ are located symmetrically with respect to, or else on, the imaginary axis. When a cut is made along the real axis,

$$0 < \mathrm{Re}\,\omega < \infty, \quad \mathrm{Im}\,\omega = -0, \tag{9}$$

the integrand in (4) is single valued. The integrand in (4) is finite at the point $\omega = 0$, and therefore near zero the contour can be deformed into the upper half plane.

Without loss of generality we can take $\tau > 0$. Then

$$X^2(\tau) = 4kT(I_1 + I_2),$$

$$I_1 = \frac{1}{2\pi i}\int_{-\infty}^{\infty}\frac{\alpha}{\omega}\left(1 - \frac{1}{2}e^{-i\omega\tau}\right)d\omega, \quad I_2 = -\frac{1}{4\pi i}\int_{-\infty}^{\infty}\frac{\alpha}{\omega}e^{i\omega\tau}\,d\omega. \tag{10}$$

The path of integration for I_2 can be closed with an infinitely large semicircle in the upper half-plane, where there are no singularities; therefore $I_2 = 0$. The path of integration for I_1 gets closed in the lower half-plane; the integral reduces to integrals around the singularities of the function $\alpha(\omega)$ ($\omega = 0$, $\omega = \sigma_k$, $\omega = \beta_s^2$) and the integral around the cut. The singularities are encircled in the negative direction; the pole $\omega = 0$ for the first term in (7) has multiplicity two, and the other poles are simple.

We finally get for I_1

$$I_1 = \frac{A_0\tau}{2} - \frac{A_k}{2\sigma_k}(1 - e^{-i\sigma_k\tau}) - 2\frac{B_s}{\beta_s}\left(1 - \frac{1}{2}e^{-i\beta_s^2\tau}\right)$$

$$+\frac{B_s}{2\pi i}\int\limits_C \frac{d\omega}{\omega(\sqrt{\omega}-\beta_s)}\left(1-\frac{1}{2}e^{-i\omega\tau}\right), \tag{11}$$

where C is a path which leaves the point $+\infty$ along the lower edge of the cut, goes around the point $\omega = 0$ in the negative direction, and then goes to $+\infty$.

Let us now consider the contour integral

$$\frac{B_s}{2\pi i}\int\limits_C \frac{d\omega}{\omega(\sqrt{\omega}-\beta_s)}\left(1-\frac{1}{2}e^{-i\omega\tau}\right)$$

$$=\frac{B_s}{2\pi i}\int\limits_0^\infty \frac{2d\omega}{\sqrt{\omega}(\omega-\beta_s^2)}+\frac{B_s}{2\pi i}\int\limits_C \frac{\beta_s(1-{}^1/_2e^{-i\omega\tau})}{\omega(\omega-\beta_s^2)}d\omega$$

$$-\frac{B_s}{2\pi i}\int\limits_0^\infty \frac{d\omega e^{-i\omega\tau}}{\sqrt{\omega}(\omega-\beta_s^2)}=\frac{B_s}{\beta_s}+\frac{1}{2}\frac{B_s}{\beta_s}-y(\tau). \tag{12}$$

Differentiating under the integral sign, we can easily verify that

$$\frac{dy}{d\tau}+i\beta_s^2 y=-\frac{B_s}{2\pi}\int\limits_0^\infty \frac{d\omega}{\sqrt{\omega}}e^{-i\omega\tau}=\frac{B_s}{2\sqrt{i\pi\tau}}, \tag{13}$$

$$y(0)=\frac{B_s}{2\pi i}\int\limits_0^\infty \frac{d\omega}{\sqrt{\omega}(\omega-\beta_s^2)}=\frac{B_s}{2\beta_s}. \tag{14}$$

Integrating the differential equation (13) and using the initial conditions (14), we have

$$y(\tau)=\frac{B_s}{2\beta_s}\exp(-i\beta_s^2\tau)-\frac{B_s}{2\sqrt{i\pi}}\int\limits_0^\tau \frac{\exp(i\beta_s^2(u-\tau))}{\sqrt{u}}du. \tag{15}$$

Accordingly, using (10)–(15), we get

$$X^2(\tau)=4kT\left[\frac{1}{2}A_0\tau-\frac{A_k}{2\sigma_k}(1-e^{-i\sigma_k\tau})-\frac{B_s}{2\beta_s}(1-e^{-i\beta_s^2\tau})\right.$$

$$\left.+\frac{B_s}{2\sqrt{i\pi}}\int\limits_0^\tau \frac{\exp(i\beta_s^2(u-\tau))}{\sqrt{u}}\right]du. \tag{16}$$

The fact that $X^2(\tau)$ is real assures that the conditions (8) are satisfied.

