

## ON MODELS OF THIXOTROPIC FLUIDS

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It is shown that phenomenological equations, having the sense of equations of coagulation kinetics for suspension, and rheological equations, describing the behavior of a mixture with a constantly changing structure, in particular, of a thixotropic medium, can be obtained within the framework of the linear thermodynamics of irreversible processes. The simplest structure of the defining equations has been considered from the viewpoint of dimensional analysis. The possible role of diffusion effects in the flows of a thixotropic medium is discussed.

1. Among fluids with non-Newtonian rheological properties the so-called thixotropic media are of considerable interest. In the general case a rheological defining equation, with coefficients which depend not only on the usual parameters of state but also on a number of "structural" parameters that satisfy the equations of "structural kinetics", holds for a thixotropic medium. In suspensions whose flow is accompanied by the formation and the destruction of coagulates of suspended particles such structural parameters are the averaged characteristics of the sizes and forms of the coagulates, while additional equations describe the kinetics of the particle coagulation processes. Interest in thixotropic media of such type is connected, in particular, with the latest researches on the rheology of blood, attesting to the strong influence of coagulation phenomena on its rheological, electrical and optical properties [1-4].

A number of approaches are known to the description of thixotropic suspensions: from the most primitive, when an empirically obtained dependence on time is assumed for the coefficient of viscosity [5], to the highly complex, when the coefficient of viscosity is provided with a memory of the prehistory of the flow [6]. The immediate closure of the system of hydrodynamic equations with the aid of an equation borrowed from the coagulation kinetics was effected in [7, 8]. More general kinetic equations, allowing for the specifics of the phenomena in blood, were considered for the same purpose in [9]. The recent article [10] contains an approximate substantiation of Kesson's rheological equation as a consequence of the kinetic equation in the case of coagulation equilibrium. We note that the idea of describing coagulation phenomena in blood by the use of Smoluchowski's equations was first expressed in the littleknown article [11]. The question of the feasibility of constructing a model of a thixotropic fluid by the usual phenomenological means, using thermodynamic concepts, has not been resolved to date (only inadequately substantiated attempts are known [12, 13]).

2. Let us consider a mixture consisting of an incompressible Newtonian fluid of suspended particles with the same true density. Under a translational flow of the

mixture the particles "collide", resulting in the formation of coagulat of finite firmness. The coagulates can disintegrate under the action of hydrodynamic forces and be interchanged with the particles [9]. The mixture's composition can be characterized by the average volume concentration  $C$  of the particles, the apparent concentration  $H$ , the average number  $n$  of particles in a coagulat and the average volume  $w$  of a coagulat. If  $w_0$  is the volume of an individual particle, then  $w = n(w_0 + w_*)$ , where  $nw_*$  is the volume of fluid trapped ("locked") in the coagulate, and  $H = C(w_0 + w_*)/w_0$ . The numerical concentrations  $N_p$  of particles and  $N_a$  of coagulat are related by  $N_p = nN_a$ ,  $N_a w = H$ ,  $N_p w_0 = C$ . By virtue of the constancy and equality of the phase densities the mass concentrations are numerically equal to the volume concentrations.

For simplicity of exposition (see Sect. 5) the particles are taken to be nondeformable and of invariable volume. In each coagulate the particles adjoin the surrounding fluid or the other particles or the bound fluid. We assume that the relations between the area elements of the corresponding separation surfaces are uniquely determined by the average size of the coagulat (for a specified concentration  $C$ ). All the arguments below are carried out in the one-fluid approximation (for the mixture as a whole) without regard to microrotations and microdeformations (i. e., in the usual kinematic variables).

