The phonon states density plotted in Fig. 3 splits into several bands. Such a situation is realistic. In some cases the phonon bands can intersect. Then, the solution of the problem of determination of the phonon spectrum from calorimetric data may become more complex. This case requires a separate analysis.

We shall conclude by stating that the density of the phonon states can sometimes be determined in the case of crystals of the cluster type with zero-dimensional anisotropy.

[1] V. V. Tarasov, Zh. Fiz. Khim. 24, 11 (1950).
[2] P. E. Stepanov, Zh. Fiz. Khim. 26, 1642 (1952).
[3] I. M. Lifshitz, Zh. Éksp. Teor. Fiz. 22, 475 (1952).
[4] K. Kopinga, P. van der Leeden, and W. J. M. de Jonge, Phys. Rev. B 14, 1519 (1976).
[5] S. M. Genensky and G. F. Newell, J. Chem. Phys. 26, 486 (1957).
[6] E. S. Syrkin and S. B. Feodos'ev, Fiz. Nizk. Temp. 11, 1001 (1985) [Sov. J. Low Temp. Phys. 11, 553 (1985)].
[7] J. M. E. Harper, R. L. Greene, P. M. Grant, and G. B. Street, Phys. Rev. B 15, 539 (1977).
[8] J. C. Lasjaunias and P. Monceau, Solid State Commun. 41, 911 (1982).
[9] R. Provencher, C. Ayache, S. Jandl, and J. P. Jay-Gerin, Solid State Commun. 59, 553 (1986).
[10] T. Ikari, R. Provencher, S. Jandl, and M. Aubin, Solid State Commun. 45, 113 (1983).
[11] S. Furuseth, L. Brattas, and A. Kjekshus, Acta Chem. Scand. A 29, 623 (1975).
[12] L. Brattas and A. Kjekshus, Acta Chem. Scand. 26, 3441 (1972).
[13] I. M. Lifshitz, Zh. Éksp. Teor. Fiz. 26, 551 (1954).
[14] V. A. Korshunov, Fiz. Met. Metalloved. 47, 1147 (1979).
[15] J. W. Loram, J. Phys. C 19, 6113 (1986).
[16] A. Grisel, F. Levy, and T. J. Wieting, Physica B (Utrecht) 99, 365 (1980).

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Nonisothermal relaxation in a nonlocal medium

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A study is made of the thermodynamics of a nonlocal medium whose evolution is governed not only by the temperature and pressure, but also by the field of a relaxation parameter. For solid-state materials which undergo a phase transition, such a relaxation parameter is the order parameter. Heat transport equations are derived together with a thermodynamic inequality which must be satisfied during relaxation. The motion of an interphase boundary during a first-order phase transition is investigated. It is shown that, if the width of the boundary exceeds a critical value, there are steady-state conditions under which the new phase formed in an exothermal transition may be at a temperature above the equilibrium temperature.

Continuum models have been widely used to describe the evolution of nonequilibrium condensed systems. In such models, relaxation is regarded as the evolution of a spatially inhomogeneous field of some parameter characterizing the deviation of the system from equilibrium. In particular, such a method may be used to describe the evolution of a phase transition from a metastable or unstable state to a stable state and the relaxation parameter is then represented by the transition or order parameter. Changes of the transition parameter at each point are accompanied by the release of heat which then affects the rate of such evolution. The analysis of the relaxation process is thus related to the problem of describing heat release in such an inhomogeneous nonequilibrium medium. Attempts to solve this problem have been based on heuristic ideas and are unsatisfactory.[1,2]

We shall address this problem using a consistent thermodynamic approach which takes account of the nonlocal properties of the medium, i.e., we shall assume that the thermodynamic functions at each point depend not only on the value of the relaxation parameter at this point, but also on the components of the gradient of this parameter. Compared with the Mandel'shtam–Leontovich–Fastov relaxation theory (see Refs. 3-5), this represents a refinement necessary to describe interphase boundaries where gradients of the transition parameter are particularly large.

