EFFECTIVE RHEOLOGICAL PARAMETERS OF A SUSPENSION
WITH POLYFRACTIONATED FILLER

V. A. Buryachenko, Yu. V. Skorbov,   UDC 532.135:539.4:541.24
S. V. Gunin, and V. V. Lysov

We examine a microscopically inhomogeneous medium consisting of a homogeneous non-linear viscoplastic matrix and a random set of rigid ellipsoidal inclusions of various sizes. A variant of the effective field method is used to calculate the macroscopic rheological constants of the medium.

Optimization of a number of chemical technology processes for suspensions [1] requires prediction of the effective rheological properties of suspensions on the basis of carrier phase properties and the geometric structure of the filler. For monofractionated filler, this problem can be solved by various methods [1-4], including the most general: the multiparticle effective field method [3, 4]. Evidently the earliest method to account for a polyfractionated filler state is the principle of multiplication of Farnas [5], used to predict various macroscopic properties of suspensions and composites [6, 7] with infinitely large differences in the size of the filler fractions. The application of this principle to the case of inclusion fractions of commensurate size can lead to underestimation of the effective viscosity of Newtonian suspensions [7]. A second method of accounting for a polyfractionated filler state is based on either an estimate using semi-empirical models [8] with the maximum filler content c_∞ for the given grain size distribution, or on the construction of asymptotic effective viscosity in terms of the solid phase concentration c when $c/c_\infty \to 1$ and $c \to 0$ [2]. Substantial differences in the effective viscosity η^* for constant c/c_∞ with change in the grain size distribution of the filler have been noted [9]. Most of the numerous theoretical methods (see reviews in [1, 2, 10]) are single-particle and do not in principle account for the influence of differences in inclusion size on the effective viscosity. An exception is the multiparticle effective field method [3, 4], on whose bases we propose an approximate method for computing the effective rheological properties of a suspension with a polyfractionated filler.

1. Effective Field Method. We consider an unbounded, microscopically inhomogeneous medium. Initially we will assume that the carrier phase equation relating the stress tensor σ and the strain rate ε is linear:

$$\sigma = L_0 \varepsilon, \qquad (1)$$

where by using the viscosity tensor L_0 of rank four, it is possible to describe the mechanisms of bulk viscosity and anisotropy.

Let the matrix v_0 with characteristic function V_0 and tensor L_0 contain the random set $X = (V_k, x_k, a_k, \omega_k)$ of rigid ellipsoids with characteristic functions V_k centers x_k forming a Poisson point field, with semiaxes $a_k^i (a_k^1 \geqslant a_k^2 \geqslant a_k^3)$, with the set of Euler angles ω_k, and tensors $L_0 + L_1$ ($L_1 = \infty$). We assume that all random quantities are statistically uniform, are ergodic fields, and that their expectation values are equal to their average over the component volume X_α:

$$\langle (\cdot) \rangle_\alpha = \overline{v}_\alpha^{-1} \int (\cdot) V_\alpha(x)\, dx, \quad \langle (\cdot) \rangle = \overline{w} \int (\cdot) W(x)\, dx, \quad \overline{v}_\alpha \equiv \mathrm{mes}\, v_\alpha,$$
$$w = U v_\alpha, \quad W = \Sigma V_\alpha \, (\alpha = 0, 1, \ldots).$$

We define $\langle (\cdot) | x_1 \rangle$ as the conditional average over the ensemble field X assuming that inclusion v_1 is located at point x_1. We will assume that the hydrodynamics of the components is

described by the equations of creep flow, and that the inclusions interact only hydrodynamically: Brownian movement is not taken into account.

We assign the composite structure with the help of $\varphi(v_m|v_1, ..., v_n)$ — the conditional density distribution of the m-th inclusion in region v_m for fixed inclusions in regions v_1, ..., v_n. Here $\varphi(v_m|v_1, ..., v_n) \to \varphi(v^m)$ if $|x_i - x_m| \to \infty$ $(i = 1, ..., n)$ and $\varphi(v_m|v_1, ..., v_n) = 0$ if x_m lies within some correlation well consisting of the union of the regions $v_j^0 \supset v_j (j = 1, ..., n)$ with characteristic functions V_j^0.

