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Thermodynamic stability of phases and transition kinetics under adiabatic conditions

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A study of equilibrium states of a thermodynamic system whose evolution is governed not only by the temperature, but also by the ordering field is carried out. It is found that an adiabatically insulated system may have a new type of nonuniform state of equilibrium which is inhomogeneous in temperature. The comparison is made of the stability conditions in isothermal and adiabatic systems. The steady motion of an interface boundary during a first-order phase transition is investigated. It is shown, that depending upon the values of the diffusion coefficients, different regimes can exist. For small thermal diffusivity, the temperature of the final phase after the exothermal transition can be above the equilibrium point. The kinetic problem is reformulated to a dynamical system, and a numerical procedure to solve the latter is presented. Numerical results are discussed in comparison with analytic ones.

I. INTRODUCTION

Field theory has been widely used to describe dynamics of phase transitions. In such theory, it is assumed that the state of a system at a given time t, in addition to temperature T, and pressure, must be described by one more function of the position vector $\mathbf{x}$. We shall call it the ordering field $\xi(\mathbf{x},t)$. The Gibbs free energy of the system as a whole is given by Ginzburg–Landau functional

$$\Phi\{\xi,T\} \equiv \int \hat{\varphi}\, d^3x. \tag{1.1}$$

Here the Gibbs free energy per unit volume $\hat{\varphi}$ of the medium capable of undergoing a first-order phase transition can be written in the form of the differential expression

$$\hat{\varphi} = \varphi(\xi,T) + \frac{\kappa}{2}(\nabla\xi)^2, \tag{1.2}$$

with the homogeneous part $\varphi(\xi,T)$ of the free energy density and the square gradient approximation for the inhomogeneous part where the parameter κ characterizes the nonlocal properties of the medium (interactions between neighboring areas). To stabilize a homogeneous state κ must be positive.

Metiu, Kitahara, and Ross[1] showed, that depending upon the nature of the ordering field, its evolution is governed by equations of different types: the Cahn–Hilliard equation, if this field obeys the law of conservation (conserved order parameter), or the relaxation one, if the ordering field is not obliged to be conserved in space and time (nonconserved order parameter). The latter case is considered in this article.

Recently much attention has been devoted to this problem in the presence of the conservation of energy,[2,3] which may be the case in an adiabatically insulated system. Umantsev and Roitburd[4] developed a thermodynamically consistent approach to these models and *derived* the evolution equation for the energy of the nonlocal medium.

In this paper, the thermodynamic stability of different equilibrium states of such a system is studied under adiabatic and isothermal conditions with constant pressure. The evolutionary problem of the stationary, one-dimensional transition is reduced to a dynamical system. For small deviations from equilibrium, analytical solutions are obtained with the help of the perturbation theory, while for arbitrary deviations, numerical results for a concrete potential φ were computed. This type of theory can be applied to various phase transitions such as ferromagnetic, ferroelectric, structural, or even solidification. The results can also be used to discuss the dynamics of reaction-diffusion systems.

II. EQUILIBRIUM STATES UNDER ADIABATIC CONDITIONS

If adiabatic conditions are maintained for a nonlocal inhomogeneous system at constant pressure then its enthalpy W, which can be written as a functional, is conserved, i.e.,

$$W\{\xi,T\} \equiv \int \hat{w}\, d^3x = \text{const}, \tag{2.1}$$

where $\hat{w} = \hat{\varphi} - T(\partial\hat{\varphi}/\partial T)_\xi$ is the enthalpy per unit volume of the system. The entropy functional of such a system takes on a maximum at the equilibrium state[5,6]

$$S\{\xi,T\} \equiv \int \hat{s}\, d^3x \to \text{maximum}, \tag{2.2}$$

where $\hat{s} = -(\partial\hat{\varphi}/\partial T)_\xi$ is the entropy per unit volume. Equilibrium states of an adiabatically insulated system thus obey the conditions which are known as the isoperimetric problem in the calculus of variations.[7] The integration in Eqs. (1.1), (2.1), and (2.2) is over the whole volume (assumed to be constant) occupied by the system.

Changes of entropy s and enthalpy w per unit volume in a *homogeneous* system are connected by the relation

$$ds = \frac{1}{T}\,dw + \left(\frac{\partial s}{\partial \xi}\right)_w d\xi. \tag{2.3}$$

Thus solutions of an isoperimetric problem (2.1) and (2.2) for this system satisfy the equation

$$\left(\frac{\partial s}{\partial \xi}\right)_w = 0. \tag{2.4}$$

Taking into account the theorem of small increments,[5] we obtain that

$$-\frac{1}{T}\left(\frac{\partial \varphi}{\partial \xi}\right)_T \equiv \left(\frac{\partial s}{\partial \xi}\right)_w = 0, \tag{2.5}$$

i.e., an equilibrium state of a homogeneous thermodynamic system under adiabatic conditions obeys the same relation as that under isothermal conditions.

