$\Delta M(z)$, mass of substance absorbed on the section $z - z + \Delta z$ of the gas-liquid layer, kg; $k = u/v$, slope tangent of velocity vector to the vertical axis; V_0, velocity of flow on the axis of the secondary eddy, m/sec; v_i, tangential velocity on the boundary of the eddy, m/sec; W, corrected velocity of gas across the reaction zone, m/sec; $\bar{r} = (r - D_0/2)/\Delta R$, dimensionless coordinate reckoned from the wall of the gas-conducting tube.

LITERATURE CITED

1. Kh. O. Nurste, Yu. V. Ivanov, and Kh. O. Lubi, Teploenergetika, No. 1, 37-39 (1978).
2. S. Chandrasekhar, Hydrodynamic and Hydromagnetic Stability, Oxford (1961).
3. V. K Shchukin, Heat Transfer and Hydrodynamics of Internal Flows in Fields of Body Forces, Moscow (1970).
4. V. B. Kozub, A. E. Gulin, and A. K. Rudenko, Intensification of Heat and Mass Transfer in Chemical Process Units [in Russian], Leningrad (1985), pp. 67-73.

THE HYDROMECHANICS OF SUSPENSIONS

Yu. A. Buevich, A. Yu. Zubarev, and A. M. Isaev

UDC 532.545

Thermodynamic forces are introduced into the momentum conservation equations for the phases of a monodisperse suspension of fine particles in order to permit effective description of the presence of diffusion processes in flows, thus circumventing the main difficulty encountered in the hydromechanics of suspensions.

The phases in flows of suspensions and other disperse systems undergo convective and diffusional redistribution, resulting in the formation of completely determined fields of concentration of the suspended particles. The concentration field, as the fields of mean pressure and mean velocity of the phases, is an unknown function. All of these unknowns should be determined simultaneously from the solution of the boundary-value problem corresponding to the given flow for the system of equations of the hydromechanics of disperse systems.

In actuality, in the overwhelming majority of specific situations the system of hydrodynamic equations traditionally used for suspensions does not have physically admissible solutions. Thus, the flows are approximately described at the cost of completely ignoring some of these equations and postulating certain a priori and usually poorly-substantiated assumptions regarding the character of the concentration distribution.

Below, we will limit ourselves to analyzing a finely-dispersed medium with identical particles. The medium is not necessarily uniform in the macroscopic sense. We write the system of conservation equations for its phases in the form [1]:

$$\begin{gathered}\varepsilon d_0(\partial/\partial t + \mathbf{v}\nabla)\mathbf{v} = -\nabla p + \nabla(\mu\nabla\mathbf{v}) - \mathbf{f} - \varepsilon d_0\nabla\Pi,\\ \rho d_1(\partial/\partial t + \mathbf{w}\nabla)\mathbf{w} = \mathbf{f} - \rho d_1\nabla\Pi,\\ \partial\varepsilon/\partial t + \nabla(\varepsilon\mathbf{v}) = 0,\ \partial\rho/\partial t + \nabla(\rho\mathbf{v}) = 0.\end{gathered} \tag{1}$$

Adding these equations in pairs, we can also obtain the momentum and mass conservation equations for the suspension as a whole.

The phase interaction force, calculated per unit volume, is usually represented in the following form for sufficiently small particles

$$\mathbf{f} = \mathbf{f}_A + \mathbf{f}_S + \mathbf{f}_B + \mathbf{f}_F + \mathbf{f}_I, \tag{2}$$

where the components in the right side describe the effective forces associated with buoyancy (Archimedes force), viscous interaction (Stokes force), the Basse force, the Faxon force, and the inertial force connected with acceleration of the apparent additional mass of the fluid

---

A. M. Gorky Ural State University, Sverdlovsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 57, No. 3, pp. 402-412, September, 1989. Original article submitted March 23, 1988.

when the velocity of the disperse phase changes. The variants of Eq. (1) proposed in the literature differ basically in the expressions adopted for the force components (2) (see the survey in [2], for example). The properties of the solutions obtained may depend significantly (the opinions of some investigators [2] notwithstanding) on the specific form of these expressions (this applies in particular to whether $\mathbf{f}_A$ is represented through the gradient of mean pressure or directly through the gradient of the potential of the external field). The study [1] obtained consistent relations for all of the force components in (2) in the flow of a macroscopically uniform suspension of identical small spheres of moderate concentration, as well as for the effective viscosity of this suspension [1]:

$$\mathbf{f}_A = \rho d\left[\Delta\Pi + \left(\frac{\partial}{\partial t} + \mathbf{w}\nabla\right)\mathbf{w}\right], \quad \mathbf{f}_S = \frac{9}{2}\rho M\frac{\mu_0}{a^2}(\mathbf{v}-\mathbf{w}),$$

