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EFFECT OF HYDRODYNAMIC INTERACTIONS BETWEEN THE PARTICLES ON THE RHEOLOGICAL PROPERTIES OF DILUTE EMULSIONS*

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The form of mean stress tensor in monodisperse emulsions is studied in the second-order approximation with respect to the volume density of the particles, for a number of flows which are of rheological interest. It is shown how the particular features of the two-particle interaction between liquid spheres, especially the non-zero differences between the normal stresses in shear flows, give rise to non-Newtonian properties of the emulsion.

We know /1, 2/ that in the case of the second-order approximation with respect to the volume concentration of the suspended disperse phase the mean stress tensor is expressed in terms of two-particle interactions in a linear velocity field, and of the binary correlation function. The binary function is formed under the action of the macroscopic flow. Specific results, however, were obtained only for suspensions and rigid spheres /1, 2/. The present paper deals with the structural model of fluid spheres of equal radius, with hydrodynamic and "contact" interactions. A number of fundamental deviations from /1/ exist in the case of rheologically strong flows, since drop flocculation-deflocculation processes must be considered (i.e. the formation and disruption of aggregates). A strict analysis is given within the framework of the model, of the effect of these processes on the binary correlation function. A connection between the model of "contact" interaction and the result of the D.L.V.O. theory /3—5/ is considered. Numerical values are obtained for the Trouton viscosity in strong rheologically axisymmetric expanding flows. The differences in normal stresses in a strong shear flow are obtained and an approximate estimate is given for the shear viscosity and compared with experimental data /6/. A method given in /2/ is used to compute the effective viscosity of the emulsion in arbitrary, rheologically weak flows in which Brownian motion predomaintes. Considerable use is made of the exact computational methods and asymptotic representations of hydrodynamic functions determining the pairwise interaction of fluid spheres /7—9/.

1. A general expression for the mean stress tensor. Consider a locally homogeneous monodisperse emulsion of drops of radius a and viscosity μ' freely suspended in a

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medium of viscosity μ_e. The particles are assumed to be spherical due to relatively high surface tension. Let the flow be described at the macro level by quasistationary Stokes equations. We assume that there are no factors hindering the development of circulation within the drops. The possibility that such a model can be realized in practice is pointed out in /6/.

Under the above conditions the mean stress tensor has the form /10/

$$\Sigma_{ij} = I.T. + 2\mu_e E_{ij} + \Sigma_{ij}^p, \quad \Sigma_{ij}^p = \frac{1}{V} \sum S_{ij} \tag{1.1}$$

$$S_{ij} = \int_S \left\{ (\sigma_m)_i x_j - \frac{1}{3} \delta_{ij} (\sigma_m \cdot \mathbf{x}) - \mu_e (v_i m_j + v_j m_i) \right\} dS$$

Here $I.T.$ represents the spherical part which is of no interest, E_{ij} is the mean deformation rate tensor, S_{ij} is the force dipole intensity of a single particle (S and $\mathbf{m}$ denote the particle surface and external normal to this surface, $\mathbf{v}$ is the local velocity of the fluid and σ_m is the stress vector on the outside of the surface). The summation in (1.1) is carried out over all particles within a macroscopically small volume V.

Disregarding the Brownian motion, we have, in the quadratic approximation with respect to the volume density c /1/

$$\Sigma^p = 2\mu_e \left(\frac{5}{2} \alpha c + \frac{5}{2} \alpha^2 c^2 \right) \mathbf{E} + \frac{15 c^2 \alpha \mu_e}{4\pi a^3} \times \tag{1.2}$$

$$\int_{r \geqslant 2a} \left[\left\{ \frac{\mathbf{S}(\mathbf{x}_0, \mathbf{x}_0 + \mathbf{r})}{{}^{20}/_3 \pi a^3 \alpha \mu_e} - \mathbf{E} \right\} p(\mathbf{r}) - \{ \mathbf{e}(\mathbf{x}_0, \mathbf{x}_0 + \mathbf{r}) - \mathbf{E} \} \right] d\mathbf{r} + o(c^2)$$

$$c \ll 1, \quad \alpha = \frac{\lambda + {}^2/_5}{1 + \lambda}, \quad \lambda = \frac{\mu'}{\mu_e}, \quad p(\mathbf{r}) = n^{-1} P(\mathbf{x}_0 + \mathbf{r} \mid \mathbf{x}_0)$$

Here $P(\mathbf{x}_0 + \mathbf{r} \mid \mathbf{x}_0)$ is the probability density of detecting a particle with the centre at $\mathbf{x}_0 + \mathbf{r}$, provided that a particle exists with centre at $\mathbf{x}_0$; n is the number of particles and $\mathbf{e}(\mathbf{x}_0, \mathbf{x}_0 + \mathbf{r}) - \mathbf{E}$ is the perturbation in the deformation rate tensor at the point $\mathbf{x}_0$ caused by a single, freely suspended sphere with centre at $\mathbf{x}_0 + \mathbf{r}$. When $r \gg a$, we have $\mathbf{e} - \mathbf{E} = O((a/r)^3)$. The value of $\mathbf{e} - \mathbf{E}$ averaged over any sphere $r = \text{const} > 2a$ is zero /1/. The explicit expression given in /1/ for $\mathbf{e}(\mathbf{x}_0, \mathbf{x}_0 + \mathbf{r}) - \mathbf{E}$ will not be required. The expression $\mathbf{S}(\mathbf{x}_0, \mathbf{x}_0 + \mathbf{r})$ in (1.2) denotes the force dipole intensity of particle 1 with its centre at $\mathbf{x}_0$ in the presence of a second sphere with centre at $\mathbf{x}_0 + \mathbf{r}$ in the case when both particles are freely suspended in an unbounded fluid with unperturbed deformation rate tensor $\mathbf{E}$. The following general rpersentation /1/ holds:

$$\mathbf{S}(\mathbf{x}_0, \mathbf{x}_0 + \mathbf{r}) = {}^{20}/_3 \pi a^3 \alpha \mu_e \{ (1 + K) \mathbf{E} + [(\mathbf{E} \cdot \mathbf{n}) \mathbf{n} + \mathbf{n} (\mathbf{E} \cdot \mathbf{n})] L + \tag{1.3}$$

$$(\mathbf{n} \cdot \mathbf{E} \cdot \mathbf{n}) [\mathbf{nn} M - ({}^2/_3 L + {}^1/_3 M) \mathbf{I}] \}, \quad \mathbf{n} = \mathbf{r}/r$$

The functions K, L, M, which depend on ζ, λ $(\zeta = r/a)$, were studied in /7/. Their numerical values as well as their remote and most significant near asymptotic representations are all known.

