## DIFFUSION IN DISPERSE MEDIUM WITH HETEROGENEOUS

TRANSFORMATIONS

Yu. A. Buevich, A. Yu. Zubarev, and S. L. Komarinskii

Mean macroscopic diffusion equations are obtained for a medium with foreign spherical inclusions in the presence of a source and a concentration discontinuity at their surfaces, and a method for closure of these equations is given.

The problem of mean description of the effective mass transfer in heterogeneous media, which is sufficiently difficult even when there are no mass sources, is even more complicated when chemical or phase transformations occur in the phase volumes or at their interfaces. In the latter case, there arises the general question of the extent to which the diffusional and mass-transfer characteristics obtained for a medium without transformations are suitable for the description of diffusion in the same medium in the presence of chemical reactions or phase transformations. It is also unclear how correct traditional concepts following from Fick's law, which lead to a parabolic diffusion equation in a homogeneous medium, are in analyzing significantly nonsteady mass transfer in heterogeneous media.

A constructive solution of these problems is of interest for many applications. Only one of the most important problems is considered here: modeling catalytic reactors with a disperse or porous catalyst [1, 2]; in investigating this problem, it is found that the parameters characterizing mass transfer in the same systems in the presence and absence of reaction may differ very greatly. Theoretical analysis of related problems also leads to the conclusion that mass and heat sources at the phase interface exert a fundamental influence on the heat and mass transfer in disperse media [3]. Both the heterogeneity of the medium and the given sources result in change in the type of nonsteady diffusion or heatconduction equation, which becomes elliptical or hyperbolic [4]. In addition, in some situations, this equation ceases to be local in time: memory integrals which depend on the previous history of the transfer process appear [4]. The utility of introducing these integrals for more adequate description of the diffusional processes follows from [5, 6].

Below, the given problem is considered for a moderately concentrated disperse medium containing identical spherical inclusions. The material of the inclusions and the continuous matrix is assumed to be homogeneous. For the sake of simplicity, the two phases are regarded as motionless, or in any case the Peclet number based on the relative velocity of the phases is assumed to be small in comparison with unity. This offers the possibility, when using a coordinate system associated with the volume-mean velocity of the dispersion medium, of neglecting the convective mass transfer by the mean fluxes, the convective dispersion due to pulsations, and also some convective cross effects discussed in [7]. It is natural to conduct the analysis by the universal method of averaging over the configurational ensemble of the particle system, using the basic concept of self-consistent field theory [8, 9]. However, this method must be generalized to the situation in which the concentration and flux of diffusing impurity undergo discontinuities of the first kind at the particle surfaces; that forms the subject of the present work.

The presence of discontinuities at the particle surfaces is taken into account by introducing a thin surface layer in which the detail concentration C(t, R), flux Q(t, R), and power density of the volume sources H(t, R) vary continuously between the corresponding boundary values, while the thickness  $\delta$  of this layer subsequently tends to zero. This procedure corresponds to one of the possible methods of introducing generalized functions and is sufficiently well developed [10].

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$$\Theta_{0} (\mathbf{R} | \mathbf{R}_{i}) = 1 - \Sigma \eta (a + \delta_{0} - |\mathbf{R} - \mathbf{R}_{i}|),$$

$$\Theta_{1} (\mathbf{R} | \mathbf{R}_{i}) = 1 - \Sigma \eta (a - \delta_{1} - |\mathbf{R} - \mathbf{R}_{i}|),$$
(1)

where  $\eta(x)$  is the Heaviside function and the summation is taken over all the particles, the Fick diffusion equation, valid in each of the phases outside the  $\delta$  layers at the particles, is written in the common form

$$\frac{\partial C}{\partial t} \approx -\nabla \mathbf{Q} + H, \quad {C \\ H} \approx \Theta_0 {C_0 \\ H_0} + (1 - \Theta_1) {C_1 \\ H_1}, \qquad (2)$$
$$\mathbf{Q} \approx -[\Theta_0 D_0 + (1 - \Theta_1) D_1] \nabla C.$$

The quantities  $\Theta_0$  and  $\Theta_1$  vanish inside spheres with centers at the points  $R_i$  (i = 1, 2, ..., N, where N is the total number of particles) and radii  $\underline{a} + \delta_0$  and  $\underline{a} - \delta_1$ , respectively, and are equal to unity outside these spheres,  $\delta = \delta_0 + \delta_1$ ; the relation between  $\delta_0$  and  $\delta_1$  may be arbitrary. In Eq. (2), the approximate equality sign is used; this reflects the fact that accurate equality is achieved as  $\delta \rightarrow 0$ .