Let us make some asymptotic estimates. The pole terms in (16) are always of the form

$$(1-e^{-i\omega_k\tau})\to(1-e^{-\tau/\tau_0})=\begin{cases}\tau, & \tau\ll\tau_0\\ 1, & \tau\gg\tau_0\end{cases}. \tag{17}$$

At the more complicated branch points only the last term in (6) changes. It has the asymptotic values

$$\int\limits_0^\tau \frac{\exp(i\beta_s^2(u-\tau))}{\sqrt{u}}du=\begin{cases}\sqrt{\tau}, & \tau\ll\tau_0\\ 1/\sqrt{\tau}, & \tau\gg\tau_0\end{cases};$$

$$\tau_0^{-1}=-\operatorname{Im}\beta_s^2. \tag{18}$$

The special case of zero roots is easily obtained from (16) by going to a limit $\sigma_k \to 0$, $\beta_s \to 0$. The corresponding terms in (16) are then

$${}^1/_2 iA_k \quad (\sigma_k\to 0), \tag{19}$$

$$B_s\sqrt{\tau/i\pi} \quad (\beta_s\to 0). \tag{20}$$

3. THE HYDRODYNAMIC APPROXIMATION

The complete system of linearized hydrodynamic equations is

$$\rho_0\partial \mathbf{v}/\partial t=-\nabla p+\eta\Delta\mathbf{v}+(\eta/3+\zeta)\operatorname{grad}\operatorname{div}\mathbf{v},$$

$$\partial\rho/\partial t=-\rho_0\operatorname{div}\mathbf{v},\quad \nabla p=(\partial p/\partial\rho)_T\nabla\rho. \tag{21}$$

In this equation the temperature is regarded as constant, which is a sufficiently good approximation in the immediate neighborhood of the critical point. In fact, as the critical point is approached there is an unlimited increase of both the specific heat at constant pressure[2] and that at constant volume,[4] and therefore hydrodynamic processes are almost isothermal. Numerical estimates of the Peclét number give

$$\frac{vl}{\lambda/\rho C_v}\approx\frac{D\rho C_v}{\lambda}\gg 1.$$

There is also no special difficulty in treating the general case.[6] The hydrodynamical problem of determining the susceptibility $\alpha(\omega)$ is solved only for one particle. In studying the correlation of the motions of several particles it is necessary to look for the correlation functions of the force. In the present section it is assumed that the speed of sound and all the parameters that appear in the equations are independent of the frequency.

We shall regard the Brownian particle as a small sphere of radius R floating in a compressible liquid. The boundary conditions for the equations (21) are of the form

$$\mathbf{v}|_{r=R}=\mathbf{u}=\mathbf{u}_0e^{-i\omega t},\quad \mathbf{v}|_{r=\infty}=0. \tag{22}$$

We shall look for the solution of the equations (21) in the form of the sum of lamellar and solenoidal parts:

$$\mathbf{v}=\mathbf{v}_1+\mathbf{v}_2,\quad \operatorname{div}\mathbf{v}_1=0,\quad \operatorname{rot}\mathbf{v}_2=0. \tag{23*}$$

Applying the operations curl and $\partial/\partial t$ to the first of the equations (21) and using the other two equations, we get

$$\frac{\partial^2}{\partial t^2}\operatorname{div}\mathbf{v}_2=\left(\frac{\partial p}{\partial\rho}\right)_T\Delta\operatorname{div}\mathbf{v}_2+\left(\frac{4}{3}\eta+\zeta\right)\frac{1}{\rho_0}\frac{\partial}{\partial t}\Delta\operatorname{div}\mathbf{v}_2, \tag{24a}$$

$$\frac{\partial}{\partial t}\operatorname{rot}\mathbf{v}_1=\frac{\eta}{\rho_0}\Delta\operatorname{rot}\mathbf{v}_1. \tag{24b}$$

*rot ≡ curl.