The fundamental hypothesis is that the total energy of the mixture per unit of mass is given by the formula

$$E \equiv \frac{u^2}{2} + U = \frac{u^2}{2} + U_V + U_\Sigma \quad (2.1)$$

Here  $u_i$  is the barycentric velocity of the mixture and  $U_V$  and  $U_\Sigma$  are the "volume" and the "surface" parts of the internal energy. The latter includes the total energy of the surfaces (free and connected) of all particles. By analogy with the reasonings in [14] we assume that

$$\begin{aligned} U_V &= U_T(S_T, C) + U_F(S_F, w, N_a) \\ U_\Sigma &= U_\Sigma(S_\Sigma, w, N_a), \quad S = S_T + S_F + S_\Sigma \\ \frac{\partial U_T}{\partial S_T} &= T_T, \quad \frac{\partial U_T}{\partial C} = \mu, \quad \frac{\partial U_F}{\partial S_F} = T_F, \quad \frac{\partial U_\Sigma}{\partial S_\Sigma} = T_\Sigma \end{aligned} \quad (2.2)$$

We also introduce notation for the derivatives of  $U_F$  and  $U_\Sigma$

$$\frac{\partial U_F}{\partial w} = \lambda_F, \quad \frac{\partial U_\Sigma}{\partial w} = \lambda_\Sigma, \quad \frac{\partial U_F}{\partial N_a} = \mu_F, \quad \frac{\partial U_\Sigma}{\partial N_a} = \mu_\Sigma \quad (2.3)$$

The indices  $T$  and  $F$  denote the components of the internal energy  $U$  and of entropy  $S$ , as well as other quantities that correspond to thermal and fluctuation motions in the mixture (here the concept of fluctuation motion is applied to the particles and the coagulates; fluctuations are the hydrodynamical consequences of the interactions of the coagulat [14]).

From the equations of conservation of mass, momentum and energy for the mixture we now successively obtain the equations of heat intake and of entropy balance. The original equations have the form

$$\begin{aligned} \partial_t u_l &= 0, \quad d_t C = -\partial_l J_l \\ \rho d_t u_k &= -\partial_l p_{lk} + \rho f_k \\ \rho d_t E &= -\partial_l (q_l + u_k p_{lk}) + \rho f_k u_k \end{aligned} \tag{2.4}$$

Here  $J_l$  is the diffusion flux of the particles,  $f_k$  is the external mass force,  $q_l$  is the heat flux,  $\partial_l = \partial/\partial x_l$ ,  $d_t = d/dt$ ,  $\partial_t = \partial/\partial t$ . Besides Eqs.(2.4) we still need to make use of additional coagulate diffusion equations. Starting from the results in [9], it is convenient to write latter equations in variables  $N_a$  and  $H = N_a w$

$$d_t N_a = -\partial_l J_l' + G, \quad d_t H = -\partial_l J_l'' + g \tag{2.5}$$

Here  $J_l'$  and  $J_l''$  are, respectively, the numerical and the volume flows of the coagulat,  $G$  is the coagulate formation rate,  $g$  is the rate of fluid entrapment the coagulates. The fluxes in (2.4) and (2.5) are related the equalities  $J_l = w_a n J_l' = C J_l' / N_a$  and  $J_l'' = w J_l'$ . From Eqs. (2.5) it follows that

$$d_t w = -\frac{J_l'}{N_a} \partial_l w + \frac{1}{N_a} (g - Gw) \tag{2.6}$$

From the energy Eqs. (2.4) we find, in the usual manner,

$$\rho d_t U = -\partial_l q_l - p_{lk} e_{lk}, \quad e_{lk} = 1/2 (\partial_k u_l + \partial_l u_k)$$

After a formal decomposition into "different-temperature" components we have ( $\theta$  defines the energy exchange between the degrees of freedom)

$$\rho d_t (U_T + U_\Sigma) = -\partial_l q_{Tl} - p_{Tlk} e_{lk} + \theta \tag{2.7}$$

$$\begin{aligned} \rho d_t U_F &= -\partial_l q_{Fl} - p_{Flk} e_{lk} - \theta \\ q_l &= q_{Tl} + q_{Fl}, \quad p_{lk} = p_{Tlk} + p_{Flk} \end{aligned}$$

