THEORY OF STRUCTURAL TRANSFORMATIONS IN FLOWING SYSTEMS

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The process of structural transformations in flowing systems is described on the basis of joint examination of the flow and mutual-transformation kinetics of kinetic-molecular units.

Activation and structural theories of viscosity have been widely used to describe viscosity anomalies in the flow of rheological systems.

Activation theory examines elementary flow events interpreted as the transition of a kinetic-molecular unit through a potential barrier, the height of which depends on the applied load. The presence of different types of kinetic units is allowed for in the generalization of this theory, but the possibility of their mutual transformation (i.e., the kinetics of the process of structural transformations) is not taken into account.

Structural theory explains viscosity anomaly on the basis of examination of structural transformations under the influence of deformation. The latter is described by the kinetic equation of the analogous chemical reaction. However, the displacement of structural units is not taken into account in this theory [2, 3].

A joint examination of the flow and mutual-transformation kinetics of structural units makes it possible to explain interesting rheological features of structured systems. Such an approach was used in [4] to describe the phenomenon of viscosity superanomaly. Taking this approach further, we describe regions corresponding to different types of viscosity anomaly. The model is checked against published experimental data.

1. We will examine the flow of a two-component liquid as our model. Assuming that the flow occurs as a result of an activated transition across a potential barrier, according to Eyring's representations [1] it may be shown that in this case the connection between the strain rate $\dot{\gamma}$ and the shear stress τ has the form:

$$\dot{\gamma} = a\nu_{10}\,\mathrm{sh}\,(\gamma_1\tau/kT) + (1-a)\,\nu_{20}\,\mathrm{sh}\,(\gamma_2\tau/kT). \tag{1}$$

Expression (1) is Eyring's equation [1] for microscopic shear rate averaged over the aggregate of particles of each component. The equation was derived from examination of the elementary event of the jump of the particles across the potential barrier. The parameters ν_{i0} and γ_i in the equation are the result of averaging over all of the particles of a given type, so that (1) describes the behavior of a continuous medium.

We will account for the process of change of the structure during deformation, which may be intepreted as the destruction and formation of each of the structures A and B. In this case, Eq. (1) must be closed by a kinetic equation describing the change in a over time:

$$da/dt = -k_1\varphi(a) + k_2\psi(a). \tag{2}$$

Equation (2) reflects the interaction of the kinetic-molecular units capable of change with the medium characterized by Eq. (1). If the process of the conversion of structure A into structure B occurs in a complex manner, as through a large number of intermediate stages, then (2) should be regarded as the equation of the net process of structural transformations, with effective constants k_1 and k_2 (the simplest case).

It is natural to suggest that the process of destruction of the structure is an activation process and that its effective activation energy U_0 is reduced under the influence of a mechanical field. As is known [5], the energy of this field E is spent mainly on deformation

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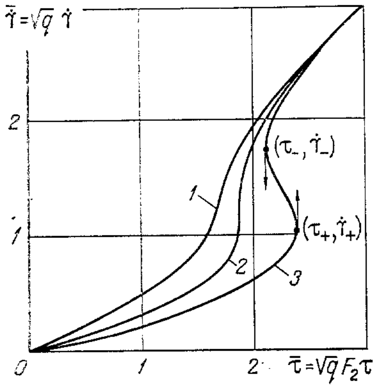

Fig. 1

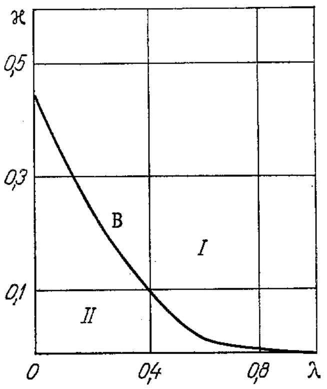

Fig. 2

Fig. 1. Rheological curves with different rates of structural transformations: 1) $\lambda = 0.1$, $\varkappa = 0.6 > \varkappa_*(\lambda)$; 2) $\lambda = 0.1$, $\varkappa = 0.342 = \varkappa_*(\lambda)$; 3) $\lambda = 0.1$, $\varkappa = 0.2 < \varkappa_*(\lambda)$.