The solution of Eq. (24b) under the condition $\operatorname{div} \mathbf{v}_1 = 0$ is given in [5]. Equation (24a) can be solved in analogous fashion. From $\operatorname{curl} \mathbf{v}_2 = 0$ it follows that $\mathbf{v}_2 = \nabla\varphi$ and $\operatorname{div} \mathbf{v}_2 = \Delta\varphi$, and the scalar function φ, with linear dependence on the polar vector $\mathbf{u}$, can be represented in the form $\varphi = \mathbf{u}\nabla f(r)$. Then (24a) reduces to a biquadratic equation for the function f(r), which can be solved with the boundary conditions (22).

The solutions of (21) so obtained for the time Fourier components v_ω of the velocity and p_ω of the pressure are

$$\mathbf{v}_\omega = \mathbf{v}_{1\omega} + \mathbf{v}_{2\omega} = \{-C_1 f(k_2 r) + C_2[k_1 r f'(k_1 r) + 2f(k_1 r)]\}\mathbf{u} - [C_1 f'(k_2 r) k_2 r + C_2 f'(k_1 r) k_1 r](\mathbf{un})\mathbf{n},$$

$$p_\omega = C_1(\mathbf{ur}) f(k_2 r)[(^4/_3\eta + \zeta)k_2^2 - \eta k_1^2],$$

$$f(x) = \frac{ix - 1}{x^3} e^{ix}, \tag{25}$$

where the wave numbers can be determined from the dispersion equations (24):

$$k_1^2 = \frac{i\omega\rho_0}{\eta}, \quad k_2^2 = \omega^2\left[\left(\frac{\partial p}{\partial \rho}\right)_T - \frac{i\omega(^4/_3\eta + \zeta)}{\rho_0}\right]^{-1}, \tag{26}$$

and the constant coefficients C_1 and C_2 are determined from the boundary conditions (22):

$$C_1 = \frac{(3 - 3ik_1R - k_1^2R^2)k_2^3R^3e^{-ik_2R}}{k_2^2R^2(1 - ik_1R) + k_1^2R^2(2 - 2ik_2R - k_2^2R^2)},$$

$$C_2 = -\frac{(3 - 3ik_2R - k_2^2R^2)k_1^3R^3e^{-ik_1R}}{k_2^2R^2(1 - ik_1R) + k_1^2R^2(2 - 2ik_2R - k_2^2R^2)}$$

The resistance force acting on the sphere moving in the liquid can be found from (25) and turns out to be

$$F_\omega = \psi_\omega u_\omega = 6\pi\eta R u_\omega \times \frac{^1/_3(1 - ik_2R)(1 - ik_1R - k_1^2R^2/3) + ^2/_3(1 - ik_1R)(1 - ik_2R - k_2^2R^2/3)}{(k_2^2/k_1^2)(1 - ik_1R) + (1 - ik_2R - k_2^2R^2/2)}. \tag{27}$$

We shall now show how from the quantity ψ_ω found in this section we can determine the function $\alpha(\omega)$ introduced in Sec. 2. The Langevin equation for the motion of a Brownian particle of mass M is

$$(-M\omega^2 - i\omega\psi_\omega)x_\omega = f_\omega. \tag{28}$$

Comparing (28) with the definition of the function $\alpha(\omega)$, namely $x_\omega = \alpha(\omega)f_\omega$, we find

$$\alpha(\omega) = -(M\omega^2 + i\omega\psi_\omega)^{-1}. \tag{29}$$

Substituting ψ_ω from (27) in (29) and using the fact that $M = 4\pi\rho_1 R^3/3$, where ρ_1 is the density of the material of the sphere, we have

