MOBILITY OF A BROWNIAN PARTICLE NEAR THE CRITICAL POINT

L. P. LUKIN, A. Z. PATASHINSKIĬ, and T. A. CHEREPANOVA

Institute of Physico-optical Measurements

Submitted June 19, 1967

Zh. Eksp. Teor. Fiz. 53, 1622–1629 (November, 1967)

Corrections are found to the mobility of a small (10^{-6} cm) Brownian particle, which arise close to the liquid-gas critical point, and which are associated with the increase in the compressibility of the liquid for a given viscosity. It is shown that the account of Brownian motion of a particle decreases the mobility under the action of a constant force; this decrease increases with increase in the compressibility. The characteristic times of the Brownian motion are also investigated with account of heat conduction in the liquid.

1. INTRODUCTION

IN experiments on the study of diffusion and Brownian motion, a slowing of these processes was observed near the critical point.[1,2] M. Leontovich[3] showed that the slowing of diffusion takes place as the result of a decrease in the thermodynamic quantity $(\partial\mu/\partial c)_{T,V}$ for the case of unchanged mobility of the individual particle. Giterman and Gertsenshteĭn[4] investigated the Brownian motion was in the neighborhood of the critical point of a liquid; it was found that the coefficient of Brownian diffusion D does not depend on the compressibility but is determined by the usual formula

$$D = kT / 6\pi\eta a = bkT, \tag{1.1}$$

where a is the dimension of the particle, η the ordinary (shear) viscosity, b the mobility of the particle. According to these authors,[4] the increase in the compressibility near the critical point leads only to a decrease in the characteristic times of Brownian motion.

The fluctuation-dissipation theorem[5,3] reduces the problem of Brownian motion to the problem of finding the resistance force for the motion of a particle with velocity $U \to 0$. In view of the complexity of determination of this quantity from the microscopic properties of the system, use is made of the phenomenological equations of motion—the equations of hydrodynamics. The usual scheme of calculation, used, for example, in[4] (see also Sec. 2), linearizes the nonlinear hydrodynamic equations and the mobility of the particle is found in the linear approximation.

We note the formulation of the fluctuation-dissipation theorem[5] uses the mobility of a real particle, i.e., a particle in thermal equilibrium with the liquid and therefore undergoing Brownian motion. In the linear approximation, the resistive force in the given motion does not depend on the Brownian motion of the particle. However, there is an interference effect between the given motion and the Brownian motion in the nonlinear equations. The aim of the present work is the calculation of the mobility with account of this effect. Here we shall assume that the interference effect is small and shall find the correction to the mobility in first approximation.

As is shown below, the correction increases like $kT_c/\rho_0 a^3 C_T^2$ as $C_T^2 = (\partial P/\partial\rho)_T \to 0$. From the results of the research it follows that the mobility of the particle decreases upon approach to the critical point. For particles of a given dimension, the degree of closeness to the critical point is found for which this decrease becomes appreciable. Because of the rapid growth of the correction near the critical point, our formulas lose their applicability when the charge of the mobility becomes large.

2. CHARACTERISTIC FREQUENCIES OF BROWNIAN MOTION AND THE GENERALIZED SUSCEPTIBILITY

We shall assume that the equations of hydrodynamics of a viscous compressible liquid are applicable for the description of Brownian motion. Neglecting terms that are small in terms of the Reynolds number, we write down the linearized set of hydrodynamic equations in the form

$$\rho_0 \partial \mathbf{V} / \partial t = -\operatorname{grad} P + \lambda \operatorname{grad} \operatorname{div} \mathbf{V} - \eta \operatorname{rot} \operatorname{rot} \mathbf{V}, \tag{2.1}$$

$$\partial\rho / \partial t + \rho_0 \operatorname{div} \mathbf{V} = 0, \tag{2.2}$$

