3. G. R. Luckhurst and P. Simpson, Chem. Phys. Lett., 95, No. 2, 149-152 (1983).
4. A. D. Bagmet, Proc. 5th Conf. of the Socialist Countries on Liquid Crystals [in Russian], Vol. 1, Part 1, Odessa (1983), pp. 123-124.
5. P. A. Lebwohl and G. Lasher, Phys. Rev., 6, No. 1, 426-429 (1972).
6. G. R. Luckhurst and S. Romano, Proc. R. Soc. London, A373, 111-130 (1980).
7. C. Zannoni, The Molecular Physics of Liquid Crystals, Academic Press, London (1977), Chap. 9.
8. P. G. de Gennes, The Physics of Liquid Crystals, Claredon Press, Oxford (1974).
9. V. De Ge, Physical Properties of Liquid-Crystal Materials [Russian translation], Moscow (1982).
10. H. C. Anderson, J. Chem. Phys., 72, No. 4, 2384-2393 (1980).
11. A. L. Tsykalo and A. D. Bagmet, Inzh.-Fiz. Zh., 38, No. 4, 658-691 (1980).
12. A. S. Sonin, Introduction to the Physics of Liquid Crystals [Russian translation], Moscow (1983).
13. G. R. Luckhurst, The Molecular Physics of Liquid Crystals, Academic Press, London (1979), pp. 85-119.

PRECRITICAL NUCLEUS FORMATION IN A LIQUID WITH SURFACTANT

Yu. A. Buevich

Equilibrium states of a liquid containing dissolved gas and a surfactant are considered. It is shown that the presence of the surfactant makes possible appearance of stable gas (and vapor) bubbles at pressures exceeding the saturation pressure.

Many Newtonian liquids and their mixtures with a dispersed heavy impurity have significantly non-Newtonian relaxation properties. Thus, after sudden compression of a mixture of glycerine containing a dissolved gas with a quartz filament a significant reduction in pressure at constant mixture volume can be observed, with the characteristic time of this process comprising tens of minutes [1]. On the other hand, after a sudden volume extension isochoric pressure increase occurs in the mixture. Similar volume creep properties appear in multicomponent liquid mixtures, for example, heavy petroleums with a high paraffin content and asphaltene-resin fractions [2-4]. Pressure processing of homogeneous and inhomogeneous media, in particular, petroleums, also leads to changes in their rheologic properties [5]. Relaxation phenomena of this type are also met in studies of the thermodynamic properties of various gas—liquid systems [6, 7]. In the latter case one can clearly distinguish two relaxation processes having different time scales. The first of these, with a characteristic time of the order of seconds or minutes, is related to conventional liberation or absorption of the free gas phase, while the second, with a characteristic time sometimes reaching several hours, is apparently of the same nature as the volume relaxation of gas—liquid solutions mentioned above. These phenomena usually prove to be more strongly expressed if the system has a well-developed liquid—solid boundary surface. Such conditions can be produced not only by introducing solid particles into the liquid, but also when a liquid saturates a porous body, which latter case is of greater practical importance [8].

On the whole the situation appears as though formation of macroscopic vapor or gas bubbles occurs even in the precritical region, i.e., in region of stable existence of the degasified liquid phase or at pressures above the saturation pressure for liquids containing dissolved gases. Although the physical cause and corresponding mechanisms of such precritical development of new phase volumes remain unclear at present, the phenomenon itself has been used effectively in technology, especially in the petroleum industry [4, 8]. In the present study it will be assumed that liquid media manifesting these effects contain all possible impurities, and a model will be proposed to explain the origin of these effects, thus defining paths for their further study and practical application. As follows from the model,
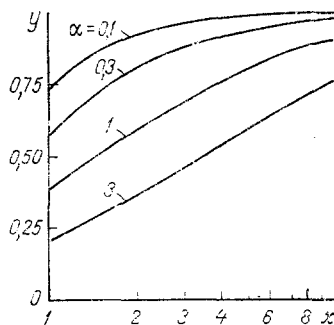
Fig. 1. Fraction of gas molecules retained in solution vs dimensionless pressure for various α.

stabilization of bubbles under precritical conditions can in principle be explained by liberation on the bubble surface of surfactant with formation of quasisolid films having negative surface tension [9, 10].