Multiplying Eq. (2) by  $\Theta_0$  and  $1 - \Theta_1$ , averaging over the ensemble of configurations (positions of the particle centers), and passing to the limit as  $\delta \rightarrow 0$ , the following result is obtained, making use of the transition properties of the operators of ensemble averaging and differentiating with respect to the time and the coordinate (here and below,  $d\underline{a}/dt \gtrsim 0$  is assumed)

$$\lim_{\delta_0 \to 0} \frac{\partial}{\partial t} \langle \Theta_0 C \rangle = \lim_{\delta \to 0} \{ -\nabla \langle \mathbf{Q} \rangle + \langle (1 - \Theta_0) \nabla \mathbf{Q} \rangle + \langle \Theta_0 H \rangle \},$$
$$\lim_{\delta_1 \to 0} \frac{\partial}{\partial t} \langle (1 - \Theta_1) C \rangle = \lim_{\delta \to 0} \{ -\langle (1 - \Theta_1) \nabla \mathbf{Q} \rangle + \langle (1 - \Theta_1) H \rangle \}.$$

Taking account of Eq. (2), it is found that

$$-\langle \mathbf{Q} \rangle \approx D_0 \langle \Theta_2 \nabla C \rangle + D_1 \langle (1 - \Theta_1) \nabla C \rangle =$$
  
=  $D_0 \nabla \langle C \rangle + (D_1 - D_0) \langle (1 - \Theta_1) \nabla C \rangle + D_0 \langle (\Theta_0 - \Theta_1) \nabla C \rangle,$   
 $\langle (1 - \Theta_0) \nabla \mathbf{Q} \rangle \approx \langle (1 - \Theta_1) \nabla \mathbf{Q} \rangle - \langle (\Theta_0 - \Theta_1) \nabla \mathbf{Q} \rangle.$ 

The formulas of [8, 9] hold for the means over the discrete phase with excluded or added surface  $\delta$  layers

$$\langle (1 - \Theta_0) F \rangle = n \int_{|\mathbf{R} - \mathbf{R}'| \leq a + \delta_0} f^*(t, \mathbf{R} | \mathbf{R}') d\mathbf{R}',$$
  
$$\langle (1 - \Theta_1) F \rangle = n \int_{|\mathbf{R} - \mathbf{R}'| \leq a - \delta_1} f^*(t, \mathbf{R} | \mathbf{R}') d\mathbf{R}',$$

where the integration is taken over the positions R' of the center of the isolated (trial) particle, and f\* denotes the result of averaging an arbitrary detail function F(t, R) over the configurations in which the position of the center of one of the particles (the trial particle) is fixed. Hence

$$\langle (\Theta_0 - \Theta_1) F \rangle = n \int_{a - \delta_1 \leq |\mathbf{R} - \mathbf{R}'| \leq a + \delta_0} f^*(t, \mathbf{R} | \mathbf{R}') d\mathbf{R}'.$$

When  $\delta_0$  and  $\delta_1$  tend to zero, means of the form  $\langle (1-\theta_1)F \rangle$  transform to those considered and investigated in [8, 9]. The corresponding limits of the means of type  $\langle (\theta_0-\theta_1)F \rangle$  are now calculated. If F(t, R) is continuous at the particle surfaces or has a discontinuity of the first kind, then these means evidently vanish as  $\delta = \delta_0 + \delta_1 \rightarrow 0$ . If F = VC, however, where C(t, R) has discontinuities of the first kind at the particle surfaces, then introducing the notation

$$\lim_{\substack{\delta_0 = |\mathbf{R} - \mathbf{R}_i| \to a \to 0}} C(t, \mathbf{R}) = C_i^+, \lim_{\substack{\delta_1 = a - |\mathbf{R} - \mathbf{R}_i| \to 0}} C(t, \mathbf{R}) = C_i^-,$$