The thermodynamic stability (TS) of such states under adiabatic conditions is determined by the sign of $d^2 s$ for admissible states, obeying the condition $w = \text{const}$. Since

$$d^2 s = \left(\frac{\partial^2 s}{\partial w^2}\right)_\xi dw^2 + 2\frac{\partial^2 s}{\partial w\, \partial \xi} dw\, d\xi + \left(\frac{\partial^2 s}{\partial \xi^2}\right)_w d\xi^2, \tag{2.6}$$

we have the condition of TS of such states,

$$\left(\frac{\partial^2 s}{\partial \xi^2}\right)_w < 0. \tag{2.7}$$

Changing to the variables (ξ, T) we may write

$$T\left(\frac{\partial^2 s}{\partial \xi^2}\right)_w = -\left(\frac{\partial^2 \varphi}{\partial \xi^2}\right)_T + \left[\frac{1}{T}\left(\frac{\partial \varphi}{\partial \xi}\right)_T - \left(\frac{\partial^2 \varphi}{\partial \xi\, \partial T}\right)\right]\left(\frac{dT}{d\xi}\right)_w. \tag{2.8}$$

Then taking into account that

$$\left(\frac{\partial w}{\partial T}\right)_\xi \left(\frac{dT}{d\xi}\right)_w = T\left(\frac{\partial^2 \varphi}{\partial \xi\, \partial T}\right) - \left(\frac{\partial \varphi}{\partial \xi}\right)_T, \tag{2.9}$$

we deduce from Eqs. (2.7) and (2.8) the adiabatic condition of TS of equilibrium states (2.5) in the form

$$\varphi_{\xi\xi} - \frac{\varphi_{\xi T}^2}{\varphi_{TT}} > 0, \tag{2.10}$$

where the left-hand side may be called the adiabatic modulus. For equilibrium states with $(\partial^2 \varphi / \partial T\, \partial \xi) = 0$, the adiabatic and isothermal conditions of TS coincide and have the form of the positivity of the isothermal modulus

$$\left(\frac{\partial^2 \varphi}{\partial \xi^2}\right)_T > 0. \tag{2.11}$$

For states with $(\partial^2 \varphi / \partial T\, \partial \xi) > 0$, condition (2.10) can also be written in the form

$$0 < \left(\frac{dT}{d\xi}\right)_{\text{EQUIL}} < \left(\frac{dT}{d\xi}\right)_w, \tag{2.12}$$

where the relation

$$\left(\frac{\partial^2 \varphi}{\partial \xi^2}\right)_T = -\left(\frac{\partial^2 \varphi}{\partial \xi\, \partial T}\right)\left(\frac{dT}{d\xi}\right)_{\text{EQUIL}}$$

has been taken into consideration.

Since the specific heat is always positive

$$C = \left(\frac{\partial w}{\partial T}\right)_\xi > 0 \tag{2.13}$$

the adiabatic modulus is not less than the isothermal one. Thus the equilibrium state with $(\partial^2 \varphi / \partial T\, \partial \xi) \neq 0$ can be stable under adiabatic conditions [i.e., the adiabatic modulus (2.10) is positive] and unstable under isothermal conditions at the same temperature [i.e., the isothermal modulus (2.11) is negative].

Equilibrium states which are stable and homogeneous with respect to the ordering field ξ [stable solutions of Eq. (2.5)] we shall call phases. The present (TS) analysis gives the stability condition of the equilibrium states only with respect to small static fluctuations. The dynamic stability analysis, (normal modes)[8] shows that the positivity of the adiabatic modulus (2.10) is not enough for the stability of a state with respect to the certain packet of "quasiisothermal" dynamical fluctuations, but condition (2.11) is required also. Therefore, this "adiabatic state" cannot be considered a phase.

We shall now study *inhomogeneous* equilibrium states of a thermodynamic system under adiabatic conditions, which also must obey the isoperimetric problem (2.1) and (2.2). In this case, it is known[7] that if the state under consideration is not an extremal of the enthalpy functional (2.1), then there exists a constant β such that the state sought is the extremal of the functional $\int(\hat{s} + \beta\hat{w})d^3x$, i.e., for the distributions of temperature T and ordering fields $\xi(\mathbf{x})$ the relation

$$\delta S + \beta\delta W = 0 \tag{2.14}$$

is satisfied. Since this relation is true for arbitrary variations $\delta\xi$ then, as a consequence of the definition of an absolute temperature,[5] the state under consideration is homogeneous with respect to temperature and $\beta = -1/T$. Hence this inhomogeneous equilibrium state $\xi(\mathbf{x})$ of an adiabatic system yields a minimum for the Gibbs free energy $\Phi\{\xi, T\} = W - TS$, i.e., satisfies the same necessary condition as in the isothermal system

$$\frac{\delta\Phi}{\delta\xi}\{\xi, T\} = 0, \quad T = \text{const}, \tag{2.15}$$

where $\delta\Phi/\delta\xi$ denotes a variational derivative of a functional. As is known, the one-dimensional (1D) distribution of the ordering field $\xi(x)$ in this state satisfies the equation

$$\varphi(\xi, T) - \frac{\kappa}{2}\left(\frac{d\xi}{dx}\right)^2 = \text{const}. \tag{2.16}$$

