

c) In the relativistic case θ does not coincide either with the Otto-Arzeliès temperature or with the Planck-Einstein temperature. For θ the law of transformation from one frame of reference to the other has the form

$$\theta = \theta_0 \sqrt{1 + p^{*2}/c^2} - p^{*2} \quad \theta_0 = \rho c^2 \quad (p^* = 0)$$

The temperature is not needed, generally speaking, for the construction of relativistic hydrodynamics.

In conclusion, it is my pleasant duty to thank A. V. Bobylev for a useful discussion.

¹N. N. Bogolyubov. Problems of a dynamical theory in statistical physics in: Studies in Statistical Mechanics (ed. by J. H. de Boer and G. E.

Uhlenbeck). Vol. 1, Wiley, New York (1961) pp 5-515

²N. N. Bogolyubov. Selected Works on Statistical Physics [in Russian] Moscow (1979)

³S. Chapman and I. G. Cowling, The Mathematical Theory of Non-Uniform Gases 2nd ed. Cambridge University Press (1952)

⁴I. P. Pavlotskii. Weakly relativistic kinetic equations for neutral particles. Preprint No. 165. Institute of Applied Mathematics, Academy of Sciences of the USSR, Moscow (1979)

⁵H. Arzeliès. Thermodynamique Relativiste et Quantique Gauthier-Villars, Paris (1968)

Translated by Edward U. Oldham

Critical nuclei in the van der Waals model

L. M. Truskinovskii

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences of the USSR, Moscow

(Presented by Academician L. I. Sedov, August 10, 1982)

(Submitted November 18, 1982)

Dokl. Akad. Nauk SSSR 269:587-592 (March 1983)

PACS numbers: 05.70.Fh, 64.10.+h

The classical theory of heterophase equilibria assumes the introduction of the idea of a mathematical surface separating the phases, at which the density of the substance has a finite discontinuity. An energy proportional to the area is ascribed to the interphase surface, and the location of the surface is considered as an independent degree of freedom.¹ The problem of a continuous description of the interphase layer was considered by van der Waals,² who first used the model of a substance with a weakly nonlocal equation of state¹:

$$\rho \tilde{F}(\rho, \nabla \rho, T) = \rho F(\rho, T) + \epsilon(\rho, T)(\nabla \rho)^2/2 \quad (1)$$

where $\tilde{F}(\rho, \nabla \rho, T)$ is the specific free energy, ρ is the density, T is the temperature, $(\nabla \rho)^2 = \nabla^i \rho \nabla_i \rho$, ∇_i is the operator of covariant differentiation in the metric g_{ij} of the observer, $F(\rho, T)$ is the specific free energy of the homogeneous substance,³ and $\epsilon(\rho, T)$ is a positive function, monotonic in ρ . We shall assume that the quantity $\lambda = (\epsilon \rho / F)^{1/2}$, having the dimensions of length, is much smaller than the characteristic size of the region occupied by the medium. If the function F is convex in ρ , the presence of the second term in (1) has practically no effect because of the smallness of λ . To model liquids experiencing first-order phase transitions, van der Waals proposed the use of functions F that are nonconvex in ρ , e.g., for the van der Waals gas²:

$$F(\rho, T) = f(T) - a\rho - RT \ln(1/\rho - b) \quad (2)$$

where a , b , and R are constants. The van der Waals theory has recently been justified in the statistical theory of inhomogeneous liquids⁴ and has been used to describe both plane^{2,5,6} and curved^{2,7} interphase boundaries. However, these works lacked general equilibrium equations for media with energy given by (1); in particular, the expression for the stress tensor in the interphase zone was not obtained.

1. General methods for constructing models of continuous media with higher derivatives were developed in Refs. 3 and 8-11. We introduce the following notation: x^i , $i = 1, 2, 3$ are the coordinates of the observer, and ξ^a , $a = 1, 2, 3$ are the Lagrangian coordinates; the law of motion (deformation) of the medium is $x^i = x^i(\xi^a)$. The density ρ is expressed in terms of the determinant $\Delta = \det(\partial x^i / \partial \xi^a)$ by the formula $\rho = \hat{\rho} \Delta^{-1}$, where $\hat{\rho}(\xi^a)$ is a specified function of the Lagrangian coordinates. Let the free-energy density \tilde{F} be a known function of ρ , $\nabla \rho$, and T . The equilibrium conditions follow from the variational equation³:

$$\delta \int_V \rho \tilde{F} dv + \delta W = 0 \quad T = T_0 \quad (3)$$

The variations $\delta x^i(\xi^a)$ of the law of motion with fixed Lagrangian coordinates are taken as independent.