and taking account of the definitions in Eq. (1), it is found that

$$\lim_{\delta \to 0} \langle (\Theta_0 - \Theta_1) \nabla C \rangle = \lim_{\delta \to 0} \{ \nabla \langle (\Theta_0 - \Theta_1) C \rangle - \langle C \nabla (\Theta_0 - \Theta_1) \rangle \} =$$
$$= -\lim_{\delta \to 0} \langle \Sigma C_i^+ n_i \delta (a + \delta_0 - |\mathbf{R} - \mathbf{R}_i| \rangle + \lim_{\delta \to 0} \langle \Sigma C_i^- n_i \delta (a - \delta_1 - |\mathbf{R} - \mathbf{R}_i|) \rangle =$$
$$= -n \int_{|\mathbf{R} - \mathbf{R}'| = a} [c^{*+}(t, \mathbf{R} | \mathbf{R}') - c^{*-}(t, \mathbf{R} | \mathbf{R}')] \mathbf{n}' d\mathbf{R}',$$

where  $c^{*+}$ ,  $c^{*-}$  are the results of averaging  $C^+$ ,  $C^-$  over conditional configurations with a fixed position of the center of the trial particle;  $\delta(x)$  is a delta function. Therefore, introducing the means over the mixture as a whole and over its individual phases in the usual manner, according to the equations

$$c = \varepsilon c_{0} + \rho c_{1} = \langle C \rangle, \ \varepsilon c_{0} = \lim_{\delta_{0} \to 0} \langle \Theta_{0} C \rangle,$$
$$\rho c_{1} = \lim_{\delta_{1} \to 0} \langle (1 - \Theta_{1}) C \rangle, \ \rho = 1 - \varepsilon$$

(the detail and mean values are denoted by the same symbols, but upper or lower case, respectively), the total mean impurity flux due to diffusion is obtained in the form

$$\mathbf{q} = \langle \mathbf{Q} \rangle = -D_0 \nabla c - (D_1 - D_0) n \int_{|\mathbf{R} - \mathbf{R}'| < a} \nabla c^*(t, \mathbf{R} | \mathbf{R}') d\mathbf{R}' + D_0 n \int_{|\mathbf{R} - \mathbf{R}'| = a} [c^{*+}(t, \mathbf{R} | \mathbf{R}') - c^{*-}(t, \mathbf{R} | \mathbf{R}')] \mathbf{n}' d\mathbf{R}'.$$
<sup>(3)</sup>

Completely analogously

$$u_{1} = u = \lim_{\delta_{1} \to 0} \langle (1 - \Theta_{1}) \nabla \mathbf{Q} \rangle = n \int_{|\mathbf{R} - \mathbf{R}'| < a} \nabla \mathbf{q}^{*}(t, \mathbf{R} | \mathbf{R}') d\mathbf{R}',$$

$$u_{0} = \lim_{\delta_{0} \to 0} \langle (1 - \Theta_{0}) \nabla \mathbf{Q} \rangle = u + h_{s},$$

$$h_{s} = -\lim_{\delta \to 0} \langle (\Theta_{0} - \Theta_{1}) \nabla \mathbf{Q} \rangle = n \int_{|\mathbf{R} - \mathbf{R}'| = a} [\mathbf{q}^{*+}(t, \mathbf{R} | \mathbf{R}') - \mathbf{q}^{*-}(t, \mathbf{R} | \mathbf{R}')] \mathbf{n}' d\mathbf{R}'.$$
(4)

Here w<sup>\*+</sup> and q<sup>\*-</sup> denote the limiting values of the flux at the surface of a trial particle when  $|R - R'| = \underline{a} \pm 0$ , respectively. Thus, the diffusion equation following from Eq. (2), which determines the mean concentrations in the continuous and discrete phases, is written in the form

$$\varepsilon \frac{(\partial c_0)}{\partial t} = -\nabla \mathbf{q} + u + h_s + \varepsilon h_0, \quad \rho \frac{(\partial c_1)}{\partial t} = -u + \rho h_1, \tag{5}$$

where the mean flux q, the density of interphase transfer u, and the density of surface impurity sources  $h_s$  are formally defined in Eqs. (3) and (4).

The densities of volume sources  $h_0$  and  $h_1$  are assumed to be specified functions of the time and coordinates (ultimately, they may also depend on the mean concentrations  $c_0$  and  $c_1$ ). Complete determination of the density of surface sources entails, generally speaking, considering the kinetics of the processes of impurity emission and absorption in the  $\delta$  layers.