The problem under study is especially topical for magnetic and superconducting first-order phase transitions and also for structural phase transitions with a wide boundary. The results could be also used to discuss the macroscopic dynamics of solid-state chemical reactions.[6]

1. THERMODYNAMIC RELATIONS FOR A NONLOCAL MEDIUM

We shall consider a nonequilibrium thermodynamic system whose state is described at each moment of time not only by the temperature $T(\mathbf{r}, t)$ and pressure $P(\mathbf{r}, t)$ fields, but also by the field of a relaxation parameter $\xi(\mathbf{r}, t)$. In a nonequilibrium state, the thermodynamic potential ϕ per unit volume of the nonlocal medium depends at each point $\mathbf{r}$ on the values of T, P, and ξ, and on the components of various derivatives of ξ with respect to the coordinates $\partial\xi/\partial x_i$. The thermodynamic potential of the system as a whole can then be written as a functional

$$\Phi\{T, P, \xi\} = \int \varphi d^3r. \tag{1}$$

The integration is over the whole volume occupied by the system which is assumed to be constant.

For given temperature and pressure distributions, the thermodynamic potential in an equilibrium state should assume a minimum value with respect to the spatial distribution of the relaxation parameter, i.e.,

$$\frac{\delta\Phi}{\delta\xi} = 0 \quad \text{for} \quad \xi = \xi(T, P, \mathbf{r}), \tag{2}$$

where $\delta\Phi/\delta\xi$ is the variational derivative of the functional (1).

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We shall determine the change in the thermodynamic potential $\delta\phi$ at a point r, induced by a small continuous increase $\delta\xi$ (r, t) which is nonzero only in the vicinity of the point r. According to the definition of the variational derivative (see Ref. 7), such as increase is given by

$$\delta\varphi = \frac{\delta\Phi}{\delta\xi}\,\delta\xi. \tag{3}$$

with an accuracy up to small terms of higher order than $\delta\xi$.

If the temperature, pressure, and relaxation parameter vary simultaneously, then

$$d\varphi = -s\,dT + v\,dP + \frac{\delta\Phi}{\delta\xi}\,d\xi, \tag{4}$$

where $s = -(\partial\phi/\partial T)_{P,\xi}$ is the entropy per unit volume and $v = (\partial\phi/\partial P)_{T,\xi}$ is the relative change of the unit volume due to compression by dP.

According to the first law of thermodynamics, the amount of heat dq received by a unit volume of the system is given by

$$dq = de + P\,dv, \tag{5}$$

where e is the energy per unit volume of the system which is related to the thermodynamic potential by the usual expression

$$\varphi = e - Ts + Pv. \tag{6}$$

Substituting Eq. (6) in Eq. (4) and using Eq. (5), we obtain an expression for the entropy change

$$T\,ds = dq - \frac{\delta\Phi}{\delta\xi}\,d\xi. \tag{7}$$

It follows from the second law of thermodynamics that

$$ds \geqslant dq/T. \tag{8}$$

Comparing Eqs. (7) and (8), we obtain a condition which should be satisfied by the variation of the relaxation parameter at each point:

$$\frac{\delta\Phi}{\delta\xi}\,d\xi \leqslant 0, \tag{9}$$

where equality is possible only under the condition (2). The simplest equation describing the evolution of the parameter ξ(r, t) satisfying these requirements has the form

$$\frac{d\xi}{dt} = -\gamma\frac{\delta\Phi}{\delta\xi}, \tag{10}$$

where the coefficient $\gamma > 0$ determines the characteristic relaxation time of the parameter ξ(r, t). This equation was used in Ref. 8 and it represents a generalization of the Mandel'shtam–Leontovich relaxation equation[3] to a nonlocal case.

Combining Eqs. (4) and (7), we obtain an equation for the enthalpy change per unit volume w = ϕ + Ts,

$$dw = dq + v\,dP. \tag{11}$$

We shall now derive an equation of heat transport in a system where P = const and heat exchange is governed by heat conduction, i.e.,

$$dq = \nabla(\lambda\nabla T)\,dt, \tag{12}$$

where λ is the thermal conductivity. We shall introduce a specific heat per unit volume. $C_P = (\partial w/\partial T)_{P,\xi}$ and total enthalpy of the system $W = \int w\,d^3r$.