$$\mathbf{f}_B = \frac{9}{2}\rho\left[\frac{(1-\rho)M}{\pi}\right]^{1/2}\left(\frac{\mu_0 d_0}{a^2}\right)^{1/2}\int\limits_{-\infty}^{t}\left(\frac{\partial}{\partial\tau} + \mathbf{w}\nabla\right)(\mathbf{v}-\mathbf{w})\frac{d\tau}{\sqrt{t-\tau}},$$

$$\mathbf{f}_F = \frac{3}{4}\rho M\mu_0\Delta\mathbf{v}, \quad \mathbf{f}_I = \frac{3}{2}\rho(1-\rho)\left[1 + \rho\left(\frac{1}{2} + \frac{15}{4}M\right)\right]\times \tag{3}$$

$$\times\, d_0\left(\frac{\partial}{\partial t} + \mathbf{w}\nabla\right)(\mathbf{v}-\mathbf{w}), \quad \mu = M\mu_0, \quad M(\rho) = \frac{1}{1-5\rho/2},$$

$$d = \varepsilon d_0 + \rho d_1.$$

Equation (2) does not consider the nonlinear components of the phase interaction force connected with nonuniformity of the phase-velocity fields and particle rotation. These forces are small for dispersions with sufficiently small particles. However, allowing for them becomes fundamentally important when the other components in (2) vanish — as occurs, for example, in the flow of suspensions in vertical channels.

Let us write the equations which describe the steady uniform flow of a suspension in an inclined plane channel of constant cross section in a gravitational field (we direct the longitudinal x and transverse y axes along the corresponding components of the vector $\mathbf{g} = -\nabla\Pi$). We follow the usual procedure to obtain two equations from (1-3). These two equations follow from the x-components of the momentum conservation equations of the suspension and its disperse phase:

$$\mu_0\frac{d}{dy}\left(M\frac{dv}{dy}\right) - \frac{\partial p}{\partial x} + dg\sin\alpha = 0, \tag{4}$$

$$\rho\beta M(v-w) + \rho(1-\rho)(d_1-d_0)g\sin\alpha = 0, \quad \beta = 9\mu_0/2a^2,$$

while $\partial p/\partial x$ is regarded as constant. It can readily be seen from this that Eqs. (4) determine the distribution of the mean velocities of the phases $v = v_x$ and $w = w_x$ with an arbitrary distribution of the concentration of the suspension in a section in which these equations are in principle incapable of describing the flow. Also, we actually ignored the y-component of the momentum conservation equation of the disperse phase, which in the present case has the form

$$\rho(1-\rho)(d_1-d_0)g\cos\alpha = 0. \tag{5}$$

This equation is obviously satisfied only in the trivial cases $\cos\alpha = 0$ or $d_1 = d_0$. It becomes clear that system (1) has no steady-state solution for a suspension of particles (as opposed to a packed layer of particles) in the case of flow of the type being examined here. The unsteady analog of Eq. (5) would simply describe settling of the particles (at $d_1 > d_0$) on the bottom of the channel.

Such settling, leading to the formation of a nonuniform concentration profile in the channel and then in the deposited layer, prevents the suspended particles from forming a diffusion flow in the direction opposite the concentration gradient. Under steady-state conditions, a concentration distribution is established such that this diffusion flow exactly compensates for the counter-directed convection of particles and their deposition in a gravitational field under the influence of the force written in (5).

In principle, the diffusional movement of particles is the result of their random fluctuating motion, which can in turn be due to sharply different physical causes. Only Brownian motion is actually important for colloidal dispersions, this motion having been subjected to detailed analysis [3] in dilute dispersions. In flows of finely-dispersed suspensions, anisotropic diffusion becomes important in addition to Brownian diffusion. Anisotropic diffusion is attributable to specific pseudo-turbulent motion. A relatively simple theory of this type of diffusion was proposed in [4]. The energy for the pseudo-turbulence is supplied by the work of the mean relative flow of the carrier phase on fluctuations of suspension concentration, and the role of pseudo-turbulence increases rapidly with an increase in particle size. Ultimately, of course, the ordinary turbulent diffusion of the suspended particles is the most important factor in turbulent flows of suspensions.

Attempts were made in [5, 6] to improve the equations of hydromechanics of suspensions by explicitly introducing diffusion flows into the mass conservation equations for the phases. These attempts were basically unsound, as indicated by I. G. Shaposhnikov in [7]. The error arises from the fact that these equations contain the mean mass phase velocities, so that the quantities $\varepsilon \mathbf{v}$ and $\rho \mathbf{w}$ in (1) describe the total mass flows – regardless of their origins.