The standard variational procedure³ leads to the equilibrium equations $\nabla_i P_j^i = 0$ and to the following expression for the functional δW :

$$\delta W = \int_V (P^i n_i \nabla_k \delta x^k - P_k^i n_i \delta x^k) d\sigma \quad (4)$$

where n^i are the components of the normal vector to the surface ∂V , and P^i and P_k^i are given by the following equations of state:

$$P^i = \rho^2 \frac{\partial \tilde{F}}{\partial \nabla_i \rho} \quad P_j^i = \pi \delta_j^i + \pi_j^i \quad \pi_j^i = -\rho \frac{\partial \tilde{F}}{\partial \nabla_i \rho} \nabla_j \rho$$

$$\pi = -\rho^2 \frac{\partial \tilde{F}}{\partial \rho} + \rho \frac{\partial \tilde{F}}{\partial \nabla_i \rho} \nabla_i \rho + \rho^2 \nabla_i \left(\frac{\partial \tilde{F}}{\partial \nabla_i \rho} \right)$$

To obtain the boundary conditions we shall specify the functional δW when V is the entire region occupied by the medium:

$$\delta W = \int_{\partial V} (\tilde{Q}_i \frac{\partial}{\partial n} \delta x^i + \tilde{R}_i \delta x^i) d\sigma = \int_{\partial V} P_0 \delta x^i n_i d\sigma \quad (5)$$

where P_0 is the fixed pressure at the boundary of the region. Let the surface ∂V be specified by the equations $x^i = r^i(u^1, u^2)$; $a_{AB} = g_{ij}r^i_A r^j_B$ is the metric induced on the surface, $r^i_A = \partial r^i / \partial u^A$, $A, B = 1, 2$. We define the tensor u^i_A by the formulas $u^i_A \tilde{a}_{AB} = r^i_B$. A comparison of (4) and (5) leads to the following boundary condition for the equilibrium equations:

$$P^A n_k = 0 \quad P_i^k n_k - \nabla_A (P^k n_k u^i_A) = -P_0 n_i \quad (6)$$

We note that a stress tensor depending on the density gradients was evidently first considered by Korteweg¹² (see also Ref. 13).

2. Although the stress tensor is not spherical in the general case, its structure is special. In view of this we have:

Assertion 1. The equilibrium equations $\nabla_i P_j^i = 0$ where the general integral

$$\rho \frac{\partial \tilde{F}}{\partial \rho} + \tilde{F} - \frac{\partial \tilde{F}}{\partial \nabla_i \rho} \nabla_i \rho - \rho \nabla_i \left(\frac{\partial \tilde{F}}{\partial \nabla_i \rho} \right) = \mu_0 = \text{const.} \quad (7)$$

Remark. An analogous assertion is also true for the case when the free-energy density depends on higher derivatives of the density. Let $\Lambda = \rho^F(\rho, \nabla_i \rho, \nabla_i \nabla_j \rho, \dots, T)$ then

$$P = \left(\Lambda - \rho \frac{\delta \Lambda}{\delta \rho} \right) \delta_i^i - \left[\frac{\partial \Lambda}{\partial \nabla_i \rho} - \nabla_p \left(\frac{\partial \Lambda}{\partial \nabla_p \nabla_i \rho} \right) - \nabla_i \nabla_p \left(\frac{\partial \Lambda}{\partial \nabla_i \nabla_p \nabla_j \rho} \right) - \dots \right] \nabla_j \rho - \left[\frac{\partial \Lambda}{\partial \nabla_i \nabla_j \rho} - \nabla_p \left(\frac{\partial \Lambda}{\partial \nabla_p \nabla_i \nabla_j \rho} \right) - \dots \right] \nabla_i \nabla_j \rho - \left[\frac{\partial \Lambda}{\partial \nabla_i \nabla_p \nabla_j \rho} - \dots \right] \nabla_p \nabla_s \nabla_j \rho - \dots$$

and the equality $\nabla_i P_j^i = -\rho \nabla_j (\delta \Lambda / \delta \rho) = 0$ is valid, where $\delta / \delta \rho$ is the variational derivative. For specific flows of the medium under consideration one can easily obtain generalizations of the Bernoulli and Cauchy-Lagrange integrals with the pressure function replaced by $\delta \Lambda / \delta \rho$.