By analogy with Eq. (4), we obtain the following expression for the enthalpy change:

$$dw = C_P\,dT + \left(\frac{\delta W}{\delta\xi}\right)_T d\xi. \tag{13}$$

Using Eqs. (11)-(13), we obtain an equation for heat transport in an immobile medium:

$$C_P\frac{\partial T}{\partial t} = \nabla(\lambda\nabla T) + Q(\mathbf{r}, t), \tag{14}$$

where the density of instantaneous heat release in the medium is given by

$$Q(\mathbf{r}, t) = -\left(\frac{\delta W}{\delta\xi}\right)_T\frac{\partial\xi}{\partial t} = -\frac{\delta\Phi}{\delta\xi}\frac{\partial\xi}{\partial t} - T\frac{\delta S}{\delta\xi}\frac{\partial\xi}{\partial t}, \tag{15}$$

where $S = \int s\,d^3r$ is the total entropy of the system.

The heat source Q(r, t) consists of a dissipation term which is always positive because of Eq. (9) and of an entropy contribution which may be either positiver or negative, depending on the direction of the process. The system (14) and (15) represents the fulfillment of our task to derive an equation governing heat transport in a nonequilibrium nonlocal medium. This equation can then be generalized to a moving medium and to solid-state materials with pressure or stress varying from point to point using standard procedures.

2. CONDITION ON THE INTERPHASE BOUNDARY (GENERALIZED GIBBS–THOMSON EQUATION)

As an example, we shall consider a two-phase system formed during a first-order phase transition. The thermodynamic potential of such a system can be the Ginzburg–Landau functional[9] and the Cahn–Hilliard functional[10], i.e.,

$$\varphi = \varphi_1(T) + \Delta\varphi(T, \xi) + \frac{\varkappa}{2}(\nabla\xi)^2, \tag{16}$$

where $\varkappa > 0$. Homogeneous solutions of Eq. (2) at a constant temperature T, i.e., the solutions of the equation

$$\frac{\partial\Delta\varphi}{\partial\xi} = 0, \tag{17}$$

describe metastable ξ_1, stable ξ_2, and unstable ξ^* states of the system. Here, ϕ_1(T) is the thermodynamic potential of the phase ξ_1, i.e., $\Delta\phi(T, \xi_1) \equiv 0$. At the equilibrium temperature T_0, we have $\phi(T_0, \xi_1) = \phi(T_0, \xi_2)$, i.e.,

$$\Delta\varphi(T_0, \xi_2) = 0. \tag{18}$$

Equation (10) describing the evolution of a system with the thermodynamic potential defined by Eq. (16) is given by

$$\frac{1}{\gamma}\frac{\partial\xi}{\partial t} = -\frac{\partial\Delta\varphi}{\partial\xi} + \varkappa\nabla^2\xi. \tag{19}$$

Isothermal solutions of this equation are known.[8,11] In the one-dimensional case at $T \neq T_0$, the solution varying from ξ_1 to ξ_2 is represented by a solitary wave of half-width

$$\delta \sim |\xi_2 - \xi_1|\sqrt{\varkappa/\Delta\varphi(T, \xi^*)}. \tag{20}$$

We can use this result and seek the solution of Eq. (19) for an arbitrary temperature distribution in the form of a function

$$\xi = \xi(u) \tag{21}$$

of a scalar field

$$u = U(\mathbf{r}, t). \tag{22}$$

The velocity V_n(r, t) of motion of the surface U(r, t) = const is given by

$$\frac{\partial U}{\partial t} + V_n|\nabla U| = 0. \tag{23}$$

The unit vector **n** normal to this surface, which is oriented from the state ξ_2 toward the state ξ_1, satisfies the relation[12,13]

$$\nabla n = k_1 + k_2, \tag{24}$$

where k_1 and k_2 are the principal curvatures of the surface U = const.