However, the diffusion effects being discussed can be described by using the main idea underlying the well-known Einstein method. In accordance with this notion, the diffusion flow is the same as would exist if a particle were acted upon by a certain force proportional to the concentration gradient. Such a force characterizes the actual rate of approach of the system to equilibrium and is usually termed the thermodynamic force. It was used successfully by Batchelor [3] to describe the Brownian diffusion of particles in dilute monodisperse suspensions. In the flow in an inclined channel examined above, this force was introduced into Eq. (5) together with gravity and buoyancy. In this case, (5) changes to an equation which can not only be satisfied, but which also determines the particle distribution in the cross section of the channel.

To calculate the thermodynamic force in the general case, we will use the method in [3] and generalize it to concentrated systems and to situations involving anisotropic fluctuating motion. It follows from the requirement of uniformity of the chemical potential φ of a particle in an equilibrium system located in an external field of body forces that the external force acting on the particle must be balanced by the thermodynamic force $\mathbf{H}=-\nabla\varphi(n, p, T)$. Limiting ourselves to analysis of isothermal flows, we have

$$\mathbf{H}=-\left(\frac{\partial\varphi}{\partial n}\right)_{p,T}\nabla n-\left(\frac{\partial\varphi}{\partial p}\right)_{n,T}\nabla p.$$

The derivative $(\partial\varphi/\partial p)_{n,T}$ is equal to the volume of the particle, so the last term in this relation simply describes the buoyant force in the equilibrium system that corresponds to the determination of $\mathbf{f}_A$ in (3). Since this force has no relation to diffusion processes even in the situations, already accounted for in (2), that differ substantially from equilibrium, we see that we should use the following as the sought thermodynamic force acting on a single particle:

$$\mathbf{H}=-\left(\frac{\partial\varphi}{\partial n}\right)_{p,T}\nabla n=-\left(\frac{\partial\varphi}{\partial\rho}\right)_{p,T}\nabla\rho.$$

As was shown in [3], the corresponding thermodynamic force acting on one molecule of liquid under the same conditions is equal to

$$\mathbf{H}_0=-\left(\frac{\partial\varphi_0}{\partial n}\right)_{p,T}=-\frac{n}{n_0}\mathbf{H}.$$

Introducing the analogous forces applied to the particles and liquid in a unit volume of the dispersion, we see that the thermodynamic force can be regarded essentially as one component of the phase interaction force manifest in a macroscopically nonuniform dispersion and not considered in (2). Thus, the conservation equations (1) retain their form, but the expression for $\mathbf{f}$ in (2) must be replaced by

$$\mathbf{f}=\mathbf{f}_A+\mathbf{f}_S+\mathbf{f}_B+\mathbf{f}_F+\mathbf{f}_I+\mathbf{f}_T,\quad \mathbf{f}_T=-n\left(\frac{\partial\varphi}{\partial n}\right)_{p,T}\nabla n=-\frac{\rho}{v}\left(\frac{\partial\varphi}{\partial\rho}\right)_{p,T}\nabla\rho \tag{6}$$

(here, we used the identity $n\mathbf{H} \equiv -n_0\mathbf{H}_0$).

To close the system of equations of the hydromechanics of suspensions, it is necessary to find an explicit expression for φ and then for $\mathbf{f}_T$ through the unknowns of this system. First let us examine the situation when only isotropic Brownian motion of the particles is important. This situation is characteristic of colloidal dispersions. The calculations are elementary for a limitingly dilute dispersion, and the expression for φ formally coincides with the same expression for an ideal gas consisting of noninteracting particles. In this case, we have $\varphi = \varphi^\circ + kT(\ln\rho - \rho)$, where $\partial\varphi^\circ/\partial\rho = 0$. For dispersions that are close to dilute, we can use the standard form of the method of group expansions [8]. If we restrict ourselves to allowing only for the second virial coefficient, we obtain the result in [3]. In accordance with the latter, the term $8kT\rho$ is added to φ. There is no rigorous theory for dispersions of high concentration, so it is best to resort to one of the approximate theories of the statistical physics of dense gases and liquids. Preference should be given to the Perkins–Yevick theory, since the equations of this theory permit an analytical description for a gas of hard spheres [9]. Using the semi-empirical Carnahan–Starling variant of this theory for the sake of definiteness [9, 10], we write the equation of state of such a gas in the form

$$PV = NkTG(\rho), \quad G = \frac{1 + \rho + \rho^2 - \rho^3}{(1-\rho)^3}, \quad V = \frac{vN}{\rho}, \tag{7}$$

where P and V are the pressure and volume of the gas; N is the total number of particles. The dependence of G on ρ is shown in Fig. 1; it agrees well with the numerical results obtained by the method of molecular dynamics [9]. The value G = 1 corresponds to an ideal gas.