So as to be specific, these processes are modeled at the external and internal  $\delta$ -layer surfaces as first-order chemical reactions [11]. Then the surface-source density at the i-th particle may be written in the form

$$H_{s,i} \approx -k_0 [C(t, \mathbf{R}) - c_{*0}] \delta(a + \delta_0 - |\mathbf{R} - \mathbf{R}_i|) - k_1 [C(t, \mathbf{R}) - c_{*1}] \delta(a - \delta_1 - |\mathbf{R} - \mathbf{R}_i|),$$

and the detail surface-source density in the source is the sum of  $H_{s,i}$  over all the particles. Averaging the latter quantity and passing to the limit as  $\delta \rightarrow 0$ , the above method gives the result

$$h_{s} = -n \int_{|R-R'|=a} \left\{ k_{0} \left[ c^{*+}(t, \mathbf{R} | \mathbf{R'}) - c_{*0} \right] - k_{1} \left[ c^{*-}(t, \mathbf{R} | \mathbf{R'}) - c_{*1} \right] \right\} d\mathbf{R'}.$$
 (6)

Here the equilibrium concentrations  $c_{*0}$  and  $c_{*1}$  have been introduced for each phase; they are uniquely determined by the temperature and pressure in the system.

Comparing the last relation in Eq. (4) and Eq. (6), it follows from the additivity of the integral over the source that

$$\mathbf{n}'(\mathbf{q}^{*+}-\mathbf{q}^{*-}) = -k_0(c^{*+}-c_{*0}) - k_1(c^{*-}-c_{*1}).$$
(7)

In addition, in the presence of impurity absorption from both phases at the phase boundary, the following conditions must be satisfied separately

$$\mathbf{n}'\mathbf{q}^{*+} = -k_0(c^{*+} - c_{*0}), \ \mathbf{n}'\mathbf{q}^{*-} = k_1(c^{*-} - c_{*1})$$
(8)

This is the situation when chemical reaction with the participation of impurity molecules from both phases occurs at the particle surfaces and also in cases where there is no reaction but sorption-desorption processes do not reach equilibrium on both sides of the surface layer.

In systems which are in a state of complete thermodynamic equilibrium, it must be the case that  $c_0 \equiv c^{*+} = c_{*0}$ ,  $c_1 \equiv c^{*-} = c_{*1}$ ; if so, there is obviously no transfer at all.

If thermodynamic equilibrium is established on only one side of the phase interface, the concentration is homogeneous in the corresponding phase and coincides with the equilibrium value, while a condition of the type in Eq. (8) is retained for the other phase. This situation is usual for systems with phase transitions, for example, for drop suspensions in the presence of evaporation and condensation at their surfaces. In this case, the mean concentration in the discrete phase  $c_1 \equiv c_{1*}$  is simply equal to the homogeneous density of the liquid, and the condition of the type in Eq. (8) in a vapor-gas mixture describes the kinetics of evaporation-condensation;  $c_{*0}$  uniquely determines the partial pressure of saturated vapor at the specified temperature and pressure in the mixture.

If, finally, thermodynamic equilibrium is not attained in the volumes of both phases, but there is no heterogeneous transformation (i.e.,  $h_s = 0$ ), and the surface layer is in a state of local equilibrium (i.e., adsorptional equilibrium is established on both sides of this layer), the condition of continuity of the normal component of the flow at the particle surfaces follows directly from Eq. (7). The second condition follows from the requirement of local equilibrium, according to which  $c^{*-} = \alpha c^{*+}$ , where  $\alpha$  is the known equilibrium distribution coefficient of the impurity. Note that  $\alpha$  is not necessarily unity, as is groundlessly assumed in many investigations.

The requirement  $k_0c_{*0} = k_1c_{*1}$ , relating the properties of the equilibrium state with the kinetic coefficients characterizing the rate of establishment of this state, is not imposed here, in contrast to [11]. From a physical viewpoint, there is no basis to expect that a relation of this type will exist, and therefore such a requirement is incorrect.