If the inhomogeneous state of equilibrium not only imparts a maximum to the entropy functional (2.2), but at the same time *is an extremal* of the enthalpy functional (2.1) (Lagrange multiplier does not exist), then instead of Eq. (2.14) this state satisfies relations

$$\delta W = 0, \tag{2.17a}$$

$$\delta S = 0, \tag{2.17b}$$

which result in the system of equations

$$\left(\frac{\delta W}{\delta \xi}\right)_T + \frac{\partial \hat{w}}{\partial T}\frac{dT}{d\xi} = 0, \tag{2.18a}$$

$$\left(\frac{\delta S}{\delta \xi}\right)_T + \frac{\partial \hat{s}}{\partial T}\frac{dT}{d\xi} = 0. \tag{2.18b}$$

Herewith the temperature distribution in this state need not be homogeneous. One can see that for this state

$$\frac{\delta\Phi}{\delta\xi}\{\xi,T\} = \frac{\partial\hat{s}}{\partial\nabla\xi}\nabla T. \tag{2.19}$$

In the medium which is described by the differential expression (1.2), with the parameter κ, independent of temperature, as assumed below, the entropy density $\hat{s} = -(\partial\varphi/\partial T)_\xi$ does not depend upon gradients of ξ, i.e., has a local character. Thus $\delta\Phi/\delta\xi$ vanishes, but even in this case Eq. (2.19) is not equivalent to Eq. (2.15), because now the temperature distribution is inhomogeneous. For the 1D state, Eq. (2.18) instead of Eq. (2.16), yields the system of equations

$$w(\xi,T) - \frac{\kappa}{2}\left(\frac{d\xi}{dx}\right)^2 = \text{const}, \tag{2.20a}$$

$$s(\xi,T) = \text{const}. \tag{2.20b}$$

The first equation shows that far from the transitional region, this state has the same enthalpy and describes the inhomogeneous ordering field distribution. The second one shows that the state has the same entropy in all points, and therefore, it must also be inhomogeneous in temperature. We shall further call it the "inhomogeneous in temperature" equilibrium state (ITES) and denote the distributions of ordering and temperature fields as $\{\overline{\xi},\overline{T}\}$, so as to distinguish from the "homogeneous in temperature" equilibrium state (HTES). It is obvious that the ITES could be attained only in an ideal insulator, i.e., without any heat exchange between neighboring areas (vanishing thermal conductivity). The possibility of existence of such states was mentioned by Leontovich.[6]

TS of inhomogeneous equilibrium states in the adiabatic system is determined by the sign of the second variation of the entropy functional

$$\delta^2 S\{\xi,T\} = \int\left(\frac{\partial^2 s}{\partial T^2}\delta T^2 + 2\frac{\partial^2 s}{\partial\xi\,\partial T}\delta T\,\delta\xi + \frac{\partial^2 s}{\partial\xi^2}\delta\xi^2\right)d^3x < 0 \tag{2.21}$$

for admissible increments of ordering and temperature fields. Because of the vanishing of the first variation of the enthalpy functional, the admissible increments $\delta\xi$ and δT are related as

$$\delta T = -\frac{\varphi_{T\xi}}{\varphi_{TT}}\delta\xi + O(\delta\xi^2) \tag{2.22}$$

both for HTES (2.15) and ITES (2.18). In the homogeneous case (2.22) results in Eq. (2.9).

For the ITES $\delta\xi$ is an arbitrary increment, as this state is an extremal of the functional W. Then substitution of Eq. (2.22) in Eq. (2.21) yields the TS condition in the form

$$\frac{\partial^2 s}{\partial\xi^2} - 2\frac{\partial^2 s}{\partial\xi\,\partial T}\frac{\partial s/\partial\xi}{\partial s/\partial T} + \frac{\partial^2 s}{\partial T^2}\left(\frac{\partial s/\partial\xi}{\partial s/\partial T}\right)^2 < 0. \tag{2.23}$$

For the HTES, condition (2.1) means vanishing not only of the first variation of the enthalpy functional, but of the second variation also

$$\begin{aligned}0 = \delta^2 W\{\xi,T\} &\equiv \int\left[\frac{\partial^2 w}{\partial T^2}\delta T^2 + 2\frac{\partial^2 w}{\partial\xi\,\partial T}\delta T\,\delta\xi + \frac{\partial^2 w}{\partial\xi^2}\delta\xi^2 + \kappa(\delta\nabla\xi)^2\right]d^3x\\ &= T\delta^2 S\{\xi,T\} + \int\left[\frac{\partial^2\varphi}{\partial\xi^2}\delta\xi^2 - \frac{\partial^2\varphi}{\partial T^2}\delta T^2 + \kappa(\delta\nabla\xi)^2\right]d^3x.\end{aligned} \tag{2.24}$$

Then from Eqs. (2.21), (2.22), and (2.24) we deduce the adiabatic condition of the TS for this state,

$$\delta^2 S = -\frac{1}{T}\int\left[\left(\varphi_{\xi\xi} - \frac{\varphi_{\xi T}^2}{\varphi_{TT}}\right)\delta\xi^2 + \kappa(\delta\nabla\xi)^2\right]d^3x < 0, \tag{2.25}$$

which differs from the condition obtained by Khachaturyan and Suris for isothermal systems[9] in that the adiabatic modulus replaces the isothermal one. Hence the positivity of the adiabatic modulus at all points of the HTES (2.15) is a sufficient (but not necessary) condition of its TS.