The chemical potential of a spherical particle differs from the above-cited value for an ideal gas by the amount $\Delta\varphi = -kT\partial\ln Q_N/\partial N$, where Q_N is the configurational integral referred to V^N for the gas being examined. Differentiation is performed with constant T and the total number N_0 of liquid molecules in the system. The requirement that N_0 be constant is very important: the result obtained for φ must apply to one of the particles of the system surrounded by liquid molecules, not to a sphere of gas consisting of identical hard spheres that do not contain liquid [3]. It can be argued that molecules of a dissolved substance are a closer analog of suspended particles than a one-component gas.

The value of Q_N is most easily calculated by considering that the right side of equation of state (7) is by definition equal to $kTV\partial\ln V^N Q_N)/\partial V$. From here, we successively obtain

$$\frac{\partial\ln(V^N Q_N)}{\partial V} = \frac{N}{V}G, \quad \frac{\partial\ln Q_N}{\partial V} = \frac{N}{V}(G-1),$$

$$\frac{\partial\ln Q_N}{\partial\rho} = -N\frac{G-1}{\rho}, \quad \ln Q_N = -N\int_0^\rho \frac{G-1}{\rho}\,d\rho,$$

and then

$$\left(\frac{\partial\ln Q_N}{\partial N}\right)_{p,T,N_0} = -\int_0^\rho \frac{G-1}{\rho}\,d\rho - N\frac{G-1}{\rho}\left(\frac{\partial\rho}{\partial N}\right)_{p,T,N_0}$$

Considering the expression for G from (7) and the fact that ρ can be expressed as $vN(vN + v_0N_0)^{-1}$ and, thus, $(\partial\rho/\partial N)_{p,T,N_0} = \rho(1-\rho)/N$, we write:

$$\left(\frac{\partial\ln Q_N}{\partial N}\right)_{p,T,N_0} = -\rho\frac{8-5\rho}{(1-\rho)^2},$$

so that the final representation for φ has the form

$$\varphi = \varphi^\circ + kTF(\rho), \quad F = \ln\rho - \rho + \rho\frac{8-5\rho}{(1-\rho)^2}, \tag{8}$$

which determines the thermodynamic force. The dependence of F on ρ is also shown in Fig. 1.

Thus, we have made the necessary generalization to concentrated dispersions subjected to Brownian motion. The above-calculated addition $\Delta\varphi$ to the chemical potential of the particles of an ideal gas describes the effect of purely geometric factors due to the influence of the excluded volume, i.e., due to the reduction in the fraction of the volume accessible to particles in a concentrated system.

The thermodynamic force $\mathfrak{f}_T$ can also be written in the form $-\nabla(JP)$, where J is a yet-to-be-determined function of ρ. Comparing this expression with P from (7) and comparing the representation for $\mathfrak{f}_T$ from (6) with φ from (8), we arrive at the equation $d(\rho JG)/\partial\rho = \rho dF/d\rho$. From this

$$\rho JG = \int_0^\rho \rho \frac{dF}{d\rho} d\rho = \rho F \Big|_0^\rho - \int_0^\rho F d\rho.$$

Performing calculations with G and F from (7) and (8), we obtain:

$$L = JG = 2\,\frac{\ln(1-\rho)}{\rho} + 3\,\frac{1-2\rho}{1-\rho} + \frac{\rho}{2}\,\frac{15-8\rho-\rho^2}{(1-\rho)^2}, \qquad (9)$$
$$J = (1-\rho)^3(1+\rho+\rho^2-\rho^3)^{-1}L.$$

At $\rho \to 0$, we have $L \to 1$, $J \to 1$. Thus, considering that $kT = m < w_i'^2>$, where w_i' is one of the components of fluctuation velocity, we have the following in a dilute dispersion

$$\mathfrak{f}_T \to -\nabla P \to -\nabla\,[(\rho/v)\,kT] = -\nabla\,(d_1\rho\,\langle w_i'^2\rangle),$$

i.e., we obtain a familiar (and completely natural) representation for this force in terms of the effective pressure of an ideal gas of suspended particles to characterize the momentum flux of the disperse phase due to its fluctuating motion. For a concentrated dispersion, we can write

$$P = d_1\rho G\,\langle w_i'^2\rangle, \quad \mathfrak{f}_T = -\nabla\,(JP) = -\nabla\,(d_1\rho L\,\langle w_i'^2\rangle). \qquad (10)$$

These formulas link the pressure and thermodynamic force directly with the mean squares of the components of fluctuation velocity. Thus, the presence of the effects of the excluded volume in a concentrated dispersion lead to increases in both the pressure of the system of suspended particles and the thermodynamic force acting on them compared to the values of these two quantities that correspond to an ideal gas. The increase in pressure due to crowding is well known for dense gases and is usually described by introducing the concentration-dependent Enskog multiplier χ [11] into the equation of state. This multiplier is formally determined from the equality $1 + 4\rho\chi = G$. An additional multiplier J appears with P in the expression for $\mathfrak{f}_T$ in the approximation being considered. Figure 1 also shows the dependences of J and L on ρ corresponding to (9). The difference of J from unity is connected with the fact that the presence of liquid in the interstices between particles causes the effective properties of the system of suspended particles to differ from the properties of the analogous gas [3]. Another factor in the deviation from unity is the fact that the model being used is approximate [10].