We shall choose the scalar field (22) so that it satisfies the eikonal equation

$$(\nabla U)^2 = 1. \tag{25}$$

Solutions of Eq. (25) form a set of equidistant surfaces U(r, t) = const that are parallel to some chosen surface which will be denoted by U = 0. We shall choose this surface to satisfy $\xi(0) = (\xi_1 + \xi_2)/2$ and call it the interphase surface. The orthogonal trajectories are straight lines and the distance from a point (r, t) to the interphase surface is equal to u (see Ref. 14). The value of V_n is independent of the eikonal u and the principal curvatures $k_{1,2}$ satisfy the relation

$$k_i = 1/(R_{i0} + u), \tag{26}$$

where i = 1, 2; R_{i0} are the principal radii of curvature of the interphase surface.

Using the Eqs. (21)-(25), we can transform Eq. (19) to the form

$$-\frac{V_n}{\gamma}\frac{d\xi}{du} + \frac{\partial \Delta\varphi}{\partial \xi} = \varkappa\left(\frac{d^2\xi}{du^2} + 2K\frac{d\xi}{du}\right), \tag{27}$$

where $K = (k_1 + k_2)/2$ is the average curvature of the surface U = const.

We shall multiply all the terms of this equation by $d\xi/du$ and integrate the equation over the interval (u_2, u_1), where $\xi_1 = \xi(u_1)$ and $\xi_2 = \xi(u_2)$. If the characteristic length of the temperature field $\lambda/C_p V_n$ is much greater than the width of the transition region 2δ, i.e., if the Peclet number of the system satisfies

$$Pe = V_n C_p \delta/\lambda \ll 1, \tag{28}$$

then

$$\int_{u_2}^{u_1} \frac{\partial \Delta\varphi}{\partial \xi}\frac{d\xi}{du}\,du \approx -\Delta\varphi(T, \xi_2). \tag{29}$$

We shall assume that the coefficients γ and κ depend only weakly on temperature and are independent of the relaxation parameter ξ. We obtain

$$\int_{u_2}^{u_1} \varkappa\frac{d^2\xi}{du^2}\frac{d\xi}{du}\,du \approx \frac{\varkappa}{2}\int_{u_2}^{u_1}\frac{d}{du}\left(\frac{d\xi}{du}\right)^2 du = 0, \tag{30}$$

since $(d\xi/du) = 0$ for $\xi = \xi_1$ and $\xi = \xi_2$. If the principal radii of curvature are much greater than the width of the transition region 2δ, we obtain from Eq. (26)

$$\int_{u_2}^{u_1}\left(\frac{V_n}{\gamma} + 2K\varkappa\right)\left(\frac{d\xi}{du}\right)^2 du \approx \left(\frac{V_n}{\gamma\varkappa} + 2K_0\right)\sigma, \tag{31}$$

where K_0 is the average curvature of the interphase surface and

$$\sigma = \int_{u_2}^{u_1} \varkappa\left(\frac{d\xi}{du}\right)^2 du. \tag{32}$$

We thus obtain from Eqs. (27)-(31) the following condition for the boundary (i.e., transition region)) whose width is small compared with the thermal length:

$$\frac{\sigma}{\gamma\varkappa}V_n + 2\sigma K_0 + \Delta\varphi(T, \xi_2) = 0. \tag{33}$$

In equilibrium, i.e., for $V_n = 0$, Eq. (33) reduces to the Gibbs–Thomson equation which relates the phase equilibrium temperature of phases separated by a curved surface to the curvature of this surface.

We shall now evaluate the change of the thermodynamic potential of the system unrelated to a change in temperature. Using Eqs. (1), (3), (16), and (29)-(32), we obtain

$$d\Phi = dt\int\left(\frac{\partial \Delta\varphi}{\partial \xi} - \varkappa\nabla^2\xi\right)\frac{\partial \xi}{\partial t}\,d^3r = \Delta\varphi(T, \xi_2)\,dt\int_{\Omega} V_n d\Omega + \sigma dt\int_{\Omega} 2K_0 V_n d\Omega, \tag{34}$$

where the integration is over the whole interphased surface $\Omega(U = 0)$. The first term is proportional to the total volume of the region ~~and~~ which is modified during a time dt and the second to the change in the area of interphase surface during the same time interval dt (see Ref. 12). It can be seen from Eq. (34) that σ is the surface thermodynamic potential of a nonequilibrium nonisothermal system.