Concerning ourselves only with the principles involved, we will consider below only equilibrium states of a mixture of nonvolatile liquid (solvent), a gas, and a surfactant (with the mixture containing N, N_{g0}, and N_{s0} molecules of the respective components). The initial concentrations $c_{g0} = N_{g0}/N$ and $c_{s0} = N_{s0}/N$ will be assumed low, so that the solution of gas and surfactant in liquid can be considered dilute. We assume that at the given temperature and pressure existence of the mixture in the form of a homogeneous true solution is impossible — separation occurs into a true solution with reduced concentrations of gas and surfactant, equal to c_g and c_s, and macroscopic bubbles of liberated gas surrounded by thin surfactant films. In view of the extremely sharp maxima of the bubble distribution over radius and the film distribution over thickness, which in principle can be obtained from the Gibbs distribution, it will be permissible to consider the stable bubbles and films identical, having a radius a and thickness h $<<$ a respectively.

In the thermodynamic equilibrium state mechanical and chemical equilibrium conditions must be satisfied. The first of these has the form

$$p = p' + 2\gamma(h)/a \tag{1}$$

(the question of mechanical stability of the bubbles relative to distortion of their spherical form will be considered below). The chemical equilibrium conditions for gas and surfactant can be written as follows [11]: $\mu_g = \mu'_g$ and $\mu_s = \mu'_s$.* Considering that the solution is dilute, assuming the gas in the bubbles ideal, and using known representations of the chemical potentials of the molecules in this system [11], we transform the chemical equilibrium conditions to the form

$$p' = p_s(c_g/c_{g0}) < p_s, \tag{2}$$

where the saturation pressure p_s is referenced to a planar solution surface with molecular gas concentration c_{g0}

$$kT \ln c_s + \psi_s = \mu'_s(h), \tag{3}$$

where ψ_s depends only on pressure p and temperature T of the mixture, while the chemical potential of the surfactant molecules in the film is also determined by the film thickness [9]. Within the framework of the theory under consideration the functions $\gamma(h)$ and $\mu'_s(h)$ can be considered known.

The material balance conditions for gas and surfactant lead to the following equations:

$$N_g + M \frac{4\pi}{3} \frac{a^3 p'}{kT} = N_{g0} \quad \text{or} \quad c_g = c_{g0} - \frac{4\pi}{3} \frac{M}{N} \frac{a^3 p'}{kT} \tag{4}$$

---

*Generally speaking, the surfactant films contain liquid and gas molecules in a dissolved state, while the bubbles themselves contain liquid and surfactant molecules, i.e., the chemical equilibrium conditions must be satisfied for a three-phase solution—film—bubble system, while there must be two such conditions for each of the materials. However, for the purposes of the present study the presence of foreign molecules in the films and bubbles is not significant, and may be neglected in a manner similar to our original assumption that the liquid is nonvolatile.
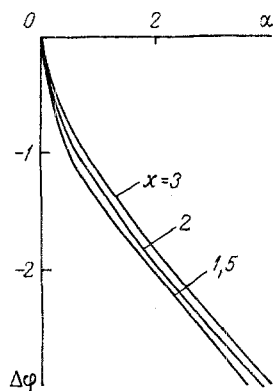
Fig. 2. Quantity $\Delta\varphi$ from Eq. (14) vs α for various x.

and

$$N_s + M 4\pi \frac{a^2 h}{v_s} = N_{s0} \quad \text{or} \quad c_s = c_{s0} - 4\pi \frac{M}{N} \frac{a^2 h}{v_s}. \tag{5}$$

We thus have five equations, Eqs. (1)-(5), for the six unknown quantities a, h, M, p', c_g and c_s, which completely define the thermodynamic equilibrium state of the inhomogeneous three-component system under consideration. As is usual in the equilibrium statistical physics method, it is natural to obtain the missing sixth equation from the condition of a minimum in the thermodynamic potential corresponding to the specified conditions. In an isothermal isobaric system we must minimize the Gibbs thermodynamic potential $\Phi = \Phi_0 + \Delta\Phi$, where $\Delta\Phi$ is the change in this potential upon transition from the fictitious true solution with concentrations c_{g0}, c_{s0} to the inhomogeneous system.