3. We now consider spherically symmetric equilibrium configurations. We take the simplest expression (1) as \tilde{F} . The equilibrium equation in spherical coordinates has the form

$$\frac{dP}{dR} \equiv \frac{d}{dR} \left[\rho^2 \frac{\partial F}{\partial \rho} - \frac{1}{2} \rho^2 \frac{\partial(\epsilon/\rho)}{\partial \rho} \left(\frac{d\rho}{dR} \right)^2 - \rho \epsilon \left(\frac{d^2 \rho}{dR^2} + \frac{2}{R} \frac{d\rho}{dR} \right) \right] = - \frac{2\epsilon}{R} \left(\frac{d\rho}{dR} \right)^2 \quad (8)$$

To describe nuclei (localized density inhomogeneities) with a characteristic size much less than $|V|^{1/3}$ it is natural to go over to the problem in an infinite region. According to (6), one should seek the solutions in the class of sufficiently smooth functions such that $|\nabla \rho| \rightarrow 0$ as $R \rightarrow \infty$. The pressure at infinity is fixed by the second boundary condition: $\rho^2 (\partial F / \partial \rho)|_{\rho_*} = P_0 = P(\infty)$, $\rho_0(P_0, T_0) = \rho(\infty)$. Integrating (8), we obtain the relation $P(R) - P(\infty) =$

$$2 \int_0^R \epsilon (d\rho/dR)^2 dR/R, \text{ which goes over into the classical}$$

formula of Laplace¹ if the density gradient is localized in the vicinity of a certain $R = R^*$.

Let us write out the equation (7):

$$\epsilon \left(\frac{d^2 \rho}{dR^2} + \frac{2}{R} \frac{d\rho}{dR} \right) + \frac{1}{2} \frac{\partial \epsilon}{\partial \rho} \left(\frac{d\rho}{dR} \right)^2 = \frac{\partial}{\partial \rho} \{ \rho(F - \mu_0) \} \quad (9)$$

As $R \rightarrow \infty$, we obtain $\rho^2 (\partial F / \partial \rho) = P_0$, $\rho (\partial F / \partial \rho) + F \rightarrow \mu_0$, and therefore $\mu_0(P_0, T_0)$ has the meaning of the chemical potential. Thus the problem reduces to integration of (9); the stresses are then recovered from the known function $\rho(R)$:

$$P_{RR} = -P - \epsilon (d\rho/dR)^2 \quad P_{\theta\theta} = P_{\varphi\varphi} = -P.$$

For nonconvex functions $F(\rho, T_0)$ of the type under consideration [e.g., the van der Waals function (2) at temperatures below the critical temperature] there exist spinodal points P_1 and P_2 defined by the conditions (Fig. 1): $\partial F / \partial (1/\rho)|_{\rho_1, \rho_2} = -P_1$, $\partial^2 F / \partial^2 (1/\rho)|_{\rho_1, \rho_2} = 0$. A qualitative investigation of the behavior of the integral curves of Eq. (9) permits us to prove the following assertion:

Assertion 2. For $P_1 < P_0 < P_2$ there exists a unique inhomogeneous "soliton" solution of Eq. (9).

