Metastable region in the scaling theory of critical phenomena

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The possibility of describing the metastable region near the liquid-vapor critical point by means of the scaling-theory equations of state is considered. It is shown that these equations imply the existence of a line bounding a region to which no equilibrium state of the substance corresponds. On this line, unlike the classical spinodal, the elasticity of the system vanishes only at the critical point. This line is calculated from the authors' data for ^{4}He and compared with the spinodal obtained from other theories.

The widely known and numerically well confirmed scaling theory of critical phenomena describes satisfactorily the behavior of fluid systems in the stable region near the critical point of vapor formation.[1] However, as far as we know, with the exception of Refs. 2 and 3 there has as yet been no serious attempt, for specific substances, to use scaling dependences to describe the metastable region, including the spinodal, even though the authors of the first papers[4,5] devoted to the scaling equation of state elucidated the presence on the isotherms of turning points bounding the region of equilibrium states of the substance. The classical theory defines a spinodal as a line bounding a region in which the existence of the uniform substance is impossible because the pressure satisfies $(\partial P/\partial V)_T > 0$, which implies loss of stability of the substance. However, the classical theory is based on the assumption that on the spinodal the thermodynamic potentials have no singularity, i.e., they can be expanded in a series in integer powers of small deviations of the thermodynamic parameters from their values on the spinodal. At the same time, Landau and Lifshitz[6] had noted that there is every reason to suppose that the spinodal is a line of singular points of the thermodynamic potentials. In this case the classical definition of the spinodal may be inaccurate.

We shall consider the question of the spinodal from the standpoint of the modern theory of critical phenomena. A consequence of scaling is the fact that the thermodynamic potentials are generalized homogeneous functions, i.e., e.g., for the Helmholtz free energy, we can write

$$F(\lambda^{a_\tau}\tau,\ \lambda^{a_M}M)=\lambda F(\tau,\ M). \tag{1}$$

Here $\tau = (T - T_k)/T_k$. Choosing as the scaling factor the susceptibility of the system, we arrive at Migdal's formulation of the scaling hypothesis:

$$H\chi^{(\beta+\gamma)/\gamma}=\varphi(m),\quad m=M\chi^{\beta/\gamma}. \tag{2}$$

Here H is the field, M is the moment, $\chi = (\partial M/\partial H)_T$, and β and γ are critical indices. For convenience in comparing with the results of Ref. 2 we shall use the terminology for a ferromagnet, with the understanding that we can go over to fluids by means of the replacements

$$H\leftrightarrow(\mu-\mu(\rho_k,\ \tau))/\mu_k,\quad M\leftrightarrow(\rho-\rho_k)/\rho_k,\quad \chi\leftrightarrow(\partial\rho/\partial\mu)_T.$$

The relation (2) is an implicit differential equation for the isotherms. It can be solved in general form, and all observable quantities can be expressed in terms of the function $\varphi(m)$. It should be noted that the function $\varphi(m)$ possesses simple properties. Reference 5 indicates the conditions which it should satisfy: $\varphi(0) = 0$, in order that the moment vanish above the transition point as $H\to 0$; $\varphi'(0) = 1$, i.e., at zero the function $\varphi(m)$ has a positive slope; finally, at some $m = m_1$ we must have $\varphi(m_1) = 0$, in order that, in zero field for $\tau < 0$, there exist a spontaneous moment. We emphasize that these properties of the function $\varphi(m)$ are very general and stem from our knowledge of the character of the behavior of matter near a critical point.

We shall consider the behavior of the field H on the isochores. It follows from (2) that

$$H=\varphi(m)\,(M/m)^{(\beta+\gamma)/\beta}. \tag{3}$$

It turns out that the behavior of $H(m)$ is complicated. Differentiating (3) with respect to m and finding the extremum of $H(m)$, we find that at a certain point $m = m_c$, determined from the condition