The quantity $\Delta\Phi$ is defined first by the effective work of macroscopic nucleus formation with consideration of the appearance of interphase boundaries coated by a surfactant film, second, by the change in thermodynamic potential of the solution itself upon decrease in concentrations to the values c_g and c_s and liberation of a portion of the dissolved materials into bubbles and films, and third, by entropy factors related to the multiplicity of possible organizations of the inhomogeneous system from the original hypothetical homogeneous mixture. For the first of these components we can immediately write [9-11]

$$(\Delta\Phi)_1 = M \left[\frac{4\pi}{3} a^3 (p - p') - 4\pi a^2 \gamma (h) \right] = -\frac{4\pi}{3} a^2 \gamma (h) M, \tag{6}$$

the second equality having been obtained with consideration of condition (1).

The thermodynamic potential of the dilute solution is equal to [11]

$$N [\mu - kT (c_g + c_s)] + N_g (\psi_g + kT \ln c_g) + N_s (\psi_s + kT \ln c_s). \tag{7}$$

The chemical potentials of gas and surfactant molecules in the bubbles and films in equilibrium with the solution coincide with the potentials of these same molecules in the solution, equal to the cofactors of N_g and N_s in Eq. (7). Therefore the second component of the quantity $\Delta\Phi$ with neglect of changes in specific volumes upon decrease in solution concentration and liberation of surfactant to films can be expressed as the difference between Eq. (7) with N_g and N_s replaced by N_{g0} and N_{s0} and the same quantity for a solution with concentrations c_{g0} and c_{s0}. We then have

$$(\Delta\Phi)_2 = kTN [c_{g0} - c_g + c_{s0} - c_s + c_{g0} \ln (c_g/c_{g0}) + c_{s0} \ln (c_s/c_{s0})]. \tag{8}$$

Finally, the number of methods of selecting gas and surfactant molecules entering the composition of the bubbles and films, considering the indistinguishability of these molecules,* is equal to

---

*In view of the fact that the bubbles and films are assumed identical, consideration of the number of methods of division of all gas and surfactant molecules into individual bubbles and films, as was done, for example, in [12], in studying aggregates in an initially homogeneous system, is not necessary. However such a division must be considered explicitly if it is assumed apriori that the bubbles and films are not all identical. This is particularly important in generalizing the theory under consideration to nonequilibrium conditions for the purpose of determining kinetic and relaxation parameters which describe transitions between various equilibrium states of the inhomogeneous system corresponding to different temperatures and pressures. In this case the methods of [12] can be used directly.

287

$$W = \frac{N_{g0}!}{N_g!\,(N_{g0} - N_g)!}\ \frac{N_{s0}!}{N_s!\,(N_{s0} - N_s)!}\ . \tag{9}$$

Calculating the "conformation" entropy corresponding to Eq. (9) and transforming to the thermodynamic limit in the conventional manner, we obtain

$$(\Delta\Phi)_3 = kTN\left[c_g \ln \frac{c_g}{c_{g0}} + (c_{g0} - c_g)\ln\left(1 - \frac{c_g}{c_{g0}}\right) + c_s \ln \frac{c_s}{c_{s0}} + (c_{s0} - c_s)\ln\left(1 - \frac{c_s}{c_{s0}}\right)\right]. \tag{10}$$

The sum of Eqs. (6), (8), and (10) defines the desired Gibbs thermodynamic potential of the system, relative to its value for the fictitious initial solution.

A serious difficulty develops involving the fact that the film properties, in particular, the functions $\gamma(h)$, for various materials are not sufficiently well known, while reliable information on the chemical potentials of the molecules entering into the composition of the films is extremely limited. Therefore, with the goal of obtaining concrete conclusions, we propose that $c_{s0} \ll c_g \sim c_{g0}$ and $c_s \ll c_{s0}$. The first inequality concerns the mixture composition and is satisfied in many real situations, while the second is quite usual for poorly soluble surfactants. These inequalities make it possible, first, to neglect terms proportional to c_s and c_{s0} in Eqs. (8) and (10), and second, to take $c_{s0} - c_s \approx c_{s0}$ in Eq. (5). Then, in particular, from Eq. (5) there follows a simple expression for M/N, containing no ill-defined quantities. Substituting this expression in Eq. (4) and expressing a with Eq. (1), from Eq. (2) we obtain an equation for the dimensionless gas pressure in the bubbles,

$$y = 1 - \frac{\alpha y}{x - y}, \quad x = \frac{p}{p_s}, \quad y = \frac{p'}{p_s}, \quad \alpha \approx \frac{2}{3}\,\frac{v_s \gamma(h)}{kTh}\,\frac{c_{s0}}{c_{g0}}, \tag{11}$$

the physically meaningful solution of which has the form

$$y = \frac{x + 1 + \alpha}{2}\left[1 - \left(1 - \frac{4x}{(x + 1 + \alpha)^2}\right)^{1/2}\right]. \tag{12}$$

As $\alpha \to 0$ we have $y \to 1$, and as $\alpha \to \infty$ for x = const we have $y \sim \alpha^{-1}$ (see Fig. 1).