$$\begin{aligned}\alpha(\omega) = &-\frac{1}{6\pi\eta R i\omega}\left[1 + \frac{1}{2\beta^2}\frac{\omega}{\omega - \omega_{01}} - y\sqrt{\frac{\omega}{\omega - \omega_{01}}}\left(1 + \frac{1}{2\beta}\sqrt{\frac{\omega}{\omega - \omega_{01}}}\right) + \frac{y^2}{2}\frac{\omega}{\omega - \omega_{01}}\right] \\ &\times\left\{1 - y\left(\beta + \sqrt{\frac{\omega}{\omega - \omega_{01}}}\right) + y^2\left[\frac{2}{9}\frac{\omega}{\omega - \omega_{01}} + \beta\sqrt{\frac{\omega}{\omega - \omega_{01}}} + \frac{\beta^2}{9} + \frac{\rho_1}{\rho_0}\left(\frac{2}{9}\beta^2 + \frac{1}{9}\frac{\omega}{\omega - \omega_{01}}\right)\right]\right. \\ &- y^3\left[\frac{\beta^2}{9}\sqrt{\frac{\omega}{\omega - \omega_{01}}} + \frac{2\beta}{9}\frac{\omega}{\omega - \omega_{01}} + \frac{\rho_1}{\rho_0}\sqrt{\frac{\omega}{\omega - \omega_{01}}}\left(\frac{2\beta^2}{9} + \frac{\beta}{9}\sqrt{\frac{\omega}{\omega - \omega_{01}}}\right)\right] \\ &\left. + y^4\frac{\omega\beta^2\rho_1}{9\rho_0(\omega - \omega_{01})}\right\}^{-1}.\end{aligned} \tag{30}$$

Here we have introduced the characteristic frequency $|\omega_{01}|$ and the dimensionless quantities y and β:

$$\omega_{01} = -i\frac{(\partial p/\partial \rho)_T \rho_0}{^4/_3\eta + \zeta},$$

$$y = i\left(\frac{i\omega\rho_0}{^4/_3\eta + \zeta}\right)^{1/2} R, \quad \beta^2 = \frac{\zeta}{\eta} + \frac{4}{3}. \tag{31}$$

The location of the roots of the denominator in (30) depends on the quantity $\omega/(\omega - \omega_{01})$, i.e., on the degree of closeness to the critical point, and two dimensionless parameters—the ratio of the densities ρ_1 and ρ_0 of the sphere and the liquid, and also the ratio of the shear and volume viscosities. For $y \to 0$ we have

$$\alpha(\omega) = -\frac{1}{6\pi\eta R i\omega}\left(1 + \frac{1}{2\beta^2}\frac{\omega}{\omega - \omega_{01}}\right), \tag{32}$$

i.e., ω_{01} is a pole of $\alpha(\omega)$ at small frequencies for spheres of small size. At large frequencies ($\omega \gg \omega_{01}$) we have approximately $\alpha(\omega) = -1/M^2$ —the inertial properties of the sphere are determined by its mass M alone. In the case of an incompressible liquid ($\omega_{01} \to \infty$)

$$\alpha(\omega) = -[(M + M')\omega^2]^{-1},$$

i.e., the inertial properties of the Brownian particle come also from the apparent additional mass $M' = 2\pi\rho_0 R^3/3$.

This difference in the limiting values of $\alpha(\omega)$ for high frequencies, that is for small times, has the consequence that only for a compressible liquid does one get from (4) the theorem of equipartition of energy $Mv^2/2 = kT/2$, while for an incompressible liquid there is an effect of entrainment of the liquid and $(M + M')v^2/2 = kT/2$ (on this point see also [7]).

4. BROWNIAN MOTION IN A LIQUID

As an example of the use of the hydrodynamical calculation of Sec. 3 and the methods of Sec. 2 we shall consider various limiting cases of Eqs. (27) and (30). The general method for treating the Brownian motion is extremely simple. The generalized susceptibility $\alpha(\omega)$ which appears in the fluctuation-dissipation theorem is to be found either directly or through the quantity ψ_ω according to (29). Then $\alpha(\omega)$ is to be expanded in the simple fractions (7), and by (16) the coefficients of this expansion [see also (17)–(20)] completely determine the mean square displacement of the Brownian particle.

