Metastable states near a tricritical point

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It is established that in the vicinity of the tricritical point there are nonequilibrium states whose lifetimes greatly exceed the equilibrium relaxation time.

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If the thermodynamic parameters of a system in equilibrium are suddenly changed, then the system leaves its previous state and goes into a new state characterized by altered parameters. In first-order phase transitions, a situation is possible in which the system, rather than go over to an equilibrium state, "strays" into a metastable state which does not correspond to the absolute minimum of the energy (see, e.g.,[1]). In the present communication we consider homogeneous metastable states that arise near the tricritical point as the result of nonequilibrium relaxation of the system. It is interesting that for these states to occur it is not mandatory to have an energy barrier that separates them from the equilibrium position.

The free-energy density of the investigated system (compressible magnet, metamagnet, etc.) is given by the Landau expansion (T is the temperature, P is the pressure, and Ψ is a single-component order parameter)

$$\Phi = \Phi_0(P, T) + A(P, T)\Psi^2 + B(P,T)\Psi^4 + D(P, T)\Psi^6. \quad (1)$$

In the tricritical point $T=T_t$, $P=P_t$, corresponding to intersection with the line $B(P,T)=0$, the line of second-order transitoins $A(P,T)=0$ (shown dashed in Fig. 1) goes over into the phase-coexistence curve $B^2=4AD$. The thermodynamic stability is ensured in this case by the coefficient $D>0$.

Let an equilibrium system with a homogeneous order parameter Ψ_0 at the instant $t=0$ be suddenly taken out of equilibrium into a region corresponding to negative values of B. The establishment of the new equilibrium in the system is described by the equation

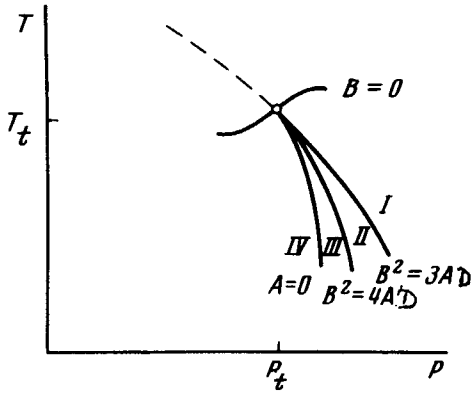

FIG. 1.

$$\frac{\partial \Psi}{\partial t} = -\frac{1}{t_s}\frac{\delta}{\delta \Psi}\left(\int \Phi\, dv\right). \tag{2}$$

Here t_s is the bare relaxation time, which specifies the time scale. We change over in this equation to spatial Fourier components and assume that the fluctuations with wave vector $k \neq 0$ are small in comparison with the homogeneous ($k=0$) Fourier component m for which Eq. (2) is written in the form

$$-\frac{\partial m}{\partial t} = Am + 2Bm^3 + 3Dm^5. \tag{3}$$

The time is measured here in units $t_s/2$. It is easy to establish that the thermodynamic force $\delta\Phi/\sigma\Psi$ is equal to zero at the following values of m:

$$m_1 = 0; \quad m_{2,3} = \pm \frac{(-B + \sqrt{B^2 - 3AD})^{1/2}}{D}; \quad m_{4,5} = \pm \frac{(-B - \sqrt{B^2 - 3AD})^{1/2}}{D}.$$

The quantities m_1, m_2, and m_3 yield the possible equilibrium positions. The system relaxes to the state m_3 if the initial value is $m_0 < m_5$, to the state m_2 if $m_0 > m_4$, and to the state m_1 if $m_5 < m_0 < m_4$.

It is easily seen that for each state between the lines $A=0$ and $B^2=3AD$ there exist two values of $|m|$ corresponding to the extrema of the free energy. In the region II (see Fig. 1), the equilibrium phase corresponds to m_1, and in region III it corresponds to $m_2(m_3)$. On the other hand, the metastable states in these regions are respectively $m_2(m_3)$ and m_1. We call the lines $A=0$ and $B^2=3AD$ the lower and upper metastability limits.