Substituting M/N from Eq. (5) in Eqs. (4), (6), we also obtain

$$c_g = \left(1 - \frac{\alpha y}{x - y}\right)c_{g0} = yc_{g0}, \quad -\frac{4\pi}{3}a^2\gamma(h)M = -\frac{\alpha kT}{2}N_{g0}, \tag{13}$$

where α and y are defined by Eqs. (11) and (12) respectively. Considering these equalities and the assumptions made, on the basis of Eqs. (6), (8), (10) we write the quantity $\Delta\Phi/kT$ for a single gas molecule in the following dimensionless form:

$$\Delta\varphi = \frac{\Delta\Phi}{kTN_{g0}} = -\frac{\alpha}{2} + (1 - y)[1 + \ln(1 - y)] + (1 + y)\ln y \tag{14}$$

(where Eq. (11) has been used). The dependence of this quantity on α for various x is shown in Fig. 2, whence it is evident that $\Delta\varphi$ is a decreasing function of α, i.e., the minimum thermodynamic potential is attained at maximum α.

The characteristic expected [9, 10] dependence of γ on h is shown in Fig. 3. As $h \to 0$ (i.e., absence of a surfactant film), there acts upon the solution-gas boundary surface a surface tension σ, which decreases with increase in quantity of absorbed surfactant and changes sign at h values of the order of molecular dimensions ($h^\circ \sim v_s^{1/3}$). As h tends to infinity γ tends to some effective value γ° characteristic of thick wetting films [9]. (In the region $h < h^\circ$ film thickness determination is naturally somewhat arbitrary, for here we deal with a surface not completely filled by surfactant molecules). The condition for extremality of α, according to the definition of Eq. (11), has the form

$$\frac{d}{dh}\left(\frac{\gamma}{h}\right)_{h = h_*} = \frac{\gamma'_* h_* - \gamma_*}{h_*^2} = 0 \quad \text{or} \quad \gamma_* = \gamma'_* h_*, \tag{15}$$

where γ_* and γ'_* are the values of γ and its first derivative at $h = h_*$ (see Fig. 3), while $\gamma'_* > 0$ in view of the necessary film thermodynamic stability condition [9]. As can easily be seen from Fig. 3, the extremum in γ/h or α corresponds to a minimum in these quantities in the region of positive definition of the surface pressure.

In Eq. (13) the quantity $1 - y$ has the meaning of the fraction of gas molecules liberated into bubbles; the character of this quantity's dependence on x and α is clear from Fig.
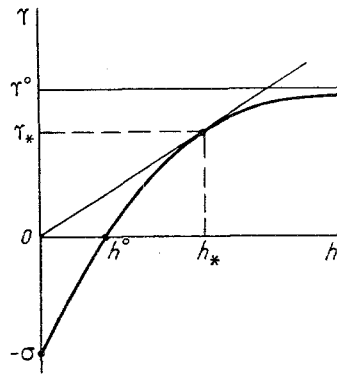
Fig. 3. Diagram for determination of film thickness.

1. A second important characteristic of the equilibrium imhomogeneous system is the radius of the bubbles formed, which can be expressed by

$$R = \frac{a p_s}{\gamma_*} = \frac{2}{x - y} ,$$ (16)

which follows from Eqs. (1) and (11); the dependence of this quantity on x and α is illustrated by Fig. 4.

