

Because of internal diffusion effects, the rheological equation of state of a suspension of elastic particles has a dispersive form. The characteristic time of the dispersive effect can fall in the range from a fraction of a second to tens of minutes.

The hydromechanical behavior of suspensions is usually described using a continuum approximation involving effective coefficients of viscosity, particle mobility, etc. It is well known that the rheological properties of aggregated colloids depend considerably on the features of their flow [1, 2]. However, in the great majority of papers dealing with the rheology of suspensions of neutral particles, the interactions between which are reduced to hydrodynamic and steric effects, it is assumed that the effective viscosity of the suspension is a constant quantity depending only on the properties of the solvent and the concentration and form of the particles.

It is obvious, as shown first by Batchelor [3, 4], that the effective viscosity of a suspension of spherical particles depends on the magnitude and geometry of the flow. The physical reason for this dependence is that the deforming motion of the suspension tends to deform the equilibrium distribution function of the particles in such a way as to decrease the dissipation of energy of the flow. The Brownian motion of the particles opposes this, tending to make their mutual spacing completely uniform. If the first trend predominates the effective viscosity assumes the minimum possible value for the given suspension. If the second trend predominates then the viscosity is a maximum.

An analysis has been carried out [3, 4] only for suspensions of low concentration, in which it is possible to isolate two interacting particles while neglecting the effect of the other particles on their behavior. In [5, 6] a model has been assumed which makes it possible to evaluate the influence of the Brownian effect in concentrated suspensions. The calculations according to these models are in poor quantitative agreement with comparable experiments [7], in which it has been shown that the low- and high-velocity limits of the effective viscosities of concentrated suspensions differ by several times.

It is not difficult to see that the Brownian effect must lead not only to a dependence of the viscosity on the flow velocity, but also to the appearance of dispersive phenomena in unsteady-state flows of the suspension. In fact, to each value of the tensor of the rate of deformation of the flow  $e$  there corresponds a particular steady-state configuration of the relative arrangement of the particles [3-6]. If  $e$  varies with time, the function of pairwise distribution will follow this change, but because of the finitude of the time of the diffusion processes this following occurs with a delay, which on the macro-level must lead to the appearance of dispersive effects in the rheological behavior of the suspension. In order of magnitude, the characteristic time  $\tau_p$  of such effects must be equal to  $a^2/D \sim 6\pi\eta_0 a^3/T$ . A simple evaluation shows that for aqueous suspensions of micron-sized particles  $\tau_p \sim 10$  sec, while for larger particles ( $a \sim 10 \mu\text{m}$ ),  $\tau_p \sim 10^4$  sec. Hence, the dispersive effects can make themselves felt significantly in real flows. Below an approximate model is proposed for the unsteady-state flow of a suspension of neutral Brownian particles considered as ideal rigid spheres.

By definition, the effective viscosity  $\eta$  is the coefficient of proportionality between the mean deviatoric value of the hydrodynamic stress tensor  $\sigma$  and the rate of deformation  $e$ , i.e.,

$$\sigma = 2\eta e - pI. \quad (1)$$

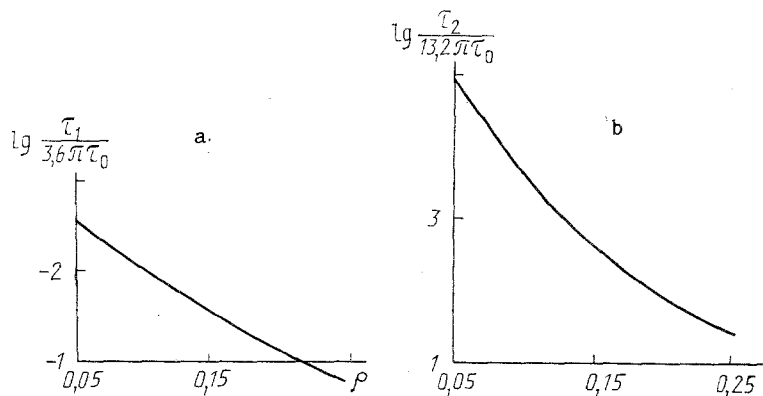


Fig. 1. Dependence of the relaxation time  $\tau_1$  (a) and the memory time  $\tau_2$  (b) on the volumetric concentration of particles  $\rho$ .  $\tau_0 = a^3\eta_0/T$ .