Relaxation to the ith state is usually characterized[11] by a relaxation function $\phi_i = (m - m_i)/(m_0 - m_i)$, where $i=1,2,3$, and the relaxation time is characterized by the quantity

$$\tau_R^{(i)} = \int_0^\infty \phi_i(t)\, dt.$$

The metastable-state lifetime corresponding to the gently-sloping section of the function is defined as

$$\tau_{ms}^{(i)} = \tau_R^{(i)}(m_0 - m_i)/(m_{ms} - m_i).$$

Solution of (3) leads to the conclusion that the lifetimes of the metastable states $m_2(m_3)$ in the region II near the upper metastability limit diverge like $\ln(T_0 - T)$, where the temperature $T_0(P)$ corresponds to the condition $B^2 = 3AD$. Particular interest attaches to the region III above the upper metastability limit, where $B^2 < 3AD$. The corresponding values of m_2^2 acquire an imaginary part b ($m_2 = y + iz$), which is small near the metastable boundary in comparison with the real part a. Under these conditions we have for the relaxation function

$$\phi_1 = \exp[-t(a^2 + b^2) + 2\ln F], \tag{4}$$

where

$$\ln F = \frac{1}{4}\ln\left[\frac{(m^2 - a)^2 + b^2}{(m_0^2 - a)^2 + b^2}\right] + \frac{a}{4b}\left(\operatorname{arc\,tg}\frac{b}{m^2 - a} - \operatorname{arc\,tg}\frac{b}{m_0^2 - a}\right)$$

It is easy to verify that this corresponds to a rapid decrease (within a time of the equilibrium relaxation $\sim(a^2+b^2)^{-1} \sim (B/3D)^2$) of m from m_0 to $m = m_{ms} \approx y = \sqrt{-B/3D}$ and to a prolonged stay of the system in this metastable state. Its time variation is proportional to z^2—the square of the imaginary part of the order parameter, the value of which is of the order of smallness

$$\left(z \approx \frac{1}{2}\sqrt{\frac{3AD - B^2}{3|B|D}}\right)$$

The lifetime of this metastable state is inversely proportional to z, namely

$$\tau_{ms}^{(1)} \approx \frac{\pi}{4z}a^{-3/2} \approx \frac{\pi}{2y^2}\sqrt{\frac{3D}{a_0}}(T - T_0)^{-1/2}, \tag{5}$$

where $a_0 = (\partial A/\partial T)_{T=T_0}$. It is interesting that the only requirement that m_0 must satisfy in order to land in this metastable state is the inequality $m_0 > y$. The difference in the behavior of the times τ_R and τ_{ms} below and above the upper metastability limit is due to the fact that above this limit the metastable states are separated from the stable ones by a barrier, and below this limit there is no such barrier. Therefore, whereas in the former case there exists near m_2 a region where the nonequilibrium relaxation goes over to an equilibrium exponential regime, in the latter case there is no such region (it lies near m_1).

Near the lower metastability limit, the corresponding lifetimes also increase without limit (with decreasing m_4^2), but the region of the initial values of m_0 from which are reached such states $m_0^2 < m_4^2$ contracts to a point in this case.

In conclusion, let us examine the causes of the finite lifetimes of the metastable states. The first cause is the interaction of the fluctuations of the order parameter, which we did not take into account. It is known,[2] however, that near the tricritical point, the action of the fluctuations of the order parameter is insignificant, and this makes our results at least qualitatively correct. The second cause is the decay of the homogeneous metastable state on account of the increase of the inhomogeneous order-parameter fluctuations with time. An appropriate analysis has shown that this instability arises in the case of motion over the convex section of the potential relief $\Phi(m)$, to which the system goes over already after leaving the metastable state.

[1]K. Binder, Phys. Rev. **B8**, 3423 (1973).
[2]L.D. Landau and E.M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1976 [Pergamon].