Thus, for fixed mixture pressure and temperature the fraction of gas liberated from the solution increases and the size of stable bubbles decreases with increase in the dimensionless parameter α from Eq. (11), i.e., with increase in size of the surfactant molecules, their concentration in the system, and the analog of the three-dimensional pressure γ_*/h_* in the film, and with decrease in the gas content in the mixture. However the absolute mass of gas forming bubbles is proportional to $(1 - y)c_{g0}$ and increases with increase in initial content. With increase in pressure, the quantity y from Eq. (12) increases, asymptotically tending to unity, which corresponds to a fall in the fraction of liberated gas to zero. The dimensionless bubble radius R of Eq. (16) then decreases. In reality, for sufficiently small a the theory thus far developed loses validity due to disruption of the assumption h << a. Moreover, for very small bubbles Laplace equation (1) loses meaning and even a conventional surface pressure or tension is lacking for the replacement [13].

Similar phenomena should also be observed in degasified liquids containing a surfactant. In this case the bubbles are completely filled with vapor, and in the region $p > p_S$ of liquid thermodynamic stability as before mechanical equilibrium condition (1) is satisfied. Chemical equilibrium with respect to the solvent leads to the replacement of Eq. (2) by the equality $p' = p_S(y = 1)$, while the corresponding balance condition leads to the replacement of Eq. (4) by the equation

$$z = 1 - \frac{4\pi}{3} \frac{M}{N} \frac{a^3 p'}{kT} ,$$ (17)

where the quantity $1 - z$ has the meaning of the fraction of liquid molecules entering into the gaseous phase. Equations (3) and (5) retain their form. It is also simple to express and study the relationship for $\Delta \varphi$ which replaces Eq. (14).

Performing substitutions as above, in the final outcome we obtain the expressions

$$1 - z = \frac{\beta}{x - 1} , \quad R = \frac{2}{x - 1} , \quad \beta \approx \frac{2}{3} \frac{v_s \gamma (h)}{kTh} c_{s0},$$ (18)

replacing Eqs. (11) and (16), while the quantity γ/h figuring in the determination of β as before is defined at the point $h = h_*$ of Fig. 3. The general character of the dependences of z and R on the parameters for formation of vapor bubbles is the same as that of the analogous dependences for y and R for liberation of gas bubbles.

Thus, the basic cause of the phenomena noted above involving volume creep and relaxation in fact is the appearance in the system of significant inhomogeneity due to appearance of gas or vapor bubbles stabilized by surfactant films. As can easily be seen, the presence in the system of significant volumes of the free gas phase permits a qualitative explanation of practically all phenomena observed in [1-8]. From the heuristic viewpoint this explanation
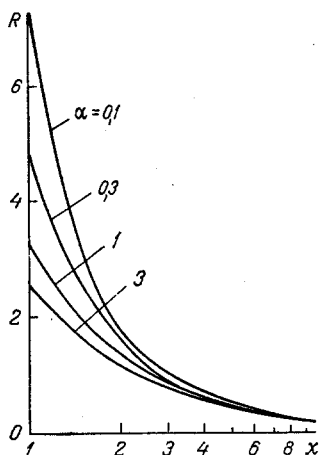
Fig. 4. Bubble size vs dimensionless pressure
for various α

agrees completely with the opinion offered in [8] that the relaxation properties under discussion are related to "redistribution of phases, which leads to formation of an energetically more favorable ordered structure" of the system.

The most unusual feature of the proposed theory is the postulation of definite, somewhat "exotic" properties intrinsic to the surfactant films on the bubble surfaces. If these films were quasiliquid, i.e., had no form resistance, then the bubbles would not be stable with respect to perturbations of their original spherical boundaries — whatever small perturbation of this boundary, retaining the gas volume within the bubble, would lead to a decrease in free surface energy, and therefore would increase [13]. In reality the theory makes an implicit assumption as to mechanical stability, which can be valid only if the films are quasisolid, i.e., behave like thin elastic shells manifesting a resistance to distortions of their form.

In reality, this assumption is indirectly supported by actual experimental material for many surfactants. There exist a large number of observations in which the experimental value of film surface viscosity proved to be approximately 10^6 times greater than the value determined theoretically on the basis of known volume properties of the material forming the film [10]. This then implies that such films must react to external mechanical perturbations like solid shells. As a result, the question of stability of the bubbles under consideration naturally proves to be related to the well studied problem of stability of thin elastic shells, the analysis of which is an independent problem within the context of the proposed theory.