Systems in which the particles are either completely impermeable to the impurity and do not conduct it  $(D_1 = 0)$  or contain a uniform concentration of impurity (as is the case, for example, for drop suspensions in vapor-gas mixtures) are now considered in more detail. In this case, taking account of Eqs. (3) and (6), the system in Eq. (5) yields a single equation for the mean concentration in the continuous phase (for simplicity, volume sources are neglected)

$$\varepsilon \frac{(\partial c_0)}{\partial t} = -\nabla \mathbf{q} + h_s, \ h_s = -k_0 n \int_{|\mathbf{R} - \mathbf{R}'| = a} [c^{*+}(t, \mathbf{R} | \mathbf{R}') - c_{*0}] d\mathbf{R}',$$

$$\mathbf{q} = -D_0 \left\{ \nabla(\varepsilon c_0) - n \int_{|\mathbf{R} - \mathbf{R}'| = a} c^{*+}(t, \mathbf{R} | \mathbf{R}') \mathbf{n}' d\mathbf{R}' \right\}.$$
(9)

Note in this connection an alternative approach to describing diffusion in heterogeneous media with inert (in diffusional terms) particles:  $D_1 = 0$ ,  $h_s = 0$ . This approach is based on solving the problem of effective transfer in a system of permeable particles with no surface transformation, in conditions of continuity of the concentration and the normal component of the impurity flux at the particle surfaces, using the transition to the limit  $D_1/D_0 \rightarrow 0$  in the final results. In this case, the mean flux q is expressed in terms of the integral (over the volume of the trial particle) of the concentration gradient inside the particle. It may be shown that, in steady conditions, both approaches are equivalent, but this is not the case for nonsteady diffusion processes.

To close the system in Eq. (5), the quantities defined in Eqs. (3) and (4) must be written in the form of functions or functionals of unknown fields of mean concentrations  $c_0(t, R)$  and  $c_1(t, R)$ . In accordance with the general method [8, 9], the requirement of selfconsistency of the theory is used for this purpose, and a special problem concerning the perturbations introduced into the mean field by the trial particles is formulated in order to find the conditional means in the integrands in Eqs. (3) and (4). Within the framework of this approach, it is usual to use Fourier (or Laplace) transformation, which offers the possibility of limiting consideration at first to functions rather than functionals. Fourier transformations of q, u, and  $h_S$  with respect to the time are represented in the form of linear functions of transformations of the concentrations  $c_0$  and  $c_1$  (and also in the general case, of  $c_{0x}$ ,  $c_{1x}$ ) with coefficients depending only on the parameters and not on the Fourier variable  $\omega$ . Such nonlinear dependences between Fourier transformations of different functions reflect functional linear relations between the functions themselves.

For the sake of simplicity, only the model of a disperse medium with moderate concentration, when the fact that the particles do not overlap may be neglected, is considered here. This is equivalent to neglecting the existence of a layer of reduced particle concentration close to the surface of the trial particle. In this case, the equations for the conditional means of the concentrations  $c_3^*$  and  $c_3^*$  in the vicinity of the trial particle are the same as the equations for the unconditional means  $c_0$  and  $c_1$ . Note however that, even in this case,  $c^{*+}$  in Eqs. (6)-(8) must be understood to mean the quantity  $c_3^{*+}$  associated with the continuous phase, because in fact the conditional particle concentration  $\rho^*$  at the trial-particle surface when  $R - R' = \underline{a}$  vanishes. The generalization to a high-concentration system is not considered here, since it may easily be undertaken using the results in [8, 9].

Following discussions analogous to [12], the linear relations between the Fourier transformations (retaining the notation of the corresponding untransformed quantities) are written in the form

$$\mathbf{q} = -D_{\nabla}c_0, \ h_s = K(c_{*0} - c_0) + K'c_{*1} - Lc_0, \ u = -Mc_0.$$
(10)

Terms proportional to  $c_1$  are not introduced in Eq. (10) since these quantities may always be expressed in terms of  $c_0$  from the Fourier-transformed second relation in Eq. (5). The coefficients D, K, K' and L, M depend on the transformation parameter  $\omega$ . Using Eqs. (5) and (10), and supposing that  $\varepsilon$  does not depend on the time and the coordinates, the following equation is obtained for the Fourier transformations of the mean concentrations  $c_0^*$  and  $c_1^*$  in the continuous and discrete phases in the vicinity of the trial particle and the impurity concentration  $c_2^*$  inside this particle

$$-D\Delta c_0^* = -(i\varepsilon\omega + K + L + M)c_0^* + Kc_{*0} + K'c_{*1} + \varepsilon h_0^*,$$
(11)  
$$i\rho\omega c_1^* = Mc_0^* + \rho h_1^*, \ r = |\mathbf{R} - \mathbf{R}'| > a; \ D_1 \Delta c^* = i\omega c^* - H_1, \ r < a$$