$$(\beta+\gamma)\varphi(m_c)=\beta m_c\varphi'(m_c), \tag{4}$$

$H(m)$ has a minimum. Thus, analysis of the behavior of the system for $M =$ const leads to an interesting result: As m increases the field H first decreases to zero (the bounding curve), then becomes negative (corresponding to the metastable region), and, finally, for $m > m_c$, begins to grow; i.e., the point $m = m_c$ is a turning point for the isochore ($M =$ const). An analogous result was obtained in Ref. 5 for isotherms with $\tau < 0$ (see Fig. 1), and the condition for the turning points of the isotherms coincides with (4). On the T-M diagram the points corresponding to $m = m_c$ form a continuous line that lies entirely inside the bounding curve. The equation of this line in the coordinates M, H can be written as

$$M_c=m_c\left(\frac{\beta+\gamma}{\beta m_c\varphi'(m_c)}\right)^{\beta/(\beta+\gamma)}H_c^{\beta/(\beta+\gamma)}. \tag{5}$$

In the coordinates M, τ it will have the form

$$M_c=m_c[C_+f(m_c)]^{-\beta/\gamma}\tau^{\beta}. \tag{6}$$

Here C_+ is a constant, determined by the dependence $\chi_+(\tau) = C_+\tau^{-\gamma}$ $(\tau > 0)$, and

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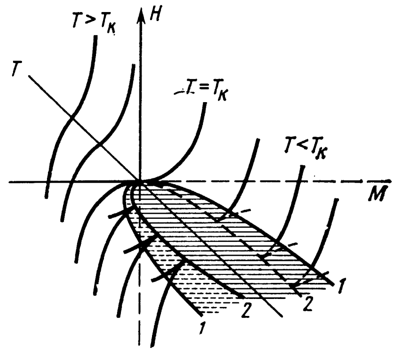

FIG. 1. Isotherms for a magnet, drawn using the Migdal equation. 1) The binodal; 2) the line of turning points ("spinodal"). The region inside the binodal ($H=0$) is shaded.

$$f(m_c)=\exp\left\{\gamma\int_0^{m_c}\frac{\varphi'(m)-1}{(\beta+\gamma)\varphi(m)-\beta m}dm\right\}.$$

We now elucidate how the line of turning points is characterized. It follows from (2) and (4) that the susceptibility on the turning-point curve is written as

$$\chi_c=\left(\frac{\beta m_c\varphi'(m_c)}{\beta+\gamma}\right)^{\gamma/(\beta+\gamma)}H_c^{-\gamma/(\beta+\gamma)}, \qquad (7)$$

i.e., on this curve χ diverges only at the critical point, at which this curve touches the bounding curve. In Ref. 5 it was shown that the point $m=m_c$ is characterized by the simultaneous vanishing of the numerator and denominator of the expression

$$\chi=(\partial M/\partial m)/(\partial H/\partial m).$$

A consequence of this is the singular behavior of $(\partial^2H/\partial M^2)_T$ on the turning-point curve:

$$\left(\frac{\partial^2H}{\partial M^2}\right)_T=\left(\frac{\partial\chi^{-1}}{\partial M}\right)_T=\left(\frac{\partial\chi^{-1}}{\partial m}\Big/\frac{\partial M}{\partial m}\right)_T.$$

The quantity $\partial\chi^{-1}/\partial m$ on this curve is equal to a certain negative constant:

$$\frac{\partial\chi^{-1}}{\partial m}\Big|_c=\frac{\partial}{\partial m}\left[\left(\frac{M}{m}\right)^{\gamma/\beta}\right]\Big|=-\frac{\gamma}{\beta m}\left(\frac{M}{m}\right)^{\gamma/\beta}\Big|_c, \qquad (8)$$

and since $\partial M/\partial m$ tends to zero from the negative side as $m\to m_c$, it follows that $(\partial^2H/\partial M^2)_T|_c=\infty$.