In view of the great practical importance of the phenomena considered herein and the novelty of the concepts proposed concerning their physical nature, it is desirable to indicate possible approaches for their further study. First of all, it will be necessary to extend the theory of equilibrium heterogeneous states occurring under isothermal—isobaric conditions to situations in which such states are established adiabatically at constant volume or pressure, as well as under isothermal—isochoric conditions. The importance of this problem as regards real processes of new phase formation was discussed in detail in [13], where principal methods for its solution were also indicated. Further, the theory must be generalized to the situation in which the system has a well-developed liquid—solid surface, i.e., to suspensions and to a liquid within a porous body. The presence of such a surface significantly changes the work involved in bubble formation; if the surface has marked hydrophobic properties, then primarily heterogeneous bubbles will be formed [13]. In this case the total volume of gas or vapor liberated should increase, thus insuring, for example, "gas wetting" of the walls of pore channels, or on the contrary, their sealing by gas bubbles. The paths to be followed toward such a generalization are quite obvious [13].

Finally, the kinetics of the transition from one equilibrium state to another upon change in external conditions are of significant interest. For slight deviations from equilibrium or for the general response of the system to nonsteady state external perturbations, it is natural to describe transitions of this sort by the relaxation formalism of the thermodynamics of irreversible processes [14, 15]. Concrete calculations of the coefficient figuring therein requires analysis of independent problems of the transport rates of gas molecules into bubbles and surfactant molecules into films from the surrounding solution. A more precise

theory will naturally include analysis of bubble and film size distributions under significantly nonsteady state conditions and could in principle be constructed in analogy to the classical theory of new phase formation of [16].

NOTATION

a, bubble radius; c, numerical molecular concentration; h, surfactant film thickness; k, Boltzmann's constant; M, total number of bubbles; N, total number of molecules; p, pressure; Pa, saturation pressure; R, dimensionless radius; T, temperature; v_s, specific volume of surfactant molecules in film; W, number of states; z, fraction of liquid molecules not liberated into vapor phase; γ, surface pressure; μ, chemical potential; Φ, φ, dimensional and dimensionless Gibbs thermodynamic potential; ψ, function appearing in definition of the chemical potential of the dissolved substances. Subscripts: g and s indicate gas and surfactant molecules; ', bubbles or film.

LITERATURE CITED

1. B. M. Yakubov, Inzh.-Fiz. Zh., 35, No. 5, 872-876 (1978).
2. M. I. Khaddur, Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 9, 37-40 (1980).
3. Yu. A. Spiridonov, Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 9, 39-45 (1982).
4. I. M. Ametov, Yu. N. Baidikov, L. M. Ruzin, and Yu. A. Spiridonov, Heavy and High Viscosity Petroluem Refining [in Russian], Moscow (1985).
5. A. Kh. Mirzadzhanzade and I. M. Ametov, Prediction of Industrial Efficiency of Thermal Action Methods on Petroleum Strata [in Russian], Moscow (1983).
6. G. Kh. Melikov, Collected Works of the M. Azizbekov Azerbaidzhan Institute of Petroluem Engineering [in Russian], Baku (1984), pp. 86-92.
7. I. M. Ametov, A. M. Mamed-zade, and G. Kh. Melikov, Dokl. Akad. Nauk Azerbaidzh. SSSR, 41, No. 1, 20-24 (1985).
8. A. Kh. Miradzhanzade, F. G. Maksudov, R. I. Nigmatulin, et al., Theory and Practice of Use of Nonequilibrium Systems in Petroleum Extraction [in Russian], Baku (1985).
9. Ya. I. Frenkel', Kinetic Theory of Liquids: Collected Works, Vol. III [in Russian], Moscow—Leningrad (1959).
10. A. Adamson, Physical Chemistry of Surfaces [Russian translation], Moscow (1979).
11. L. D. Landau and E. M. Lifshits, Statistical Physics [in Russian], Moscow (1964).
12. Yu. A. Buevich, Inzh.-Fiz. Zh., 43, No. 2, 280-287 (1982).
13. A. I. Rusanov, Phase Equilibria and Surface Phenomena [in Russian], Leningrad (1967).
14. Yu. A. Buevich and G. P. Yasnikov, Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 10, 54-59 (1981).
15. Yu. A. Buevich and G. P. Yasnikov, Inzh.-Fiz. Zh., 44, No. 3, 489-504 (1983).
16. Ya. B. Zel'dovich, Zh. Eksp. Teor. Fiz., 12, No. 11/12, 525-538 (1942).