Now using (2.2) –(2.6), from (2.7) we first obtain expressions for  $d_t(S_T + S_\Sigma)$   $d_t S_F$  and then, finally,

$$\begin{aligned} \rho \partial_t S + \partial_t G_l &= R, \quad R = \sum_{s=1}^7 Y^s X^s \\ G_l &= \rho S u_l + \frac{q_{Tl}}{T_T} + \frac{q_{Fl}}{T_F} - J_l' \left( m + \frac{\mu}{T_T} \frac{C}{N_a} \right) \\ m &= \mu_\Sigma / T_T + \mu_F / T_F \end{aligned} \tag{2.8}$$

The thermodynamic forces  $X^s$  and fluxes  $Y^s$  occurring in the dissipative function  $R$  are defined by the formulas:

$$\begin{aligned}
 X^1 &= T_F - T_T, & Y^1 &= T_T^{-1} T_F^{-1} \theta & (2.9) \\
 X^2 &= -m + \Lambda \frac{w}{N_a}, & Y^2 &= G \left( \Lambda = \frac{\lambda_{\Sigma}}{T_T} + \frac{\lambda_F}{T_F} \right) \\
 X^3 &= \Lambda / N_a, & Y^3 &= g \\
 X_i^4 &= \partial_i T_T, & Y_i^4 &= -\frac{1}{T_T^2} \left( q_{Ti} - \frac{\mu C}{N_a} J_i' \right) \\
 X_i^5 &= \partial_i T_F, & Y_i^5 &= -\frac{1}{T_F^2} q_{Fi} \\
 X_i^6 &= \frac{C}{T_T N_a} \partial_i \mu + \partial_i m - \frac{\Lambda}{N_a} \partial_i w, & Y_i^6 &= -J_i' \\
 X_{ik}^7 &= e_{ik}, & Y_{ik}^7 &= -\left( \frac{p_{Tik}}{T_T} + \frac{p_{Fik}}{T_F} - A \delta_{ik} \right)
 \end{aligned}$$

Here  $A$  is an undetermined scalar introduced to allow for the incompressibility of the mixture. Let us now write out the linear relations between the fluxes and the forces, with due regard to the symmetry principle and the medium's isotropy. Omitting the summands not germane to the subsequent arguments and not contributing to the dissipation (see [14]), we obtain

$$\begin{aligned}
 Y^r &= \sum_s A^{r,s} X^s, & A^{s,r} &= A^{r,s} \quad (s, r = 1, 2, 3) & (2.10) \\
 Y_i^r &= \sum_s A^{r,s} X_i^s \quad (s, r = 4, 5, 6) \\
 Y_{ik}^7 &= A^{7,7} X_{ik}^7 + \sum_{s=1}^3 A^{7,s} X^s \delta_{ik} \\
 p_{ik} &= -A_*^{7,7} e_{ik} - \sum_{s=1}^3 A_*^{7,s} X^s \delta_{ik} + A_* \delta_{ik} \\
 p_{Fik} &= -A_F^{7,7} e_{ik} - \sum_{s=1}^3 A_F^{7,s} X^s \delta_{ik} + A_F \delta_{ik} \\
 A_*^{r,s} &= T_T A_T^{r,s} + T_F A_F^{r,s}, & A_* &= A_T T_T + A_F T_F \\
 A^{r,s} &= A_T^{r,s} + A_F^{r,s}, & A_*^{s,r} &= A_*^{r,s}
 \end{aligned}$$

Without loss of generality, here we can assume  $A_F = 0$  and identify  $A_*$  with the hydrostatic pressure  $p$ . The transfer coefficients  $A^{r,s}$  can depend on the state parameters that are:  $C$  one of the temperature  $T_T$  or  $T_F$ , and, under specific conditions, also the quantities  $w$  and  $N_a$ . These conditions consist of the possibility of thermodynamic equilibrium when  $T_T = T_F$  and of arbitrary  $C$ ,  $w$  and  $N_a$  and are realized for systems in which a spontaneous (at the expense of forces  $X^2$  and

$X^3$ ) variation of the coagulation state takes place sufficiently slowly. An example is suspensions of coarse particles, wherein Brownian coagulation can be neglected in comparison with the shear one.