Thus the stress tensor can be calculated with accuracy to $o(c^2)$, provided that the distribution $p(\mathbf{r})$ to the zeroth approximation in $c \ll 1$ is known. Generally speaking, the determination of $p(\mathbf{r})$ is too complicated since the microstructure depends on the past history of the deformations. Below we consider two special cases of steady flows.

2. Expanding axisymmetric steady flows. According to /1/ the problem of determining $p(\mathbf{r})$ involves examining the relative motion of a pair of particles suspended in a fluid with unperturbed deformation rate tensor $\mathbf{E}$ and vorticity $\mathbf{\Omega}$. In the zeroth approximation in $c \ll 1$ $\mathbf{E}$ and $\mathbf{\Omega}$ are equal to the corresponding mean values for the emulsion. The velocity $\mathbf{V}$ of sphere 2 relative to sphere 1 has the form /1/

$$\mathbf{V} = r [\mathbf{\Omega} \times \mathbf{n} + (1 - B) \mathbf{E} \cdot \mathbf{n} + (B - A)(\mathbf{n} \cdot \mathbf{E} \cdot \mathbf{n}) \mathbf{n}] \tag{2.1}$$

The functions $A(\zeta, \lambda), B(\zeta, \lambda)$ were investigated in /7/. In particular we have

$$1 > A > B \geqslant 0, \quad A = O(\zeta^{-3}), \quad B = O(\zeta^{-5}) \quad (\zeta \to \infty) \tag{2.2}$$

$$(1 - A)^{-1} = O(\varepsilon^{-1/2}), \quad 1 - B, \ dB/d\zeta = O(1), \quad (\varepsilon = \zeta - 2 \to 0, \lambda < \infty)$$

Let us consider the axisymmetric flows with $\mathbf{\Omega} = 0$, $\mathbf{E} = \text{const}$. Let x_1, x_2, x_3 by the system of principal axes of the tensor $\mathbf{E}$ with origin at the centre of sphere 1, $E_{11} = E_{22} = -E_{33}/2$, $E_{ij} = 0$ $(i \neq j)$. The pattern of relative trajectories is symmetrical about the x_3 axis and the plane $x_3 = 0$. The form of the trajectories is given by (2.1)

$$\zeta^3 \sin^2 \theta \cos \theta = C \varphi^3 (\zeta) \tag{2.3}$$

$$\varphi(\zeta) = \exp \left[\int_\zeta^\infty \frac{A(\zeta') - B(\zeta')}{1 - A(\zeta')} \frac{d\zeta'}{\zeta'} \right]$$

Here θ is the angle between the $\mathbf{r}$ and x_3 axis, and C is the intergration constant. From (2.2) it follows that $\varphi(2) < \infty$. When $|C| > C_{cr} = 16/(3\sqrt{3}\varphi^3(2))$, the corresponding trajectory arrives from infinity and returns to infinity without reaching the sphere $r = 2a$. We also have trajectories arriving from infinity at the sphere $r = 2a$, and trajectories departing from the sphere to infinity. In both cases $|C| < C_{cr}$. The critical trajectories with $C = \pm C_{cr}$ touch the sphere $r = 2a$ at $\theta = \theta_0$ or at $\pi - \theta_0$ $(\theta_0 = \operatorname{arc\,tg} \sqrt{2})$. The pattern of relative motion in the meridianal half-space is shown in Fig.1 for $E_{33} < 0$. When $E_{33} > 0$, the directions of the trajectories become reversed.

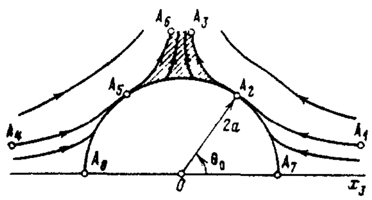

Fig.1

The possibility of the particles coming into contact under the action of macroscopic deformation constitutes the principal difference between the case of liquid and rigid spheres. When $\lambda = \infty$, we have $1 - A = O(\varepsilon)$ as $\varepsilon \to 0$ /11/, so that $\varphi(2) = \infty$ and every relative trajectory with $C \neq 0$ begins and ends at infinity.

Certain additional assumptions must be made about the non-hydrodynamic short range interactions between the particles. Following the D.L.F.O. theory /3–5/, we assume the when $\varepsilon \ll 1$, the molecular attraction forces and stabilizing repulsion forces between the double electric layers of the sphere surfaces act along the line joining the centres. The resultant F of these forces causes the second particle to acquire an additional relative radial velocity $B_0 G F$ where

$$B_0 = (3\pi\mu_e a\chi)^{-1}, \quad G = \chi(2\Lambda_{11} - \Lambda_{12})^{-1}$$
$$\chi = (\lambda + {}^2/_3)(1 + \lambda)^{-1}$$

Here $\Lambda_{11}(\lambda, \varepsilon)$, $\Lambda_{12}(\lambda, \varepsilon)$ are the coefficients of resistance /7, 12/. According to /7/ we have, when $\varepsilon \to 0$,

$$1 - A \simeq D^*\chi^{-1}G, \quad 1.097 \leqslant D^*(\lambda) < 2.039 \tag{2.4}$$

From (2.1) and (2.4) it follows that when $\varepsilon \ll 1$ and the force F is taken into account, we have

$$dr/dt \simeq B_0 G\,[6\pi\mu_e a^2 D^*(\mathbf{n}\cdot\mathbf{E}\cdot\mathbf{n}) + F] \tag{2.5}$$