Fig. 2. Regions of viscosity anomaly (I) and superanomaly (II). B is the boundary curve defining $\varkappa_*(\lambda)$ for the case $\mu = 0.01$.

of bonds in the structure being destroyed and on the orientation of chaotically directed kinetic-molecular units.

In the deformation of the bonds, the determining parameter is the stress acting in the medium. In the orientational rotation, the determining factor is the velocity gradient, since the orientation of a kinetic unit in the flow is the result of differences in the velocities of different sections of the unit. Assuming that these two processes occur independently of each other, we can write $E = p\tau + q\dot\gamma^2$. Here p and q are constants, respectively, expressing the rates of the processes. If the process of rotation of a kinetic unit is hindered (the case of a solid), it may be assumed that the reduction in effective activation energy takes place only as a result of tensile stress. This fact is reflected in the description in [6, 7] of the features of mechanical degradation of solid polymers.

Let us suppose that the process of restoration of the structure is also an activation process and is retarded under the influence of the same factors. Then the destruction and restoration constants may be written in the form

$$k_1 = k_{01}\exp\left[-\frac{U_0 - E}{RT}\right],\quad k_2 = k_{02}\exp\left[-\frac{U_0 + E}{RT}\right],\quad k_{0i} = \text{const}. \tag{3}$$

Thus, in general form, the model of deformation of a structured liquid contains two equations: rheological equation (1) and kinetic equation (2), with the constant relation in the form of (3).

Strictly speaking, not only flow but also structural transformations should be regarded as the result of elementary events consisting of the destruction (restoration) of bonds.

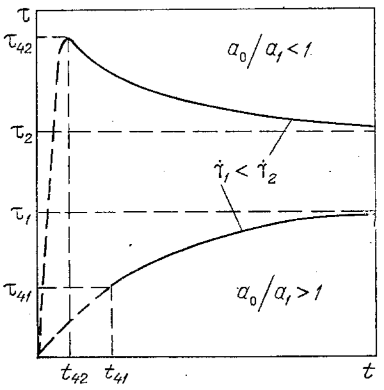

Fig. 3. Transient features of the proposed kinetic model.

TABLE 1. Values of the Parameters $\varkappa$, p, and q for Several Flowing Systems, δ — mean relative deviation

Material investigated	Source in literature	$\varkappa$	p	q	δ, %
Printer's ink No.54	[10]	0,633	0,003	1,6	7
Grade III asphalt	[11]	0,3	0,03	$7{,}5\cdot 10^{-4}$	10
Polyester + aerosol (3%)	[12]	0,19	0,006	0,001	6
s-polyacrylic acid	[13]	0,006	0,56	0,008	1,5
Emulsion: 10%	[15]	0,0026	0,171	$3{,}3\cdot 10^{-5}$	8
Methacrylate (MA)+ 20%		0,0036	0,045	$0{,}01\cdot 10^{-5}$	12
+ methylmethacrylate (MMA) 30%		0,00026	0,011	$0{,}01\cdot 10^{-5}$	3
+ acetophenone 40%		0,00006	0,007	$0{,}3\cdot 10^{-5}$	1,5
Emulsion: acetophenone	[15]	0,00006	0,007	$0{,}3\cdot 10^{-5}$	1,5
MA + MAA + benzene		0,0007	0,07	$100\cdot 10^{-5}$	1,5
+ 40 wt.% toluene		0,002	0,06	$220\cdot 10^{-5}$	6
Polyisobutylene + 60%	[14]	$0{,}7\cdot 10^{-5}$	7,3	7,25	10
+ channel black, 20%		$5{,}6\cdot 10^{-5}$	4 5	5,5	13
wt.% 10%		$77\cdot 10^{-5}$	4,3	6	12
0%		$140\cdot 10^{-5}$	3,8	8	11

