RHEOLOGICAL PROPERTIES OF FINELY DISPERSED SUSPENSIONS

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The influence exerted by the physical interaction of particles, their Brownian motion, and the fluctuations in porosity on the effective viscosity of suspensions and colloids is evaluated.

A fundamental problem, not yet rigorously solved, pertaining to the physical mechanics of mixtures, involves the problem of determining the effective characteristics of a disperse medium on the basis of the known features of its structure at the level of individual particles. Analysis of the rheological properties of suspensions in most of the works with which we are familiar is limited to an investigation of two extreme cases. First of all, the investigation involves a system of neutral particles where interaction arises between these particles only as a consequence of perturbations which they themselves have introduced into the flow of the carrier fluid. Secondly, the investigations deal with strongly structured colloids, and their flow is described by means of various modifications of the Frenkel–Eyring theory [1, 2]. Here the location of the particles and their concentration in each region of space is assumed to be determined by the characteristics of the medium.

Real suspensions and colloids are more complex systems than is assumed within the framework of such idealizations. Thus, the molecular and hydrodynamic interaction between particles may be comparable. It is not evident in advance that they combine to achieve a total hydrodynamic stress, as was assumed in [1]. There have been virtually no studies into the influence exerted by the Brownian motion in finely dispersed suspensions on the rheological properties of these suspensions [3, 4]. Within the scope of a single physicomathematical model it is impossible to take into consideration the great multiplicity of mechanisms affecting the rheology of disperse systems. In the following we will individually examine the influence of the combined molecular and hydrodynamic interactions of particles, as well as certain of the consequences resulting from their Brownian motion on the effective viscosity of suspensions and colloids. The particles are represented by identical solid spheres, and the dispersion fluid is assumed to be Newtonian and incompressible.

Physical Particle Interaction. We are quite familiar with the fact that the energy of interaction between the colloidal particles, as a function of the distance between the particles, is a nonmonotonic function. Therefore, in the motion of a particle along a layer of other particles, said particle will have to overcome a "potential crest" (see Fig. 1). A portion of the flow energy, which is dissipated into heat, is spent on overcoming these potential barriers, thus leading to an increase in the effective viscosity of the suspension, relative to the situation in which there is no potential interaction between the particles.

In continuous approximation the flow of an incompressible suspension can be described by means of the following equations:

$$-\nabla p+\nabla\sigma,\ \operatorname{div}\mathbf{v}=0,\ \sigma=2\eta\mathbf{e},\ \sigma=\sigma_h+\sigma_f,\ \eta=\eta_h+\eta_f. \tag{1}$$

Here σ_h and σ_f represent the deviator components of the mean stress $\sigma-p\mathbf{I}$, ascribed to the hydrodynamic effects and molecular interparticle interaction, respectively. The strain rate tensor $\mathbf{e}$ is associated in the usual fashion with the average velocity of the flow [5].

The effective viscosity η of the suspension represents the sum of the "hydrodynamic" viscosity η_h, i.e., a factor of proportionality between σ_h and e, as well as of the "molecular" viscosity linking σ_f to e. The "hydrodynamic" viscosity η_h can be calculated from the following relationship which flows directly out of its definition [6, 7]:

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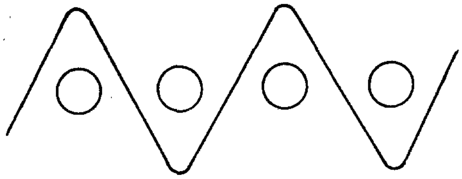

Fig. 1. Schematic representation of the "crests" of potential barriers, formed by an isolated layer of particles.

$$2(\eta_h - \eta_0)\mathbf{e} = \frac{3\rho}{4\pi a^3} \int\limits_{r \leqslant a} \mathbf{\Sigma}^* d\mathbf{r}, \tag{2}$$

where $\mathbf{\Sigma}^*$ represents the total stress within some arbitrary test particle, and which arises in the shear flow of the suspension, with an average strain rate tensor $\mathbf{e}$.