$$\delta P = \left(\frac{\partial P}{\partial\rho}\right)_S \delta\rho + \left(\frac{\partial P}{\partial S}\right)_\rho \delta S = C_S^2 \delta\rho + \alpha\delta S, \tag{2.3}$$

$$\delta T = \left(\frac{\partial T}{\partial\rho}\right)_S \delta\rho + \left(\frac{\partial T}{\partial S}\right)_\rho \delta S = \beta\delta\rho + \gamma\delta S, \tag{2.4}$$

$$\rho_0 T_0 \partial S / \partial t = \varkappa \nabla^2 T. \tag{2.5}$$

The characteristics of Brownian motion for the linearized hydrodynamic equations, close to the critical point and without account of the equation of thermal conduction (2.5), are found in[4]. It is shown there that there exist two characteristic frequencies ω_0 and ω_1:

$$\omega_0 = -\frac{i\rho_0}{\lambda}\left(\frac{\partial P}{\partial\rho}\right)_\omega, \quad \omega_1 = -\frac{i\lambda}{\rho_0 a^2}, \tag{2.6}$$

where $\lambda = (4/3)\eta + \zeta$. We consider the case $\omega_0/\omega_1 \gg 1$, i.e., $a^2 \ll \rho_0^2(\partial P/\partial\rho)_\omega/\lambda^2$.

Let us consider the effect of thermal conduction on the motion of a Brownian particle. First of all, we note that one can neglect the term $\rho_0 \partial V/\partial t$ in Eq. (2.1) in comparison with the remaining terms. Actually, we transform to the temporal Fourier harmonics and obtain the relation

$$\frac{|(\rho_0 \partial \mathbf{V}/\partial t)_\omega|}{|(\operatorname{grad} P)_\omega|} \approx \frac{\rho_0 U\omega a}{P} \sim \frac{\omega^2 a^2}{C_S^2}. \tag{2.7}$$

Thus the term $(\rho_0 \partial V/\partial\tau)_\omega$ in the region of frequencies $\sim\omega_0$ is small in terms of the parameter $\beta = \omega_0^2/\omega_1^2$ and we get in place of (2.1)

$$-\operatorname{grad} P + \lambda \operatorname{grad} \operatorname{div} \mathbf{V} - \eta \operatorname{rot} \operatorname{rot} \mathbf{V} = 0. \tag{2.1'}$$

It follows from (2.1′) that

$$-P+\lambda\,\mathrm{div}\,\mathbf{V}_d=\Gamma, \tag{2.8}$$

where curl $\mathbf{V}_d = 0$, Γ is some harmonic function. By using (2.8), we transform the system (2.1′)–(2.5) to the form

$$-\mathrm{rot}\,\mathrm{rot}\,\mathbf{V}_r=-\frac{1}{\eta}\,\mathrm{grad}\,\Gamma, \tag{2.9}$$

$$\mathrm{div}\,\mathbf{V}_d=-(\Gamma+\alpha S)\left(C_S{}^2\frac{\rho_0}{i\omega}-\lambda\right)^{-1}, \tag{2.10}$$

$$\nabla^2 S+k^2 S=0, \tag{2.11}$$

where div $\mathbf{V}_r = 0$ and

$$k^2=\frac{i\omega\rho_0 T_0}{\varkappa}\left\{\gamma-\beta\frac{\rho_0}{i\omega}\alpha\left(C_S{}^2\frac{\rho_0}{i\omega}-\lambda\right)^{-1}\right\}^{-1}. \tag{2.12}$$

In particular, let us consider the case of a large thermal conductivity of the Brownian particle. In this case, it is necessary to require the satisfaction of the boundary conditions

$$T|_{r=a}=T_0=\mathrm{const}, \tag{2.13}$$

$$\mathbf{V}|_{r=a}=\mathbf{U}_\omega,\quad \mathbf{V}|_{r=\infty}=0. \tag{2.14}$$