These events have their own constants (activation energy, oscillation frequency, etc.). The kinetic law of change in the structure in this case would depend on the aggregate of all of these constants. The simplification being made in the present approach consists of allowing for hydrodynamic and rheological quasistationariness. In this case, the velocity field can be formulated up to the beginning of the structural transformations, so that the latter process (of structural transformations) is affected by the properties of an already formed medium (e.g., particle rotation depends on the velocity distribution). This situation is actually realized when the characteristic times of change in the hydrodynamic and rheological characteristics t_1 and t_2 are much shorter than the characteristic time of change in the structure t_3:

$$t_1,\ t_2 \ll t_3. \tag{4}$$

It should be noted that such a "nonuniform" examination of different processes is encountered fairly often and yields good results. We should remind the reader, however, of the study of the dependence of viscosity on chain length [8].

2. We will examine features of rheological behavior connected with the process of structural transformations, the simplest form of the net scheme of which is as follows:

$$A \overset{k_1}{\underset{k_2}{\rightleftarrows}} B.$$

This scheme corresponds to the kinetic equation

$$\frac{da}{dt} = -k_{10} a \exp\left[\frac{p_1\tau + q_1\dot{\gamma}^2}{RT}\right] + k_{20}(1-a)\exp\left[-\frac{p_1\tau + q_1\dot{\gamma}^2}{RT}\right], \tag{5}$$

$$k_{i0} = k_{0i}\exp(-U_0/RT).$$

It should be noted that at $p_1 = 0$ we obtain the model examined in [4]. Assuming the triviality of γ_i/RT (γ_i is usually small), we will use the first term of the expansion $\operatorname{sh}(x) = x + \ldots$. Then Eq. (1) takes the form

$$\dot{\gamma} = [aF_1 + (1-a)F_2]\,\tau, \tag{6}$$

where F_i is the flow of the i-th component. It is evident from this that the viscosity of such a liquid

$$\eta = [aF_1 + (1-a)F_2]^{-1},$$

or, in other words, the flow of such a liquid is the cumulative result of the flows of the various fractions of its components. Such an expression for the flow of a mixture of different liquids was found experimentally by Bingham [9].

Let us examine the steady-state solution of the system (5), (6). Excluding a, we obtain the flow curve

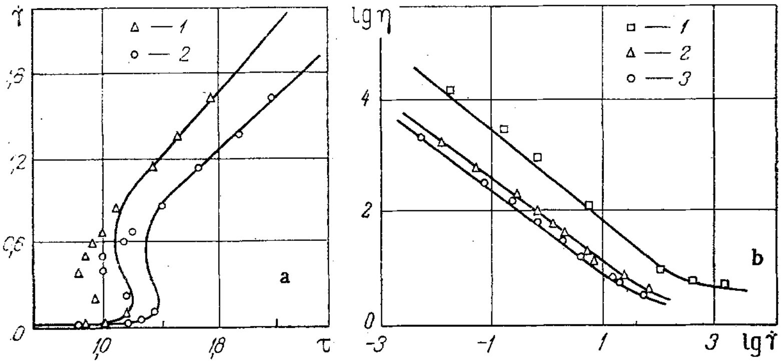

Fig. 4. Comparison of theoretical (solid lines) and experimental (points) flow curves: a) polyisobutylene + channel black [14] (1 — 60%, 2 — 0); b) emulsion MA + MMA in different solvents [15] (1 — acetophenone; 2 — benzene; 3 — toluene). $\dot{\gamma}$, $\sec^{-1}$; τ, $\mathrm{kgf/cm^2}$; $\log\eta$, P; $\log\dot{\gamma}$, $\sec^{-1}$.