In tensor form, Eqs. (10) can be represented as:

$$P_{ij} = d_1\rho G\,\langle w_i' w_j'\rangle, \qquad (11)$$
$$\mathfrak{f}_{T,i} = -\frac{\partial}{\partial x_j}(JP_{ij}) = -\frac{\partial}{\partial x_j}(d_1\rho L\,\langle w_i' w_j'\rangle),$$

while for Brownian motion $P_{ij} = P\delta_{ij}$. Equations (11) make it possible to generalize the theory to situations in which the particle fluctuations are due to factors other than just Brownian motion and are not necessarily isotropic.

In fact, the functions G, J, and L describe the manner in which the effective thermodynamic characteristics of a system of suspended particles are influenced by purely geometric factors, i.e., the presence of excluded volume and the associated crowding. In a first approximation, they should be independent of the origin and characteristics of the fluctuating motion of the particles if the fluctuations of adjacent particles are not correlative. Given this situation, Eqs. (11) are still valid, as if the tensor $\langle w_i' w_j' \rangle$ of random fluctuating motion did not exist.

If the particle fluctuations are pseudo-turbulent in character and Brownian motion can be ignored, then the tensor $\langle w_i' w_j' \rangle$ is diagonal and axisymmetric in a coordinate system in which one axis is directed along $\mathbf{u}=\mathbf{v}-\mathbf{w}$; the principal values of this tensor were calculated in [4]*

Now let us examine disperse systems in which Brownian motion and pseudo-turbulence are simultaneously important. In this case, fluctuation velocity can be represented in the form $\mathbf{w}'=\mathbf{w}^{(b)}+\mathbf{w}^{(p)}$. The physical mechanisms responsible for generating fluctuations of these two types $\mathbf{w}^{(b)}$ and $\mathbf{w}^{(p)}$ are completely different and are independent of one another. This immediately leads us to the equality

$$\langle w_i' w_j' \rangle = (kT/m)\delta_{ij} + \langle w_i^{(p)} w_j^{(p)} \rangle, \tag{12}$$

which should also be used in (11). Thus, a solution has been found for the problem of determining the thermodynamic force in flows of monodisperse media with sufficiently fine spherical particles.

Let us take a closer look at the particle diffusion caused by Brownian and pseudo-turbulent motion. Here, we should differentiate between self-diffusion — which also takes place in microscopically uniform suspensions and describes the average mixing of the particles relative to their nearest neighbors — and gradient diffusion — which occurs in macroscopically nonuniform dispersions and leads to a nontrivial mean flow of the disperse phase [3]. Coefficients of self-diffusion were calculated in [4] for conditions under which Brownian motion can be ignored.

For simplicity, we will assume that a particle moving relative to its neighboring particles in a macroscopically uniform dispersion is acted upon by a force whose components are dependent on concentration in a manner similar to (3). The linearity of the equation of fluctuating motion obviously allows us to examine $\mathbf{w}^{(b)}$ and $\mathbf{w}^{(p)}$ separately. With allowance for (3), we have the following Lagrangian equation for Brownian motion (we will use a coordinate system connected with the mean motion of the dispersion — when the convective inertial terms can be ignored — and we will take $\mathbf{v}^{(b)} = 0$).

$$m^{(b)} d\mathbf{w}^{(b)}/dt + 6\pi\mu_0 a M \mathbf{w}^{(b)} - \mathbf{R}\{\mathbf{w}^{(b)}\} = \mathbf{A}, \quad m^{(b)} = (1-\rho)\left\{d_1 + \frac{d_0}{2}\left[1 + 3\rho\left(1 + \frac{15}{2}M\right)\right]\right\} v,$$
$$\mathbf{R}\{\mathbf{w}^{(b)}\} = \frac{9}{2}\left[\frac{(1-\rho)M}{\pi}\right]^{1/2}\left(\frac{\mu_0 d_0}{a^2}\right)^{1/2} v \int_{-\infty}^{t} \frac{d\mathbf{w}'}{d\tau}\frac{d\tau}{\sqrt{t-\tau}} \tag{13}$$