It is convenient to transform the volume integral (2) into a surface integral, for which purpose we will write

$$\int\limits_{r \leqslant a} \mathbf{\Sigma}^* d\mathbf{r} = \int\limits_{r \leqslant a} (\nabla : \mathbf{r}\mathbf{\Sigma}^* - \mathbf{r} : \nabla\mathbf{\Sigma}^*)\, d\mathbf{r},$$

where : represents dyad multiplication. Having subsequently applied the Ostrogradskii–Guass theorem, bearing in mind that in steady-state processes $\nabla\Sigma^* = 0$, and also taking into consideration the continuity of the force density at the surface of the particle, we obtain

$$\int\limits_{r \leqslant a} \mathbf{\Sigma}^*_{ij} d\mathbf{r} = \frac{1}{a} \int\limits_{r=a} \mathbf{r}_i \mathbf{r}_k (\sigma^+_{kj} - p^+ \delta_{ik})\, d\mathbf{r},\ i,\ j,\ k = x,\ y,\ z, \tag{3}$$

where δ_{ik} is the Kronecker delta.

The parameter η_f, generated by the scattering of the flow energy as the particles skip through the potential barriers, is evaluated in the Eyring–Frenkel theory (see, for example [1]). Thus, as we can see from (1)-(3), to determined the effective viscosity η of the suspension it is necessary to find the stress $\sigma^+ - p^+\mathbf{I}$ near the surface of the test particle. It is impossible to achieve an exact solution for this problem because of the need to take into consideration the presence of numerous particles in the vicinity of the test sphere. Later on we will make use of an approximation of a self-consistent field within whose scope it is assumed that the isolated particle is submerged into a uniform medium whose properties coincide with the effective properties of the suspension, while the structure of the flow at an infinite distance from the test sphere is specified on the basis of the average values of $\mathbf{v}$ and $\mathbf{e}$. It has been demonstrated in [8] that such an approximation gives good results when $\rho \leq 0.20$-0.25. It is additionally assumed that the relationship between η_f and $\mathbf{e}$ can be neglected in the vicinity of the test sphere.

Within the framework of the approximations adopted here, the problem of a test particle is formulated in precisely the same way as in [8]:

$$\begin{gathered} -\nabla p^+ + \eta\Delta\mathbf{v}^+ = 0;\ \operatorname{div}\mathbf{v}^+ = 0,\ r > a;\ \ \mathbf{v}^+\mathbf{n} = 0,\ \ r = a;\ \ \sigma^+\mathbf{n} - \mathbf{I}p^+ = \mathbf{\Sigma}^*\mathbf{n}, \\ r = a;\ \mathbf{v}^+ \to \mathbf{v} - \mathbf{v}_1 + \mathbf{e}\mathbf{r},\ r \to \infty;\ \sigma^+ = 2\eta\mathbf{e}^+;\ \eta = \eta_h + \eta_f, \end{gathered} \tag{4}$$

where $\mathbf{v}_1$ is the velocity of motion for the test sphere. In the absence of mass forces we have $\mathbf{v} = \mathbf{v}_1$. The plus sign here denotes the corresponding quantities near the test particle, and the tensor $\mathbf{e}^+$ is associated with $\mathbf{v}^+$ just as $\mathbf{e}$ is associated with $\mathbf{v}$. After calculations analogous to those performed in [8], we will determine the values of σ^+ and p^+, dependent on η as well as on the parameter, and then we will find from (3) that

$$\eta_h = \frac{\eta_0 + 2.5\rho\eta_f}{1 - 2.5\rho},\quad \eta = \frac{\eta_0 + \eta_f}{1 - 2.5\rho}. \tag{5}$$

We can see from (5) that when $\eta_0 \ll \eta_f$ the total viscosity of the colloid is not equal to the magnitude of η_f determined from the analogy between the colloid and the molecular fluid. This can be explained by the fact that in the shear flow of the suspension mechanical stresses Σ^* are generated within the particles, and these contribute to the average stress σ and have not been taken into consideration in the Eyring theory.

<u>Brownian Particle Motion.</u> The strain of the suspension leads to a change in the configuration of the particles relative to their equilibrium position [3]. The diffusion pro-

cesses in turn seek to cause this configuration to become uniform. The "diffusion stresses" which arise in this case increase the dissipation of the mechanical energy of the flow, as a consequence of which the effective viscosity of the suspension increases. Such phenomena were initially analyzed in [3] for exceedingly dilute systems. In the following we will examine moderately concentrated suspensions.

We will once again calculate the effective viscosity with formulas (2) and (3). To determine Σ^* we will formulate the problem dealing with the streamlining of the test particle in a uniform medium, where the properties of the medium coincide with the effective properties of the suspension (we will not take into consideration the nonhydrodynamic interaction of the particles, and therefore $\eta_f = 0$). This problem is analogous to (4); however, the diffusion effects must be taken into consideration here.