(the coordinate origin is at the center of the trial particle). The boundary conditions on the solution of the first and third relations in Eq. (11) take the form

$$c_{0}^{*}(\omega, \mathbf{R}) \rightarrow c_{0}(\omega, \mathbf{R} - \mathbf{R}'), \ r \rightarrow \infty; \ c^{*} < \infty, \ r = 0;$$

$$\mathbf{n}'\mathbf{q}^{*+} = -D\mathbf{n}'\nabla c_{0}^{*} = -k_{0}(c_{0}^{*} - c_{*0}), \ \mathbf{n}'\mathbf{q}^{*-} = -D_{1}\mathbf{n}'\nabla c^{*} = k_{1}(c^{*} - c_{*1}), \ r = a,$$
(12)

while the conditions on the fluxes follow directly from Eq. (8). The unconditional mean concentration co in the continuous phase is understood to be the external expansion of the conditional mean concentration c<sup>\*</sup> when r >> <u>a</u>. The quantity c<sup>\*</sup> is found in terms of the known c<sup>\*</sup> from the second relation in Eq. (11).

The solution of the problem in Eqs. (11) and (12) completely determines the expressions for the Fourier transformations of the quantities appearing in the integrands in Eqs. (3) and (4), also Fourier-transformed. Calculating the integrals, representations for the Fourier transformations of q, u, and h<sub>s</sub> depending on D, K, K', L, and M as parameters are obtained. Equating these results to the corresponding expressions in Eq. (10) yields a system of equations - transcendental in the general case - whose solution determines the parameters introduced in Eq. (10). Then applying an inverse Fourier transformation to Eq. (10), a functional dependence is obtained between the mean fluxes and densities of the interphase mass transfer and surface sources and the unknowns  $c_0$  and  $c_1$  of Eq. (5); this completely closes the given system. Both time derivatives of higher than first order and memory integrals may appear here in Eq. (5), as noted in [4, 12].

The solution of the problem for a trial particle and analysis of the system of mean diffusion equations for systems of specific classes will be undertaken in the future. Note, in conclusion, that the generalization of the theory here developed to more complex situations, in which the heterogeneous reaction includes several simultaneously diffusing materials or simultaneous heat and mass transfer processes are significant but the kinetics of the transformation at the particle surfaces may be linearized, is associated with fairly unwieldy computations but does not involve any fundamental difficulties.

Equally, it is simple to consider situations of partial equilibrium: in this case, the boundary conditions when r = a in Eq. (12) must be replaced by other, simpler, conditions, in accordance with the discussion following Eq. (8).

## NOTATION

a, particle radius; c, impurity concentration; c\*, equilibrium concentration; D, diffusion coefficient; h, density of sources; k, rate constant of reaction; n, numerical concentration of particles; n', n<sub>j</sub>, unit vector of external normal at the surfaces of the trial and j-th particles; R, t, radius vector and time; R',  $R_j$ , radius vectors of centers of trial and j-th particles; r = R - R'; u, density of interphase mass transfer;  $\alpha$ , impurity distribution coefficient;  $\delta = \delta_0 + \delta_1$ , thickness of surface layer;  $\varepsilon$ , volume fraction of continuous phase;  $\theta_0$ ,  $\theta_1$ , structural functions;  $\rho = 1 - \epsilon$ ;  $\omega$ , parameter of Fourier transformation with respect to the time; the results of averaging detail functions denoted by upper-case letters are denoted by the corresponding lower-case letters; subscripts 0 and 1 denote the continuous and discrete phases, respectively; s, particle surface; angle brackets denote averaging over a configurational ensemble; \*, conditional means.