The density of instantaneous heat release (15) for the thermodynamic potential (16) and a relaxation parameter $\xi(r, t)$ satisfying Eqs. (21)-(25) has the form

$$Q = \left[\frac{\partial \Delta w}{\partial \xi} - \left(\varkappa - T\frac{d\varkappa}{dT}\right)\left(\frac{d^2\xi}{du^2} + 2K\frac{d\xi}{du}\right)\right]V_n\frac{d\xi}{du},$$

where $\Delta w(T, \xi) = \Delta\phi - T(\partial\Delta\phi/\partial T)_\xi$ is the difference enthalpies of an arbitrary homogeneous state of the system and of the state for which $\xi = \xi_1$ at the same temperature T. We shall integrate this expression in the interval (u_2, u_1) assuming that the width of the transition region is small compared with the thermal length and with the radius of curvature of the interphase surface. Using Eqs. (29)-(32), we then obtain the following expression for the total power of the heat released in the system:

$$\bar{Q} = V_n\left[L(T) - 2K_0\left(\sigma - T\frac{d\sigma}{dT}\right)\right], \tag{35}$$

where

$$L(T) = T\partial\Delta\varphi(T, \xi_2)/\partial T - \Delta\varphi(T, \xi_2) \tag{36}$$

is the latent heat of the transition at a temperature T. The second term in Eq. (35) is the heat released in the system due to changes in the area of the interphase boundaries and is the only source of heat for recrystallization or growth of antiphase domains.[12] The boundary condition (33) and the expression (35) for the power of released heat can be used to solve the boundary-value problems for the generalized Stefan problem.[15,16] Classical analysis of the boundary of an infinitesimal thickness corresponds to the limit $\kappa \to 0$ for $\gamma\sqrt{\kappa} = \text{const}$, $K\cdot\Delta\varphi(T_0, \xi^*) = \text{const}$.

3. STEADY-STATE MOTION OF AN INTERPHASE BOUNDARY

We shall consider stationary one-dimensional solutions of the system of equations (14) and (19) without the restriction (28) representing the requirement that the Peclet number is small. We shall express the solution of the system (14) and (19) in the form of a wave moving in the positive direction of the x axis with respect to the medium with a constant velocity $V \geq 0$ so that all the functions depend only on the ~~external~~ eikonal (22) which now assumes the form $u = x - Vt$ and varies within the limits $-\infty < u < +\infty$. We shall further replace Eq. (14) by the equivalent equation (11). We shall introduce the enthalpy $w_1(T) = (\phi_1 - T d\phi_1/dT)$ of the homogeneous state ξ_1.

In the case $\varkappa = \text{const}$, we can write the correction to the enthalpy w of a unit volume for an arbitrary state in the form

$$dw = dw_1 + d\Delta w - \varkappa \nabla^2 \xi d\xi. \tag{37}$$

We thus find from Eq. (11), (19), and (37) that the distributions of temperature T(u) and of the relaxation parameter $\xi(u)$ in a system of coordinates moving with the wave satisfy the system of equations

$$\frac{1}{V}\frac{d}{du}\left(\lambda \frac{dT}{du}\right) + \frac{dw_1}{du} + \frac{d\Delta w}{du} - \varkappa \frac{d^2\xi}{du^2}\frac{d\xi}{du} = 0, \tag{38}$$

$$\frac{V}{\gamma}\frac{d\xi}{du} - \frac{\partial \Delta\varphi}{\partial \xi} + \varkappa \frac{d^2\xi}{du^2} = 0. \tag{39}$$

Equation (39) is identical with Eq. (27) since the surfaces U = const for a one-dimensional system are planes, i.e., $k_{1,2} = 0$.