As was demonstrated in [3], the Brownian diffusion flow is equal to the one which arises in the suspension in which Brownian motion is absent, but where each particle is acted on by a thermodynamic force $\mathbf{f}_t$, equal to

$$\mathbf{f}_t = -\beta^{-1}\frac{D}{\rho}\nabla\rho, \tag{6}$$

and here β^{-1} is the coefficient of hydrodynamic particle mobility under restricted conditions, with D representing the coefficient of particle diffusion. The force $\mathbf{f}_t$ is balanced by the force of interphase interaction $\mathbf{f}_h=\beta^{-1}(\mathbf{v}-\mathbf{v}_1)$, where $\mathbf{v}_1$ once again represents the velocity of the particle. Therefore

$$\beta^{-1}(\mathbf{v}-\mathbf{v}_1)-\beta^{-1}\frac{D}{\rho}\nabla\rho = 0. \tag{7}$$

Within the scope of the approximation for the self-consistent field we will assume that near the test sphere all of the remaining particles are acted on by the forces $\mathbf{f}_t^+$ and $\mathbf{f}_h^+$, and these are of the same form as $\mathbf{f}$ and $\mathbf{f}_h$, with the average values of $\rho, \mathbf{v}$, and $\mathbf{v}_1$ replaced by the corresponding quantities $\rho^+, \mathbf{v}^+$, and $\mathbf{v}_1^+$ near the test particle. We will then write

$$\rho^+ = \rho + \rho', \tag{8}$$

where ρ' is an addition to the equilibrium concentration due to the convective motion of the suspension near the test sphere. This function can be determined from the condition of particle flow continuity $\mathbf{j}^+ = \rho^+\mathbf{v}_1^+$ near the test particle. The solution for the equation div $\mathbf{j}^+ = 0$ coincides with the equation for the convective diffusion near the test sphere. In the following we will examine only the very slow flows in which the Peclet number Pe, equal to $|\mathbf{v}-\mathbf{v}_1|aD^{-1}$ and $\|\mathbf{e}\|a^2D^{-1}$ ($\|\mathbf{e}\|$ i.e., the norm of the tensor $\mathbf{e}$) is considerably smaller than unity. In this case, in terms of order of magnitude, $\rho'/\rho \sim \mathrm{Pe} \ll 1$.

In linear approximation of Pe the equation for the balance of forces acting on the particle near the test sphere is written as follows:

$$-\beta^{-1}\frac{D}{\rho}\nabla\rho' + \beta^{-1}(\mathbf{v}^+ - \mathbf{v}_1^+) = 0. \tag{9}$$

The thermodynamic force acting on the particle per unit volume of the mixture is written in the form of the pressure gradient ∇p_B^+, which we will refer to as Brownian

$$n\mathbf{f}_t^+ = -\nabla p_B^+ = -\beta^{-1}n\frac{D}{\rho}\nabla\rho', \quad n = \frac{3}{4\pi a^3}\rho, \tag{10}$$

where n is the numerical concentration of the particle.

Because of the impermeability of the particles the radial velocity v_{1r}^+ is equal to zero when $r = 2a$, i.e., when the nearest spheres are in contact with each other. According to Newton's third law, the particles which are brought to a stop near the test sphere act on that sphere with a force $-n\mathbf{f}_t^+ = \nabla p_B^+$. The second of the boundary conditions in (4) must therefore now be rewritten as follows:

$$\sigma^+\mathbf{n} - (p_B^+ + p^+)\mathbf{I} = \Sigma^*\mathbf{n}, \tag{11}$$

and in integral (3) in the place of p^+ we have to write the sum $p^+ + p_B^+$.

We note immediately that in the layer $a < r < 2a$ the dispersion phase executes no radial motion, and p_B^+ is therefore constant for $a < r < 2a$.

We determine the concentration ρ' from the linearized equation of diffusion and from the condition $v_{1r}^+ = 0$ for $r = 2a$, which in combination with (9) yields

$$\Delta\rho' = 0,\ r > 2a;\ -\frac{D}{\rho}\,\frac{\partial\rho'}{\partial r} + v_r^+ = 0,\ r = 2a. \tag{12}$$