To estimate the dimensionless non-hydrodynamic force $f = F(6\pi\mu_e a^2 D^* |E_{33}|)^{-1}$, we use the results of /3, 5/

$$F(\varepsilon) = 2\pi\varepsilon_0 e\Psi_0^2 ak\,\frac{e^{-ak\varepsilon}}{1 + e^{-ak\varepsilon}} - A_{12}\,\frac{g(p_w)}{12a\varepsilon^2}$$
$$p_w = \frac{2\pi\varepsilon a}{\lambda_w}$$
$$g(p_w) = \begin{cases} (1 + 3.54p_w)(1 + 1.77p_w)^{-2}, & p_w < 2 \\ (5p_w)^{-1}(4.9 - 2.17p_w^{-1} + 0.337p_w^{-2}), & p_w > 2 \end{cases}$$

Here $\varepsilon_0 = 8.85\cdot10^{-12}$ Ф/m, e is the relative permittivity of the disperse medium, Ψ_0 is the surface potential, k^{-1} denotes the thickness of the double layer, A_{12} is the Hamaker constant and λ_w $(\approx 10^{-7}$ m) is the London wavelength. The stabilized systems are characterized by the presence of a positive maximum f_{max} and negative minimum f_{min} for large values of ε.

For example, when $e = 80$, $\Psi_0 = 25$ mv, $k^{-1} = 0.002$ um (which agrees with the order of magnitude of the quantities usually adopted in the theory of the stability of emulsions M/B [4]), $A_{12} = 10^{-20}$ J, $a = 2$ um, $D^* = 1.45$ $(\lambda = 1)$, $|E_{33}| = 500$ sec^{-1}, $\mu_e = 10^{-3}$ N·sec·m^{-2}, we have $f_{max} \approx 6.7$ $(\varepsilon \approx 1.2\cdot10^{-3})$ and $f_{min} \approx -0.05$ $(\varepsilon \approx 7.5\cdot10^{-3})$. Already, when $\varepsilon = 0.1$ we have $f = -6\cdot10^{-6}$, so that the radius of action of the force F is very small. The value of A_{12} depending on the combination of the disperse and dispersing medium and on the presence of an adsorbed monolayer of emulsifier /4/, show considerable indeterminacy. When $A_{12} = 10^{-21}$ J, we have $f_{max} \approx 16$ $(\varepsilon \approx 4.6\cdot10^{-4})$ and $f_{min} \approx -0.002$ $(\varepsilon \approx 0.01)$.

Leaving aside these estimates, we will assume that $f_{max} > 1$, $|f_{min}| \ll 1$. This justifies the idealized model of "contact" interaction. After achieving the contact the centre of the second sphere moves along the surface $r = 2a$ as long as $\mathbf{n}\cdot\mathbf{E}\cdot\mathbf{n} < 0$ (it follows from (2.5) that here the hydrodynamic force $6\pi\mu_e a^2 D^*(\mathbf{n}\cdot\mathbf{E}\cdot\mathbf{n})$ is balanced by the "contact" force). When $\mathbf{n}\cdot\mathbf{E}\cdot\mathbf{n} = 0$ $(\theta = \theta_0$ or $\pi - \theta_0)$, the corresponding trajectory becomes detached (i.e. the spheres separate) and the centre of the second sphere begins to move freely in accordance with (2.3). The relative velocity $\mathbf{V}^*$ of contact motion is found from (2.1) as $\varepsilon \to 0$ (since F influences V_r) only)

$$\mathbf{V}^* = 2a(1 - B^*)[\mathbf{E}\cdot\mathbf{n} - (\mathbf{n}\cdot\mathbf{E}\cdot\mathbf{n})\mathbf{n}] \tag{2.6}$$

Henceforth, the asterisk denotes the limiting values of the hydrodynamic functions and other qualities for the spheres in contact.

Let us now turn our attention to the problem of determining the binary correlation function, assuming at first that $E_{33} < 0$ (Fig.1). The set of relative trajectories of the interacting pairs is best represented as a flow of a certain (compressible) phase "fluid" past the sphere $r = 2a$. Let us construct a film formed by rotating the trajectories A_2A_3, A_5A_6 about the x_3 axis. In the "shadow" region bounded by the film we have, in the steady state, $p(\mathbf{r}) \equiv 0$ in accordance with the model of "contact" interaction. In the remaining part of the $\mathbf{r}$ space the volume distribution $p(\mathbf{r})$ can be found from the Liouville equation /1/

$$\operatorname{div}[p(\mathbf{r})\mathbf{V}(\mathbf{r})] = q\mathbf{V}\cdot\nabla[p(\mathbf{r})/q(r)] = 0 \tag{2.7}$$
$$q = (1 - A)^{-1}\varphi^{-3}(\zeta), \quad q = 1 + O(\zeta^{-6}) \quad (\zeta \to \infty)$$

In accordance with the boundary condition $p \to 1$, when $r \to \infty$ (there are no remote statistical constants /1/) we find, that the volume distribution $p(\mathbf{r}) \equiv q(r)$ everywhere at $r > 2a$ except the shadow region. We have non-zero density $\lim\,[q(r)V_r]$ $(\varepsilon \to 0)$ of the flux of the phase fluid arriving at the sphere $r = 2a$, at the segments where $\mathbf{n}\cdot\mathbf{E}\cdot\mathbf{n} < 0$ and where the surface phase denisty P^* must be brought in. The region $P^* \neq 0$ is formed by rotating the arcs A_2A_7, A_5A_8 about the x_3 axis. The density P^* is defined by the balance equation

$$\operatorname{div}_s[P^*\mathbf{V}^*] = -2a\varphi^{-3}(2)\,\mathbf{n}\cdot\mathbf{E}\cdot\mathbf{n} \tag{2.8}$$

Here div_s is the surface divergence. Using (2.6) we find the particular solution

$$P^* = {}^2/_3 a\varphi^{-3}(2)(1 - B^*)^{-1} \tag{2.9}$$

The general solution $P^* = \mathrm{const}\cdot\sin^{-2}\theta\cos^{-1}\theta$ of the homogeneous equation generates a surface source at $\theta = 0$, and should be neglected.