Starting from this definition it is possible by using the well-known method of Eshelby [8] to obtain the expression

$$(\eta - \eta_0) \mathbf{e} \cdot \mathbf{e} = \frac{3\rho}{8\pi a^3} \int_{r=a} (\sigma_{rr}^+ u_r + \sigma_{r\theta}^+ u_\theta + \sigma_{r\varphi}^+ u_\varphi) dr. \quad (2)$$

Here and subsequently the crosses denote the values of the quantities close to an arbitrarily selected (specimen) sphere. The integration in Eq. (2) is carried out over its surface. The subscripts  $r$ ,  $\theta$ , and  $\varphi$  denote the components of the tensors and vectors in a spherical system of coordinates with the origin at the center of the specimen particle. The components of  $\mathbf{e}$  and  $\mathbf{u}$  are interrelated in the standard way. For example, in the Cartesian system of coordinates,

$$e_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right), \quad i, j = x, y, z. \quad (3)$$

It must be emphasized that the mean values of  $\mathbf{e}$  and  $\mathbf{u}$  refer to the suspension as a homogeneous fluid while the quantities indicated by crosses take into account the perturbations introduced by the specimen particle into the corresponding mean field.

As shown in [3-6], the stress  $\sigma^+$  close to the specimen sphere is the sum of the hydrodynamic stress  $\sigma_H^+$  produced by the perturbed stream flowing around the specimen sphere, and the Brownian stress  $\sigma_B^+$ , generated by the diffusional motion of the disperse phase close to the specimen particle.

In order to determine  $\sigma^+$  it is necessary to solve a multiparticle problem taking into account the effects of all the particles on the hydrodynamic conditions close to the specimen sphere. In the general case the exact solution of this problem is no simpler than the detailed description of the flow of many particles. Even for very dilute systems [3, 4] it has not yielded to strictly analytical investigations. In the case of concentrated systems the mathematical complexities which arise become insurmountable.

An approximate analysis can be carried out by using a model of self-consistent fields, where the specimen sphere is assumed to be submerged in a homogeneous medium the properties of which are equivalent to the effective properties of the suspension. Within the framework of this model, the parameter  $\sigma^+$  depends on the effective viscosity  $\eta$  as well as on the parameters which make it possible by using Eq. (2) to obtain an equation relative to  $\eta$  and to calculate it by self-consistent means. As shown in [9] such an approximation corresponds well with experiments for suspensions in which the volumetric concentration of particles  $\rho$  falls in the range 0.2-0.25. Within the framework of this approximation the distribution of the disperse phase in the vicinity of the specimen sphere will comply with the equations of convective diffusion, the solution of which differs considerably at large and small values of the Peclet number. Below we will restrict our attention to an analysis of small flow velocities, when the Brenner number  $Br = \|e\|a^2/D$  (which is the analog of the Peclet number in shear flows) is much smaller than unity.

$$\begin{aligned}
\nabla \sigma_H^+ &= 0, \operatorname{div} \mathbf{u}^+ = 0, r > a; \mathbf{u}^+ = 0, r = a; \mathbf{u}^+ \rightarrow \mathbf{u}, r \rightarrow \infty; \\
\sigma_H^+ &= -p_H^+ \mathbf{I} + 2\eta \mathbf{e}^+; \\
\sigma_B^+ &= \begin{cases} -p_B^+ \mathbf{I}, & r > 2a; \\ -p_B^+(2a) \mathbf{I}, & r \leq 2a; \end{cases} \\
\nabla p_B^+ &= \rho \frac{3}{4\pi a^3} \frac{\partial \mu(\rho)}{\partial \rho} \nabla \rho', r > 2a; \frac{\rho'}{\rho} \sim \operatorname{Br} \ll 1; \\
\sigma^+ &= \sigma_H^+ + \sigma_B^+.
\end{aligned} \tag{4}$$