Omitting the simple calculations, we write out the solution of the system in the form

$$\mathbf{V}_d=-\frac{1}{3}A\frac{1}{C_S{}^2\rho_0/i\omega-\lambda}\left\{\mathbf{N}_2{}^2\int_a^r x\,dx-\mathbf{N}_0{}^1\int_\infty^r\frac{dx}{x^2}\right\}$$

$$-\frac{1}{3}\frac{\alpha c}{C_S{}^2\rho_0/i\omega-\lambda}\left\{\mathbf{N}_2{}^2\int_a^r x^2\,dx\,h_1(kx)-\mathbf{N}_0{}^1\int_\infty^r dx\,h_1(kx)\right\}, \tag{2.15}$$

$$V_r=\frac{A}{2\eta}\left\{\mathbf{N}_2{}^2\frac{a^2-r^2}{3}+\frac{4}{3}\mathbf{G}_0{}^2\right\}, \tag{2.16}$$

where

$$c=\varepsilon A,\quad \varepsilon=\frac{\beta\rho_0}{a^2h_1(ka)}\left[i\omega\left(C_S{}^2\frac{\rho_0}{i\omega}-\lambda\right)\gamma-\rho_0\beta\alpha\right]^{-1}, \tag{2.17}$$

$$A=\left\{\frac{1}{3}\left(C_S{}^2\frac{\rho_0}{i\omega}-\lambda\right)^{-1}\int_\infty^a\frac{dx}{x^2}\right.$$

$$\left.+\frac{1}{3}\varepsilon\alpha\left(C_S{}^2\frac{\rho_0}{i\omega}-\lambda\right)^{-1}\int_\infty^a dx\,h_1(kx)+\frac{2}{3}\frac{1}{\eta a}\right\}^{-1},$$

$$\mathbf{N}_0{}^1=\mathbf{U}_\omega,\quad \mathbf{G}_0{}^2=r^{-1}\mathbf{U}_\omega,$$

$$\mathbf{N}_2{}^2=\frac{1}{r^3}[\mathbf{U}_\omega-3\mathbf{n}(\mathbf{n}\mathbf{U}_\omega)],\quad h_1(z)=-\frac{z+i}{z^2}e^{iz}.$$

From (2.15) and (2.16), we find the resistive force:

$$F_\omega=4\pi AU_\omega. \tag{2.18}$$

Using (2.18) and thermodynamic identities (see [5]), we find the generalized susceptibility

$$\alpha(\omega)=-\frac{1}{6\pi\eta ai\omega}\left[1+\frac{i\omega\eta}{2(i\omega\lambda-\rho_0C_S{}^2)}+\frac{B}{2}\frac{1}{1-ika}\right], \tag{2.19}$$

where

$$B=\frac{i\omega\eta\alpha\beta\rho_0}{\gamma(i\omega\lambda-\rho_0C_S{}^2)(i\omega\lambda-\rho_0C_T{}^2)}, \tag{2.20}$$

$$k^2=\frac{i\omega\rho_0T_0(C_S{}^2\rho_0-i\omega\lambda)}{\varkappa\gamma(C_T{}^2\rho_0-i\omega\lambda)}. \tag{2.21}$$

For $ka \gg 1$, we have, from (2.19),

$$\alpha(\omega)=-\frac{1}{6\pi\eta ai\omega}\left(1+\frac{1}{2}\frac{i\omega\eta}{i\omega\lambda-\rho_0C_S{}^2}\right), \tag{2.22}$$

while for $ka \ll 1$,

$$\alpha(\omega)=-\frac{1}{6\pi\eta ai\omega}\left(1+\frac{1}{2}\frac{i\omega\eta}{i\omega\lambda-\rho_0C_T{}^2}\right). \tag{2.23}$$

In the region of extremely low frequencies (for the zeroth harmonic) the condition of isothermal behavior is satisfied, inasmuch as $\kappa \neq 0$ near the critical point. In the frequency range $\omega \sim C_T^2\rho_0/\lambda$, the isothermal condition has the form

$$\varkappa \gg \rho_0{}^2C_S{}^2C_Va^2/\lambda, \tag{2.24}$$

where C_V is the heat capacity at constant volume.