We shall consider a thermodynamic system with a positive latent heat at arbitrary temperatures in the vicinity of the phase equilibrium temperature T_0. Assuming that the original homogeneous phase ξ_1 far from the transition region for $u \to +\infty$ is at a temperature T_1 such that $\Delta\phi(T_1, \xi_2) < 0$, we find from Eqs. (18) and (36) that $T_1 < T_0$, i.e, this phase is supercooled. The system of equations (38) and (39) describes the rate and conditions for which the system undergoes a steady-state transition to a new state (T_2, ξ_2).

Using the procedure applied to Eq. (27), we again multiply all the terms of Eq. (39) by $d\xi/du$ and integrate them with respect to u over the interval $(-\infty, +\infty)$. The expression in Eq. (30) is identically equal to zero for $\varkappa = \text{const}$. Using the equality $d\Delta\phi = (\partial\Delta\phi/\partial\xi)_T d\xi + (\partial\Delta\phi/\partial T)_\xi dT$, we obtain an equation which determines the velocity V of motion of a nonisothermal stationary wave

$$\Delta\varphi(T_2, \xi_2) + V\int_{-\infty}^{\infty} \frac{1}{\gamma}\left(\frac{d\xi}{du}\right)^2 du + \int_{-\infty}^{\infty} \left(\frac{\partial \Delta\varphi}{\partial T}\right)_\xi \frac{dT}{du} du = 0. \tag{40}$$

In the limit of an infinitesimally thin boundary and for an isothermal transition region, the last term in Eq. (40) vanishes and the velocity is proportional to the discontinuity of the thermodynamic potential at the boundary taken with opposite sign (see Refs. 8 and 11), i.e., such boundaries may undergo steady-state motion ($V > 0$) only if $\Delta\phi(T_2, \xi_2) < 0$ ($T_2 < T_0$).[17] Considering nonisothermal transition regions, we find that the system (38) and (39) may have solutions for large values of $\varkappa$ such that $\Delta\phi(T_2, \xi_2) \geq 0$ for $V > 0$. In fact, Eq. (38) can be integrated analytically. Its first integral

$$w_1(T) + \Delta w(T, \xi) + \frac{\lambda}{V}\frac{dT}{du} - \frac{\varkappa}{2}\left(\frac{d\xi}{du}\right)^2 = \text{const} \tag{41}$$

expresses the law of conservation of the enthalpy between homogeneous states of the system far from the boundary

$$w_1(T_1) = w_1(T_2) - L(T_2)$$

and determines the temperature T_2 of the new phase ξ_2. Since $L(T) > 0$, we find that $T_2 > T_1$ and, therefore, $dT/du < 0$. Moreover, it follows from Eq. (36) that the inequality $\partial\Delta(T, \xi_2)/\partial T > 0$ is satisfied near $T = T_0$. It follows that the last term in Eq. (40) is negative and, therefore, positive values of V are possible even for $\Delta\phi(T_2, \xi_2) \geq 0$, i.e., for $T_2 \geq T_0$.

We shall find a critical value $\varkappa^*$ such that Eq. (39) has a stationary solution for $\Delta\phi(T_2, \xi_2) = 0$, with $V > 0$ even for $T_2 = T_0$. We can write $\Delta\phi$ in the form

$$\Delta\varphi = \Delta\varphi_0 + \frac{L_0}{T_0} f(T, \xi), \tag{42}$$

where $\Delta\phi_0 = \Delta\phi(T_0, \xi)$, and $L_0 = L(T_0)$, i.e., $f(T_0, \xi) = f(T, \xi_1) = 0$ and $\partial f(T_0, \xi_2)/\partial T = 1$. It follows that $\partial f(T_0, \xi)/\partial T$ is positive in some neighborhood of $\xi = \xi_2$ and $\partial f(T_0, \xi_1)/\partial T = 0$. Let $\partial^2 f(T_0, \xi)/\partial T \partial \xi \geq 0$ be satisfied for all ξ such that $\xi_1 \leq \xi \leq \xi_2$. For $T_2 = T_0$ and $\varkappa \to \varkappa^* + 0$, we have $V \to 0 + 0$ and the function $\xi(u)$ approaches its equilibrium form $\xi_e(u)$ for which [see Eqs. (39) and (42)]

$$\frac{\varkappa}{2}\left(\frac{d\xi_e}{du}\right)^2 = \Delta\varphi_0. \tag{43}$$