Here, $\mathbf{A}$ is an isotropic random force having the spectral properties of white noise, $m^{(b)}$ serves as the effective mass of a particle with allowance for the apparent additional mass and effects connected with the frequency dispersion of viscosity (accounted for in the force f_I in (3) [1]); $\mathbf{R}\{\mathbf{w}^{(b)}\}$ is a functional which describes the effective hereditary Basse force. In the equation for the velocity $\mathbf{w}^{(p)}$ of fine particles which is analogous to (13), it turns out to be possible to use a noninertial approximation, i.e., to ignore all of the components

---

*In these discussions, the hypothesis of the statistical independence of the random forces acting on different particles is important. In pseudo-turbulent motion, these forces are generated by a change in the hydrodynamic situation (by concentration fluctuations) in the neighborhood of the particles. This hypothesis is approximately valid if the linear scale of the fluctuations is on the order of the mean distance between adjacent particles. The study [4] examined motion of this type, which is seen for fairly finely-dispersed suspensions. An increase in particle size and the difference in the densities of the phases are accompanied by the occurrence of correlated fluctuating motion of groups of large numbers of particles and the corresponding large-scale fluctuations (up to the point where gas bubbles are formed in the pseudo-fluidized layers). The theory currently being developed is ultimately inadequate for such flows. This theory must also be invalid for turbulent flows of liquid and gas suspensions in which the scale of the fluctuations is determined by the turbulence structure. In these flows, with large-scale irregularities, the tensors $\langle v_i' v_j' \rangle$ and $\langle w_i' w_j' \rangle$ are introduced into the theory by averaging the momentum conservation equations of the phases and are used to determine the corresponding Reynolds stresses.

of the total force except the viscous component [4]. This cannot be done for $w^{(b)}$ since the characteristic frequency of this random function cannot be considered small.

We use a standard method and represent $w^{(b)}$ and $\mathbf{A}$ in the form of stochastic Fourier–Stieltjes integrals, as was done in [4] for pseudo-turbulent random variables. Here (just to simplify the calculations), we ignore the force $R\{w^{(b)}\}$. We can do this because this force can be regarded as small in the ranges of frequency ω in which one of the two forces—viscous and inertial — remaining in the left side of (13) will be much larger than the other. Then we use (13) to obtain the following for the random measures $dZ_w^{(b)}$ and $d\mathbf{Z}_A$ in the stochastic integrals:

$$(i\omega m^{(b)} + 6\pi\mu_0 aM)\, d\mathbf{Z}_w^{(b)} = d\mathbf{Z}_A$$

and we have the corresponding relation for the spectral densities of the random processes $w^{(b)}$ and $\mathbf{A}$ (compare with [4]):

$$\Psi^{(b)}_{wi,wj}(\omega) = \frac{6\pi\mu_0 aM/m^{(b)}}{\omega^2 + (6\pi\mu_0 aM/m^{(b)})^2}\,\frac{\Psi_{Ai,Aj}(\omega)}{m^{(b)}}. \tag{14}$$

Since the force A is isotropic and has the statistical properties of white noise ($\Psi_{Ai,Aj} = A^2\delta_{ij}$, where A^2 depends on ω), we use the condition

$$m^{(b)}\,\langle w_i^{(b)2}\rangle = m^{(b)}\int_{-\infty}^{\infty}\Psi^{(b)}_{wi,wj}(\omega)\,d\omega = kT$$

to then obtain $A^2 = kT/\pi$. For the Brownian coefficient of self-diffusion, by definition we have

$$D^{(b)} = \pi\Psi_{wi,wi}(0) = D_0/M,\quad D_0 = kT/6\pi\mu_0 a \tag{15}$$

(here, no tensor summation is performed over i). In connection with the assumptions made above, Eq. (15) must ultimately be regarded as sequential estimate of the Brownian self-diffusion coefficient.

It should be emphasized that Brownian self-diffusion of particles is independent of the degree of development of pseudo-turbulence. However, the inverse is not true. In fact, pseudo-turbulent motion is determined by the work of the carrier flow on concentration fluctuations, and the kinetics of the formation and decay of these concentrations depends on the intensity not only of pseudo-turbulent self-diffusion, but also Brownian self-diffusion. Thus, the principal coefficients of pseudo-turbulent self-diffusion $D_{11}^{(p)}$ and $D_{22}^{(p)} = D_{33}^{(p)}$ which figure in the determination of the spectral density of the concentration fluctuations in [4]

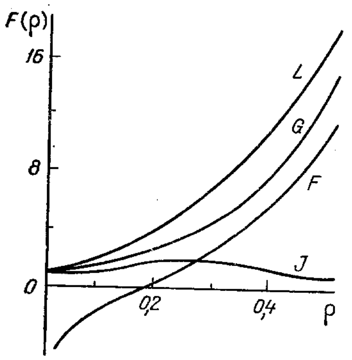

Fig. 1

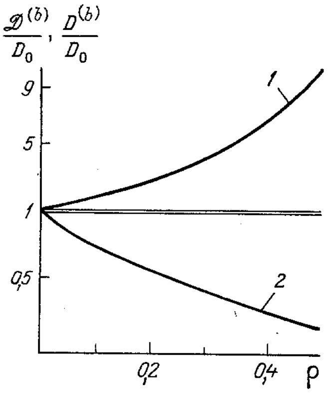

Fig. 2

Fig. 1. Dependence of the introduced functions on the concentration of the suspension.