The region lying inside the turning-point line is not described by the equation of state (2); i.e., from the standpoint of Eq. (2), which is a formulation of the scaling hypothesis, equilibrium states of the substance that correspond to this region are simply impossible. Thus, the turning-point curve corresponds to the classical spinodal, which also bounds the region of physically impossible equilibrium states of the system. It should be noted that for the classical index values $\beta=\frac{1}{2}$ and $\gamma=1$ this line goes over naturally into the classical spinodal, since it follows from (4) that in this case $\varphi(m)\to Am^3$ as $m\to m_c$, and, consequently, the simplest function $\varphi(m)$ satisfying the required limiting behavior at the points $m=0$ and $m=m_c$ will be $\varphi(m)=m+Am^3$, and it is obvious that the asymptotic behavior $\varphi(m)\to Am^3$ will be found only for $m\to m_c\to\infty$. This asymptotically exact form of $\varphi(m)$ leads to the result that for $\beta=\frac{1}{2}$ and $\gamma=1$ the isotherm, as easily found from (2), will have the form of a cubic parabola $H=-AM^3/2+C_+\tau M$, and for $m\to m_c$

$$\chi=\chi(0,\ \tau)(1+3Am_c^2/2),$$

i.e., χ becomes infinite (together with m_c) on the turning-point curve, which in this case coincides with the classical spinodal.

The term "spinodal" was introduced by van der Waals from the Latin *spina* (thorn, or spine), because the section of the free-energy surface cut by the tangent plane at this point possesses a turning point, or spine. It can be seen from Fig. 1 that the isotherms of the Migdal equation also have a similar spine; i.e., from the etymological point of view the turning-point curve can also be called a spinodal. However, in order to distinguish this line from the classical spinodal we shall call it the turning-point curve.

Thus, in contrast to the classical equations of state of the van der Waals type, for which isotherms also exist in the region of absolute instability and the boundary between the metastable and labile regions is determined by the condition $(\partial H/\partial M)_T=0$, in scaling equations of state with nonclassical indices the turning-point curve simply bounds the region that is not describable by the equation of state, i.e., the region in which, from the standpoint of scaling [since Eq. (2) is a formulation of scaling], equilibrium states of the substance are not possible. It is obvious that the existence of such a region follows from the scaling hypothesis itself, since the turning-point curve in Eq. (2) is obtained without any assumptions concerning the choice of the specific form of the scaling function $\varphi(m)$.

In his paper Migdal also points out the possibility of the existence of metastable states in which the spontaneous moment is several times larger than that in the stable state. However, the existence of such states is dubious, since they correspond to zeros of the function $\varphi(m)$ at $m>m_c$, the presence of which in Migdal's paper arose entirely from the specific choice of $\varphi(m)$ in the form of a power polynomial.

We now consider Schofield's parametric equation of state[4]:

$$H=Ar^{\gamma+\beta}\theta(1-\theta^2), \qquad (9)$$

$$\tau=r(1-B^2\theta^2), \qquad (10)$$

$$M=gr^\beta\theta. \qquad (11)$$

As shown in Ref. 7, this equation, like the Migdal equation, is based on the scaling theory of critical phenomena. Moreover, it coincides exactly with the Migdal equation in the approximation $\beta+\gamma=3/2$ and differes from the latter only by terms of higher order than ε^2 (Ref. 7). Consequently, the Schofield equation should also describe the metastable state of a system, and its isotherms should have turning points. Indeed, an investigation of Eqs. (9)–(11) has shown that for parameter values $|\theta|>1$ the isotherms drawn using this equation fall into the region of metastable states, and for $\theta^2=\gamma/(\gamma-2\beta)$ have turning points; i.e., the value $\theta^2=\gamma/(\gamma-2\beta)$ corresponds to the turning-point curve and the properties of this curve coincide fully with the properties of the similar curve from the Migdal equation.

Thus, the scaling hypothesis implies the existence of a certain analog of the spinodal, on which, in contrast to the classical definition, the susceptibility becomes infinite only at the critical point.

Having investigated the general properties of the turning-point curve, we attempted to determine it from the experimental P, ρ, T data near the critical point of ^{4}He (Ref. 8). For this we made use of the Schofield equation of state (9)–(11), which for the liquid-vapor critical point can be written as follows[9]:

$$\Delta P \equiv (P-P_k)/P_k = (S_k T_k/P_k V_k - a)\tau + Ar^{\gamma+\beta}(\theta-\theta^3) + Agr^{\gamma+2\beta}(z_0+z_2\theta^2+z_4\theta^4), \quad (12)$$

$$\tau = r(1-B^2\theta^2), \quad (13)$$

$$\Delta\rho \equiv (\rho-\rho_k)/\rho_k = gr^\beta\theta. \quad (14)$$

We had determined the constants of this equation for ^{4}He previously.[10] Substituting into (12)–(14) the value $\theta^2 = \gamma/(\gamma - 2\beta)$, we obtained the turning-point curve of ^{4}He; see Fig. 2.