$$\tau=\frac{1}{F_2}\frac{k+1}{k+\lambda}\dot{\gamma},\quad k=\varkappa\exp(p\tau+q\dot{\gamma}^2),\quad \varkappa=\frac{k_{10}}{k_{20}},\tag{7}$$

$$\lambda=F_1/F_2,\quad p=2p_1/RT,\quad q=2q_1/RT.$$

The following may be said in regard to the parameters λ and $\varkappa$. Viscosity usually decreases during structural transformations, so that we will assume $\lambda<1$ $(F_1<F_2)$. The parameter $\varkappa$ is the ratio of the constants of the rates of destruction and restoration of the structure at rest, so that $\varkappa<1$ also. It can be seen from (7) that the relation $\tau(\dot{\gamma})$ cannot be obtained in explicit form, but all of its characteristic features can be studied. We should note first of all the limiting relations $(\eta=\tau/\dot{\gamma})$:

$$\lim_{\tau,\,\dot{\gamma}\to\infty}\eta=F_2^{-1},\quad \lim_{\tau,\,\dot{\gamma}\to 0}\eta=F_2^{-1}(\varkappa+1)/(\varkappa+\lambda).\tag{8}$$

The first relation means that at large τ (or $\dot{\gamma}$) a flow regime with the lowest Newtonian viscosity $\eta_\infty=F_2^{-1}$ — coinciding the viscosity of structure B — is realized. At small values of τ (or $\dot{\gamma}$) the highest Newtonian viscosity η_0 is realized. As shown by the second equation of (8), this value generally does not coincide with the viscosity of structure A. Only at $\varkappa\ll\lambda$ do we have $\eta_0=F_1^{-1}$.

Equation (7) makes it possible to qualitatively describe the phenomenon of viscosity superanomaly. In this case, the curve of $\dot{\gamma}(\tau)$ is a multivalued function in a certain interval of τ, and there may be abrupt transitions from one branch to another (curve 3, Fig. 1). To find the extremums of function (7), the equation $d\tau/d\dot{\gamma}=0$ is conveniently written in the form

$$2x=\frac{(k+1)(k+\lambda)}{k(1-\lambda)},\quad x=q\dot{\gamma}^2.\tag{9}$$

For $x>0$, Eq. (9) either has no roots or has up to two roots. In the region of the parameters where Eq. (9) has two roots, the superanomaly phenomenon is observed. The boundaries of this region may be found from the condition of tangency of the left and right sides of Eq. (9). It is given with allowance for $k>0$

$$k_*=\varkappa_*\exp(p\tau+q\dot{\gamma}^2)=1-\lambda+\sqrt{(1-\lambda)^2+\lambda}.\tag{10}$$

Thus, to find the boundary of $\varkappa_*(\lambda)$, dividing the regions of monotonic and nonmonotonic relations $\tau(\dot{\gamma})$, it is necessary to solve a system of three equations: (7), (9), and (10). Excluding τ and $\dot{\gamma}$ from them, we obtain

$$\varkappa_*(\lambda)=k_*\exp\left\{-\frac{k_*+1}{\sqrt{2k_*(1-\lambda)}}\left(\frac{p}{F_2\sqrt{q}}\sqrt{\frac{k_*+1}{k_*+\lambda}}+\frac{k_*+\lambda}{\sqrt{2k_*(1-\lambda)}}\right)\right\}.\tag{11}$$

At $p=0$, Eq. (11) coincides with the corresponding work function in [4]. It should also be noted that at $k=k_*(\lambda)$, the viscosity of the system is expressed only through λ:

$$\eta_* = \frac{1}{F_2}\frac{k_*+1}{k_*+\lambda} = \frac{1}{F_2}\frac{2-\lambda+\sqrt{(1-\lambda)^2+\lambda}}{1+\sqrt{(1-\lambda)^2+\lambda}}.$$

The condition $\varkappa < \varkappa_*(\lambda)$ defines the region of the superanomaly (region II in Fig. 2). It has already been noted in [4] that the superanomaly effect is intrinsically of a hysteresis nature. This means that at $\varkappa < \varkappa_*(\lambda)$, the critical points of the transitions (the points of extremum (7)) $(\tau_+, \dot{\gamma}_+)$ and $(\tau_-, \dot{\gamma}_-)$ (see Fig. 1) do not coincide. At $\tau = \tau_+$, there is an abrupt shift in the flow regime, from an almost intact structure to a flow regime with a nearly destroyed structure. At $\tau = \tau_-$, the reverse shift of regimes takes place. At $\varkappa = \varkappa_*(\lambda)$ (curve B in Fig. 2), the critical conditions of the transitions coincide and the hysteresis character of the phenomenon degenerates. At $\varkappa > \varkappa_*(\lambda)$ (region I in Fig. 2), the transitions from regime to regime are of a crisis-free nature (curve 1, Fig. 1).