3. In the case of a quasistationary mode for the fluctuation temperature [14] with the conduction terms neglected the second equation in (2.7) approximately reduces to the finite relation  $\Theta(X^1, X^2, X^3) = -p_{Fik}e_{ik}$ . According to (2.10) the right hand side here is proportional to  $I_2 = e_{ik}e_{ik}$ ; hence for  $T_F$  follows the expression:  $T_F = T_F(I_2, C, T_T, w, N_a)$ . Then the formulas for  $Y^2$  and  $Y^3$  in (2.10) can also be written as  $G = G(I_2, C, T_T, w, N_a)$  and  $g = g(I_2, C, T_T, w, N_a)$ . Thus, the fluctuation intensity, the growth rate of the number of coagulates and the rate of fluid entrapment are represented as functions of the second invariant of the deformation rate tensor. When  $J_1 = 0$  (the diffusion is negligibly weak)

$$\frac{dN_a}{dt} = G, \quad \frac{dH}{dt} = g, \quad \frac{dw}{dt} = z \tag{3.1}$$

$$\left( z = \frac{g - Gw}{N_a} \right)$$

Consequently, using a linear (in the sense of the relation between forces and fluxes) formalism of nonequilibrium thermodynamics, for  $N_a, H$  and  $w$  we obtain nonlinear equations of coagulation kinetics of a very general form (the right hand sides in (3.1) virtually become arbitrary functions of their arguments if we complement the first three of relations in (2.10) by nonlinear nondissipative terms). Equations (3.1) are comparable with the first moment equations in [9], so that we can trace the connection between  $G, g$  and the probability characteristics of the coagulation interactions (the entrapment of the fluid was not taken into account in [9]; this is not difficult to do by keeping in mind the analogy of with the condensation process [15]).

Only two equations are independent in (3.1) (see Sect. 2). In the particular case when the fluid entrapment is uniquely determined by the coagulation process we should assume  $w = w(C, N_a)$  and then only one of these equations remains independent. If we additionally accept that  $C = \text{const}$  and do not consider the heat exchange ( $T_T \approx \text{const}$ ), then the first and third equations in (2.4), the formula for  $p_{ik}$  in (2.10) with coefficients  $A_{*}^{2,3}$  independent of  $T_F$ , and one of the equations in (3.1) form a system describing the motion of the simplest thixotropic fluid, viz., with one structural parameter.

4. In the model considered above it is possible to specify concretely the functions  $G$  and  $g$  and the transfer coefficients using empirical data or detailed physical considerations including the investigation of the hydrodynamics of fine-scale motions. Methods of dimensional analysis can be used for investigating the structure of the functions occurring in the description of the medium.

As an example let us consider a simple shear flow of a generalized thixotropic medium with one structural parameter. We make the dependence of the transfer coefficients on the fluctuation temperature under the assumption of the latter quasistationarity,

i. e., actually on the rate of shear. According to (2.10) and (3.1), for such flow

$$\tau = 2\eta(w, \dots)e, \quad dw/dt = z(w, \dots) \quad (\eta \equiv A_*^{7,7}) \quad (4.1)$$