An estimate of the effective viscosity tensor L* in the relation (analogous to (1)) $\langle \sigma \rangle = L^* \langle \varepsilon \rangle$ can be obtained using the effective field method [3, 4]:

$$L^* = L_0 + \sum_{i,j=1} n_i (Y^{-1})_{ij} \langle R_j \rangle_\omega, \tag{2}$$

where n_i is the number concentration of inclusions of component i, and $\langle (\cdot) \rangle_\omega$ is the average over the orientation of inclusions of the j-th component. The tensor $R_j = P^{-1}{}_j$ is determined from the solution to the hydrodynamic problem of an isolated inclusion. In turn, $P_j = -\int U (x-y) V_j(y) dy \equiv L_0 S_0^j$, $x \in v_j$. Here $S^j{}_0$ is the Eshelby tensor, which is independent of the size (but not the form) of ellipsoid v_j. This tensor is well-known in isotropic [10] and transversally isotropic [11] media. U is the second derivative of Green's tensor [2, 3]. The tensor $(Y^{-1})_{ij}$ describes the concentration of the strain-rate field at the inclusions v_j caused by neighboring inclusions:

$$\langle \bar{\varepsilon} \rangle_i = \langle R_i \rangle_\omega^{-1} \sum_{j=1} (Y^{-1})_{ij} \langle R_j \rangle_\omega \langle \varepsilon \rangle,$$

$$Y_{ij} = \delta_{ij}(I - \langle R_i \rangle_\omega \int \langle S(x_i - x_j) Z_{ji} \rangle_\omega \varphi(v_j|x_j; x_i) dx_j) +$$

$$+ (-1 + \delta_{ij}) \langle R_i \rangle_\omega \int \{ \langle S(x_i - x_j) Z_{ji} \rangle_\omega \varphi(v_j|x_j; x_i) - \tag{3}$$

$$- \langle S_i(x_i - x_j) \rangle_\omega n_i \} V(x_j; x_i) dx_j - \langle R_i \rangle_\omega \langle P(v_i^0) \rangle_\omega n_j,$$

$$S(x_i - x_j) \equiv (\bar{v}_i \bar{v}_j)^{-1} \iint U(x - y) V_i(x) V_j(y) dx dy,$$

$$S_i(x_i - x_j) \equiv (\bar{v}_i)^{-1} \int U(x - x_j) V_i(x) dx, \quad V(x_j; x_i) = V(x_j) - V(x_i).$$

The matrix $Z = (Z_{ji}) (j, i = 1, ..., N)$ accounts for the binary interaction of inclusions v_i and v_j, and has an inverse Z^{-1} with elements

$$(Z^{-1})_{ij} = I\delta_{ij} - (1 - \delta_{ij}) R_i S(x_i - x_j). \tag{4}$$

For definiteness in (4) i, j take on only two values: i, j = 1, 2. The matrix Z can be constructed by the method of successive approximations, taking the first two iterations into account:

$$Z_{ij} = I\delta_{ij} + (1 - \delta_{ij}) R_i S(x_i - x_j). \tag{5}$$

Using (5), the expression for Y_{ij} in (3) simplifies to

$$Y_{ij} = \delta_{ij} I + (\delta_{ij} - 1) \langle R_i \rangle_\omega \int \{ \langle S(x_i - x_j) \rangle_\omega \langle R_j \rangle_\omega \langle S(x_i - \tag{6}$$

$$- x_j) \rangle_\omega \varphi(v_j|x_j; x_i) - \langle S_i(x_i - x_j) \rangle_\omega n_j \} V(x_j; x_i) dx_j - \langle R_i \rangle_\omega \langle P(v_i^0) \rangle_\omega n_j.$$

For equiprobably oriented inclusions the tensors $\langle S(x_i - x_j) \rangle_\omega$, $\langle R_j \rangle_\omega$ and $J_{ij} \equiv \langle R_i \rangle_\omega \langle S(x_i - x_j) \rangle_\omega \langle R_j \rangle_\omega \langle S(x_i - x_j) \rangle_\omega$ are isotropic [3]:

$$J_{ij} = (3J_{ij}^1, 2J_{ij}^2) \equiv 3J_{ij}^1 N_1 + 2J_{ij}^2 N_2, \quad N_1 = \delta_{ij}\delta_{kl}/3,$$

$$N_2 = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - 2\delta_{ij}\delta_{kl}/3)/2.$$

The components J_{ij} are given in [3].

2. Approximation Methods. Analysis of (5) and (6) shows that, independently of the precision of the solution to the problem with binary inclusion interaction, with the assumption

$$\varphi(v_j|x_j; x_i) = n_j V(x_j; x_i) \tag{7}$$

the values of the integrals in (5) and (6) are directly proportional to the inclusion concentration c. This is the principle limitation of the two-particle effective field method. It is possible to make the method more accurate by accounting for a greater number of interacting inclusions, but then the difficulty of assigning the conditional density distributions $\varphi(v_j|x_j; x_1, ..., x_n)$ arises. We note that at present, $\varphi(v_j|x_j; x_1, ..., x_n)$ is known only for n = 1 and spherical inclusions of uniform size [12]. An estimate of the nonlinear effects of the dependence on c of the integral terms in (5) and (6) is possible only by using an approximate approach based on identification of the coefficients-moduli from certain model experiments.