To find the correction to the mobility of the Brownian particle, we need the solution of the hydrodynamic equations at zero frequency and in the frequency region $\omega \sim C_\omega^2\rho_0/\lambda$. In the first case, the isothermal condition is always satisfied; therefore, $C_\omega^2|_{\omega=0} = C_T^2$. In the second case, by $(\partial P/\partial\rho)_\omega$ we imply C_T^2 if the inequality (2.24) is satisfied, and C_S^2 in the opposite case.

3. CORRECTIONS TO THE MOBILITY OF THE BROWNIAN PARTICLE

Near the critical point $\beta = \omega_0^2/\omega_1^2 \ll 1$ for $a \ll \rho_0 C_S/\lambda$. Moreover, it can be shown that the principal contribution to the mobility correction is made by Brownian motion with frequencies $\omega \sim \omega_0$, while for $\omega \gg \omega_0$ the size of the contribution connected with Brownian motion at frequency ω falls off as $1/\omega^2$. Discarding terms that are small in β, in the approximation $\beta \ll 1$ we write out the set of hydrodynamic equations in the form

$$-\mathrm{grad}\,P+\lambda\,\mathrm{grad}\,\mathrm{div}\,\mathbf{V}-\eta\,\mathrm{rot}\,\mathrm{rot}\,\mathbf{V}=0, \tag{3.1}$$

$$\partial\rho/\partial t+\mathrm{div}\,(\rho\mathbf{V})=0, \tag{3.2}$$

$$P-P_0=C_\omega{}^2(\rho-\rho_0); \tag{3.3}$$

Here ρ_0 and P_0 are the equilibrium density and the pressure in the liquid, respectively.

The velocity field $\mathbf{V}$ must satisfy the boundary conditions

$$\mathbf{V}|_{r=a}=\mathbf{U},\quad \mathbf{V}|_{r=\infty}=0.$$

Here $\mathbf{U}$ is the velocity of a sphere of radius a:

$$\mathbf{U}=\mathbf{U}_0+\mathbf{U}_\Phi,$$

where $\mathbf{U}_0$ = const is the constant velocity and $\mathbf{U}_\Phi$ is the Brownian velocity of the sphere:

$$\mathbf{U}_\Phi(t)=\int d\omega\,\mathbf{U}_\omega e^{-i\omega t}.$$

In the linear approximation we have in place of (3.2),

$$\partial\rho_1/\partial t+\rho_0\,\mathrm{div}\,\mathbf{V}_1=0. \tag{3.4}$$

In this approximation we get for the temporal Fourier components of the velocity and density:

$$\mathbf{V}_{01}=\mathbf{U}_0\left(1-\frac{3a}{4r}-\frac{a^3}{4r^3}\right)+\mathbf{n}(\mathbf{U}_0\mathbf{n})\left(\frac{3a^3}{4r^3}-\frac{3a}{4r}\right), \tag{3.5}$$

$$\rho_{01}=-\frac{3}{2}\frac{\eta}{C_T{}^2}\frac{a}{r^2}(\mathbf{U}_0\mathbf{n}), \tag{3.6}$$

$$\mathbf{V}_{\omega1}=\mathbf{U}_\omega\left[1-\frac{3(1+k)}{2(2+k)}\frac{a}{r}+\frac{1-k}{2(2+k)}\frac{a^3}{r^3}\right]$$

$$+\mathbf{n}(\mathbf{U}_\omega\mathbf{n})\left[\frac{3(1-k)}{2(2+k)}\frac{a^3}{r^3}-\frac{3(1-k)}{2(2+k)}\frac{a}{r}\right], \tag{3.7}$$

$$\rho_{\omega1}=\frac{\rho_0}{i\omega}\frac{3k}{2+k}\frac{a}{r^2}(\mathbf{U}_\omega\mathbf{n}); \tag{3.8}$$

here

$$k=k_2{}^2/k_1{}^2, \tag{3.9}$$

$$k_1{}^2=\frac{i\omega\rho_0}{\eta},\quad k_2{}^2=\frac{\omega^2}{C_\omega{}^2-i\omega\lambda/\rho_0}. \tag{3.10}$$