Below we shall consider thermodynamic systems described by a functional (1.1) and (1.2) and capable of undergoing a first-order phase transition. Being under isothermal conditions close to the equilibrium temperature, the system has two stable equilibrium states (phases) ξ_i; $i = 1,2$, separated by an unstable equilibrium state ξ^*: $\xi_1 < \xi^* < \xi_2$, i.e., ξ_i satisfy relations (2.5) and (2.12) and ξ^* only Eq. (2.5). For this type of systems depending upon T and const, Eq. (2.16) is known to have periodic (periodon), nontopological soliton (critical nucleus), and topological soliton (two-phase kink) solutions.[9,10] But none of them satisfies the criterion of the isothermal stability, except for the topological soliton with boundary conditions

$$\xi(-\infty) = \xi_2,\quad \xi(+\infty) = \xi_1,\quad d\xi(\pm\infty)/dx = 0 \tag{2.26a}$$

and the temperature obeying the condition

$$\varphi(\xi_1,T_0) = \varphi(\xi_2,T_0), \tag{2.26b}$$

where T_0 is the equilibrium point of the transition, i.e., the temperature under which the stable inhomogeneous with respect to the ordering field state can exist in a system. (Note that within the continuous framework, the equilibrium temperature T_0 can be determined only in the thermodynamical limit of infinite system.) In this case, Eq. (2.16) has a solution in the form of the two-phase state with a transitional region of half-width $\delta \sim |\xi_2 - \xi_1|\sqrt{\kappa/\Delta\varphi(\xi^*,T_0)}$, where

$$\Delta\varphi(\xi,T) = \varphi(\xi,T) - \varphi(\xi_1,T). \tag{2.27}$$

Adiabatic conditions can change stability of these states. For instance, the critical nucleus or a periodic solution can be thermodynamically stable, Eq. (2.25) if the adiabatic modulus is positive at all points of the state. Thus an equilibrium state (uniform or nonuniform) can be thermodynamically stable under adiabatic conditions and unstable under isothermal ones. Hence we can say that the adiabatic system is "more stable" than the isothermal one. This does not mean the absolute stability of these states, because they may be unstable dynamically.

III. GIBBS FREE ENERGY OF SYSTEMS UNDERGOING A FIRST-ORDER PHASE TRANSITION

To analyze the phase-transition kinetics, we shall use further the Gibbs free energy (1.2) and (2.27) in the form

$$\Delta\varphi(\xi,T) = \tfrac{1}{2}a(T)\omega^2(\xi) + f(T)v(\xi), \tag{3.1a}$$

$$v(\xi) = \frac{1}{\Omega}\int_{\xi_1}^{\xi} \omega(\tilde{\xi})\, d\tilde{\xi}, \quad \Omega = \int_{\xi_1}^{\xi_2} \omega(\tilde{\xi})\, d\tilde{\xi}, \tag{3.1b}$$

where $\omega(\xi)$ is a differentiable function which has exactly two roots ξ_1 and ξ_2 in the domain of the parameter ξ and is positive on $\xi_1 < \xi < \xi_2$. We shall call $\omega(\xi)$ the generating function for the potential (3.1). In order to describe a first-order phase transition with equilibrium temperature T_0 it is necessary to require that

$$a(T) > 0 \text{ and } f(T_0) = 0. \tag{3.1c}$$

Equilibrium states of potential (3.1) can be described by the solutions of Eq. (2.5)

$$\left(\frac{\partial\Delta\varphi}{\partial\xi}\right)_T = \omega(\xi)\left[a(T)\frac{d\omega}{d\xi} + \frac{f(T)}{\Omega}\right] = 0. \tag{3.2}$$

Thus ξ_i; $i = 1,2$ certainly are states of equilibrium at any temperature. Moreover, this system may have other states of equilibrium. They are described by the equation

$$a(T)\frac{d\omega}{d\xi} + \frac{f(T)}{\Omega} = 0. \tag{3.3}$$

According to Rolle's theorem for a function $\omega(\xi)$, there exists a ξ^* in the interval (ξ_1,ξ_2) for which $\omega'(\xi^*) = 0$. Hence, for $T = T_0$, and in the vicinity of this temperature, there is at least one solution $\xi = \xi^*(T)$ of Eq. (3.3) which describes an intermediate state of equilibrium.

In order to find conditions under which homogeneous equilibrium states of potential (3.1) are thermodynamically stable, we determine

$$\left(\frac{\partial^2\Delta\varphi}{\partial\xi^2}\right)_T = a(T)\left[\omega(\xi)\frac{d^2\omega}{d\xi^2} + \left(\frac{d\omega}{d\xi}\right)^2\right] + \frac{f(T)}{\Omega}\frac{d\omega}{d\xi}. \tag{3.4}$$

Since $\partial^2\varphi(\xi_i,T)/\partial T\,\partial\xi = 0$, the isothermal and adiabatic conditions of the TS coincide for the states ξ_i and the inequality (2.11) has the form

$$\frac{d\omega}{d\xi}\left[a(T)\frac{d\omega}{d\xi} + \frac{f(T)}{\Omega}\right] > 0. \tag{3.5}$$

The critical temperatures T_i^* (spinodal points) for potential (3.1) can be determined according to the equation

$$\xi^*(T_i^*) = \xi_i. \tag{3.6}$$

By the definition of the generating function we know that $\omega'(\xi_1) > 0$ and $\omega'(\xi_2) < 0$. Then from Eqs. (3.3), (3.5), and (3.6) we see that the inequalities

$$\frac{f(T)}{a(T)} > \frac{f(T_1^*)}{a(T_1^*)} \quad \text{for } \xi = \xi_1,$$
$$\frac{f(T)}{a(T)} < \frac{f(T_2^*)}{a(T_2^*)} \quad \text{for } \xi = \xi_2 \tag{3.7}$$

are the necessary and sufficient conditions of stability for these equilibrium states.

