Critical nuclei in the van der Waals model

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The classical theory of heterogeneous 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. The problem of a continuous description of the interphase layer was considered by van der Waals, who first used the model of a substance with a weakly nonlocal equation of state:

\[ \rho F(\rho, \nabla \rho, T) = \rho f(\rho, T) + e(\rho, T)(\nabla \rho)^2/2 \]  

(1)

where \( F(\rho, \nabla \rho, T) \) is the free energy density, \( \rho \) is the density, \( T \) is the temperature, \( \nabla \rho \) is the gradient of \( \rho \), and \( \nabla \rho \) 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, and \( e(\rho, T) \) is a positive function, monotonic in \( \rho \). We shall assume that the quantity \( \lambda = (\rho f'/f)^{1/2} \), 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 \( \rho \), the presence of the second term in (1) has practically no effect because of the smallness of \( \lambda \). To model liquids experiencing first-order phase transitions, van der Waals proposed the use of functions \( F \) that are nonconvex in \( \rho \), e.g., for the van der Waals gas:

\[ F(\rho, T) = f(T) - \alpha \rho - RT \ln(1/\rho) - b, \]

(2)

where \( \alpha, b, \) and \( R \) are constants. The van der Waals theory has recently been justified in the statistical theory of inhomogeneous liquids and has been used to describe both plane\(^5\) and curved\(^6\) 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 \( \xi^a, a = 1, 2, 3 \) are the Lagrangian coordinates; the law of motion (deformation) of the medium is \( \frac{dx^i}{dt} = \xi^a \frac{\partial F}{\partial \xi^a} \). The density \( \rho \) is expressed in terms of the determinant \( \Delta = \det(\partial x^i/\partial \xi^a) \) by the formula \( \rho = \delta \Delta^{-1} \), where \( \delta \xi(a) \) is a specified function of the Lagrangian coordinates. Let the free-energy density \( F \) be a known function of \( \rho, \nabla \rho, \) and \( T \). The equilibrium conditions follow from the variational equation:

\[ \delta \int \rho F d\nu + \delta W = 0 \quad T = T_0 \]  

(3)

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

The standard variational procedure\(^3\) leads to the equilibrium equations \( \Delta F = 0 \) and to the following expression for the functional \( \delta W \):

\[ \delta W = \int \left( \rho' \nabla \cdot V - \nabla \cdot P + \frac{1}{2} \rho'' \nabla \cdot V \right) d\nu \]  

(4)

where \( \rho' \) and \( \rho'' \) are the components of the normal vector to the surface \( \delta V \), and \( P \) and \( P' \) are given by the following equations of state:

\[ \rho' = \rho^2 \frac{\partial F}{\partial \rho} \quad \rho'' = \rho \frac{\partial F}{\partial \rho} \quad \frac{\partial F}{\partial \rho} \]

To obtain the boundary conditions we shall specify the functional \( \delta W \) when \( V \) is the entire region occupied by the medium:

\[ \delta W = \int \left( \frac{\partial F}{\partial \rho} \frac{\partial \rho}{\partial \rho} \right) d\nu \]  

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where $P_0$ is the fixed pressure at the boundary of the region. Let the surface $dV$ be specified by the equations $x^1 = 1/2(a^1, u^1)$; $a_{AB} = g_{ij} x^i x^j$. $1B$ is the metric induced on the surface, $1A = \partial A/\partial u^A$, $A, B = 1, 2$. We define the tensor $u^i_1$ by the formulas $u^i_1 a_{AB} = 11B$. A comparison of (1) and (5) leads to the following boundary condition for the equilibrium equations:

$$P_n + 0 = \rho \nabla_d (\rho P u^i_1) = -\rho n_i$$

We note that a stress tensor depending on the density gradient was evidently first considered by Korteweg ([7], 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 $\nabla_d P^1 = 0$ have the general integral

$$\frac{\partial \rho}{\partial \rho} + \dot{\rho} = \frac{\partial \rho}{\partial \nabla_d \rho} \nabla_d \rho - \frac{\partial \rho}{\partial \nabla_d \rho} \nabla_d \rho$$

Remark. An analogous assertion is also true for the case when the free-energy density depends on higher derivatives of the density. Let $\Lambda = \rho F(\rho)$ and $\nabla_d \rho$.

$$\rho = \left( \Lambda - \dot{\rho} \right) \frac{\partial \rho}{\partial \rho} - \frac{\partial \Lambda}{\partial \nabla_d \rho} \nabla_d \rho$$

and the equality $\nabla_d P^1 = -\rho \partial_p (\partial \Lambda/\partial \rho) = 0$ is valid, where $\partial / \partial \rho$ 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 $\partial \Lambda / \partial \rho$.