In the case of stationary flow of an incompressible liquid (27) reduces to the Stokes formula $F_\omega = 6\pi\eta R u_\omega$, i.e., $\psi_\omega = 6\pi\eta R = \psi_0$. Exactly the same sort of result is obtained for stationary flow with finite, nonvanishing, compressibility. With neglect of the inertial terms in (30) we then get $\alpha(\omega) = -1/i\omega\psi_0$, i.e., by (7) $A_0 = 1/\psi_0$, and according to (16) we get for the squared displacement of the Brownian particle the Einstein formula

$$X^2(\tau) = \frac{2kT}{6\pi\eta R}\tau. \tag{33}$$

As the next example we turn to the case of nonstationary flow of an incompressible liquid $[(\partial p/\partial\rho)_T = \infty]$. Equation (27) then reduces to

$$F_\omega = \psi_\omega u_\omega = 6\pi\eta R u_\omega(1 - ik_1R - k_1^2R^2/9). \tag{34}$$

This formula agrees with the result of the calculation made in (5). The corresponding substitution in (30) is $\omega_{01} = \infty$, and we get

$$\alpha(\omega) = -\frac{1}{6\pi\eta R i\omega}\left[1 - iR\left(\frac{i\rho_0\omega}{\eta}\right)^{1/2} - \frac{iR^2(\rho_0 + 2\rho_1)\omega}{9\eta}\right]^{-1}. \tag{35}$$

Let β_1 and β_2 be the roots of the quadratic expression in $\omega^{1/2}$ in the denominator of (35). After expanding $\alpha(\omega)$ in simple fractions we get an expression of the form (7) with the coefficients

$$A_0 = \frac{i}{M+M'}\frac{1}{\beta_1\beta_2}, \quad B_0 = -\frac{1}{M+M'}\frac{\beta_1+\beta_2}{\beta_1^2\beta_2^2}$$

$$B_1 = -\frac{1}{M+M'}\frac{1}{(\beta_1-\beta_2)\beta_1^2},$$

$$B_2 = \frac{1}{M+M'}\frac{1}{(\beta_1-\beta_2)\beta_2^2}, \quad \beta_0 = 0,$$

$$\beta_{1,2} = \frac{9(i\eta/\rho_0)^{1/2}}{2R(1+2\rho_1/\rho_0)}\left\{1 \pm \left[1 - \frac{4}{9}\left(1 + \frac{2\rho_1}{\rho_0}\right)\right]^{1/2}\right\}. \tag{36}$$

Substituting these coefficients in (16), we have finally

$$X^2(\tau) = \frac{2kT}{6\pi\eta R}\left\{\tau + i\frac{\beta_1+\beta_2}{\beta_1\beta_2}\sqrt{\frac{\pi\tau}{i}} - i\frac{\beta_1^2+\beta_2^2+\beta_1\beta_2}{\beta_1^2\beta_2^2} - \frac{i\beta_2\exp(-i\beta_1^2\tau)}{\beta_1(\beta_1-\beta_2)}\left[\frac{1}{\beta_1} - \frac{1}{2\sqrt{\pi i}}\int_0^\tau \frac{\exp(i\beta_1^2u)}{\sqrt{u}}du\right] + \frac{i\beta_1\exp(-i\beta_2^2\tau)}{\beta_2(\beta_1-\beta_2)}\left[\frac{1}{\beta_2} - \frac{1}{2\sqrt{\pi i}}\int_0^\tau \frac{\exp(i\beta_2^2u)}{\sqrt{u}}du\right]\right\}. \tag{37}$$

This formula had been obtained previously[7] in a different way. The paper[7] was based on a theorem of Vladimirskiĭ,[8] which for the classical case is equivalent to the fluctuation-dissipation theorem. Vladimirskiĭ was evidently the first to construct a hydrodynamical theory of the Brownian motion.