Here  $\rho^+ = \rho + \rho'$  is the volumetric concentration of the disperse phase close to the specimen particle. The perturbation  $\rho'$  to the equilibrium distribution  $\rho$  can be derived in the model chosen from a solution of the problem of the convective diffusion of the disperse phase close to the specimen sphere, which to a linear approximation with respect to  $\operatorname{Br}$  can be written as:

$$\begin{aligned}
\frac{\partial \rho'}{\partial t} &= D \Delta \rho', r > 2a, \\
-D \frac{\partial \rho'}{\partial r} + \rho u_r^+ &= 0, r = 2a; \rho' \rightarrow 0, r \rightarrow \infty.
\end{aligned} \tag{5}$$

The first boundary condition here follows from the fact that the particles cannot overlap, as a result of which the normal component of the diffusion flux of the disperse phase on the specimen sphere at  $r = 2a$  (i.e., when the particles are as close together as is possible) is equal to zero. The second boundary condition is a consequence of the principle of correlation attenuation.

The right side of Eq. (2) is denoted by  $J$  and is represented in the form of two terms

$$\begin{aligned}
J &= J_H + J_B, \\
J_H &= \frac{3\rho}{8\pi a^3} \int_{r=a} (\sigma_{Hr}^+ u_r + \sigma_{Hr\theta}^+ u_\theta + \sigma_{Hr\varphi}^+ u_\varphi) dr; \\
J_B &= \frac{3\rho}{8\pi a^3} \int_{r=a} \sigma_{Brr}^+ u_r dr.
\end{aligned} \tag{6}$$

The condition for using the continuum approximation is the smallness of the particle size compared with the scale of measurement of  $\mathbf{u}$ , which is assumed. In this case it can be assumed that close to the specimen particle

$$\mathbf{u} = e \mathbf{r}. \tag{7}$$

For clarity it will be assumed that  $e$  is represented in the form

$$e_{xx} = e, e_{yy} = -e, e = \text{const}, \tag{8}$$

and that all the other components  $e_{ij}$  in the Cartesian system of coordinates with the origin at the center of the particle are equal to zero. Here the choice of Eq. (8) has been made in order to facilitate the calculations. Its specific variant cannot influence the final solution of the problem.

The determination of  $\sigma_H^+$  from Eq. (4) with the conditions (7) and (8) does not differ from the solution of the classical problem of Einstein on the state of the deformational flow close to a single particle (see, for instance, [3, 10]). The only difference (but one which is absolutely non-essential) consists of the fact that the effective viscosity  $\eta$  of the suspension appears in Eq. (4), and not the viscosity of the dispersing medium  $\eta_0$ , as in [3, 10]. By using the classical result it is possible to write directly

$$J_H = \frac{5}{2} \rho \eta e \cdot e. \quad (9)$$

In order to calculate  $\sigma_B^+$  and  $J_B$ , it is necessary, as can be seen from Eq. (4), to determine the hydrodynamic perturbation  $\rho'$  to the equilibrium concentration of the disperse phase close to the specimen sphere, which coincides with  $\rho$  within the framework of the model which has been chosen. The function  $\rho'$  can be estimated approximately from Eq. (5). In order to solve this problem use is made of a Fourier transform with respect to time, which leads to the replacement of the operator  $\partial/\partial t$  by the multiplier  $i\omega$ , where  $i = \sqrt{-1}$ , and  $\omega$  is the Fourier frequency. By introducing a spherical system of coordinates with the origin at the center of the particle and a polar axis directed along  $z$ , and using (7) and (8), it is found from Eq. (4) that

$$u_r^+ = U(r) \sin^2 \theta \cos 2\varphi, \quad r > a; \quad (10)$$

$$U(r) = \left[ 1 - \frac{5}{2} \left( \frac{a}{r} \right)^3 + \frac{3}{2} \left( \frac{a}{r} \right)^5 \right] e^{\kappa r}.$$