Let the shearstress be a function of the shear rate  $e$ , of the liquid phase viscosity  $\eta_0$ , the true concentration  $C$  of the particles, the density  $\rho$  of the mixture, the mean volume  $w$  of coagulate, the parameter  $kT_T$  ( $k$  is the Boltzmann constant), which characterizes the intensity of Brownian motion, and of the dimensionless quantities  $\kappa_1, \kappa_2, \dots, w/l_1^3, w/l_2^3, \dots$ . The dimensionless constants  $\kappa_i$  and the constants  $l_i$  with the dimension of length are, by their origins, bound by the additional relations by which the parameter  $w$  is connected with the other essential structural parameters (we recall that by assumption the model contains only one independent structural parameter). It is evident that instead of all these constants we can directly include the dependent structural parameters themselves among the arguments of  $\tau$ . Among these are: the apparent concentration  $H = H(C, w)$ , the coagulat asymmetry index  $\lambda = w^{1/3}/l_{\max}(w)$  ( $l_{\max}$  is the maximum linear dimension of the coagulat), the relative dispersion of coagulates  $\delta(w) = (w_{\max} - w_{\min})/w$  with respect to dimensions, etc.

With due regard to these remarks we can write

$$\tau = 2\eta_0 e f \left( H, \lambda, \delta, \dots; \frac{\eta_0 e w}{kT_T}, \frac{\rho e w^{1/3}}{\eta_0} \right) \quad (4.2)$$

Further, we assume that  $C = \text{const}$  and occurs in  $f$  only in terms of  $H, \lambda, \dots$  since the "phase" composition of the mixture is determined precisely by the apparent concentration  $H$ . The last of the arguments in  $f$  is the Reynolds number  $R_a$  for the coagulat. The mechanisms of thixotropy and nonlinear viscosity, as a rule, are not connected with the inertial effects (for blood, for instance, the modes when  $R_a \leq 10^{-2}$ ) are of interest); therefore, from now on we assume

$$\tau = 2\eta_0 e f \left( H, \lambda, \delta, \dots; \frac{\eta_0 e w}{kT_T} \right) \quad (4.3)$$

We see that two essentially distinct mechanisms of nonlinearity of function  $\tau(e)$  exist. One of them is due to Brownian motion and is accompanied by the dependence of the viscosity on the size of the particles (see the last argument in  $f$ ), which is fully consistent with microrheological representations [16,17]. The second mechanism is independent of Brownian effects and is caused by the dependence of the structural parameters  $H, \lambda, \delta, \dots$  on  $e$  by virtue of the second equation in (4.1). It is precisely the second mechanism that corresponds to the case of a purely thixotropic medium:

$\tau = 2\eta_0 e f(H, \lambda, \delta, \dots)$ . From (4.3) it follows that when there is no entrapment of the liquid ( $H = C = \text{const}$ ) in a monodisperse suspension ( $\delta = 0$ ) the viscosity is independent of the absolute size of particles if they vary in a geometrically similar manner ( $\lambda = \text{const}$ ). For spherical particles this conclusion has been confirmed experimentally and was repeatedly obtained on other considerations [18].

Formula (4.3) shows also that for a polydisperse suspension the viscosity is determined not only by concentration but also by the fractional composition (related empirical data have been presented, for instance, in [19]).

Let us now turn to the second equation in (4.1) which describes the variation of the average volume of a coagulate. First, we note that for  $w = w(C, N_a), C = \text{const}$  and  $H = H(C, w)$  the functions  $z, g$  and  $G$  differ by factors depending only on  $C$  and  $w$ . According to [9] the function  $G$ , and, consequently,  $z$ , can be represented as a sum of three summands  $z_a, z_f$  and  $z_e$  which correspond, respectively, to the fusion, disintegration, and exchange interactions of the coagulat. For simplicity we assume that the exchange interactions are such that the numerical concentration of the coagulata is not changed; then  $z_e = 0$ .