To determine p^+, p_B^+, σ^+ we again specify the tensor $\mathbf{e}$ and solve (4) in a manner analogous to the way this was done earlier (it should be remembered that now $\eta_f = 0$). Having determined the velocity $\mathbf{v}^+$, from the first three equations in (4), from (12) we find ρ', after which we calculate p_B^+ from (10), with p_B^+ corresponding to ρ' when $r = 2a$. After the calculations, from (2), (3), we arrive at an equation for the effective viscosity, namely:

$$\eta = \eta_0 + \frac{5}{2}\rho\eta + \frac{9}{40\pi\beta}\rho^2. \tag{13}$$

We will now find the mobility β of the particles. This quantity is defined as a proportionality factor between the relative velocity of the particle and the suspension $\mathbf{v}-\mathbf{v}_1$ and that force acting on the particle. Taking into consideration the Brownian pressure p_B^+ after application of standard concepts [5] we obtain

$$\beta^{-1}(\mathbf{v}-\mathbf{v}_1) = \int\limits_{r=a} [(\sigma_{rr}^+ - p^+ - p_B^+)\cos\theta - \sigma_{r\theta}^+\sin\theta]\,d\mathbf{r}, \tag{14}$$

where the integration is conducted over the surface of the test sphere and θ represents the angle between the direction of the vector $\mathbf{v}-\mathbf{v}_1$ and the radius vector directed from out of the center of sphere to some point on its surface.

To determine β we will specify the vector $\mathbf{v}-\mathbf{v}_1$ in (4) and assume that $\mathbf{e} = 0$. Subsequent to the calculations we obtain the following equation for β:

$$\beta^{-1} = 6\pi\eta a + \frac{8}{5}\pi a\rho\beta^{-1}. \tag{15}$$

Having combined (13) and (15), we obtain

$$\eta = \frac{\eta_0}{1 - 2{,}5\rho + 1{,}35\rho^2(1 - 1{,}2\rho)^{-1}},\quad \beta = \frac{1 - 1{,}2\rho}{6\pi\eta a}. \tag{16}$$

Within the scope of this same self-consistancy model, but without consideration of the Brownian motion, it was found in [8] that

$$\eta = \frac{\eta_0}{1 - 2{,}5\rho},\quad \beta = \frac{1}{6\pi\eta a}. \tag{17}$$

If we compare (16) and (17), we see that the Brownian diffusion elevates the effective viscosity of the suspension and reduces particle mobility. For suspensions that are weakly concentrated ($\rho \ll 1$) the correction factor $\delta\rho$, introduced through Brownian motion into the effective viscosity η and determined by comparison of (16) and (17), is equal to $\delta\eta \approx 1.35\rho^2$, which is in rather good agreement with the analogous correction factor found in [3] and equals to $0.97\rho^2$. The difference in our results for $\rho \ll 1$ from the rigorous formula in [3] is explained by the fact that in the selected version of the self-consistancy model the correlations in the positions of the particles in the formulation of (4) are neglected. It is the intention of the authors to undertake a more exact calculation in the future to make provision for these correlations.

Velocity Fluctuations. The fluctuations in the concentration of the dispersed phase introduce additional perturbations into the flow of the suspension, which leads to an increase in its effective viscosity. Apparently, the influence of such processes on the rheological properties of suspensions was initially analyzed in [9]. However, only small fluctuations were dealt with in [9], these arising in neutral syspensions or in colloids whose state was considerably distant from the critical point of transition between sol and gel.

It is a well-known fact that on approach to the critical point the fluctuations in concentration and the radius of their correlations increase.

We note from the experiment described in [10, 11] that the viscosity of the molecular solution near the critical point of condensation for a dissolved substance increases markedly. It has been demonstrated experimentally in [12] that near the critical point of stratification in a magnetic fluid the coefficient of sound attenuation increases anomalously, which can be explained by the substantial increase in the viscosity of the ferrocolloid. The physical mechanism responsible for the unique features of the critical behavior in the viscosity of solutions and colloids must be identical and associated with the great fluctuations in the concentration of dissolved molecules or impurity particles. We will subsequently examine the state of the colloid near the critical point of stratification, assuming that the correlation radius R between the positions of the particles is very large.

Analysis of the situation arising here will be conducted by the scaling method [13]. We will divide the volume occupied by the suspension into cubic blocks of ℓ such that in each block numerous particles are contained, but $\ell \ll R$. Then we will combine these blocks into others, with sides L, and $\ell \ll L \ll R$. We will use appropriate subscripts to denote the average quantities referred to the blocks ℓ and L, and we will write

$$\sigma_l = \eta_l(\delta\rho_l)\mathbf{e}_l, \quad \sigma_L = \eta_L(\delta\rho_L)\mathbf{e}_L, \tag{18}$$

$$\delta\rho_i = \frac{\rho_i - \rho_c}{\rho_c}, \quad i = l, \ L,$$

where ρ_c is the critical concentration of the dispersed phase.