It then follows from Eq. (5) that

$$\rho' = Bh(r) \sin^2 \theta \cos 2\varphi, \quad h(r) = r^{-1/2} H_{5/2}(\kappa r), \quad (11)$$

$$\kappa = \sqrt{i \frac{\omega}{D}},$$

where  $H_{5/2}$  is a Hankel function of the first type, and  $B$  is an integration constant which is determined from the boundary condition (5):

$$B = \rho \frac{U(2a)}{f(2a)}, \quad f = \frac{\partial}{\partial r} h. \quad (12)$$

Taking into account that  $D = \beta \rho \partial \mu / \partial \rho$  [11], where  $\beta(\rho)$  is the hydrodynamic mobility of the particles under hindered conditions, it is found from Eqs. (11) and (12), using the explicit form of the Hankel function, that

$$\sigma_{Brr}^+|_{r \leq 2a} = -\rho \frac{Uh}{\beta f} \sin^2 \theta \cos 2\varphi, \quad (13)$$

$$U, h, f \equiv \{U, h, f\}(2a).$$

By substituting Eq. (13) into the integral  $J_B$  in Eq. (6), and using the representation  $u_r = e^{\kappa r} \sin^2 \theta \cos 2\varphi$ , obtained from Eqs. (7), (8) by the standard conversion from the Cartesian system of coordinates to spherical coordinates, it is found after simple computations that

$$J_B = \rho^2 \frac{81}{20} \eta \frac{3 + 3\xi + \xi^2}{9 + 9\xi + 4\xi^2 + \xi^3}, \quad \xi = 2\kappa a, \quad (14)$$

where for evaluating  $\beta$  use is made of the formula  $\beta = (6\pi\eta a)^{-1}$  [7].

By substituting Eqs. (9), (14) into Eq. (6) and also into Eq. (2), a Fourier representation is obtained for  $\eta$ :

$$\eta = \frac{\eta_0}{1 - \frac{5}{2} \rho - \rho^2} \frac{81}{20} \frac{3 + 3\xi + \xi^2}{9 + 9\xi + 4\xi^2 + \xi^3},$$

$$\xi = 2a \sqrt{i \frac{\omega}{D}} = 2a \sqrt{i \frac{6\pi\eta a \omega}{\rho \frac{\partial \mu}{\partial \rho}}}. \quad (15)$$

In principle it is possible to find  $\eta$  as a function of  $\rho$  and  $\omega$  from the system (15). In the absence of the Brownian effect ( $J_B = 0$ ) instead of Eq. (15) the formula  $\eta = \eta_0(1 - \frac{5}{2}\rho)^{-1}$  is found, which was obtained earlier in [7, 12]. In the steady state ( $\omega = 0$ ), the formula of [5] is obtained from Eq. (15).

The fact that  $\eta$  depends on  $\omega$  means that in unsteady-state flows dispersive effects appear. For harmonic processes the rheological equation of state has the form

$$\tilde{\sigma}(\omega) = 2\eta(\omega) e(\omega) \quad (\tilde{\sigma} = \sigma + p\mathbf{1}). \quad (16)$$

In the general case the relationship between  $\sigma$  and  $e$  is obtained from Eq. (16) by means of the inverse Fourier transform

$$\tilde{\sigma} = \frac{1}{\pi} \int_{-\infty}^{+\infty} \eta(\omega) e(\omega) \exp(-i\omega t) d\omega. \quad (17)$$

The system (15) reduces to an algebraic equation of the fifth power with respect to  $\sqrt{\eta}$ , so that it cannot be solved in terms of roots. However, it is not difficult to analyze Eq. (15) by numerical methods, and the same is true for the numerical inversion of (17).