For the state $\xi = \xi^*(T)$ we have $\partial^2\varphi(\xi^*,T)/\partial T\,\partial\xi \neq 0$. That is why isothermal and adiabatic conditions of the TS for this state differ. From Eqs. (2.10), (2.11), (2.13), (3.3), and (3.4) it follows that

$$\omega(\xi^*)\omega''(\xi^*) > 0 \quad \text{isothermal TS,} \tag{3.8a}$$

$$\frac{\omega''(\xi^*)}{\omega(\xi^*)} > -\frac{Ta(T)}{\Omega^2 C}\left[\left(\frac{f}{a}\right)'\right]^2 \quad \text{adiabatic TS.} \tag{3.8b}$$

Potentials of the form

$$\Delta\varphi = \frac{\tilde{a}}{2}\xi^2 + \frac{\tilde{b}}{n+2}\xi^{n+2} + \frac{\tilde{c}}{2n+2}\xi^{2n+2}$$

have been commonly used.[11-13] These potentials can be put in form (3.1) if and only if $\tilde{a},\tilde{b},\tilde{c}$ are linearly dependent functions of temperature with coefficients $(1,k,k^2)$, respectively. In this case, the generating function is $\omega(\xi) = \xi(1 - \xi^n/k)$ and $a(T) = \tilde{c}k^2/(n+1)$, $f(T) = \tilde{a} - \tilde{c}k^2/(n+1)$. In our work specifically, we shall use the Gibbs free energy (3.1) with the generating function

$$\omega(\xi) = \xi(1-\xi). \tag{3.9}$$

In this case $\xi_1 = 0$, $\xi_2 = 1$, $v(\xi) = \xi^2(3 - 2\xi)$, and $\Omega = 1/6$. The function

$$\omega(\xi) = \cos(\pi\xi), \quad -1 < \xi < 1 \tag{3.10}$$

also can be used as the generating function for potential (3.1).

The latent heat of the transition from ξ_1 to ξ_2 and the difference between specific heats (2.13) of these states are, respectively,

$$L(T) \equiv -\Delta w(\xi_2,T) = Tf' - f,$$
$$\Delta w(\xi,T) = w(\xi,T) - w(\xi_1,T), \tag{3.11a}$$

$$\Delta C \equiv C_1 - C_2 = \frac{dL}{dT} = Tf'', \quad C_i \equiv C(\xi_i,T). \tag{3.11b}$$

We shall further consider exothermal transitions with $L(T_0) > 0$. Employing the simplest possible functions $a(T) = \text{const}$ and $f \sim (T - T_0)$ we obtain

$$a(T) = a_0 > 0, \quad f = L_0(T - T_0)/T_0,$$
$$L(T) = L_0, \quad \Delta C = 0. \tag{3.12}$$

Equation (3.6) has a single solution for each i in case of potential (3.1) with Eqs. (3.9) and (3.12). Each solution determines the critical temperature

$$T_1^* = T_0(1-E), \quad T_2^* = T_0(1+E), \quad E = \Omega \frac{a_0}{L_0}. \tag{3.13}$$

From (3.7) one can see that at $T > T_1^*$ the state $\xi = \xi_1$ is stable, at $T < T_2^*$ the state $\xi = \xi_2$ is stable, and at $T_1^* < T < T_2^*$ both states ξ_i are stable (isothermally and adiabatically). Moreover, because $\omega''(\xi) < 0$ for Eq. (3.9) the isothermal condition (3.8a) is true for $\xi^*(T) < \xi_1$ or $\xi^*(T) > \xi_2$. And the adiabatic condition (3.8b) is fulfilled under this constraint. Thus, the state $\xi^*(T)$ is stable at $T < T_1^*$ or $T > T_2^*$ under isothermal and adiabatic conditions. At $T_1^* < T < T_2^*$ $(\xi_1 < \xi^* < \xi_2)$, condition (3.8a) is not true and this state is not stable isothermally, but it can be thermodynamically stable under adiabatic conditions [the inequality (3.8b) is satisfied, i.e., the adiabatic modulus (2.10) is positive] if there exists the temperature for which $[(T-T_0)/ET_0]^2 + 8\Omega E/QT < 1$. Analysis shows that the latter can be true and the state $\xi^*(T)$ at this temperature is the adiabatic one, if parameters of the system satisfy the condition

$$\frac{8\Omega}{Q} < \begin{cases} \dfrac{1}{E} + \dfrac{E}{4} + \cdots, & E \to 0 \\ \dfrac{2}{3\sqrt{3}} + \cdots, & E \to \infty \end{cases}, \quad Q = \frac{L_0}{C_1 T_0}. \tag{3.14}$$

For the generating function (3.10) with Eq. (3.12), condition (3.8a) cannot be fulfilled at any temperature, the inequality (3.8b) becomes $T > 4a_0 C_1 T_0^2 L_0^2$ and is the condition for the adiabatic state existence.