We should note certain transient features of Eqs. (5) and (6). Usually the deformation of flowing systems occurs in two regimes: a) with a constant shear rate ($\dot{\gamma} = \text{const}$); b) with a constant stress ($\tau = \text{const}$). In the first case, the pre-steady-state behavior of $\tau(t)$ depends on the value of a_0/a_1 (a_0 is the initial value of a, a_1 is the steady-state value of a). At $a_0/a_1 > 1$, $\tau(t)$ monotonically increases, approaching its steady-state value at $t \to \infty$. At $a_0/a_1 < 1$, the stress over time falls to its steady-state value. It should be remembered, however, that, due to the quasistationary character of rheological equations (1) and (6), the initial value of $\tau(0)$ will be different from zero. Thus, the curve of $\tau(t)$ will qualitatively correspond with the experimental curve beginning with a certain moment of time t_4 after the beginning of deformation. In actual systems, during this period the system is going through the stage of elastic deformation, accompanied by an increase in stress over time. The quasistationary value of the stress τ_4 is reached by the moment t_4. If this value of stress is greater than the steady-state value, then the complete curve of $\tau(t)$, including its initial section, will have a maximum. If this value of stress is less than the steady-state value, then the curve will be monotonic (Fig. 3). It should be remarked that τ_4 increases with an increase in the shear rate and t_4 decreases.

The analogous transient features are retained on the curve of $\dot{\gamma}(t)$ in the case $\tau = \text{const}$. There will then be several (two stable and one unstable) steady-state values of a in the superanomaly region. The proper choice of initial conditions may lead to one of the stable steady-state values of a, which are determined from the equation

$$\varkappa a \exp\{p\tau + q\tau^2[F_2 - a(F_2 - F_1)]^2\} = 1 - a.$$

3. The proposed kinetic model of the process of structural transformations contains several constants (λ, p, q, $\varkappa$) having a clear physical meaning. Knowledge of these constants makes it possible to qualitatively evaluate the rate of the structural transformation process in the investigated system and to make comparative estimates of the rate of the process in different systems. It may be noted for the flow curve in the coordinates $\eta - \dot{\gamma}^2$ that the width of the zone of intensive structural transformations is characterized by the parameter $\mu = p/F_2\sqrt{q}$ (with a change in $(\dot{\gamma}^2/\mu)$ to unity, $\dot{\gamma}_2$ changes to the value of μ). In these same coordinates, the quantity $\varkappa^{-1}$ qualitatively characterizes the region of slight change of initial viscosity. The quantity λ^{-1} characterizes the limits of the change in viscosity during deformation. Table 1 shows the values of these parameters calculated from the complete flow curves of several polymer systems.

Analysis of the tabular data shows that an increase in the percentage content of filler leads to "reinforcement" of the initial structure ($\varkappa$ decreases). The substitution of one filler for another in certain cases leads to an abrupt change in the probability of orientational rotation (q changes strongly), which might characterize the nature of the solvent.

Figure 4 shows a comparison of experimental data from [14, 15] with flow curves (the solid lines) calculated with the constants found. It can be seen that the theoretical and experimental curves diverge somewhat in the superanomaly region (Fig. 4a), which is quite admissible in view of the simple kinetic scheme adopted for the structural transformation process. There is good agreement between the theoretical and experimental data for conventional s-shaped curves (Fig. 4b). Table 1 and Fig. 4 show that the proposed kinetic model can be used not only for qualitative estimates of superanomaly conditions, the rate of the structural transformation process, etc., but for quantitative description of viscometric data for a broad class of structured flowing systems.