We also have a concentrated phase density P^{**} at the film surface, which can be found from the Liouville surface equation $\operatorname{div}_s[P^{**}\mathbf{V}] = 0$ having first computed the phase fluid flux from the sphere $r = 2a$. Along the film we have

$$P^{**}\,|\mathbf{V}|\,\zeta\sin\theta = (8\sqrt{3}/9)\,|E_{33}|\,a^2\varphi^{-3}(2) \tag{2.10}$$

When $E_{33} > 0$, the film is formed by rotation of the trajectories A_2A_1, A_5A_4, and the region with surface density of P^* by rotating the arc A_2A_5 about the x_3 axis; formulas (2.9) and (2.10) both hold.

Although in (1.1) and (1.2) the spheres were assumed to be separate and free of external forces (in this case the integral (1.1) is invariant with respect to the choice of the reference origin $\mathbf{x}$), however /10/ implies that (1.1) also holds in the case when aggregates with internal contact forces acting between the particles are present, provided that the origin of reference $\mathbf{x}$ in integral (1.1) is the same for all particles of the aggregate. Thus a specific total force dipole for a doublet is equal to twice the limit of expression (1.3) as $\varepsilon \to 0$, since the free relative motion along the line connecting the centres, in the limit as $\varepsilon \to 0$, makes no contribution to the total dipole (see (4.5) of /7/). As a result we can use (1.2) in the generalized sense, adding to the volume integral the corresponding surface integrals in which $p(\mathbf{r})\,d\mathbf{r}$ have been replaced by P^*dS and $P^{**}dS$. The term containing $\mathbf{e}(\mathbf{x}_0, \mathbf{x}_0 + \mathbf{r}) - \mathbf{E}$ contributes nothing to the surface integrals, nor to the volume integral provided that in the latter integral we carry out the first integration over the angle variables (which is allowed by virtue of the absolute convergence of the integral).

In the case in question the axial symmetry implies that $\Sigma_{11}^p = \Sigma_{22}^p = -\Sigma_{33}^p/2$, therefore

$$\Sigma_{ij} = I_{.}T_{.} + 2\mu_\pm E_{ij} \tag{2.11}$$
$$\mu_\pm \simeq \mu_e\left(1 + \frac{5}{2}\alpha c + k_\pm(\lambda)c^2\right)$$

The upper sign corresponds to $E_{33} > 0$ and the lower one to $E_{33} < 0$. The quantity $\mu_\pm$ is three times as small as the corresponding Trouton viscosity /13/.

Using (1.2) and (2.9)–(2.10) and the method described above, we obtain

$$k_\pm = \frac{5}{2}\alpha^2 + \frac{20\alpha}{\varphi^3(2)(1 - B^*)}\left[J_\pm^* \pm \frac{1}{\sqrt{3}}\left(K^* + \frac{4}{9}L^* + \frac{4}{45}M^*\right)\right] + \frac{40\alpha}{\sqrt{3}\,\varphi^3(2)} \times \tag{2.12}$$
$$\int_2^\infty \left[K + \left(\nu_\pm^2 + \frac{1}{3}\right)L + \frac{1}{6}(3\nu_\pm^2 - 1)^2 M\right]\frac{d\zeta}{\zeta(1 - A)\,|1 - 3\nu_\pm^2|} +$$
$$\frac{15\alpha}{2}\int_2^\infty \left\{J_\pm \pm \nu_\pm\left[K + \frac{(\nu_\pm^2 + 1)}{3}L + \frac{1}{6}\left(\frac{9}{5}\nu_\pm^4 - 2\nu_\pm^2 + 1\right)M\right]\right\} q(\zeta)\,\zeta^2\,d\zeta$$
$$J_+ = 0, \quad J_- = J = K + \frac{2}{3}L + \frac{2}{15}M$$
$$\nu_\pm(1 - \nu_\pm^2) = \frac{C_{cr}\varphi^3(\zeta)}{\zeta^3}, \quad 0 < \nu_- < \frac{1}{\sqrt{3}} < \nu_+ < 1$$

To calculate K, L, M, A, B at $\zeta > 2$, we have used exact methods as well as the remote and near asymptotic representations /7/. The quantities $K^*, K^* + {}^4/_3L^* + {}^2/_3M^*$ are given in /7/, and the limiting values of the functions L and B (which have, unlike M, a finite derivative at $\varepsilon = 0$ provided that $\lambda < \infty$), were found by linear extrapolation. This yields all quantities needed in (2.12). The contribution of the remote region $\zeta \gg \zeta_0 \gg 1$ to each of the integrals of (2.12) is of order $O(\zeta_0^{-3})$.

Below we give the numerical results obtained:

$\lambda =$	0	0.25	0.5	1	2	3	5	10
$k_+ =$	1.02	1.46	1.86	2.49	3.33	3.86	4.49	5.22
$k_- =$	1.40	1.88	2.30	2.98	3.80	4.31	4.90	5.57

When $\lambda = \infty$, we have in accordance with /1/,

$$k_+ = k_- = \frac{5}{2} + \frac{15}{2}\int_2^\infty J(\zeta)\, q(\zeta)\, \zeta^2\, d\zeta$$

and (2.11) also holds for any steady-state expansion flows. At $\lambda = \infty$ the exact value of $k_\pm$ equal to 7.0, replaces the approximate estimate of 7.6 given in /1/.

The difference between the values of k_+ and k_- at $\lambda < \infty$ represents a typical non-Newtonian effect. In the case of arbitrary steady state expansion flows the above method would lead, at $\lambda < \infty$ to the disappearance of the proportionality between the stress deviator and E_{ij}.