The Gibbs free energy (3.1), (3.9), (3.12), and (3.13) can be written down in the more compact form of the potential with the correlated coefficients,

$$\begin{aligned} \Delta\varphi &= \frac{a_0}{2}\xi^2[h - \tfrac{2}{3}(h+2)\xi + \xi^2], \\ h(T) &= 1 + \frac{T-T_0}{ET_0}, \\ h(T_1^*) &= 0, \quad h(T_0) = 1, \quad h(T_2^*) = 2. \end{aligned} \tag{3.15}$$

The equilibrium phase diagrams of the Gibbs free energy (3.1) and (3.12) with the generating functions (3.9) and (3.10) are plotted in Fig. 1. The heavy lines stand for the equilibrium states, double solid: for the stable ones (phases). The spinodal points are always bifurcational for the potential (3.1). Under isothermal conditions in the system with the generating function (3.9) the equilibrium states ξ_i and $\xi^*(T)$ exchange stability at the spinodal point $T = T_i^*$, so that the transcritical bifurcation occurs in this point and the total number of stable states (phases) is conserved. In the system with the generating function (3.10) at the spinodal points $T = T_1^*$ or $T = T_2^*$ the appropriate stable state ξ_i transforms into an unstable one so that the subcritical bifurcation takes place and the total number of stable states (phases) diminishes by one. The inequality (2.12) is the geometric expression of the same condition as (2.10). To employ this condition, one must plot the line of constant energy (dashed lines in Fig. 1) and compare its slope with that of the equilibrium line $\xi^*(T)$ at the point of their intersection. Figures 1(a) and 1(b) correspond to the cases with the adiabatic states.

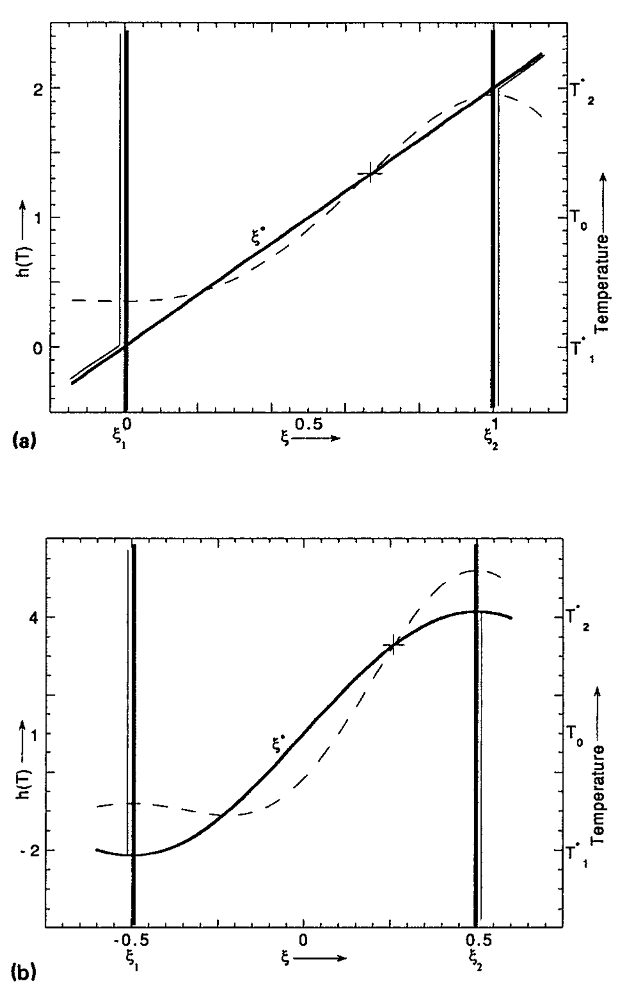

FIG. 1. The equilibrium phase diagram for the Gibbs free energy (3.1) with the generating function (3.9)—(a) and (3.10)—(b). Heavy lines: equilibrium states, double solid: stable states (phases). Dashed lines represent states with constant energy. Cross: the adiabatic state.

Cooling the system in the ξ_1 state below T_1^* may lead to a metastable mixture of coexisting domains of two different phases ξ_2 and ξ^*, where the former appears as a result of the first-order phase-transition while the latter arises from the second-order transition [Fig. 1(a)]. This may explain some of the features of the martensitic transformation behavior observed in Fe-30.1at%-Pd.[14] Strain is believed to play the role of the ordering field for this type of a transformation. X-ray and neutron scattering experiments show that below $T = 273$ K two different tetragonal phases emerge from the initial cubic parent phase which may suggest that this temperature is the spinodal point T_1^*. At $T = 265$ K the lower tetragonality phase disappears. The latter may be related to a quadratic term in the function $f(T)$, which cancels stability of the ξ^* phase.