In our approximation, the contributions of the Brownian oscillations with different frequencies to the mobility correction are additive; therefore, averaging over the polarizations of the Brownian motion reduces to the substitution

$$\overline{U_{\omega i}U_{-\omega k}} = {}^1/_3|\overline{U_\omega}|^2\delta_{ik}. \tag{3.11}$$

For the second approximation, we have

$$i\omega\rho_{\omega 2} - \rho_0 \operatorname{div} \mathbf{V}_{\omega 2} = \operatorname{div}(\rho_{01}\mathbf{V}_{\omega 1} + \rho_{\omega 1}\mathbf{V}_{01}), \tag{3.12}$$

$$\rho_0 \operatorname{div} \mathbf{V}_{02} = -\operatorname{div}(\rho_{\omega 1}\mathbf{V}_{-\omega 1} + \rho_{-\omega 1}\mathbf{V}_{\omega 1}). \tag{3.13}$$

The boundary conditions for $\mathbf{V}_2$ are zero both on the sphere and at infinity. In (3.13), we carry out averaging over the polarizations. The solution in this approximation has the form

$$\overline{\mathbf{V}}_{02} = \frac{|\overline{U_\omega}|^2}{i\omega}\frac{3m}{2+m}\left[\frac{1}{2+k}\frac{a^2}{r^3} - \frac{1-k}{3(2+k)}\frac{a^4}{r^5} - \frac{a}{3r^2}\right]\mathbf{n}, \tag{3.14}$$

$$\overline{\rho}_{02} = -\frac{|\overline{U_\omega}|^2}{i\omega}\frac{3m}{2+m}\frac{\lambda}{C_T^2}\left[\frac{1}{2+k}\frac{a^2}{r^4} - \frac{1-k}{2+k}\frac{a^4}{r^6}\right], \tag{3.15}$$

$$\mathbf{V}_{\omega 2} = \{\mathbf{U}_\omega(\mathbf{U}_0\mathbf{n}) + \mathbf{U}_0(\mathbf{U}_\omega\mathbf{n})\}f_1(r) + \mathbf{n}(\mathbf{U}_0\mathbf{n})(\mathbf{U}_\omega\mathbf{n})f_2(r) + \mathbf{n}(\mathbf{U}_0\mathbf{U}_\omega)f_3(r), \tag{3.16}$$

$$\rho_{\omega 2} = (\mathbf{U}_0\mathbf{n})(\mathbf{U}_\omega\mathbf{n})\varphi_1(r) + (\mathbf{U}_0\mathbf{U}_\omega)\varphi_2(r), \tag{3.17}$$

where m = k*

$$f_1(r) = \frac{3}{8}\frac{\eta C_\omega^2 k_2^2}{\omega^2\rho_0 C_T^2}\left[\frac{1-k}{2+k}\frac{a^4}{r^5} - \frac{3(k^2+10k+9)}{2(2+k)(3+2k)}\frac{a^3}{r^4} + \frac{3(5+3k)}{2(2+k)}\frac{a^2}{r^3} - \frac{11k^2+25k+24}{2(2+k)(3+2k)}\frac{a}{r^2}\right]$$
$$+ \frac{9}{8}\frac{iC_\omega^2 k_2^2}{\omega^3}\frac{k}{2+k}\left[\frac{a^4}{3r^5} - \frac{7k+9}{2(3+2k)}\frac{a^3}{r^4} + \frac{5a^2}{2r^3} - \frac{13k+24}{6(2k+3)}\frac{a}{r^2}\right]$$