The mathematical procedure for finding the constants from the rheological curve or part of this curve does not present particular difficulties, although it is tedious. It is simplified appreciably by using the empirically established and partially valid assumption $F_1 \ll F_2$ $(F_2 = \eta_\infty^{-1})$. From (6) and steady-state equation (5), we have

$$q = \lim_{\dot{\gamma}\to\infty} \{\dot{\gamma}^{-2} \ln[(1-a)/a]\},\ a = \dot{\gamma}/\tau F_2.$$

Calculating these quantities from the experimental curve of $\tau(\dot{\gamma})$, we may determine q. With a known q, by rectifying the relation $\psi(\tau) \equiv \ln[(1 - a)/a] - q\dot{\gamma}^2$, we may find $\varkappa$ and p as functions of τ. In fact, in accordance with steady-state equation (5), the function $\psi(\tau)$ may be represented in the form:

$$\psi(\tau) = \ln\varkappa + p\tau.$$

It should be noted that reliable determination of q requires a sufficiently representative region of the rheological curve close to $F \to F_2$, while the same requirement holds close to F_1 for determining p. Use of the complete scheme of calculation for all of the parameters would obviously lead to more accurate results. However, it is more important that the model itself be further developed with allowance for the complete form of rheological equation (1), the non-isothermal nature of the flow in the region of high shear rates, etc. At the present stage, it is apparent that the possibility of qualitatively evaluating the rate of the structural transformation process by means of the model parameters $\varkappa$, p, q, and λ is of primary importance.

NOTATION

γ, strain rate; τ, shear stress; ν_{io}, natural vibration frequency; a, fraction of first component; γ_i, effective volume of particles of the i-th component; T, absolute temperature; k, Boltzmann's constant; A, B, initial and final structures; t, time; k_1, k_2, constants of rates of processes of destruction and restoration of structure, respectively; $\varphi(a)$, $\psi(a)$, kinetic laws of these processes; p, q, constants characterizing the rate of the processes of deformation of bonds and orientational rotation; E, energy of the mechanical effect.

LITERATURE CITED

1. H. Eyring, "Viscosity, plasticity, and diffusion as examples of absolute reaction rates," J. Phys. Chem., 4, 283-291 (1936).
2. A. P. Rebinder, Collected Works: Surface Phenomena in Disperse Systems. Physicochemical Mechanics [in Russian], Nauka, Moscow (1979).
3. O. C. C. Lin, "Thixotropic behavior of gellike systems," J. Appl. Polym. Sci., 19, No. 1, 199-215 (1975).
4. A. M. Stolin, S. I. Khudyaev, and L. M. Buchatskii, "Theory of viscosity superanomaly of structured systems," Dokl. Akad. Nauk SSSR, 243, No. 2, 430-433 (1978).
5. B. M. Smol'skii, Z. P. Shul'man, and V. M. Gorislavets, Rheological Dynamics and Heat Exchange of Nonlinearly Viscoplastic Materials [in Russian], Nauka i Tekhnika, Minsk (1970).
6. V. R. Regel', A. I. Slutsker, and É. E. Tomashevskii, Kinetic Theory of the Strength of Solids [in Russian], Nauka, Moscow (1974).
7. G. B. Manelis, L. P. Smirnov, and E. P. Polianchik, "Kinetic laws of mechanical degradation," Dokl. Akad. Nauk SSSR, 215, No. 5, 1157-1159 (1974).
8. F. Bueche, "Viscosity, self-diffusion, and allied effects in solid polymers," J. Chem. Phys., 20, No. 12, 1959-1964 (1952).
9. E. C. Bingham, Fluidity and Plasticity, Vol. 1 (1922).
10. T. I. Gudkova, L. A. Kazarovitskii, and N. V. Mikhailov, "On the effect of structural-mechanical properties of printer's inks on their behavior in the printing process," Kolloidn. Zh., 22, No. 6, 649-657 (1960).
11. P. F. Ovchinnikov and N. V. Mikhailov, "Formulas of effective viscosity of a structured liquid with allowance for thixotropy," Kolloidn. Zh., 32, No. 3, 409-415 (1970).
12. A. G. Merzhanov, A. M. Stolin, and B. N. Shatalov, "Nonisothermal method of studying the rheological properties of flowing systems in rotational viscometry," in: Heat and Mass Transfer [in Russian], Vol. 5, ITMO Akad. Nauk Belorussian SSR, Minsk (1976), pp. 18-23.