The limiting situations  $\xi \ll 1$  and  $\xi \gg 1$  are considered below. In the first case after simple computations to an accuracy of  $\xi^2$  it is found that

$$\eta = \eta^\circ \left( 1 - \frac{1,35\eta^\circ}{\eta_0} \frac{\xi^2}{9} \right) \equiv \eta^\circ (1 - i\omega\tau_1), \quad (18)$$

$$\tau_1 = 3,6\pi\rho^2 \left( \frac{\eta^\circ}{\eta_0} \right)^2 \frac{1}{\rho \frac{\partial v}{\partial \rho}} \frac{a^3\eta_0}{T}, \quad \eta^\circ = \frac{\eta_0}{1 - 2,5\rho - 1,35\rho^2}, \quad v = \frac{\mu}{T}.$$

By substituting Eq. (18) into Eq. (16) it is found that to within the accuracy chosen,

$$(1 + \tau_1 i\omega) \tilde{\sigma} = 2\eta^\circ e$$

or after the inverse Fourier transformation (17),

$$\left( 1 + \tau_1 \frac{\partial}{\partial t} \right) \tilde{\sigma} = 2\eta^\circ e. \quad (19)$$

It can be seen from Eq. (19) that the stress  $\tilde{\sigma}$  relaxes to the rate of deformation of the flow  $e$  with a relaxation time  $\tau_1$ , the dependence of which on  $\rho$  is shown in Fig. 1a. Here and subsequently the chemical potential  $\mu$  is used in the calculations in the form [13] obtained from the equation of state of a gas consisting of solid spheres in the Carnahan-Starling variant [14]:

$$\mu = T \left[ \ln \rho - \rho + \rho \frac{8 - 5\rho}{(1 - \rho)^2} \right].$$

From Fig. 1a it can be seen that  $\tau_1$  decreases very rapidly as the volumetric concentration of the solid phase decreases, so that for dilute systems the relaxational effects are practically not observed, though they can be significant for concentrated media.

In the quasi-steady-state regime ( $\xi \rightarrow 0$ ) Eq. (19) assumes the non-Newtonian form:

$$\tilde{\sigma} = 2\eta^0 e.$$

In the high-frequency approximation ( $\xi \gg 1$ ) it is found to an accuracy of  $\xi^{-1}$  from Eqs. (15), (16) that

$$\tilde{\sigma} = 2\eta^\infty \left( 1 + \frac{1}{\sqrt{i\omega\tau_2}} \right) e, \quad (20)$$

$$\tau_2 = 13,2\pi \frac{1 - 2,5\rho}{\rho^5 \frac{\partial v}{\partial \rho}} \frac{a^3 \eta_0}{T}, \quad \eta^\infty = \frac{\eta_0}{1 - 2,5\rho}.$$

By applying the inverse Fourier transformation to Eq. (20) the following equation of state is found

$$\tilde{\sigma}(t) = 2\eta^\infty \left( e(t) + \frac{1}{\sqrt{\pi\tau_2}} \int_0^t \frac{e(s)}{\sqrt{t-s}} ds \right). \quad (21)$$

Thus, when the conditions are significantly unsteady-state in nature the flow of the suspension depends on its previous history with a characteristic memory time  $\tau_2$ . Figure 1b shows the dependence of  $\tau_2$  on  $\rho$ . In the case of the limitingly rapidly varying process ( $\xi \rightarrow \infty$ ), Eqs. (20) and (21) undergo transition to the Newtonian equation of state

$$\tilde{\sigma} = 2\eta^\infty e,$$

but with an effective viscosity of  $\eta^\infty$  rather than  $\eta^0$ , as at  $\xi \rightarrow 0$ . It will be recalled that this same value of the effective viscosity, equal to  $\eta^\infty$ , was obtained in [9, 12], where the Brownian effect was not taken into account. The physical reason for this agreement is that for  $\tau_2\omega \rightarrow \infty$  the diffusion effects do not have time to appear in a time of the order of  $\omega^{-1}$ \*

It can be seen from Fig. 1b that as  $\rho$  decreases the time  $\tau_2$  increases very rapidly. Thus, in experiments carried out on suspensions of low concentration memory phenomena are not able to appear, and Newtonian behavior is detected in the experiment with an effective viscosity of  $\eta^\infty$ .