The stable heterophase 1D distribution of the ordering field in the HTES [the solution of Eq. (2.16) with boundary conditions (2.26)] of the system with potential (3.1) is described by the formula

$$x=-\delta_0\int_{\xi^*(T_0)}^{\xi}\frac{d\xi}{\omega(\xi)},\quad \delta_0=\sqrt{\frac{\kappa}{a(T_0)}}. \tag{3.16}$$

To determine the parameters of the ITES of a medium which is described by the potential (3.1) and (3.12) with $C_1=\text{const}$, we write down the entropy s and enthalpy w per unit homogeneous volume,

$$s=s(\xi_1,T_0)+C_1\ln\frac{T}{T_0}-\frac{L_0}{T_0}\nu(\xi), \tag{3.17a}$$

$$w=w(\xi_1,T_0)+C_1(T-T_0)+\frac{a_0}{2}\omega^2(\xi)-L_0\nu(\xi). \tag{3.17b}$$

Then from Eqs. (2.20) we find the distributions of temperature and ordering fields

$$\bar{T}=\bar{T}_1\exp[Q\nu(\bar{\xi})], \tag{3.18a}$$

$$\delta_0^2\left(\frac{d\bar{\xi}}{dx}\right)^2=\omega^2(\bar{\xi})+\frac{2}{e}\left\{\frac{\exp[Q\nu(\bar{\xi})]-1}{\exp Q-1}-\nu(\bar{\xi})\right\},$$

$$e=\frac{E}{\Omega} \tag{3.18b}$$

and the temperature of the initial phase in the ITES

$$\bar{T}_1=T_0\frac{Q}{\exp Q-1}. \tag{3.18c}$$

To evaluate the TS of this state we must calculate expression (2.23)

$$-C_1\frac{Q}{\Omega}\left[\frac{Q}{\Omega}\omega^2(\xi)+\omega'(\xi)\right],$$

which, according to the definition of the generating function, is alternating in the domain $\xi_1\leqslant\xi\leqslant\xi_2$. It means that the ITES is not stable but of the saddle type.

IV. DYNAMICS OF A TRANSITION PROCESS

The evolution of a thermodynamic system in disequilibrium is accompanied by processes of the ordering field relaxation and heat redistribution. To derive the equation which governs the latter process, we determine the change in the Gibbs free energy of a nonequilibrium system at a point $\mathbf{x}$, induced by small changes in temperature T and ordering field ξ

$$d\hat{\varphi}=\hat{s}\,dT+(\delta\hat{\varphi})_T.$$

If a small increment $\delta\xi(\mathbf{x},t)$ is continuous and nonvanishing only in the vicinity of the point $\mathbf{x}$, then according to the definition of the variational derivative,[7]

$$(\delta\hat{\varphi})_T=\frac{\delta\Phi}{\delta\xi}\delta\xi, \tag{4.1}$$

with an accuracy up to small terms of higher order than $\delta\xi$. The first law of thermodynamics then can be written in the form[4]

$$T\,d\hat{s}=dq-\frac{\delta\Phi}{\delta\xi}\delta\xi. \tag{4.2}$$

Taking into account Eq. (2.3) and the identity (2.5) the heat transport equation in systems, with heat conduction: $dq=\nabla(\lambda\nabla T)dt$ is given by

$$\nabla(\lambda\nabla T)=\frac{dw}{dt}-\kappa\nabla^2\xi\frac{d\xi}{dt}, \tag{4.3}$$

where $\lambda\geqslant 0$ is the thermal conductivity. Utilizing the definition of the specific heat (2.13) it can also be written in the form[4]

$$C\frac{dT}{dt}=\nabla(\lambda\nabla T)-\left(\frac{\delta W}{\delta\xi}\right)_T\frac{d\xi}{dt},$$
$$\left(\frac{\delta W}{\delta\xi}\right)_T=\frac{\partial w}{\partial\xi}-\kappa\nabla^2\xi. \tag{4.4}$$

The ordering field variations must obey the second law of thermodynamics. Then from Eq. (4.2) one can see that

$$\frac{\delta\Phi}{\delta\xi}\delta\xi\leqslant 0. \tag{4.5}$$

The simplest equation that satisfies this inequality is the relaxation one

$$\frac{d\xi}{dt}=-\gamma\frac{\delta\Phi}{\delta\xi}, \tag{4.6}$$

where the coefficient $\gamma>0$ determines the characteristic time of relaxation. Ginzburg–Landau potential (1.1) and (1.2) transforms Eq. (4.6) into a diffusion equation with the relaxation diffusivity $d=\gamma\kappa$. Thus a nonequilibrium evolution of a nonlocal medium is described by two diffusion equations (4.4) and (4.6). To estimate the relative rate of these diffusion processes the ratio

$$R=\frac{\alpha}{d} \tag{4.7}$$

can be introduced, where $\alpha=\lambda/C$ is the heat diffusivity. The ratio (4.7) is like the Lewis number in the combustion theory or the Prandtl number in hydrodynamics.