13. H. T. Kim and R. S. Brodkey, "A kinetic approach for polymer solution data," AIChE J., 14, No. 1, 61-68 (1968).
14. G. M. Bartenev and Z. G. Povarova, "Rheological properties of polyisobutylene—carbon black mixtures," Kolloidn. Zh., 28, No. 2, 171-178 (1966).
15. N. I. Seraya, L. V. Ivanova, and P. I. Zubov, "Thixotropic structure formation in acrylate complexes," Kolloidn. Zh., 28, No. 3, 450-457 (1966).

BUBBLE MOTION UNDER THE ACTION OF A GRADIENT IN SURFACE-ACTIVE MATERIAL CONCENTRATION

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The problem of bubble motion under the action of a gradient in surface-active material concentration is considered. The bubble drift velocity is determined. The possibility of calculating bubble velocity with simultaneous action of temperature and concentration gradients is considered.

The study of bubble and droplet motion in liquid and gaseous media is important in the solution of many practical technical problems (emulsion theory, solution of droplets, atomization of fuels, fuel placement in reservoirs, bubbling in air regeneration systems aboard spacecraft, etc.).

In most cases the motive force is provided by gravitation, but there are also cases in which droplet or bubble motion is caused by nonuniform surface tension on a boundary [1, 2]. This nonuniformity can develop either because of a nonuniform temperature distribution [3-5], or because of a nonuniform concentration of surface-active material [6].

Below we will study bubble motion under the action of a constant gradient in surface-active material concentration, but in contrast to [6], where the simplifications made to the fundamental equations were purely intuitive, a more formal simplification procedure will be used, based on expansion in the small parameters of the problem. We will assume that mass forces are absent, and that evaporation of the surface-active material into the bubbles does not occur. The motion is steady-state and translational. We place the origin of the coordinate system at the center of the moving bubble.

The distributions of velocity $\bar{v}$, pressure p, and surface-active material concentration are defined by a system of equations

$$\frac{\partial \bar{v}}{\partial t} + (\bar{v}\nabla)\bar{v} = -\frac{\nabla p}{\rho} + \nu\Delta\bar{v}, \quad \nabla\bar{v} = 0, \qquad (1)$$

$$\frac{\partial c}{\partial t} + \bar{v}\nabla c = D_v \Delta c.$$

On the bubble surface at $r = R_L$ the equation for conservation of surface-active material has the form [2, 7]

$$\frac{\partial \Gamma}{\partial t} + \frac{1}{R\sin\theta}\frac{\partial}{\partial\theta}(\Gamma v_\theta \sin\theta) - D_s \frac{1}{R^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Gamma}{\partial\theta}\right) = D_v \left.\frac{\partial c}{\partial r}\right|_{r=R}. \qquad (2)$$

Limiting ourselves to the case $\mathrm{Re} \ll 1$, $\mathrm{Pe} \ll 1$, we will estimate the order of magnitude of the terms of Eqs. (1), (2), transforming to dimensionless variables and choosing for the length scale the droplet radius R, for velocity $|d\sigma/dc|RE_c/\mu$, for pressure $|d\sigma/dc|E_c$, and for concentration E_cR. Performing this estimate, we find that in the zeroth approximation for small Re and Pe in Eq. (1) the inertial terms may be neglected, while in Eq. (2) (assuming also that $D_V \sim D_S$) the first two operators on the left-hand side may be dropped, these representing the change in surface concentration of the surface-active material with time and the convective transfer of the material along the surface.

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