3. Steady-state shear flow. When $\lambda < \infty$, the case is characterized by an even more complex three-dimensional pattern of relative trajectories, than that for rigid spheres /11/. Let the rate of the unperturbed flow in which the spheres 1 and 2 are immersed, have the form $\mathbf{v}_\infty = (\varkappa x_2 + \text{const}, 0, 0)$ in a Cartesian system of coordinates x_1, x_2, x_3 with origin at the centre of sphere 1 $(\varkappa < 0)$. The integrals of relative motion are obtained from (2.1) and have the form /11/

$$\frac{x_3}{a} = \xi_3 \varphi(\zeta), \quad \frac{x_2^2}{a^2} = \varphi^2(\zeta)[\xi_2 + \Psi(\zeta)] \tag{3.1}$$

$$\Psi(\zeta) = \int_\zeta^\infty \frac{B(\zeta')\,\zeta'\, d\zeta'}{[1 - A(\zeta')]\,\varphi^2(\zeta')}$$

Here $\xi_2, \xi_3 = \text{const}$ along the corresponding trajectories. From (2.2) it follows that $0 \leqslant \Psi(2) < \infty$. We separate when $r > 2a$ the following regions of $\mathbf{r}$-space:

$$D_f\colon \frac{x_2^2}{a^2} < \varphi^2(\zeta)\Psi(\zeta), \quad D_t\colon \frac{x_2^2 + x_3^2}{a^2} \leqslant \varphi^2(\zeta)\left[\frac{4}{\varphi^2(2)} - \Psi(2) + \Psi(\zeta)\right]$$

and several possible types of relative trajectories.

1°. Trajectories not belonging to $D_f \cup D_t$ $(\xi_2 > 0,\ \xi_2 + \xi_3^2 > 4/\varphi^2(2) - \Psi(2))$. The trajectories arrive from infinity and depart to infinity without reaching the sphere $r = 2a$.

2°. Trajectories arriving from infinity at the sphere $r = 2a$ (they form the region $(D_t \setminus D_f) \cap \{x_1 x_2 > 0\}$).

3°. Trajectories emerging from the sphere $r = 2a$ and going to infinity (they form the region $(D_t \setminus D_f) \cap \{x_1 x_2 < 0\}$).

4°. Trajectories emerging from the sphere $r = 2a$ and returning to it (they form the region $D_f \cap D_t$).

5°. Closed trajectories (they form the region $D_f \setminus D_t$).

When $\lambda = 0$, we have $B \equiv 0$ /7/ and region D_f vanishes. When $\lambda > 0$, the mutual distribution of the region D_f and D_t depends on whether the inequality $\varphi^2(2)\Psi(2) < 4$ holds. Numerical computations yield

$\lambda =$	0.25	0.5	1	2	3	5	10	20
$\varphi(2)\sqrt{\Psi(2)}/2 =$	0.12	0.17	0.24	0.32	0.37	0.44	0.54	0.65

When $\lambda = \infty$, we have $\varphi(2) = \infty$ (see Sect.2) and $\Psi(2) \approx 0.76$ /11/. Therefore a value $\lambda_{cr} > 20$ exists for which $\varphi(2)\sqrt{\Psi(2)}/2 = 1$. The quantity λ_{cr} is not easy to calculate exactly since when $\lambda \gg 1$ the region $\zeta - 2 \ll 1$ makes a large contribution towards the integral for $\varphi(2)$ and $\Psi(2)$.

Fig.2 shows a typical pattern of relative trajectories in the $x_3 = 0$ plane for $0 < \lambda < \lambda_{cr}$. The boundary of the region D_f is formed by rotation of the trajectories $A_1A_2, A_3A_4, A_5A_6, A_7A_8$ (with $\xi_2 = 0$) about the x_2 axis. Results obtained in /7/ imply that as $\zeta \to \infty$, the trajectories approach the x_1 axis as

$$x_2^2/a^2 \simeq {}^8/_3\lambda\,(1 + 2\lambda)\,[(2 + 3\lambda)(1 + \lambda)]^{-1}\zeta^{-3} \tag{3.2}$$

The boundary of the region D_t is formed by rotating the trajectories $A_9A_{10}A_{11}$, $A_{12}A_{13}A_{14}$ (with $\xi_2 = 4/\varphi^2(2) - \Psi(2)$) about the x_1 axis and has, as $\zeta \to \infty$, a finite thickness $2a\sqrt{\xi_2}$. The closed trajectories lie outside the limits of the plane $x_3 = 0$.

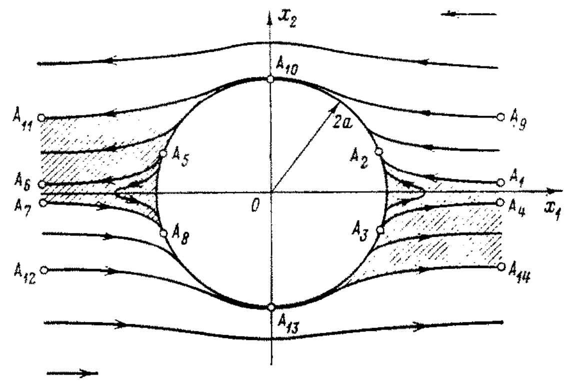

Fig.2

When $\lambda > \lambda_{cr}$, the outer boundary of D_f consists of two singly connected surfaces of revolution $\xi_2 = 0$ not reaching the sphere $r = 2a$, and the region $D_t \subset D_f$ consists of trajectories of type 4°, without any trajectories of types 2° and 3°. When $\lambda > \lambda_{cr}$, the minimum distance between the surfaces $\xi_2 = 0$ and the sphere $r = 2a$ is less than $4.7 \cdot 10^{-5} a$ (this can be found from the results of /7, 11/ by considering the limiting case of $\lambda = \infty$). The only possible trajectories for the rigid spheres /11/ $D_t = \phi$ are those of types 1° and 5°.