Let us give brief explanations. We set $\epsilon = \epsilon_1(T_0)$ for simplicity. We define the equilibrium pressure $P_0^*(T_0)$ for the given temperature T_0 using Maxwell's rule:

$$\rho^2 \frac{\partial F}{\partial \rho} \Big|_{\rho_1^*, \rho_2^*} = P_0^*(T_0) \quad \left(\rho \frac{\partial F}{\partial \rho} + F \right) \Big|_{\rho_1^*, \rho_2^*} = \mu_0(P_0^*, T_0)$$

The case when the denser phase is located at the center corresponds to the interval $P_0^* \leq P_0 \leq P_2$. The dashed lines in Fig. 2 show the integral curves of the equation

$dP/dR = 0$, where $P = \frac{\epsilon_1}{2} \left(\frac{d\rho}{dR} \right)^2 - \rho(F - \mu_0)$, with P_0 lying within the interval indicated above. A bifurcation (a co-

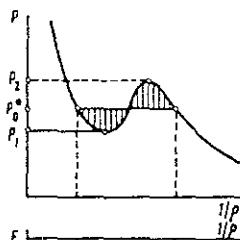


FIG. 1

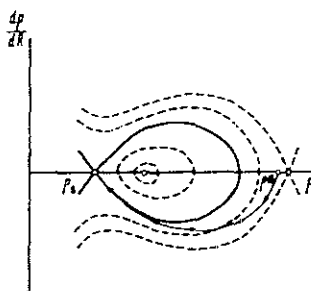


FIG. 2

occurs at a center and a saddle point) occurs at $P_0 = P_2$, while at $P_0 = P_0^*$ a separatrix joining both saddle points arises. Equation (9) can be rewritten in the form

$$\frac{dP}{dR} = -\frac{2\epsilon_1}{R} \left(\frac{d\rho}{dR} \right)^2, \text{ so that } P \text{ decreases as } R \rightarrow \infty \text{ and the}$$

integral curve of Eq. (9) will intersect the lines $P = \text{const}$. We shall indicate some properties of the critical nuclei. If at point ρ_0 the function $g = -\rho(F - \mu_0 + P_0/\rho)$ has a

$$\text{maximum } g \sim -\frac{a^2}{2} (\rho - \rho_0)^2 \quad a^2 = \rho^2 \frac{\partial^2 F}{\partial(\rho/\rho_0)^2}, \text{ then for}$$

large R we obtain $\rho \sim (1/R) \exp(-aR/\sqrt{\epsilon_1})$. With increasing degeneracy ($a \rightarrow 0$, corresponding to approach to the critical point or to the spinodal, i.e., the boundary of metastability) the density gradients decrease and the nucleus ceases to be a concentrated formation. For values of P_0 near P_0^* the density gradients are localized in the vicinity of $R = R^*$, the latter quantity being determined from the classical formulas of Gibbs.¹ As $P_0 \rightarrow P_0^*$ the density at the center ($R = 0$) tends to its maximum value, while the effective "radius" of the nucleus tends to infinity so that the phase boundary approaches a plane.

These conclusions are confirmed by the results of numerical integration of Eq. (9) for a function $F(\rho, T)$ of special form.⁷

Let us present an approximate solution, asymptotically exact in the limit $P_0 \rightarrow P_0^*$ ($P_0 \rightarrow P_2$):

$$R(\rho) = \sqrt{\epsilon_1} \int_{\rho}^{\rho(0)} \frac{d\rho}{\sqrt{2[\rho(F - \mu_0) + P_0]}} \quad (10)$$

where $\rho(0)$ is the root (differing from ρ_0) of the equation $\rho(F(\rho, T_0) - \mu_0(P_0, T_0)) + P_0 = 0$. For near-equilibrium configurations an explicit expression can be obtained for R^* . Let R^* correspond to the maximum of $d\rho/dR$. Then $R^* = R(\rho^*)$, where ρ^* is determined from the equation $\rho(\partial F/\partial \rho) + F = \mu_0$. $\rho_0 \leq \rho^* \leq \rho(0)$. The width of the inter-phase zone is specified in the standard manner:

$$2\delta = \frac{\rho_0 - \rho(0)}{(d\rho/dR)|_{\rho_0}} = \sqrt{\epsilon_1} \frac{\rho(0) - \rho_0}{\sqrt{2[\rho^*(F_0(\rho^*, T_0) - \mu_0) + P_0]}}$$

The construction of the approximate solution from a specified function $F(\rho, T)$ and fixed P_0, T_0 , and $\epsilon_1(T_0)$ thus reduces to finding the roots of nonlinear equations and calculating integrals. The values obtained for the maximum density $\rho(0)$ give a lower bound for the corresponding quantity.