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

$$\frac{dp}{dr} = \frac{d^2 P}{dr^2} + \frac{1}{2} \frac{d\rho}{dr} \frac{d\rho}{dr}$$

To describe nucleus (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 $|\nabla \rho| = 0$ as $R = \infty$. The pressure at infinity is fixed by the second boundary condition: $\rho^*(\partial \rho/\partial \rho)_{\rho^*} = P_0 = \rho^*(\rho_0, T_0) = \rho_0$. Integrating (6), we obtain the relation $P_0 - P(\rho) = 2 \frac{1}{\sigma^2} \frac{d\sigma}{dR} dR/R$, which goes over into the classical formula of Laplace [3] if the density gradient is localized in the vicinity of a certain $R = R^*$. Let us write out the integral (7):

$$\frac{dP}{dr} + \frac{2}{R} \frac{dP}{dr} = \frac{1}{2} \frac{d\rho}{dr} \left( \frac{d\rho}{dr} \right)^2 - \frac{3}{2} \frac{\partial \rho}{\partial \rho} [\rho(F - \rho_0)]$$

As $R = \infty$, we obtain $\rho^*(\partial \rho/\partial \rho) - P_0 = \rho^*(\partial \rho/\partial \rho) + \rho - \rho_0$, and therefore $\rho^*(P_0, T_0)$ has the meaning of the chemical potential. Thus the problem reduces to integration of (9); the stresses are then recovered from the known function $\rho(F)$:

$$P_{\text{ext}} = -P - \frac{d\rho}{dR} dR$$

For nonconvex functions $F(\rho, T)$ 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):

$$\frac{dP}{d\rho}(P_1, T_0) = -P_1, \quad \frac{d^2 P}{d\rho^2}(P_1, T_0) = 0.$$ A qualitative investigation of the behavior of the integral curves of Eq. (9) permits us to prove the following assertion:

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

Let us give brief explanations. We act $\epsilon = \epsilon_1(T_0)$ for simplicity. We define the equilibrium pressure $P^*_0(T_0)$ for the given temperature $T_0$ using Maxwell's rule:

$$\rho^* \frac{d\rho^*}{d\rho^*} = P^*_0(T_0) \left( \rho^* \frac{d\rho^*}{d\rho^*} + F \right) \rho^* = \mu_0(P^*_0, T_0)$$

The case when the denser phase is located at the center corresponds to the interval $P^*_0 \leq P \leq P^*_2$. The dashed lines in Fig. 2 show the integral curves of the equation $dp/dR = 0$, where $\rho = \rho_0 \left( \frac{d\rho}{dR} \right)^2 = \rho(F - \rho_0)$, with $P^*_0$ lying within the interval indicated above. A bifurcation (a co-
aleness of a center and a saddle point) occurs at \( P_0 = P_1 \), while at \( P_0 = P_2^* \) a separatrix joining both saddle points arises. Equation (6) can be rewritten in the form

\[
\frac{d^2\rho}{dR^2} = \frac{2s_1}{R} \left( \frac{d\rho}{dR} \right)^2,
\]

so that \( P \) decreases as \( R \to -\infty \) 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 \( \rho_0 \) the function \( g = -\rho (F - \mu_\rho + P_0 / \rho) \) has a maximum

\[
g \sim - \rho^2 \left( \mu - \mu_\rho \right) \quad \text{at} \quad \rho = \frac{\mu - \mu_\rho}{2s_1},
\]

then for large \( R \) we obtain \( \rho \sim (1/R)^{\exp(-\Delta /\sqrt{\epsilon_1})} \). With increasing degeneracy \( \epsilon_1 \to 0 \), corresponding to approach to the critical point or to the spinodal, i.e., the boundary of metastability) the density gradients decrease and the nuclei 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. As \( P_0 \to P_0^* \), the density at the center \( (R = 0) \) tends to its maximum value, while the effective radius \( \rho^* \) 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 \( F(\rho, r) \) and the special solution of the problem:

\[
R(\rho) = \sqrt{\epsilon_1} \int \frac{d\rho}{\sqrt{\frac{1}{2}[\rho(F - \mu_\rho) + P_0]}},
\]

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

\[
\Delta \rho = \left. \frac{\rho_0 - \rho(0)}{(d\rho/dR)_\rho} \right|_{\rho = \rho^*} = \sqrt{\epsilon_1} \sqrt{\frac{\rho(0) - \rho_0}{2[F(\rho_0 - F^*) - \mu_\rho]}}.
\]

The construction of the approximate solution from a specified function \( F(\rho, r) \) and fixed \( P_0, T_0, \) and \( \epsilon_1 \) (\( \Gamma_0 \)) 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 (3) has the form \( \delta I = 0 \), \( \delta I = \int G d\rho \)

\[
G = \rho(F - \mu_\rho) + P_0.
\]

Equation (9) is then written more compactly:

\[
\delta G / \delta \rho = 0.
\]

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 \( G^* \), \( T_0, P_0 \), \( T_0^* \) of the form \( G^* \), \( T_0 \), \( P_0 \) + \( P_0 \).

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. For the proof it is sufficient to consider the single-parameter family of perturbations concentrated in the vicinity of large gradients of the density \( \rho_0(R) = \rho_0(R_{\text{out}}) \), where \( \rho_0(R) \) is the solution being investigated for stability and \( a \) is a parameter.

The instability of critical nuclei has also been established in the classical theory of nucleation. 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: \( I = W_{\text{CF}} = \int (\rho F - \mu_\rho - P_0 \rho) \rho \)

\[
\rho_0(\rho_0, T_0) - \rho_0(T_0, T_0) - 2[F(\rho_0, T_0) - \mu_\rho] = \sqrt{[\rho_0 - \rho_0(T_0, T_0)]}.
\]

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.

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