Below, we shall assume that $\lambda < \lambda_{cr}$. As in Sect.2, the volume density on type 1° and 2° trajectories is $p(\mathbf{r}) = q(r)$. The model of contact interaction admits of contact motion of the spheres (with relative velocity $\mathbf{V}^*$ differing from (2.6) by an additional term $2a\Omega \times \mathbf{n}$) only on the segments where $x_1 x_2 > 0$, with subsequent detachment when $x_1 = 0$. This implies that in the steady state the shaded region with volume distribution $p(\mathbf{r}) \equiv 0$ consists of type 3° and 4° trajectories. The boundary condition $p \to 1$ will be restored in the shaded region at a considerable distance downstream, when the weak Brownian diffusion and (or) collective interactions are taken into account.

The surface density P^* differs from zero on the segments of the sphere $r = 2a$ on which $x_1 x_2 > 0$, $x_2^2/a^2 > \varphi^2(2)\Psi(2)$ simultaneously, and is given by the equation (2.8) with boundary condition $P^* = 0$ when $x_2^2/a^2 = \varphi^2(2)\Psi(2)$ (the latter excludes the flow of phase particles along the surface $r = 2a$ from the "forbidden" region in the steady-state mode). As a result we obtain (γ is the angle between the $\mathbf{r}$ and the x_2 axis)

$$P^* = P^*(\gamma) = \frac{2a}{3\varphi^3(2)(1 - B^*)}\left\{1 - \left[\frac{2B^* + (1 - B^*)\varphi^2(2)\Psi(2)}{2B^* + 4(1 - B^*)\cos^2\gamma}\right]^{3/2}\right\} \tag{3.3}$$

The surface of the film is formed by the trajectories (type 3°) departing from the sphere when $x_1 = 0, x_2^2/a^2 \geqslant \varphi^2(2)\Psi(2)$. The integrals (3.1) yield the parametric representation $x_i = x_i(\zeta, \gamma_0)$ of this surface; the Lagrangian variable γ_0 is equal to the angle γ at the point of detachment of the trajectory. The Liouville surface equation for the density P^{**} of the film yields (dS is the surface element)

$$P^{**}\,dS = \frac{2a^4(2 - B^*)P^*(\gamma_0)\zeta\,|\cos\gamma_0\,d\gamma_0\,d\zeta\,|}{(1 - A)\,|x_1 x_2|} \tag{3.4}$$

The volume distribution $p(\mathbf{r})$ in the region of closed trajectories remains unknown, as in the case of rigid spheres /1/. Equation (2.7) yields only $p(\mathbf{r}) = C(\xi_2, \xi_3)\,q(r)$. It was assumed in /1, 14/ that the form of the functions $C(\xi_2, \xi_3)$ is determined by weak Brownian diffusion or by the weak collective interactions. The problem of the rigorous determination of $C(\xi_2, \xi_3)$ will not be considered further.

In the shear flow only the components $\Sigma_{ii}^p, \Sigma_{12}^p$ can differ from zero. The difficulty mentioned above hinders the exact computation of Σ_{12}^p when $\lambda > 0$. The region of closed trajectories however, makes no contribution to the integrals (1.2) for $\Sigma_{11}^p, \Sigma_{22}^p, \Sigma_{33}^p$ irrespective of the form of $C(\xi_2, \xi_3)$. Using the results of /1/, we obtain

$$\frac{1}{c^2\mu_e\,|\varkappa|}\begin{pmatrix}\Sigma_{11} - \Sigma_{22}\\ \Sigma_{22} - \Sigma_{33}\end{pmatrix} = \begin{pmatrix}N_1\\ N_2\end{pmatrix} \doteq -\frac{15\alpha}{4\pi a^3}\int\begin{Bmatrix}(n_1^2 - n_2^2)M\\ L + (n_2^2 - n_3^2)M\end{Bmatrix} n_1 n_2 p(\mathbf{r})\,d\mathbf{r}$$

for the differences between the normal stresses /13/.

The integrals are considered in the generalized sense (as in Sect.2), and the volume integration extends only to the region $(D_t \setminus D_f) \cap \{x_1 x_2 > 0\}$. Using (3.3) and (3.4) we can find

$$N_1 = \Phi\left(2y - \frac{10}{3}z\right)M^* + (y - \sin^5\tau)I$$

$$N_2 = \Phi\left[\frac{8}{3}zM^* - 2y(L^* + M^*)\right] + \left(\frac{4}{5}\sin^5\tau - 2y\right)I$$

$$\tau = \arcsin\left(\frac{(1 - B^*)[4 - \varphi^2(2)\Psi(2)]}{2(2 - B^*)}\right)^{1/2}$$

$$y = \frac{\sin^3\tau}{3} + \cos^3\tau(\tau - \operatorname{tg}\tau)$$

$$z = \frac{(1 - B^*/2)}{(1 - B^*)} \left[\frac{\sin^5 \tau}{5} + \cos^3 \tau \left(\frac{3}{2} \tau - \operatorname{tg} \tau - \frac{\sin 2\tau}{4} \right) \right]$$

$$I = \frac{160\alpha}{\pi \varphi^5 (2)} \left(\frac{1 - B^*/2}{1 - B^*} \right)^{3/2} \int_2^\infty \frac{M \varphi^2 (\zeta)}{(1 - A) \zeta^3} d\zeta$$

$$\Phi = \frac{20\alpha (1 - B^*/2)^{3/2}}{\pi \varphi^3 (2) (1 - B^*)^{5/2}}$$

The contribution of the region $\zeta \geqslant \zeta_0 \gg 1$ to I is of order $O(\zeta_0^{-6})$. We note that N_1, $N_2 \to 0$ as $\lambda \to \lambda_{cr}$.