In the case of small values of  $\rho$  the analysis of Eqs. (15), (17) can be carried out for any value of  $\xi$ . Limiting ourselves to accuracies up to  $\rho^2$  inclusively, it is assumed in Eq. (15) that

$$\xi = 2a \sqrt{\frac{6\pi\eta_0 a}{T} i\omega}.$$

\*It must be stressed that the use of relationships (19) and (21) is valid only for quasi-steady-state and rapidly varying flows respectively. For example, after a stepwise change of  $e$  to some constant value the establishment of the steady-state value of  $\tilde{\sigma}$  will occur in three stages: the initial stage (rapid change of  $\tilde{\sigma}$ , for which Eq. (21) holds true), the final stage (slow change of  $\tilde{\sigma}$ , for which Eq. (19) holds true), and an intermediate stage, for which it is necessary to use the general equation of state, Eq. (17). Naturally, the total time for establishing the steady-state value of  $\tilde{\sigma}$  does not coincide with either  $\tau_1$  or  $\tau_2$ .

By substituting Eq. (15) with this value of  $\xi$  into Eq. (16), reducing the equation which is obtained to a common denominator, and transforming from the Fourier representation to the original variables, the rheological equation can be written as

$$\begin{aligned} & \left[ (1 - 2,5\rho - 1,35\rho^2) \left( 1 + \sqrt{\frac{\tau_3}{\pi}} \int_0^t \frac{\partial/\partial s}{\sqrt{t-s}} ds \right) + \left( \frac{4-10\rho}{9} - \right. \right. \\ & \quad \left. \left. - \frac{1,35}{3} \rho^2 \right) \tau_3 \frac{\partial}{\partial t} + \frac{1-2,5\rho}{9\sqrt{\pi}} \tau_3^{\frac{3}{2}} \int_0^t \frac{\partial^2/\partial s^2}{\sqrt{t-s}} ds \right] \sigma = \\ & = 2\eta_0 \left( 1 + \sqrt{\frac{\tau_3}{\pi}} \int_0^t \frac{\partial/\partial s}{\sqrt{t-s}} ds + \frac{4}{9} \tau_3 \frac{\partial}{\partial t} + \frac{1}{9\sqrt{\pi}} \tau_3^{\frac{3}{2}} \int_0^t \frac{\partial^2/\partial s^2}{\sqrt{t-s}} ds \right) \mathbf{e}, \\ & \quad \tau_3 = \frac{24\pi\eta_0 a^3}{T}, \end{aligned}$$

which contains both relaxational and memory components.

In conclusion it must be stressed that here only relatively slow flows have been considered such that  $Br \ll 1$ . If this inequality is not satisfied there must be other dispersive effects.

#### NOTATION

$a$ , particle radius;  $D$ , coefficient of Brownian diffusion of the particles;  $\mathbf{e}$ , tensor of the rate of deformation of the flow;  $\|\mathbf{e}\|$ , norm of the tensor  $\mathbf{e}$ ;  $\mathbf{I}$ , unit tensor of the second rank;  $p$ , pressure;  $\mathbf{u}$ , flow velocity of suspension;  $T$ , absolute temperature in energy units;  $\eta$ ,  $\eta_0$ , effective viscosity of suspension and viscosity of dispersing liquid;  $\rho$ , volumetric concentration of disperse phase;  $\mu$ , chemical potential of particle;  $\sigma$ , stress;  $\bar{\sigma}$ , deviator part of  $\sigma$ ; superscript crosses denote the values of quantities close to the specimen particle.

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