Fig. 2. Dependences of the dimensionless coefficients of Brownian gradient diffusion (1) and self-diffusion (2) on the concentration of the suspension.

should be replaced by $D_{11}^{(p)} + D^{(b)}$ and $D_{22}^{(p)} + D^{(b)}$ respectivly. Strictly following the method in [4], in the case being examined we obtain the below equations for these coefficients:

$$\begin{gathered}
D_{11}^{(p)} = \frac{(au)^2}{D_{11}^{(p)} - D_{22}^{(p)}} S(\rho)[(1-z)^2 I_0 + 2z(1-z) I_2 + z^2 I_4], \\
D_{22}^{(p)} = \frac{(au)^2}{2(D_{11}^{(p)} - D_{22}^{(p)})} S(\rho) z^2 (I_2 - I_4), \\
S = 3\left(\frac{2}{9\pi}\right)^{2/3} \rho^{4/3} \left(1 - \frac{\rho}{\rho_*}\right)\left(\frac{d \ln M}{d\rho}\right)^2, \\
I_n = \int_0^1 \frac{t^n dt}{t^2 + \gamma^2}, \quad \gamma^2 = \frac{D_{22}^{(p)} + D^{(b)}}{D_{11}^{(p)} - D_{22}^{(p)}}, \quad z = \frac{\rho d_1}{d},
\end{gathered} \tag{16}$$

these equations changing into the analogous equations in [4] at $D^{(b)} = 0$ (when the determination of γ in (16) coincides with the determination in [4]).*

The coefficients of Brownian and pseudo-turbulent gradient diffusion can be calculated by the method proposed and realized for dilute dispersions in [3]. In accordance with this method, the diffusion flux of particles is equal to the convective flux of settling particles under the condition that disperse phase and dispersion medium are acted upon by external forces equal to $\mathbf{H}_0/v_0$ and $\mathbf{H}/v$ when calculated per unit volume of the phases. Omitting the details of the calculations – which are completely analogous to those performed in [3] – we will present results for the coefficient of Brownian gradient diffusion in moderately concentrated dispersions (for which Eqs. (3) are valid)):

$$\mathscr{D}^{(b)} = \frac{\rho}{M} \frac{dF}{d\rho} D_0 \tag{17}$$

as well as results for principal values of the axisymmetric tensor of the coefficients of pseudo-turbulent gradient diffusion (the x_1 axis of the coordinate system being directed along the vector $\mathbf{u}$):

$$\mathscr{D}_{ii}^{(p)} = \frac{1}{6\pi\mu_0 a} \frac{\rho}{M} \frac{d}{d\rho} (Fm \langle w_i^{(p)2} \rangle) = \frac{2\rho}{9M} \frac{d}{d\rho} (F \langle w_i^{(p)2} \rangle) \frac{a^2 d_1}{\mu_0}, \tag{18}$$

where the function F is determined from (8) and no tensor summation is performed in (18). Equations (18) are formally obtained by replacing kT by m $\langle w_j^{(p)} w_j^{(p)} \rangle$, as was done earlier.

The detailed study of pseudo-turbulent diffusion is an independent problem. Here, to illustrate we present only the dependence on ρ of the coefficients $D^{(b)}/D_0$ and $\mathscr{D}^{(b)}/D_0$. For moderately concentrated suspensions, the function M is determined in (3) and has significance for values of ρ that are appreciably smaller than 0.4. To obtain qualitative results for the entire region $0 < \rho < \rho^*$ of concentration, we again use the function $M = -(1-\rho)^{-5/2}$ as a convenient approximation. The relations corresponding to this function are shown in Fig. 2. The character of the relations for the coefficients of self-diffusion and gradient diffusion turn out to be completely different, as was indicated in [3] and several other studies ([12], for example). The increase in $\mathscr{D}^{(b)}$ with an increase in concentration is due to the fact that the effects associated with the excluded volume facilitate the penetration of particles into regions where their concentration is relatively low. Meanwhile, this effect turns out to be greater than the drag effect of the particles in concentrated dispersions.