To elucidate how the turning-point curve determined from the Schofield equation differs from the classical spinodal we calculated the spinodal in several ways. The first way, described in Ref. 11, is based on the fact that in the classical case the spinodal is the envelope of the family of isochores in the variables P, T, the isochores themselves being straight lines. The latter circumstances makes it possible in this case to extrapolate the isochores into the metastable region up to the spinodal; this is important because of the sparseness of the experimental data in this region. The part of the spinodal ($\rho < \rho_k$) which we constructed in this way from the data of Ref. 8 with the use of the analytical method is shown, in comparison with the results obtained by earlier methods, in Fig. 2. It can be seen from the figure that near the critical point the spinodal obtained lies outside the binodal (the bounding curve), indicating the incorrectness of this method. Clearly, this is connected with the fact that extrapolation of the straight lines into the metastable region is not justified. Thus, the method described in Ref. 11 for determining the spinodal gives too large an error ($\sim 15\%$) and is not suitable for an exact determination of the spinodal, at least near the critical point.

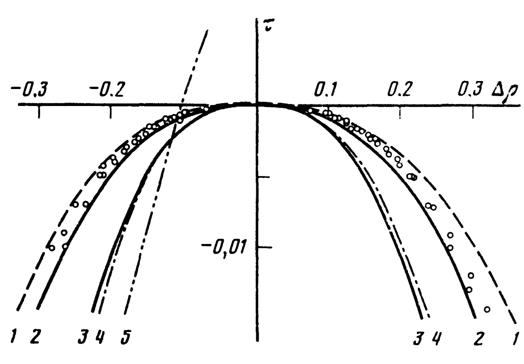

FIG. 2. Bounding curve and spinodal of ^{4}He: the small circles represent the binodal (experimental points); 1–1) the binodal from the Schofield equation; 2–2) the binodal from Eq. (15); 3–3) the turning-poing curve from the Schofield equation; 4–4) the spinodal from Eq. (16); 5–5) the spinodal plotted from Ref. 11.

Figure 2 shows one further estimate that we have made of the spinodal. It shows the coexistence and turning-point curves of ^{4}He, calculated from the Schofield equation (curves 2–2 and 3–3). Figure 2 also depicts the coexistence curve and spinodal (cruves 1–1 and 4–4) calculated from the results of Ref. 12, in which empirical equations of the following form were proposed for the binodal and spinodal:

$$\Delta\rho_6 = \pm B(-\tau)^\beta - (B-1)\tau, \quad (15)$$

$$\Delta\rho_c = \pm {}^2/_3 B(-\tau)^\beta - (B-1)\tau, \quad (16)$$

where $B = 0.505 z_k^{-1}$, $z_k = P_k V_k / RT_k$. It can be seen from the figure that, in this range of the parameters,[8] both the binodal and spinodal found from Eqs. (15) and (16) coincide, to within 5%, with the binodal and turning-point curve, respectively, determined from the Schofield equation. This is not surprising, since the value of the coefficient B in Eqs. (15)–(16) is close to the value determined from the Schofield equation, while the term linear in τ in these equations is small and ranges from $\sim 2\%$ of the principal term at $\tau = 10^{-2}$ to $\sim 4\%$ of the principal term at $\tau = 10^{-3}$.

Thus, the above account shows that the difference between the classical spinodal and its scaling analog, at least not too far from the critical point, is small, and for estimates in this region one can us, e.g., Eq. (16).

Final confirmation of the correctness of the scaling definition of the "spinodal" could be provided by the experimental observation of those branches of the isotherms that are obtained for the Migdal equation for $m > m_c$, and for the Schofield equation for $\theta^2 > \gamma/(\gamma - 2\beta)$. However, at the present time it is not clear how one should perform the experiment in order to get into this region of state of the system.

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