In accordance with the theory of similarity [13] we will assume that $\mathbf{e}_l$ and $\delta\rho_\ell$ are linear functions of $\mathbf{e}_L$ and $\delta\rho_L$, respectively, i.e.:

$$\mathbf{e}_l = \lambda^x \mathbf{e}_L, \quad \delta\rho_l = \lambda^y \delta\rho_L, \tag{19}$$

where $\lambda = \ell/L$, while x and y are quantities as yet unknown.

Within the framework of equilibrium similarity theory [13] we will assume that the thermodynamic potential of the system, an additive quantity, assumes an identical value, regardless of the dimensions of the blocks on the basis of which it was calculated. Analogous considerations allow us to state that the dissipative function of the system determined with blocks ℓ and L must be one and the same, i.e.:

$$\sum_l \sigma_l \mathbf{e}_l l^3 = \sum_L \sigma_L \mathbf{e}_L L^3, \tag{20}$$

which we will adopt as our hypothesis.

Equation (20) can be satisfied if we assume that

$$\sigma_l \mathbf{e}_l = \sigma_L \mathbf{e}_L . \tag{21}$$

If we substitute (18) into (21) and make use of (19), we obtain

$$\eta_L(\delta\rho_L) = \lambda^{2x}\eta_l(\lambda^y \delta\rho_L). \tag{22}$$

As $R/a \to \infty$, the choice of λ becomes arbitrary. Therefore, we will assume that $\lambda = (\delta\ell_L)^{-1/y}$. It then follows from (22) that

$$\eta_L(\delta\rho_L) = (\delta\rho_L)^{-2\frac{x}{y}} \eta_l(1). \tag{23}$$

It is clear from physical considerations that if $\delta\rho_L \neq 0$, the viscosity η_L is finite and that therefore the value of η_ℓ from (1) is finite. We will now determine the signs of the exponents x and y. We will write the correlation function

$$\Gamma_l(\mathbf{r}_l) = \langle \mathbf{e}_l(\mathbf{r}_l)\mathbf{e}_l(0) \rangle . \tag{24}$$

Using the concepts of similarity once again, we assume that Γ_ℓ is functionally dependent on $\mathbf{r}_l$, just as the correlator $\Gamma_L = \langle \mathbf{e}_L(\mathbf{r}_L)\mathbf{e}_L(0) \rangle$ depends on $\mathbf{r}_L$, if $\mathbf{r}_l = \lambda\mathbf{r}_L$. It follows from the definition of Γ_ℓ and Γ_L, as well as from (19) that

$$\Gamma_L(\mathbf{r}_L) = \lambda^{-2x}\Gamma_l(\lambda\mathbf{r}_l). \tag{25}$$

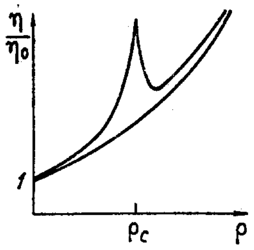

Fig. 2. Schematic diagram representing the behavior of effective colloid viscosity with an increase in the volume particle concentration.

If we set $\lambda = Lr_L^{-1}$, we then obtain

$$\Gamma_L(\mathbf{r}_L) = \mathbf{r}^{2x} L^{-2x} \Gamma_l(\mathbf{r}_\Delta). \tag{26}$$

It follows from the principle of correlation attenuation that as $\mathbf{r}_L \to \infty$ the correlator $\Gamma_L \to 0$ so that $x < 0$. Using the Ornshtein–Tsernik theory, we can demonstrate that $y = -1/2$. Denoting $x/y = m > 0$ and equating L with the dimension of the region occupied by the suspension, from (3) we obtain

$$\eta(\delta\rho) \sim (\delta\rho)^{-m}, \quad \delta\rho = \frac{\rho - \rho_c}{\rho_c} \ll 1. \tag{27}$$

Figure 2 schematically illustrates the behavior of η, constructed according to (27) and from the results of [9]. Curves of analogous form have been obtained in the experiments of [10-12], which confirms our conclusion regarding the divergence of the effective viscosity of the colloid at the critical point of structure formation. However, additional research is necessary to refine the nature of this divergence.

NOTATION

a — particle radius; $\mathbf{e}$ — average shear strain rate tensor; $\mathbf{I}$ — second-rank unit tensor; unit vector of normal two-particle surface; p, pressure; $\mathbf{r}$ — radius vector directed from the center of the particle; $\mathbf{v}$ — average velocity of suspension; ρ, volume concentration of dispersed phase; η_0, η, viscosity of dispersion fluid and effective viscosity of suspension; σ — average stress within the mixture.

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