Since the variation of temperature over the length of the transition region is small for $V \to 0 + 0$, we have $w_1(T) \approx w_1(T_2)$ and we find from Eqs. (41)-(43) that the temperature gradient in the transition region is given by the following expression with an accuracy up to terms of the order of V^2:

$$\frac{dT}{du} = -V\frac{L_0}{\lambda}\left[1 - \frac{\partial f(T_0, \xi)}{\partial T}\right]. \tag{44}$$

Equations (40), (43), and (44) then yield the following equation which determines the critical value $\varkappa^*$

$$2\frac{\lambda T_0}{L_0^2 \gamma \varkappa^*}\int_{\xi_1}^{\xi_2} \sqrt{\Delta\varphi_0}\, d\xi = \int_{\xi_1}^{\xi_2} \frac{\frac{\partial f(T_0, \xi)}{\partial T}\left[1 - \frac{\partial f(T_0, \xi)}{\partial T}\right]}{\sqrt{\Delta\varphi_0}} d\xi. \tag{45}$$

We shall now formulate the main results of this section and discuss whether they could be verified experimentally. The existing theories of the displacement of interphase boundaries assume that the boundary can always be regarded as isothermal and its velocity is given by

$$V = \mu(T_0 - T_I), \tag{46}$$

where T_I is a temperature ascribed to the boundary and μ is the growth coefficient.[8,11,17] This implies immediately that the growing phase cannot have temperature higher than T_0.

Our investigation of steady-state adiabatic motion of the boundary indicates that this conclusion holds only for boundaries whose half-width δ is smaller than a critical length δ^*. It is easy to see from Eqs. (20) and (45) that this critical length is given by

$$\delta^* = A\frac{\lambda}{\mu L_0}, \tag{47}$$

where the numerical coefficient A is of the order of unity and is governed by the actual form of the potential (42). Equations (32), (33), and (36) then imply that μ in Eqs. (46) and (47) is given by

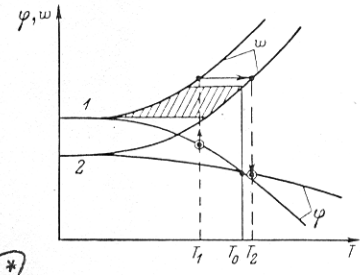

FIG. 1. Dependences of the enthalpy w and the thermodynamic potential ϕ of the initial (1) and final (2) states of the system on temperature T.

$$\mu = \frac{\gamma \varkappa L_0}{c T_0}.$$

The shaded region in Fig. 1 corresponds to steady-state phase transitions that are allowed for boundaries with $\delta < \delta^*$. For $\delta > \delta^*$ and under adiabatic conditions, steady-state transitions can take place (indicated by arrows in Fig. 1) for which $T_2 > T_0$, i.e., the superheated phase may grow. It should be emphasized that the value of the Peclet number is irrelevant for this condition and it depends only on the thermal parameters and the main characteristics of the phase transition.

The critical length (47) is expressed in terms of measurable quantities. For example, the crystallization of white phosphorus was reliably investigated[18] and it was found that this quantity amounts to $5 \cdot 10^{-8}$ m, which is clearly much greater than the width of the crystal–melt boundary. Unfortunately, data on the transport coefficients governing the evolution of phase transitions with wide interphase boundaries (superconductor–normal metal and magnetic transitions) are not available. The effects in question could be quite considerable for such transitions.