Let  $z_a = z_a(w, H, \lambda, \delta, \dots, e, \eta_0, kT_T)$  and  $z_f = z_f(w, H, \lambda, \delta, \dots, e, \eta_0, \sigma_f)$ , where  $\sigma_f$  is the mean critical stress for the coagulate and  $\eta_0$  occurs in  $z_f$  only in combination with  $e$ , namely, in terms of the stress  $\tau$  (4.3). Then

$$\frac{dw}{dt} = we \left[ \zeta_a \left( H, \lambda, \delta, \dots; \frac{\eta_0 e w}{kT_T} \right) - \zeta_f \left( H, \lambda, \delta, \dots; \frac{\sigma_f}{\tau} \right) \right] \quad (4.4)$$

A purely thixotropic medium, in which the effects of Brownian motion are negligibly small, is described by the relations

$$\tau = 2\eta_0 e f(H, \lambda, \delta, \dots), \quad H = H(w), \quad \lambda = \lambda(w), \dots \quad (4.5)$$

$$\frac{dw}{dt} = we \left[ \zeta_a(H, \lambda, \delta, \dots) - \zeta_f \left( H, \lambda, \delta, \dots, \frac{\sigma_f}{\tau} \right) \right]$$

In the absence of disintegrations ( $\zeta_f = 0$ ) and of fluid entrapment ( $H = C$ ), if,  $\lambda = \text{const}$  and  $\delta = \text{const}$  we obtain the well-known equation of shear coagulation [15]. In the general case the shear rate  $e$  is a time function  $e = e_* \varphi(t/t_*)$  characterized by not more than two dimensional constants  $e_*$  and  $t_*$ . Therefore, instead of (4.4) we can write

$$\frac{dw}{d(t/t_*)} = e_* t_* w \varphi \left( \frac{t}{t_*} \right) (\zeta_a - \zeta_f) \quad (4.6)$$

If the shear mechanism of coagulation predominates, then when  $e_* t_* \gg 1$  we obtain  $\zeta_a - \zeta_a \approx 0$ , whence follows the finite connection between  $\tau, e$  and  $w$ . Combining it with (4.3), we arrive at a model of a nonlinearly-viscous medium with a rheological equation that does not explicitly contain the particle size. The physical sense of the inequality  $e_* t_* \gg 1$  is obvious: the typical time for a change in the structure ( $\sim 1/e_*$ ) is very much less than the typical "hydrodynamic" time  $t_*$ . In the other limit case, when  $e_* t_* \ll 1$  (for example, a small amplitude or a high frequency), under a periodic variation of  $e$  we obtain  $w = w_0(1 + O(e_* t_*))$ . The constant  $w_0$  is found from Eq. (4.6) by averaging over the period.

When  $e = 0$  it is generally necessary to allow for Brownian effects. In the

absence of a spontaneous disintegration of coagulates, instead of (4.4) we have

$$\frac{dw}{dt} = \frac{kT_{\Gamma}}{\eta_0} \zeta_a^{\times}(H, \lambda, \delta, \dots)$$

We see that when  $H = \text{const}$ ,  $\lambda = \text{const}$  and  $\delta = \text{const}$  the average size of the coagulates grows linearly, while the numerical concentration  $N_a \sim t^{-1}$ . This is in complete agreement with the results of the kinetic theory of coagulation [9, 20]. Among the assumptions made we have not included any constraints on the multiplicity of interactions; nevertheless, (4.5) is consistent with the equation obtained from the general kinetic equations [9] for paired collisions. A reason for this can be the absence (in contrast, say, to the equations of chemical kinetics) of an interaction cross-section among the independent arguments of  $z_a$ . Equations of a form more general than (4.5) arise when additional independent arguments are introduced in  $z_a$  and  $z_f$ , reflecting the physical properties of the coagulates and formed by using the constants occurring in  $U_{\Sigma}$  and  $U_F$  as well as by allowing for the influence of finite  $R_a$  on the coagulation.

5. Let us note certain possible generalizations and modifications of the arguments made in Sects. 2 and 3.

1. We assumed above that the components  $U_{\Sigma}$  and  $U_F$  of the internal energy and a number of other quantities depend only upon two characteristics of the structure, viz.,  $w$  and  $H$  (or  $N_a$  and  $H$ ), i. e., on the first two moments of the distribution function of coagulate size [9]. Only one of the moments was reckoned independent in Sect. 4. However, it is possible that the quantities named depend also on the higher moments. Their introduction implies the emergence of new summands in the dissipative function, of new defining equations and of new cross effects, and leads to an increase in the order of the system of structural equations.