---

*The kinetics of spreading of the concentration fluctuations in the mean-statistical sense can be described by an effective diffusion equation with a diffusion coefficient dependent on the scale of the fluctuations. It is clear that the limiting value of this coefficient for small scales – when we are actually dealing with displacements of particles relative to their nearest neighbors – should coincide with the self-diffusion coefficient of the particles, while the limiting value for large scales should coincide with the coefficient of gradient diffusion. (The difference between these coefficients is discussed in [3, 12], for example). Since we are discussing pseudo-turbulence generated by the work of the carrier flow on small-scale fluctuation concentrations, it becomes obvious that only the coefficients of pseudo-turbulent self-diffusion – not the coefficients of gradient diffusion – figure in the determination of the spectral density of these fluctuations in [4] and, thus, in (16).

In conclusion, let us make several observations. First of all, since the Perkins—Yevick theory cannot in principle describe a phase transition of the liquid-crystal type in a system of hard spheres, the theory cannot give the concentration ρ^* of the close-packed state; this quantity must be assigned a priori on the basis of additional considerations. Forces associated with the direct contact interaction of particles (such as friction) may become important near a closely-packed region. As was noted in [4], this fact is not accounted for in the theory.

Finally, the thermodynamic force in flows of suspensions and colloidal dispersions is heavily dependent on the chemical potential of the particles. Above, we considered only "geometric" interaction between particles, preventing their overlapping. In actual dispersions, particles also interact as a result of short-range surface forces, the formation of diffuse electric layers near the charged surfaces of particles, dipole forces between magnetized particles, etc. All these factors influence the chemical potential of the particles and, thus, the distribution of their concentration in flows and the properties of the flows. External fields acting on the dispersion also lead to changes in chemical potential. This opens up highly enticing possibilities for controlling the rheological properties of dispersions in flows of different types and for controlling flows by introducing electrolytes and surfacants, superimposing external electromagnetic fields, etc. These topics merit special attention.

NOTATION

a, particle radius; D, $\mathcal{D}$ coefficients of self-diffusion and gradient diffusion; D_0, coefficient of Brownian diffusion of a single particle; d, d_0, d_1, flows of the suspension, liquid, and particle material; F, G, J, L, M, functions of ρ determined in the text; $\mathbf{f}$, phase interaction force; $\mathbf{g}$, acceleration due to external body-force field; $\mathbf{H}$, $\mathbf{H}_0$ thermodynamic force acting on one particle and one molecule, respectively; k, Boltzmann constant; m, m_0, mass of particle and molecule; N, N_0, total number of particles and molecules; n, n_0, numerical concentration of particles and molecules; P, pressure of gas of hard spheres; p, pressure of liquid; Q_N, configurational integral of gas of hard spheres referred to V^N; S, function from (16); T, temperature; $\mathbf{u} = \mathbf{v} - \mathbf{w}$; V, volume of system; $\mathbf{v}$, $\mathbf{w}$, mean velocities of the liquid and disperse phase; $\mathbf{w}'$, fluctuation velocity of particle; v, v_0, volume of particle and molecule; z, parameter introduced in (16); dZ, random measure; α, angle of inclination of channel to the horizontal; γ, parameter introduced in (16); $\varepsilon - 1 - \rho$; μ, μ_0, viscosity of suspension and homogeneous liquid; Π, potential of external body-force field; ρ, volume concentration of particles; φ, φ_0, chemical potential of particles and molecules; Ψ, spectral density; ω, frequency. The superscripts (b) and (p) denote quantities pertaining to Brownian and pseudoturbulent motion; the brackets denote averaging.

LITERATURE CITED

1. Yu. A. Buevich and V. G. Markov, Inzh. Fiz. Zh., 34, No. 6, 1007-1013 (1978).
2. R. I. Nigmatulin, Principles of the Mechanics of Heterogeneous Media [in Russian], Moscow (1978).
3. J. Batchelor, Hydrodynamic Interaction of Particles in Suspensions [Russian translation], Moscow (1980), pp. 84-123.
4. Yu. A. Buevich and A. M. Isaev, Inzh. Fiz. Zh., 57, No. 2, 239-246 (1989).
5. N. A. Slezkin, Dokl. Akad. Nauk SSSR, 77, No. 2, 205-208 (1951).
6. S. V. Vallander, Dokl. Akad. Nauk SSSR, 78, No. 1, 25-28 (1951).
7. I. G. Shaposhnikov, Zh. Éksp. Teor. Fiz., 21, No. 2, 1309-1310 (1951).
8. T. Hill, Statistical Mechanics [Russian translation], Moscow (1960).
9. J. Zaiman, Models of Disorder, Moscow (1982).
10. N. F. Carnahan and K. E. Starling, J. Chem. Phys., 51, No. 2, 635-637 (1969).
11. J. Hirschfelder, J. Curtiss, and R. Baird, Molecular Theory of Gases and Liquids, Wiley, New York (1964).
12. C. W. J. Beenakker and P. Mazur, Phys. Lett., 98A, No. 1-2, 22-24 (1983).