We shall dwell on one of the possible approximation approaches. If we consider the case of a single-component filler, then

$$L^* = L_0 + (1 - \langle R \rangle_\omega \langle P \rangle_\omega n_i - \int J_{ij}\varphi(v_j|x_j; x_i)dx_j)^{-1} \langle R \rangle_\omega n_i, \tag{8}$$

$$J^{ij} \equiv c^{-1} \int J_{ij}\varphi(v_j|x_j; x_i)dx_j = c^{-1}(I - \langle R \rangle_\omega n_i (L^* - L_0)^{-1} + \langle R \rangle_\omega \langle P \rangle_\omega n_i). \tag{9}$$

For density distribution (7), the J^{ij} in (9) are constant. In particular, for rigid spherical inclusions of uniform size in an incompressible matrix [3], we have

$$\eta^* = \eta_0 \left[1 + \frac{5}{2}c \left(1 - \frac{31}{16}c \right)^{-1} \right], \quad J_2^{ij} = \frac{15}{16}, \quad \langle R \rangle_\omega n_i = \frac{5}{2}\eta_0 c, \quad \langle R \rangle_\omega \langle P \rangle_\omega n_i = c. \tag{10}$$

where $J^{ij} = (3J^{ij}_1, 2J^{ij}_2)$. We note that the exact evaluation of $J^{ij}_2 = 1.004$, obtained for infinitesimal c [13], which is in agreement with the proposed effective field method, may be used for moderate values of the concentration c as well. The estimate of J_2 in (10) differs from the exact value by 6%. Let us examine the experimental data on the relative change in viscosity (η^*/η_0) of a suspension with spherical, rigid inclusions [7] (see Fig. 1). Because of the well-known hydrodynamic analogy of elastic problems, this corresponds to the relative change in shear modulus for a composite with rigid inclusions in an incompressible matrix. Substituting the experimental data for η^*/η_0 into the right part of (9), we rewrite it in co-

ordinates $J_2^e = \left(c^{-1} - \frac{5}{2}(\eta^*/\eta_0 - 1)^{-1} + 1 \right) \sim c$ (see Fig. 2). From Fig. 2 it is clear that for a mono-

fractionated filler, the experimental value for J^e_2 agrees satisfactorily with the calculated value $J^{ij}_2 = 1.004$ only up to a filler volume concentration of c = 0.4. Thus c = 0.4 limits the region of applicability of the two-particle effective field method of approximation. As a consequence of multiple-particle interactions of the inclusions, J^{ij}_2 decreases for c > 0.4. We take this into account with the piecewise linear relation $J^{ij}_2(c) = J^{ij}_2 f(c)$, $f(c) = \min(1, \alpha_1 - \alpha_2 c)$, which relation corresponds to a three-particle approximation. For doubly-fractionated filler, it can be shown that within the limits of the multiparticle effective field method only the dependence of the integral terms of J^{ij} on the relative size of the inclusion pair a_i/a_j affects the value of the effective modulus (12). We can conclude from Fig. 2 that there is an increase in parallel displacement of the direct-line portions of the J^{ij}_2 dependence for decreasing a_2/a_1.

Thus we take $J^{ij}_2(c) = J_2 \min (1, \alpha_1 - \alpha_2 c + \alpha(a_j/a_i)\cdot\text{sign}(1 - a_j/a_i))$, where $\alpha(1) = 0$. By minimizing the error we find $\alpha_1 = 1.57$, $\alpha_2 = 1.47$, $\alpha = 1.25(1 - a_j/a_i)$. According to experimental data [15] for a suspension with doubly-fractionated filler, the magnitude of the parallel displacement depends not only on the relative size of the fractions a_2/a_1, but also on their relative concentration, with $\alpha = 0$ for $c_2/c_1 = 0$ or $c_1/c_2 = 0$ and maximum parallel displacement α being achieved for $c_2/(c_1 + c_2) = 0.25-0.5$. Thus we can consider that approximately $\alpha = 1.25\{1 - (a_2/a_1)\min[4c_2(c_1 + c_2)^{-1}, 1, 2c_1(c_1 + c_2)^{-1}]\}$. These values for α_1, α_2, and α allow us to compute curves of the relative change in the viscosity of a suspension with a bimodal distribution of spherical inclusions (see Fig. 1), which is in satisfactory agreement with experiment. For polyfractionated filler it is necessary in (3) and (6) to use values of J^{ij}_2 interpolated from the doubly-fractionated filler values.