$$f_2(r) = -\frac{3}{2}\frac{\eta C_\omega^2 k_2^2}{\omega^2\rho_0 C_T^2}\left[\frac{5(1-k)}{2(2+k)}\frac{a^4}{r^5} - \frac{27(k^2+10k+9)}{8(2+k)(3+2k)}\frac{a^3}{r^4} + \frac{3(5+3k)}{2+k}\frac{a^2}{r^3} - \frac{77k^2+166k+177}{8(2+k)(3+2k)}\frac{a}{r^2}\right]$$
$$- \frac{9}{4}\frac{iC_\omega^2 k_2^2}{\omega^3}\frac{k}{(2+k)}\left[\frac{a^4}{r^5} - \frac{5(7k+9)}{4(3+2k)}\frac{a^3}{r^4} + \frac{5a^2}{r^3} - \frac{13k+27}{4(3+2k)}\frac{a}{r^2}\right]$$

$$f_3(r) = -\frac{9}{8}\frac{\eta C_\omega^2 k_2^2}{\omega^2\rho_0 C_T^2}\left[\frac{k^2+10k+9}{2(2+k)(3+2k)}\frac{a^3}{r^4} - \frac{3+k}{2+k}\frac{a^2}{r^3} + \frac{3k^2+8k+9}{2(2+k)(3+2k)}\frac{a}{r^2}\right]$$
$$- \frac{9}{8}\frac{iC_\omega^2 k_2^2}{\omega^3}\frac{k}{2+k}\left[\frac{7k+9}{2(3+2k)}\frac{a^3}{r^4} - \frac{3a^2}{r^3} + \frac{5k+9}{2(3+2k)}\frac{a}{r^2}\right],$$

$$\varphi_1(r) = -\frac{9}{4}\frac{i\eta C_\omega^2 k_2^2}{\omega^3 C_T^2}\left[\frac{1-k}{2+k}\frac{a^4}{r^6} - \frac{5+3k}{2+k}\frac{a^2}{r^4} + \frac{11k^2+25k+24}{2(2+k)(3+2k)}\frac{a}{r^3}\right]$$
$$+ \frac{9}{4}\frac{i\eta}{\omega C_T^2}\left[\frac{1-k}{2+k}\frac{a^4}{r^6} - \frac{5+3k}{2+k}\frac{a^2}{r^4} + \frac{2a}{r^3}\right]$$
$$+ \frac{9}{4}\frac{C_\omega^2\rho_0 k_2^2}{\omega^4}\frac{k}{2+k}\left[\frac{a^4}{r^6} - \frac{5a^2}{r^4} + \frac{13k+24}{2(3+2k)}\frac{a}{r^3}\right]$$
$$- \frac{9}{2}\frac{\rho_0}{\omega^2}\frac{k}{2+k}\left[\frac{a^4}{2r^6} - \frac{5a^2}{2r^4} + \frac{2a}{r^3}\right],$$

$$\varphi_2(r) = -\frac{3}{4}\frac{i\eta C_\omega^2 k_2^2}{\omega^3 C_T^2}\left[\frac{1-k}{2+k}\frac{a^4}{r^6} + \frac{3(1-k)}{2+k}\frac{a^2}{r^4} - \frac{11k^2+25k+24}{2(2+k)(3+2k)}\frac{a}{r^3}\right]$$
$$+ \frac{3}{4}\frac{i\eta}{\omega C_T^2}\left[\frac{1-k}{2+k}\frac{a^4}{r^6} + \frac{3(1+k)}{2+k}\frac{a^2}{r^4} - \frac{2a}{r^3}\right]$$
$$+ \frac{3}{4}\frac{C_\omega^2\rho_0 k_2^2}{\omega^4}\frac{k}{2+k}\left[\frac{a^4}{r^6} + \frac{3a^2}{r^4} - \frac{13k+24}{2(3+2k)}\frac{a}{r^3}\right]$$
$$- \frac{3}{4}\frac{\rho_0}{\omega^2}\frac{k}{2+k}\left[\frac{a^4}{r^6} + \frac{3a^2}{r^4} - \frac{4a}{r^3}\right].$$