4. In the investigation of the problem in an infinite region the variational formulation (3) requires regularization, since the integrals in (3) diverge. It is not difficult to verify that the corresponding variational problem in R^3 has the form $\delta I = 0$, $I = \int_{R^3} \tilde{G} dv$, $\tilde{G} = \rho(F - \mu_0) + P_0$. Equation (9) is then written more compactly: $\delta \tilde{G}/\delta \rho = 0$. In considering the functional I , we go over from specification of the total mass to specification of the chemical potential at infinity. For homogeneous states the problem

reduces to seeking the extrema of the Gibbs function $G(V, T_0, P_0) = F(V, T_0) + P_0 V$.

We shall consider the problem of the stability of the solutions under study. Configurations corresponding to the minimum of the functional I will be called stable. In this case it is easily proven that the density distributions obtained are unstable. This fact is known in field theory as the Derrick-Hobart theorem.¹⁴ For the proof it is sufficient to consider the single-parameter family of perturbations concentrated in the vicinity of large gradients of the density $\rho_\alpha(R) = \rho(R/\alpha)$, where $\rho(R)$ is the solution being investigated for stability and α is a parameter.

The instability of critical nuclei has also been established in the classical theory of nucleation.¹ Discussions in terms of the radius of the nucleus (a collective coordinate) do not have precise meaning in the vicinity of the spinodal points, and it is natural to consider the energy scale of the critical fluctuations: $\|W_{cr}\| = \int_{R^3} (\|\rho\tilde{G}\| - \mu_0 \|\rho\|) dv$ where $\|\cdot\|$ denotes the difference of the values for the homogeneous solution and the inhomogeneous solution that coincides with it at infinity. The calculation of $\|W_{cr}\|$ is the fundamental problem in the determination of the nucleation rate. Using the approximate solution (10), we obtain the estimate

$$\|W_{cr}\| = 4\pi\epsilon_1^{3/2} \int_{\rho(0)}^{\rho_0} \frac{\rho_0[F(\rho_0, T_0) - \mu_0] - 2\rho[F(\rho, T_0) - \mu_0] - P_0}{\sqrt{2[\rho(F - \mu_0) + P_0]}} d\rho \times \left[\int_{\rho(0)}^{\rho} \frac{d\rho'}{\sqrt{2[\rho'(F - \mu_0) + P_0]}} \right]^2 d\rho.$$

In an investigation of the problem of a small nucleus in a finite volume the solutions obtained above can be used as the inner asymptotic form.

The author thanks Academician L. L. Sedov, V. L. Berdichevskii, A. N. Golubyatnikov, and V. A. Zhelnorovich for useful discussion of the work and for remarks which are taken into account in the writing of this note.

¹An expression differing from (1) by a divergence term was considered in Ref. 2.

¹J. W. Gibbs, The Collected Works of Josiah Willard Gibbs. Elliotts, Northford Conn. (1948).

²J. D. van der Waals Z. Phys. Chem. **13**, 657 (1894).

³L. I. Sedov, A Course in Continuum Mechanics. Vol. 2. Wolters-Noordhoff Groningen (1972).

⁴F. Abraham. Phys. Rep. **53**, 93 (1979).

⁵J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **28**, 258 (1958).

⁶L. M. Truskinovskii. Dokl. Akad. Nauk SSSR **265**, 306 (1982) [Sov. Phys. Dokl. **21**, 551 (1982)].

⁷J. W. Chan and J. E. Hilliard J. Chem. Phys. **31**, 688 (1959).

⁸M. É. Églit Prikl. Mat. Mekh. **29**, 351 (1965).

⁹V. L. Berdichevskii Prikl. Mat. Mekh. **30**, 510 (1966).

¹⁰M. V. Iur'e Prikl. Mat. Mekh. **30**, (1966).

¹¹V. A. Zhelnorovich, Dokl. Akad. Nauk SSSR **184**, 55 (1969) [Sov. Phys. Dokl. **14**, 29 (1969)].

¹²D. J. Korteweg. Arch. Neerl. Sci. Exactes Nat. Ser. 11 **6**, 1 (1901).

¹³J. Serrin, in: Recent Methods in Nonlinear Analysis and Applications. Naples (1980) p. 169.

¹⁴R. Jackiw Rev. Mod. Phys. **49**, 681 (1977).

Translated by David G. Miller