2. In certain cases the internal energy is generally determined not only by the size distribution of the coagulat but also by more refined statistical characteristics, for example, by the trapped fluid distribution with respect to the elongation  $\lambda$ , to the amount of trapped fluid, etc.

3. The allowance for the internal degrees of freedom — the microrotation and the microdeformation of the coagulates — leads to a number of additional effects, in particular, the dependence of the fluctuation temperature and of the rate of change of the structure on the invariants of the micromotion tensors, without affecting the general character of the model.

4. If, as was done in [14], we examine a two-phase medium consisting of a liquid phase and of coagulat, then the fluid entrapment is described as a phase transition. In contrast to the one — phase case, in the two — phase analysis the gradients  $\partial H / \partial x_k$  (or  $\partial C / \partial x_k$ ) serve as parameters of state. Therefore, an anisotropy of the transfer processes can exist, while among the arguments of the thermodynamic fluxes in particular, of function  $G$ , there may be present also scalars of the form

$$\frac{\partial H}{\partial x_k} \frac{\partial H}{\partial x_k}, \quad \frac{\partial H}{\partial x_k} X_k^s, \quad \frac{\partial H}{\partial x_k} \frac{\partial H}{\partial x_l} X_{lk}^s$$



where  $X_k^*$  and  $X_{1k}^*$  are, respectively, tensors of first and second rank that have the meaning of thermodynamic forces (see (2.9)).

5. Also possible is a multiphase analysis when the mixture is assumed to consist of a liquid zero and of a solid phase, each of which combine coagulates of like size. Combining the arguments in Sect. 2 and in [14, 21], we can find the rate  $G^n$  of formation of coagulates of  $n$  particles as a function (in the quasistationary case) of deformations rates and of numerical concentrations  $N_a^m$  of coagulates of different sorts. The equations for  $N_a^m$ , in which  $G^n$  occurs, form an analog of the kinetic equations of coagulation for a discrete distribution by size [9]. One variant of a multiphase model of such a type has been proposed previously (see [14]).

6. For the diffusion fluxes  $J_l$ , from (2.10) we obtain representations in terms of the gradients of  $\mu, T_T, T_F, w$  and  $N_a$  with variable coefficients. As in [14], these relations take into account the fluctuation mechanism of diffusion intensification and, in addition, reflect a tendency to the smoothing of the mixture's composition both with respect to concentration and to coagulate sizes.

The discussions in Sects.3 and 4 did not take into account these diffusion effects and the conductive transfer of the fluctuation energy. Such an approximation is valid if the corresponding transfer coefficients (of the "fluctuation thermal conductivity" and the diffusion) are small and there are no zones of higher gradients of  $T_F, H, \dots$ . However, the fluxes may contain regions where the nondifferential terms of the corresponding equations are also small, for example, regions where  $I_2 \approx 0$ . From the point of view of the equations in Sects. 3 and 4, in these regions  $T_F = T_T$  and  $dw/dt \geq 0$  (a very slow Brownian growth of coagulates takes place). But if the transfer coefficients (for instance viscosity) depend strongly on  $T_F$  close to  $T_T$  and on  $w$ , then the small absolute error permitted in the computation of  $T_F$  and  $w$  leads to large errors in the determination of the other quantities. Thus, the validity of the elementary models of a thixotropic medium is violated not only in the boundary layers with large gradients but also in the boundary layers of a special type, where the conductive effects and processes induced by the shear in the flow (fluctuations, formation and disintegration of coagulates) are simultaneously weak. A more exact analysis of the processes in regions where  $I_2 \approx 0$  can be made with the use of the method of singular perturbations.