[1] J. B. Collins and H. Levine, Phys. Rev. B 31, 6119 (1985).
[2] G. Caginalp, Arch. Ration. Mech. 92, 207 (1986).
[3] L. I. Mandel'shtam and M. A. Leontovich, Zh. Éksp. Teor. Fiz. 7, 438 (1937).
[4] M. A. Leontovich, Introduction to Thermodynamics. Statistical Physics [in Russian], Nauka, Moscow (1983).
[5] N. S. Fastov, Zh. Éksp. Teor. Fiz. 22, 487 (1952).
[6] A. G. Merzhanov and É. N. Rumanov, Usp. Fiz. Nauk 151, 553 (1987) [Sov. Phys. Usp. 30, 293 (1987)].
[7] I. M. Gel'fand, and S. V. Fomin, Variational Calculus [in Russian], Izd. Fiz. Mat. Lit., Moscow (1961).
[8] H. Metiu, K. Kitahara, and J. Ross, J. Chem. Phys. 64, 292 (1976).
[9] V. L. Ginzburg and L. D. Landau, Zh. Éksp. Teor. Fiz. 20, 1064 (1950).
[10] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. 28, 258 (1958).
[11] S. K. Chan, J. Chem. Phys. 67, 5755 (1977).
[12] S. M. Allen and J. W. Cahn, Acta Metall. 27, 1085 (1979).
[13] C. E. Weatherburn, Differential Geometry of Three Dimensions, Vol. 1, Cambridge University Press (1927).
[14] R. Courant, Partial Differential Equations [Russian translation], IL, Moscow (1964).
[15] B. Ya. Lyubov, Theory of Crystallization in Large Volumes [in Russian], Nauka, Moscow (1976).
[16] L. M. Truskinovskii, Dokl. Akad. Nauk SSSR 285, 309 (1985) [Sov. Phys. Dokl. 30, 945 (1985)].
[18] M. E. Glicksman and R. J. Schaefer, J. Cryst. Growth 1, 297 (1967).
17. A.R. Umantsev, Sov. Phys. Crystallogr. 30, 87 (1985)

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Thermodynamic properties of thin films in the vicinity of a first-order phase transition

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The Landau–Ginzburg model and the mean-field approximation are used to study thermodynamic properties of thin metal films in the vicinity of a first-order phase transition resembling a continuous transition. The size dependences of the equilibrium transition temperature, surface energy density, and entropy are analyzed numerically and compared with available experimental data. It is shown that the present method provides a satisfactory description of the physical systems under study (continuous and island films). The limits of stability of metastable states are also determined within this model.

Thin films of various materials exhibit a number of unique properties and are increasingly being used in modern engineering and technology. Extensive research into properties of first-order phase transitions in thin metal films is now being undertaken. Until recently, this research has been carried out mainly experimentally.[1] It was found that the size effects lead to shifts of phase transition and polymorphic transformation points and influence the range of stability of the metastable phase for liquid-crystal transitions[2–4] and change the profile of the hysteresis curves. In particular, it was found that the melting point decreases monotonically when the film thickness is reduced and a sample changes gradually from a bulk material to a thin film (provided such a material is reasonably pure).[1] It has also been demonstrated that the surface energy is reduced in the transition from a bulk sample to a thin film.[5] It was shown in Ref. 6 that a liquid phase (water) can exist in the pores of a wetting agent at temperature much lower than the melting point for the bulk phase and the latent heat of the transition is reduced for thin films.

Thermodynamic properties of a finite system during a first-order phase transition were first studied theoretically in Refs. 8 and 7. The Landau–Ginzburg model was used in Ref. 7 to obtain the size dependence of a shift of the phase equilibrium point of a film. The distribution of the order parameter across a film thickness was studied in Ref. 8. However, many important problems remain unresolved. Among them, we could mention general understanding of the size dependences of the surface energy, latent heat of a transition, etc. and also the explanation of changes in the temperature intervals corresponding to the existence of metastable phases (in particular, supercooled liquid phase) and the limits of existence of such phases. All these problems have very important applications (for example, in adhesion of thin layers of unlike materials).

It is our aim to study the changes in thermody-

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