Finally, in the third approximation, the equation of continuity is described in the following way:

$$\rho_0 \operatorname{div} \mathbf{V}_{03} = -\operatorname{div}(\rho_{01}\mathbf{V}_{02} + \rho_{02}\mathbf{V}_{01} + \rho_{\omega 1}\mathbf{V}_{-\omega 2} + \rho_{\omega 2}\mathbf{V}_{-\omega 1} + \rho_{-\omega 1}\mathbf{V}_{\omega 2} + \rho_{-\omega 2}\mathbf{V}_{\omega 1}). \tag{3.18}$$

We average the right-hand side of (3.18) over the polarizations of the Brownian motion. By finding the solution of (3.18) consistent with (3.1) and (3.3) for zero boundary conditions, and substituting it in the expression for the resistive force in terms of the stress tensor, we obtain

$$F_3 = -3\pi\eta a\int_a^\infty\int_{-1}^1 dr\,dz\,P_1(z)\operatorname{div}\mathbf{V}_{03}. \tag{3.19}$$

In accord with the fluctuation-dissipation theorem,

$$\overline{|U_{i\omega}|^2} = \frac{kT}{\pi}\omega\alpha''(\omega), \tag{3.20}$$

where $\alpha(\omega)$ in the first nonvanishing approximation is determined by Eq. (2.22) or (2.23). As a result of simple but tedious calculations, we obtain

$$F_3 = \int_0^\infty G(\omega)\overline{|U(\omega)|^2}U_0\,d\omega, \tag{3.21}$$

where

$$G = \operatorname{Re}\left\{\frac{\pi C_\omega^2\eta k_2^2}{a^2\omega^4}\frac{3k(1002+983k-534m-356km)}{560(2+k)(2+m)(3+2k)} - \frac{\pi\eta}{a^2\omega^2}\frac{3k(167-125m)}{280(2+k)(2+m)}\right.$$
$$+ \frac{\pi i\eta^2 C_\omega^2 k_2^2}{\omega^3 a^2\rho_0 C_T^2}\frac{3(1008+435k^2+456k^2m+948km+537k+398m)}{560(2+k)(2+m)(3+2k)}$$
$$- \frac{\pi i\eta^2}{\omega a^2\rho_0 C_T^2}\frac{9(26+5k+17m-8km)}{140(2+k)(2+m)} + \frac{\pi i\eta^2}{\omega a^2\rho_0 C_T^2}\frac{9m(2+5k)}{70(2+m)(2+k)}$$
$$\left. + \frac{\pi i\eta\lambda}{\omega a^2\rho_0 C_T^2}\frac{6m(4+5k)}{35(2+k)(2+m)}\right\}. \tag{3.22}$$

The integral over the frequencies in (3.21) can be computed by closing the contour of integration in the upper half plane, with the aid of the theorem of residues. The result of the integration has the form

$$F_3 = \frac{\eta^2 U_0 kT}{C_T^2\rho_0 a^2}f\left(\frac{\zeta}{\eta}\right), \tag{3.23}$$

where f(x) is a positive bilinear function; for $\eta = \zeta$,

$$f(x) = 0{,}2. \tag{3.24}$$

Assuming that $C_T^2 \ll C_\omega^2$, $\zeta \sim \eta$, we get for the resistive force

$$F_3 = \frac{U_0 kT\eta_0}{a^2\rho_0 C_T^2}\left[\frac{\zeta_0}{\zeta_\omega}0{,}005 + \frac{\eta_0}{\eta_\omega}0{,}1\right]. \tag{3.25}$$