5. PECULIARITIES OF THE BROWNIAN MOTION NEAR THE CRITICAL POINT

In experiments on the Brownian motion it is in principle possible to measure both the asymptotic slope of the straight line $X^2(\tau)$ for $\tau \to \infty$ and the characteristic times of the nonstationary processes. As has been shown above, the poles of the function $\alpha(\omega)$ provide a complete characterization of the Brownian motion. The characteristic relaxation time is simply the reciprocal of the distance of a pole of $\alpha(\omega)$ from the real axis, and the pole $\omega = 0$, which is always present, determines the asymptotic behavior.

A specific feature of the critical region [cf. Eq. (1)] is that the compressibility increases to infinity as the temperature approaches the critical temperature, and the correlation radius of the density fluctuations increases; also, because of the increase of the characteristic times, a frequency dependence of the viscosity coefficient may appear.

The force of resistance for $\omega \to 0$ depends on which of the conditions $\omega \gg |\omega_{01}|$ or $\omega \ll |\omega_{01}|$ holds. For displacements of a Brownian particle during times larger than $\tau_1 = |\omega_{01}|^{-1}$ the resistance force has the Stokes value, and for times smaller than τ_1

$$F_\omega = 6\pi R u_\omega \eta_{\text{eff}}, \quad \eta_{\text{eff}} = \eta\frac{8\eta + 6\zeta}{11\eta + 6\zeta}. \tag{38}$$

Accordingly, the formula (33) holds as before, but with the effective viscosity η_{eff}, and $1 \gtrsim \eta_{eff}/\eta \gtrsim 0.7$. We note that (38) corresponds to the case in which we take p = const and $\nabla p = 0$ in the basic equations (21).

The nonzero poles of $\alpha(\omega)$ can be divided into two groups—"hydrodynamic" poles, determined by the fourth-degree equation in the denominator of (30) for $\eta(\omega) \neq 0$, and poles caused by zeroes of the shear viscosity.

Since all of the dimensionless coefficients of the equation that determines the hydrodynamic poles of $\alpha(\omega)$ are of the order of unity, it is to be expected that for the roots of this equation $|y_i| \approx 1$, i.e., for the characteristic relaxation times $\tau_2 = \omega_{02}^{-1}$ we have

$$|y| \approx 1, \qquad \omega_{02} \approx (4/3\eta + \zeta) / \rho_0 R^2. \tag{39}$$

We note that whereas the characteristic time τ_1 is determined only by the properties of the liquid, mainly by the distance from the critical point (in the temperature scale), the characteristic time $\tau_2 \sim R^2$, so that it depends strongly on the size of the Brownian particle. Therefore for sufficiently small radius R the Brownian motion is determined solely by the properties of the liquid and does not depend on the size and shape of the Brownian particle.

For small frequencies $\alpha(\omega)$ is of the form (32). Resolving (32) into simple fractions, we get for the coefficients of the expansion [cf. (7)]

$$A_0 = 1/\psi_0, \quad A_1 = -1/2i\beta^2\psi_0, \quad \sigma_1 = \omega_{01} \tag{40}$$

and, according to (16), we find for the mean square displacement of the Brownian particle

$$X^2(\tau) = \frac{2kT}{6\pi\eta R}\left[\tau - \frac{1}{2\beta^2}\,\frac{1-\exp(-|\omega_{01}|\tau)}{|\omega_{01}|}\right]. \tag{41}$$

In the derivation of (41) we have dropped the "hydrodynamic" terms in the denominator of (30), and also have not taken into account a possible frequency dependence of the viscosity coefficients. The "hydrodynamic" terms are important only for times $t \ll \tau_2$ which [cf. (43)] cannot be reached experimentally.

Our general formulas (27)–(30) can also be applied to the case in which there is frequency dependence of the viscosity coefficients, which leads to the appearance of new poles of the function $\alpha(\omega)$, but we do not know of any experiments which determine the form of the functions $\eta(\omega)$ and $\zeta(\omega)$.

As has already been said, near the critical point there is a decided increase of the correlations between the motions of different particles of the liquid, and therefore, generally speaking, even for a sphere at rest there can be changes of the properties of the liquid in the region adjoining the sphere. For a general orientation we have considered the following problem.