## LITERATURE CITED

- 1.
- S. H. Park and Y. G. Kim, Chem. Eng. Sci., <u>39</u>, No. 3, 523-549 (1984). P. Fott and P. Schneider, Chem. Eng. Sci., <u>39</u>, No. 4, 643-650 (1984). Yu. A. Buevich, Inzh.-Fiz. Zh., <u>32</u>, No. 4, 625-631 (1977). 2.
- 3.
- Yu. A. Buevich and Yu. A. Korneev, Inzh.-Fiz. Zh., 31, No. 1, 21-28 (1976). 4.
- L. S. Kalashnikova and I. N. Taganov, Teor. Osn. Khim. Tekhnol., 15, No. 6, 914-917 (1981). 5.
- L. S. Kalashnikova, Inzh.-Fiz. Zh., 49, No. 3, 481-486 (1985). 6.
- F. Zanotti and R. G. Carbonelli, Chem. Eng. Sci., 39, No. 2, 263-311 (1984). 7.
- Yu. A. Buevich, Yu. A. Korneev, and I. N. Shchelchkova, Inzh.-Fiz. Zh., 30, No. 6, 979-8. 985 (1976).
- Yu. A. Buevich and I. N. Shchelchkova, Prog. Aerosp. Sci., <u>18</u>, No. 2, 121-150 (1978). 9.
- L. Shvarts, Mathematical Methods for Physical Sciences [in Russian], Moscow (1965). 10.

- S. S. Borisov and Yu. I. Paskal', Izv. Vyssh. Uchebn. Zaved., Fiz., <u>28</u>, No. 6, 43-49 (1985).
- 12. Yu. A. Buevich and S. P. Fedotov, Inzh.-Fiz. Zh., 43, No. 5, 740-748 (1982).

## CLOSURE OF A CAVITY IN POLYMER LIQUID

Z. P. Shul'man and S. P. Levitskii

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The closure of a spherical cavity in a relaxing polymer liquid with nonlinear rheological equations is investigated.

Known experimental results indicate anomalous dynamics of bubbles in liquids containing polymer additives. As well as the integral effect of suppression of cavitation of various types in solutions of high-molecular compounds [1], slowing of the collapse of individual inclusions has been noted [2], together with stabilization of the spherical form and retardation of the development of microjets in the closure of bubbles close to solid boundaries [3]. The theoretical model of cavity growth and collapse in a polymer medium was formulated in [4, 5], respectively, within the framework of a spherically symmetric formulation of the problem. To describe the rheology of the liquid, the Oldroid equation with an upper convective derivative was used [6]. The equations of gas-bubble oscillation in this liquid were obtained in [7]. Note that nonlinear pulsations of the bubbles in a viscoelastic liquid were also numerically investigated in [8-10], but instead of the corresponding invariant time derivative the ordinary derivative d/dt was used for the tensor quantities in [8, 9] and the partial derivative  $\partial/\partial t$  in [10].

Numerical calculations of the nonlinear dynamics of a cavity in a relaxing polymer medium on the basis of integrodifferential equations [4, 5] are sufficiently difficult (in [5], because of the development of numerical instabilities, only the initial stage of collapse was calculated), which complicates the use of such equations, in particular, for the description of collective phenomena. It is shown below that integrodifferential equations of the type in [4, 5] may be reduced to equivalent differential equations, and on this basis the features of cavity closure in polymer liquid are analyzed.

The equation of radial bubble motion in an incompressible non-Newtonian liquid takes the form

$$I = p_{\infty} - p_g + 2\sigma R^{-1} = S, \quad I = \rho \left( R\ddot{R} + \frac{3}{2} \dot{R}^2 \right),$$
  

$$S = 2 \int_0^\infty (T_{rr} - T_{\varphi\varphi}) (3y + R^3)^{-1} dy.$$
(1)

For T, a rheological equation of Oldroid type is adopted [6]

$$T = T^{(1)} + T^{(2)}, \quad T^{(2)} = 2\eta (1 - \beta) D,$$

$$T^{(1)} + \lambda \left[ DT^{(1)} / Dt - \alpha \left( T^{(1)} \cdot D + D \cdot T^{(1)} \right) \right] = 2\eta \beta D.$$
(2)

When  $1/2 < \alpha \le 1$ , Eq. (2) provides a qualitatively correct description of the elongational flow of polymer solutions and follows from various structural models; the equations adopted in [4, 5] are identical to Eq. (2) in the particular case when  $\alpha = 1$ . Using the kinematic

A. V. Lykov Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk. Lenin-Komsomol Voronezhskii State University. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 53, No. 2, pp. 218-222, August, 1987. Original article submitted May 21, 1986.