Here η_0, ζ_0 are the viscosities at $\omega = 0$; η_ω, ζ_ω are the same for $\omega \neq 0$. For $\zeta_\omega \gg \eta_\omega$ the resistive force has the form

$$F_3 = \frac{U_0 kT\eta_0}{a^2\rho_0 C_T^2}\left[\frac{\eta_0}{\eta_\omega}0{,}02 + \frac{\zeta_0}{\zeta_\omega}0{,}005\right]. \tag{3.26}$$

Finally, with account of the corrections computed by us, we find the mobility at zero frequency:

$$b(\omega)|_{\omega=0} = \left\{6\pi\eta a\left[1 + \frac{kT}{2\pi C_T^2\rho_0 a^3}f\left(\frac{\zeta}{\eta}\right)\right]\right\}^{-1}. \tag{3.27}$$

4. DISCUSSION OF THE RESULTS

The retardation of the diffusion of the Brownian particles becomes important for $\Delta b/b \sim 1$, i.e., for $kT_c/\rho_0 \sim a^3C_T^2 f(\zeta/\eta)$. For $\rho_0 \sim 1$ g/cm³, $C_T^2 \sim 10^7\tau$ cm²/sec², $a \sim 10^{-6}$ cm, where $\tau = (T - T_c)/T_c$, we find $\tau_0 f \sim 10^{-3}$. When $\zeta_0/\zeta_\omega \sim 1$ it is necessary to come to within 10^{-2} – 10^{-3} deg of $T_c \sim 300$°K. If, for example, $\zeta_0 \sim \zeta_\omega \tau^{-1}$, then the region is extended to 0.1–0.01 deg. For particles of size 10^{-7} cm, where the hydrodynamic consideration can be only qualitative, $\tau \sim 1$, the effect of diffusion retardation is seen to be very strong over the entire range of temperatures $T \sim T_c$.

The correction to the mobility can be represented as the first nontrivial term in the expansion of the function in the parameter $r_c(\tau)/r$, where $r_c(\tau)$ is the "hydrodynamic" correlation radius. In our case, $r_c \ll a$. The appearance of a large r_c shows the limits of the hydrodynamic description of the motion of the particle. On the basis of not rigorous but descriptive considerations, it can be established that the mobility will fall upon increase in r_c. The value of the resistive force can be represented in the form $F \sim \eta R$, where R is the order of magnitude of the distance at which the presence of the particle materially changes the flow velocity. In the case $r_c < a$, the value of R is determined by the size of the particle a. Near the critical point the presence of a sufficiently strong correlation leads to an increase in R to r_c. Therefore, it can be expected that as $r_c \to \infty$ the mobility at zero frequency becomes smaller.

We note that such a result is strongly connected with the assumption on the absence of dispersion in the compressibility. The presence of such dispersion leads to a replacement of the isothermal compressibility by the compressibility of the volume of liquid with a characteristic dimension of the order of the particle dimension. This case will be considered in more detail in the following paper.

[1] I. P. Krichevskiĭ, N. E. Khazanova, L. S. Lesnevskaya and É. A. Polyakova, Khim. promyshlennost' (Chemical Industry) **2**, 29 (1962).

[2] A. Ya. Bal'tsevich, V. G. Martynets and É. V. Matizen, Zh. Eksp. Teor. Fiz. **51**, 983 (1966) [Sov. Phys.-JETP **24**, 654 (1967)].

[3] M. A. Leontovich, Zh. Eks. Teor. Fiz. **49**, 1624 (1965) [Sov. Phys.-JETP **22**, 1110 (1965)].

[4] M. M. Giterman and M. E. Gertsenshteĭn, Zh. Eks. Teor. Fiz. **50**, 1084 (1966) [Sov. Phys. JETP **23**, 722 (1966)].

[5] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics) (Fizmatgiz, 1965).

Translated by R. T. Beyer
188