A sphere of radius R in a spherical layer of thickness $l > R$ is surrounded by liquid of density ρ and viscosity η, and outside this layer the liquid has density ρ_1 and viscosity η_1. It is found that (for the case $|\omega_{01}| \ll \omega$) the force acting on a uniformly moving sphere differs from the Stokes force by the factor

$$[1 + (R/l)^3(\eta/\eta_1 - 1)]^{-1}$$

so that the difference is small and reduces to a slight renormalization of the radius of the Brownian particle

$$R_{eff} = R\left[1 + \frac{R^3}{l^3}\left(\frac{\eta}{\eta_1} - 1\right)\right]^{-1}.$$

It may be supposed that also for other types of renormalization of the parameters of the liquid owing to increase of the correlations the corrections to the Stokes force will be small. The presence of the correlations also causes changes of the basic hydrodynamic equations (24) (in the terminology of [6] "spatial dispersion" becomes important).

The addition of terms quadratic in the density gradients to the free energy of the liquid ("weak spatial dispersion") leads to a fourth-order equation instead of Eq. (24a).[2, 6] It is easy to verify that this causes no change (for small frequencies $\omega \ll \omega_{01}$) in the limiting Stokes value of the mobility, nor in the expression (38), valid for frequencies $\omega \gg \omega_{01}$. In fact, owing to the equation of continuity $\operatorname{div} \mathbf{v} = i\omega\rho$, for $\omega \to 0$ we have also $\operatorname{div} \mathbf{v} \to 0$—i.e., the liquid can be regarded as incompressible, and consequently the Stokes expression for the mobility is valid.

In the second limiting case of large frequencies it also follows from the equation of continuity that the density, and consequently also the pressure, remains unchanged, which again corresponds to Eq. (38). We make some quantitative estimates of the characteristic time $\tau_1 = |\omega_{01}|^{-1}$. Assuming that $(\partial p/\partial\rho)_T$ decreases linearly as the temperature approaches the critical temperature,[2] we have in order of magnitude

$$\left(\frac{\partial p}{\partial \rho}\right)_T \approx \left(\frac{p_k}{\rho_k T_k}\right)(T - T_k),$$

where typical critical parameters are

$$p_k = 50\ \text{atm}; \quad \rho_k = 1\ \text{g/cm}^3; \quad T_k = 200^\circ\ \text{K}.$$

[The density is assumed to have its critical value—

owing to the condition (1) the deviation of the density from the critical value is less important than that of the temperature.] In this estimate we assume that the viscosity coefficients have no important anomalies at the critical point and take the static values of these coefficients to be $(4\eta/3 + \zeta)/\rho_0 = 0.1\ \mathrm{cm}^2/\mathrm{sec}$. Then for the characteristic time τ_1 we have

$$\tau_1 = 4\cdot 10^{-6}\ \mathrm{sec} \quad \text{for} \quad T - T_k = 0.1^\circ,$$

$$\tau_1 = 4\cdot 10^{-4}\ \mathrm{sec} \quad \text{for} \quad T - T_k = 0.001^\circ. \tag{42}$$

The other characteristic time $\tau_2 = \omega_{02}^{-1}$, which depends on the size of the Brownian particle, is very small:

$$\begin{aligned} \tau_2 &= 10^{-5}\ \mathrm{sec} \quad \text{for} \quad R = 10^{-3}\ \mathrm{cm}, \\ \tau_2 &= 10^{-9}\ \mathrm{sec} \quad \text{for} \quad R = 10^{-5}\ \mathrm{cm}, \end{aligned} \tag{43}$$

For the characteristic frequencies of the viscosity coefficients it is hard to give quantitative estimates—experiments are necessary here. From what has been said it can be seen that measurement of the viscosity in the critical region will allow us to draw a number of interesting conclusions from experiments on the Brownian motion.

Other methods can also be indicated for studying the characteristic time near the critical point—measurement of the spectrum of modulation of light or sound passing through the critical phase, and also measurement of the cross-susceptibility of a suspension of elongated conducting particles. These more direct methods by no means exclude the study of the Brownian motion, which is of a local character and therefore can be used also to study the inhomogeneities near the critical point, whereas the direct methods give average values. Besides this, in the study of the Brownian motion it is evidently easier to approach the critical point very closely than in the direct methods.

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