3. Non-Newtonian Properties. We consider a Newtonian suspension based on a viscoplastic matrix whose mechanical properties are described by the dissipation function

$$D = k\sqrt{\varepsilon_{ij}\varepsilon_{ij}} + \eta(I'_2)(\varepsilon_{ij}\varepsilon_{ij})/2 + ae_{ij}\varepsilon_{ij}. \tag{11}$$
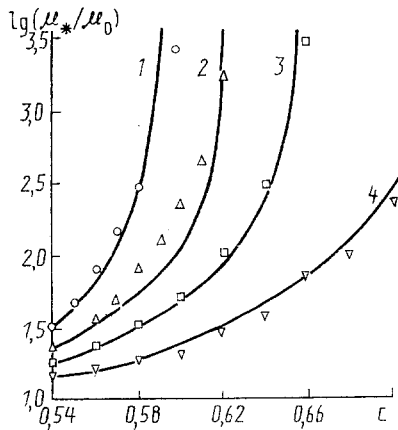
Fig. 1.   Fig. 2.

Fig. 1. Experimental data and curves calculated using the effective field method for the relative change in Newtonian viscosity of a suspension ($c_2/c \equiv 0.25$): (1) $a_2/a_1 = 1$; (2) 0.477; (3) 0.318; (4) 0.138.
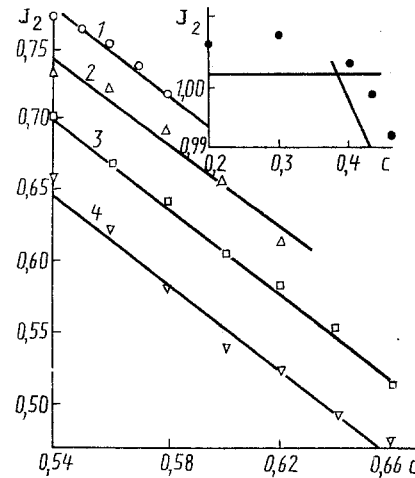
Fig. 2. Experimental data and computed curves [see Fig. 1 and [14] (filled points)], transformed to $J_2 \sim c$ coordinates.

For definiteness we will examine a variant of the power-law fluid $\eta(I'_2) \equiv \eta_0(I'_2)^{(n-1)/2}$, where $I'_2 = \vartheta_{ij}\vartheta_{ij}$ is the second invariant of the strain rate deviator $\vartheta_{ij} = \varepsilon_{ij} - \varepsilon_{kk}\delta_{ij}/3$; n is the parameter of nonlinearity; η_0 is the linear viscosity; k is the plastic limit; a is a hardening parameter, and $e_{ij} \equiv \int\limits_0^t \varepsilon(t)\,dt$.

To obtain concrete final results we assume homogeneity of the accumulated plastic strain and the second invariant of the strain rate tensor $\varepsilon_{ij}(x)\varepsilon_{ij}(x) = \langle \varepsilon_{ij}\varepsilon_{ij}\rangle_0$, $x \in v_0$ in the matrix material. With these assumptions, the problem of evaluating the effective non-Newtonian properties is linearized. Then as in [4], it can be shown that for an isotropic, incompressible matrix and inclusions with equiprobable orientations, the effective rheological properties of the suspension are described by a dissipation function of the form (11) with parameters

$$k^* = k\sqrt{(1-c)f_2(c)}\ , \quad a^* = af_2(c),$$
$$\eta^* = \eta_0 f_2(c)^{(n+1)/2}(1-c)^{(1-n)/2}(\ \langle \vartheta_{ij}\rangle\ \langle \vartheta_{ij}\rangle\ )^{(n-1)/2} \tag{12}$$

and a load function $\langle \sigma^a_{ij}\rangle \langle \sigma^a_{ij}\rangle = k^*$ with a deviatoric tensor of the active stresses $\langle \sigma^a_{ij}\rangle \equiv \langle \sigma_{ij}\rangle - \delta_{ij}\langle \sigma_{kk}\rangle/3 - \eta^*\langle \varepsilon_{ij}\rangle - a^*\langle e_{ij}\rangle$. It is evident from (12) that for a Newtonian suspension with n = 1, k = a = 0, the function $f_2(c)$ denotes the relative change of the Newtonian viscosity η^*/η_0, which depends only on the geometry of the inclusions and which may be evaluated using (8).