When $\lambda = 0$, there are no closed trajectories, and we can also obtain the shear viscosity

$$\mu_{sh}/\mu_e \simeq 1 + c + k_{sh} c^2, \quad \mu_{sh} = \Sigma_{12}/\varkappa \tag{3.5}$$

$$k_{sh} = \frac{2}{5} + \frac{4}{\varphi^3 (2)} \left[\frac{2}{3} L^* + \frac{2}{15} M^* \right] +$$

$$\frac{4}{\varphi^3 (2)} \int_2^\infty \left[\frac{1 + \nu^2}{2} L + \nu^2 (1 - \nu^2) M \right] \frac{d\zeta}{\zeta (1 - A) \nu \sqrt{1 - \nu^2}} +$$

$$\frac{3}{2} \int_2^\infty \left\{ \frac{L}{2} \left(\nu + \frac{\nu^3}{3} + \frac{4}{3} \right) + M \left(\frac{\nu^3}{3} - \frac{\nu^5}{5} + \frac{2}{15} \right) \right\} q \zeta^2 d\zeta, \quad \nu = \left[1 - \frac{4 \varphi^2 (\zeta)}{\zeta^2 \varphi^2 (2)} \right]^{1/2}$$

Here we assumed that $K \equiv 0$ when $\lambda = 0$ /7/. The contribution of the remote region $\zeta \geqslant \zeta_0 \gg 1$ to k_{sh} is of order $O(\zeta_0^{-2})$.

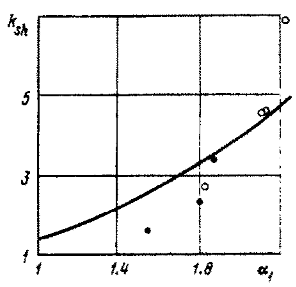

Fig.3

The numerical values of $\varphi (2) \sqrt{\Psi (2)}/2$ given above and the asymptotic forms (3.2) together show that when $\lambda \sim 1$, the region of closed trajectories is fairly "thin". At the outer boundary of the region (when $\xi_2 = 0$) $C = 1$. Therefore, to obtain an approximate value for the shear viscosity when $\lambda > 0$, we assume that $C(\xi_2, \xi_3) \approx 1$. In this case we can carry out the integration in the volume integral (1.2) for Σ_{12}^p over the angle variables analytically. In the double integral in ζ, γ_0 representing the contribution of the density P^{**} to Σ_{12}^p, integral integration in γ_0 yields incomplete elliptic integrals of first and second kind. The contribution of the density P^* to Σ_{12}^p is expressed in finite form in terms of $K^*, L^*, M^*, B^*, \varphi(2), \Psi(2)$. The final expression for the quadratic coefficient k_{sh} in the expansion of μ_{sh}/μ_e is extremely bulky and therefore not given here. In the limit $\lambda \to 0$ we have (3.5).

The numerical results are given below

$\lambda =$	0	0.25	0.5	1	2	3	5	10
$-N_1 =$	0.44	0.49	0.51	0.52	0.47	0.42	0.33	0.20
$-N_2 =$	0.31	0.31	0.29	0.25	0.19	0.15	0.10	0.05
$k_{sh} =$	1.41	1.99	2.44	3.13	3.95	4.42	4.94	5.45

Let us compare the values of k_{sh} with the experimental data. The viscosity of dilute, stable oil-water emulsions with a high degree of monodispersivity ($|\varkappa| = 200 - 900$ sec^{-1}, $c \leqslant 0.16$; $a = 1.25 - 1.75$ or 1.75–2.25 um, $\mu_e \sim 10^{-3}$ N·sec·m^{-2} was measured in /6/ in conditions of strong shear flow, and standard methods were used to calculate the linear coefficient α_1 and the quadratic coefficient k_{sh} in the expansion of μ_{sh}/μ_e; the quantities k_{sh} are extremely sensitive to experimental errors in μ_{sh}/μ_e /6/. Fig.3 uses small circles to show the experimental pairs of values (α_1, k_{sh}) for emulsions with $\alpha_1 \approx 2.5\,\alpha$ (i.e. without the factors retarding the internal circulation). The data corresponding to the black circles were obtained in /6/ by extrapolating the values of α_1, k_{sh} for emulsions with $\alpha_1 > 2.5\,\alpha$ in the limit of zero concentration of the emulsifier (when $\alpha_1 \to 2.5\,\alpha$). Judging from the results of /6/, we see that the extrapolated values of k_{sh} are less accurate.

The curve in Fig.3 shows the theoretical computation. A more detailed check of the theory would require a direct experimental determination of k_{sh} for emulsions with $\alpha_1 \approx 2{,}5\,\alpha$ for small λ (when the approximation $C(\xi_2, \xi_3) \approx 1$ does not introduce substantial errors), and the determination of N_1, N_2.

The method given above together with the results obtained in /1/ can be applied to the polydisperse case, provided that the problem of the interaction of two liquid spheres of different radii in a linear flow field is solved, and the particle size distribution function is known.

4. Weak rheological flows of deflocculated emulsions.

When there is Brownian motion, the volume distribution $p(\mathbf{r}, t)$ satisfies the relations /2/

$$\partial p/\partial t + \operatorname{div} (p\mathbf{V} - \mathbf{D} \cdot \nabla p) = 0, \; p \to 1 \; (r \to \infty) \tag{4.1}$$

As in /2/, the tensor of relative diffusion of two liquid spheres is

$$\mathbf{D}(\mathbf{r}) = B_0 kT\,[\mathbf{nn}G + (\mathbf{I} - \mathbf{nn})H], \quad H = \chi(2T_{11} - T_{12})^{-1}$$

Here k is Boltzman's constant, T is the absolute temperature and $T_{11}(\zeta, \lambda)$, $T_{12}(\zeta, \lambda)$ are the coefficients of resistance denoted in /8/ by $\Lambda_{11}, \Lambda_{12}$). We represent the presence of short-term stabilising repulsion forces by the boundary condition

$$(p\mathbf{V} - \mathbf{D}\cdot\nabla p)\cdot\mathbf{n} \to 0 \quad (r \to 2a) \tag{4.2}$$

It should be expected that the distributions $p(\mathbf{r})$, P^*, P^{**} obtained in Sects.2 and 3 (except the volume density on closed trajectories) can be obtained formally from the corresponding steady state problems (4.1), (4.2) in the limit $\mathrm{Pe} = \|\mathbf{E}\|\, a^3 \mu_e/(kT) \to \infty$. At least we can easily construct the boundary layers of thickness $\sim a\,\mathrm{Pe}^{-1}$ "blurring" the surface density P^*, and (2.8) can be obtained from the condition for matching the two-term boundary layer expansion with the outer solution $p = q(r)$. The density P^{**} is "blurred" by the subcharacteristic boundary layer of thickness $\sim a\ \mathrm{Pe}^{-1/2}$. However, the structure of the boundary layers is not required for computing Σ_{ij} in the zero approximation in $\mathrm{Pe}^{-1} \ll 1$.