As a typical example let us consider the stationary problem on flows of Poiseuille type in a plane slit  $|Y| \leq 1$  ( $Y = y/h$  is a dimensionless coordinate). Let the distribution of the velocity  $u(Y)$  be known and let it be required to find a function  $Z(Y)$  subject to the equation (all quantities below are dimensionless)

$$\varepsilon (DZ)' - W(Y, Z) = 0, \quad \varepsilon DZ' = 0 \text{ for } Y = \pm 1 \tag{6.1}$$

The "degenerate" (when  $\varepsilon = 0$ ) solution  $Z_\infty(Y)$  satisfies the equation  $W(Z_\infty, Y) = 0$ . The differences between  $Z$  and  $Z_\infty$  are localized in the "boundary layers" close to the axis and walls of the channel; here  $Z - Z_\infty = O(\varepsilon^\alpha)$ ,  $\alpha > 0$ . The main interest is in the quantity  $Z_0(\varepsilon) = Z(0)$ .

Let  $Z_\infty \approx AY^n$ ,  $W/D \approx BZ_0^m Y^k$ , and  $Z \sim Z_0$  when  $Y \ll 1$ , with  $n \geq 0$ ,  $m \geq 1$ , and  $k \geq 0$ . Then in the neighborhood of the axis  $\varepsilon Z' \approx BZ_0^m Y^k$ , whence  $Z \approx Z_0 + \varepsilon^{-1} BZ_0^m Y^{k+2} / (k+1)(k+2)$ . For some  $Y = \delta$  this solution must smoothly join up with  $Z_\infty$ ; therefore, we set

$$\begin{aligned} A\delta^n &= Z_0 + \varepsilon^{-1} BZ_0^m \delta^{k+2} / (k+1)(k+2) \\ An\delta^{n-1} &= \varepsilon^{-1} BZ_0^m \delta^{k+1} / (k+1) \end{aligned} \quad (6.2)$$

Hence  $\delta$  and  $Z_0$  are found explicitly in terms of the other parameters of the problem. The second relation in (6.2) shows that  $Z_0^m / \varepsilon \sim \delta^{n-2-k}$ ; then from the first follows an estimate of the order of  $Z_0$  and, finally, the estimates  $\delta \sim \varepsilon^{n(1-m)+k-2}$  and  $Z_0 \sim \delta^n$ . We see that the orders of smallness of  $\delta$  and  $Z_0$  may prove to be substantially lower than  $\varepsilon$ .

Analogous results are obtained when solving (6.1) by the method of integral relations.

According to (2.7) and (2.10) the simplest equation for the fluctuation temperature in a plane slit has the form

$$\varepsilon (k_F T_F')' - k_1 (T_F - T_T) + k_2 (u')^2 = 0 \quad (6.3)$$

If  $k_F(0)$ ,  $k_1(0)$  and  $k_2(0)$  are finite and nonzero and  $(u')^2 \sim Y^2$ , then  $n = 2$ ,  $m = 1$  and  $k = 0$  and, consequently,  $T_F - T_T \sim \varepsilon$  and  $\delta \sim \sqrt{\varepsilon}$ . With due regard to (2.5) and Sect. 4 we take it that the numerical concentration of coagulates satisfies the simplified equation

$$\varepsilon (DN_a')' - \zeta_{f0} |u'|^\beta N_a^b + \zeta_{a0} |u'|^\alpha N_a^a = 0 \quad (6.4)$$

Here  $D$ ,  $\zeta_{f0}$  and  $\zeta_{a0}$  are finite and nonzero on the channel's axis,  $\gamma = (\alpha - \beta) / (b - a) > 0$ ,  $a, b, \alpha$ , and  $\beta$  are nonnegative. Then  $n = \gamma$ ,  $m = b$ ,  $k = \beta$  when  $\beta < \alpha$  and  $m = a$ ,  $k = \alpha$  when  $\beta > \alpha$ , etc. It is somewhat more complicated to realize estimates for  $T_F$  and  $N_a$  in nonstationary flows, when an ordinary differential equation is obtained for  $Z_0$ .

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