NOTATION

σ_{ij}, ε_{ij}, e_{ij} are the stress, strain rate and accumulated plastic strain tensors, respectively; $X = (V_k, x_k, a_k, \omega_k)$ is the set of inclusions v_k with characteristic functions V_k, centers x_k, semi-axes a_k and aggregate Euler angles ω_k; U is the second derivative of the Green tensor of the Lame problem for homogeneous unbounded media; $\varphi(v_m|x_m; x_k)$ is the conditional density distribution of the inclusions; and n_i is their number concentration.

LITERATURE CITED

1.   R. Kristensen, Introduction to the Mechanics of Composite Materials [in Russian], Moscow (1983).

2. Stereoregular Rubbers [in Russian], Vol. 2, Moscow (1981).
3. V. A. Buryachenko and A. M. Lipanov, Zh. Prikl. Mekh. Tekh. Fiz., No. 4, 53-57 (1989).
4. V. A. Buryachenko, Inzh.-fiz. Zh., 58, No. 3, 452-455 (1990).
5. C. C. Furnas, Ind. Eng. Chem., 23, 1052-1058 (1931).
6. V. E. Zgevsky, Int. J. Polym. Mater., 6, No. 1, 109-124 (1977).
7. R. J. Farris, J. Rheol., 12, No. 2, 281-301 (1968).
8. A. Wienckowski and F. Strek, Chem. Stosow, 16, No. 1, 45-127 (1966).
9. V. V. Moshev and V A. Ivanov, Rheological Behavior of Concentrated Non-Newtonian Suspensions [in Russian], Moscow (1990).
10. T. Mura, Micromechanics of Defects in Solids, Martinus Nijhoff, The Hague (1982).
11. P. J. Withers, Phil. Mag. A, 59, No. 4, 759-781 (1989).
12. Yu. V. Sokolkin and A. A. Tashkinov, Mechanics of Deformation and Failure of Structurally Inhomogeneous Bodies [in Russian], Moscow (1984).
13. H. S. Chen and A. Acrivos, Int. J. Solid Struct., 14, No. 3, 349-364 (1978).
14. I. M. Krieger, Adv. Colloid Interface Sci., 3, No. 2, 111-136 (1972).
15. A. B. Metzner, J. Rheology, 29, No. 6, 739-775 (1985).

SOME PROPERTIES OF A PRECURSOR FILM

D. I. Vandyshev and S. G. Skakun   UDC 532.696.1

The optical, rheological, and topological properties of a precursor film, which is created by a drop lying on a surface, were studied by means of ellipsometry. The investigated liquid is glycerin; the investigated substrates were type K8 and KU1 glass. The results are in good qualitative agreement with DLFO theory.

Heterogeneous dispersive media are used in many industrial processes, which creates heightened interest in the wetting and spreading phenomena, which play a defining role in such systems. It is known that an interphase liquid—vapor surface can form near the contact of a drop with the base. If wetting is incomplete, the contact angle is finite at equilibrium; if wetting is complete, the contact angle is negligibly small [1]. It has been observed [1-3] that a submicron thick film forms on a solid substrate for any type of wetting near the interphase contact line. This film, which is called the precursor film, starts at the boundary between the phases, where its thickness is at a maximum, and slowly thins away from the boundary. In the case of complete spreading, this film has the shape of a pancake, which contains all the initial volume of the liquid. In the case of incomplete wetting, that is, when some equilibrium contact angle θ is established in the system, this film also takes on a more complex equilibruim shape, which forms a transition region between the drop and the substrate. The shape and properties of this transition region are totally determined by the balance of forces which act on the interphase boundary and, consequently, are the most important characteristics of the liquid—solid body—vapor system.

The method of ellipsometry was used to study the optical, rheological, and topological properties of the precursor film, which arises in the case of incomplete wetting. Glycerin was chosen as the liquid to be studied. The substrates in the study were plane parallel plates of optical glass of type K8 and KU1. K8 glass is a single-component borosilicate glass, which contains additives of large cations and as a result has a large porosity in its structure. KU1 glass is a simple quartz silicate glass with no additional inclusions or developed porosity. From studies on glass surfaces [4], it is known that the surface of any silicate glass under normal conditions is covered with a layer of adsorbed water with inclusions of a depolymerizing silicon oxide grid. This "gel" has a chemical composition of the type $SiO_x(OH)_y$, where $x \to 2$ and $y \to 0$ with depth. We determined the effective values of these coating thicknesses for the glasses we used. The thickness was 50 Å for K8 glass, and 20 Å for KU1 glass, which is in good agreement with other investigations [5], which give values of 55 and 20 Å, respectively. The difference in the thicknesses is explained by the different glass porosities and