In the other limiting case $\mathrm{Pe} \ll 1$ ($\mathbf{u}\,\|\partial\mathbf{E}/\partial t\| \ll \mathrm{Pe}^{-1}\|\mathbf{E}\|^2$) we have, as in /2/,

$$p(\mathbf{r}, t) = 1 - a^2 (B_0 kT)^{-1} (\mathbf{n}\cdot\mathbf{E}\cdot\mathbf{n})\, Q(\zeta) + \ldots \tag{4.3}$$

$$\frac{d}{d\zeta}\left(\zeta^2 G \frac{dQ}{d\zeta}\right) - 6HQ = \frac{d}{d\zeta}(\zeta^3 A) - 3B\zeta^2$$

$$Q \to 0 \ (\zeta \to \infty), \quad G\,dQ/d\zeta \to 0 \ (\zeta \to 2)$$

The meaning of the coefficients G and H implies that when $\zeta \to \infty$,

$$G = 1 - {}^3/_2\,\chi\zeta^{-1} + O(\zeta^{-3}) \tag{4.4}$$

$$H = 1 - {}^3/_4\,\chi\zeta^{-1} + O(\zeta^{-3})$$

Using (4.4) and the results of /7/ we find, that a particular solution $Q_0(\zeta)$ of (4.3) and solution $Q_1(\zeta)$ of the corresponding homogeneous equation exists such that when $\zeta \to \infty$

$$Q_0(\zeta) \simeq -{}^{25}/_2\,\alpha^2\zeta^{-4}, \quad Q_1(\zeta) \simeq \zeta^{-3} + {}^3/_2\,\chi\zeta^{-4} \tag{4.5}$$

Relations (4.5) were used in computing the initial values $Q_i(\zeta_0)$, $Q_i'(\zeta_0)$ for some $\zeta_0 \gg 1$. For $\zeta < \zeta_0$ the functions $Q_i(\zeta)$, $Q_i'(\zeta)$ were found by numerical integration (and here the derivatives $dG/d\zeta, dA/d\zeta$) did not have to be calculated). When $\zeta \to 2$ (and $\lambda < \infty$), we have

$$G\,dQ_1/d\zeta = C_1 + O(\varepsilon), \quad G\,dQ_0/d\zeta + 2(1 - A) = C_0 + O(\varepsilon)$$

The constants C_i were easily calculated numerically. The required solution is $Q(\zeta) = Q_0(\zeta) - C_0 Q_1(\zeta)/C_1$. It can be shown that when $\zeta_0 \to \infty$ and $\zeta \sim 1$, the computed values of $Q(\zeta)$ differ from the exact values by $O(\zeta_0^{-7})$, although for $Q_0(\zeta)$, and $Q_1(\zeta)$ the corresponding errors are of order $O(\zeta_0^{-2})$.

Using the results obtained in /2/, we find that the mean stress tensor has Newtonian form with effective viscosity

$$\mu_0 = \mu_e\,[1 + {}^5/_2\,\alpha c + k_0(\lambda)\, c^2] \tag{4.6}$$

$$k_0 = \frac{5}{2}\alpha^2 + \frac{15\alpha}{2}\int_2^\infty J\zeta^2\, d\zeta + \frac{9}{40}\chi\int_2^\infty \left[3BQ\zeta^2 + (\zeta^3 A - 8)\frac{dQ}{d\zeta}\right] d\zeta$$

Below we give numerical results

$\lambda = 0$	0.25	0.5	1	2	3	5	10	∞
$k_0 = 1.91$	2.35	2.72	3.28	3.96	4.36	4.81	5.26	5.91

The direct contribution /2/ of the Brownian motion to k_0 determined by the function $Q(\zeta)$, varies from 1.21 ($\lambda = 0$) to 0.91 ($\lambda = \infty$). The value /14/ of 6.1 for k_0 at $\lambda = \infty$ is less accurate due to the errors in determining J (see /1/).

Amongst the rheological features of the model discussed we note the weakening under shear and axisymmetric tension (for small λ) and the negative character of N_1, N_2. In this connection we find qualitative agreement with the behaviour of model suspension /15/ of rigid charged spheres (without hydrodynamic interaction) in a weak electrolyte, although, unlike in /15/. We have for the model in question $N_1 \sim N_2$ when $\lambda \lesssim 1$).

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ON THE MATHEMATICAL DESCRIPTION OF SPIRAL WAVES IN DISTRIBUTED CHEMICAL SYSTEMS*

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Selfexcited oscillatory modes in a chemically active medium of general form with diffusion are studied. The reactor is in the shape of a circle with impermeable boundaries and the medium is in mechanical equilibrium. Asymptotic forms are found for the case of a near-threshold value of the parameter for two kinds of selfexcited oscillations, rotating waves and standing symmetric waves, under the assumption that a vibrational loss of chemical equilibrium stability occurs.

Rotating spiral (reverberator) and divergent concentric (donducting centre) waves of chemical concentrations or electrical excitation have been observed in experiments on vibrational modes in distributed biological and chemical systems /1—3/. The reverberator can have several branches (several spiral wave fronts rotate around one local section of the medium). Analogous modes are detected in the combustion of cylindrical specimens /4/. Different approaches (see /5—8/ and the bibliography presented there) were used to describe such modes on the basis of diffusion equations with non-linear kinetics.** In one of the approaches, the occurence of rotating waves was associated with loss of stability of the stationary spatially homogeneous mode, and therefore, was examined from the aspect of the theory of bifurcation of solutions of non-linear equations dependent on a parameter. The analytical difficulties that occur here were successfully overcome in /7, 8/ by using group methods of bifurcation theory /9/. It was found that in the bifurcation situation examined, solutions, periodic in time,

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