We shall now consider, in such a system, kinetics of a 1D *stationary* transition from the initial phase (ξ_1,T_1) with T_1 below the equilibrium point T_0, to the final phase (ξ_2,T_2). It is described by the traveling-wave solutions of Eqs. (4.3) and (4.6) with the boundary conditions (2.26a) for the ordering field (topological solitary wave). Changing to the variable $u=x-Vt$, where $V\geqslant 0$ is a constant velocity of a transition, we arrive at the eigenvalue problem,

$$\frac{1}{V}\frac{d}{du}\left(\lambda\frac{dT}{du}\right)+\frac{dw}{du}-\kappa\frac{d\xi}{du}\frac{d^2\xi}{du^2}=0, \tag{4.8a}$$

$$\frac{V}{\gamma}\frac{d\xi}{du}-\frac{\partial\varphi}{\partial\xi}+\kappa\frac{d^2\xi}{du^2}=0, \tag{4.8b}$$

$$\xi(-\infty)=\xi_2,\quad \xi(+\infty)=\xi_1,\quad \frac{d\xi}{du}(\pm\infty)=0,$$

$$T(+\infty)=T_1<T_0,\quad \frac{dT}{du}(\pm\infty)=0. \tag{4.8c}$$

Equation (4.8a) admits the first integral

$$\frac{\lambda}{V}\frac{dT}{du}+w-\frac{\kappa}{2}\left(\frac{d\xi}{du}\right)^2=\text{const.} \tag{4.8d}$$

For the transition with $V\neq 0$ it expresses the law of conservation of enthalpy between phases of the system far from the transition region

$$w(\xi_1,T_1)=w(\xi_2,T_2). \tag{4.9}$$

Utilizing the definitions of the specific (2.13) and (3.11b) and latent (3.11a) heats it can also be written in the form

$$\int_{T_1}^{T_2} C_1\, dT = L(T_2), \tag{4.10}$$

which determines the connection between temperatures of initial T_1 and final T_2 phases of a medium.

For $V=0$ (the equilibrium state) from Eq. (4.8d) it follows that either $dT/du=0$, and the system is in the HTES (2.16) or $\lambda=0$ (an ideal insulator) and the system is in the ITES (2.20).

To determine the relationship between the velocity of a transition V, and temperature T_2 of a final phase, we multiply all terms of Eq. (4.8b) by $d\xi/du$ and integrate them with respect to u over the interval $(-\infty, +\infty)$. As a result, we obtain the solvability condition of the eigenvalue problem (4.8) in the form of the integral constraint

$$\Delta\varphi(\xi_2,T_2) + \frac{V}{\gamma}\int_{-\infty}^{+\infty}\left(\frac{d\xi}{du}\right)^2 du + \int_{-\infty}^{+\infty}\left(\frac{\partial\Delta\varphi}{\partial T}\right)_{\xi}\frac{dT}{du}\,du = 0. \tag{4.11}$$

In the isothermal system, the last term vanishes. To estimate it in the adiabatic system we must solve Eq. (4.8a) for dT/du. The solution with $C_1=\text{const}$, $\lambda=\text{const}$ has the form

$$C_1\frac{dT}{du} = -\frac{1}{l_T}\exp\left(-\frac{u}{l_T}\right)\int_{-\infty}^{u}\frac{dU}{d\tilde{u}}\exp\frac{\tilde{u}}{l_T}\,d\tilde{u}, \tag{4.12a}$$

where

$$U[\xi(u),T(u)] = \Delta w(\xi,T) + L(T_2) - \frac{\kappa}{2}\left(\frac{d\xi}{du}\right)^2 \tag{4.12b}$$

and $l_T = \alpha/V$ is a characteristic length of the thermal field.

The outer expansion of solution (4.12) can be obtained easily for $L(T)=\text{const}$. In this case, $U[\xi_2,T]=0$, $U[\xi_1,T]=L$, i.e., $U(u)$ varies essentially in the same domain as the ordering field does, and dU/du is a bell-like function of the width 2δ. Suppose we determine an axis u so that $dU(0)/du=0$, then for $|u| \gg l_T \gg \delta$ one can see that

$$C_1\frac{dT}{du} \approx -\frac{U(u)}{l_T}\exp\left(-\frac{u}{l_T}\right), \tag{4.13}$$

which agrees with the formula for the temperature field in front of and behind a stationary moving planar interface during a phase transition.[15]

The inner expansion of solution (4.12) can be obtained by integrating by parts. For $|u| \ll \delta \ll l_T$ it is a convergent asymptotic series with respect to velocity V

$$C_1\frac{dT}{du} \sim -\frac{U(u)}{l_T} + \frac{1}{l_T^2}\int_{-\infty}^{u} U(\tilde{u})\,d\tilde{u} + \cdots. \tag{4.14}$$

If $V \to 0$ then $T_2 \to T_0$, $\xi(u)$ is described by Eq. (2.16), and the series (4.14) for the temperature distribution in the transition region can be restricted to the first term. The analysis of constraint (4.11) in this case shows[4] that there exists a critical value κ^* such that for $\kappa > \kappa^*$ the eigenvalue problem (4.8) has a solution with $V>0$, even for $T_2 = T_0$. If we define the Peclet number

$$\text{Pe} = \frac{\delta}{l_T}, \tag{4.15}$$

we can give the definition of the critical ratio

$$R^* = \text{supp}\{R{:}\text{Pe}(T_2 = T_0,R) > 0\}. \tag{4.16}$$

in other worlds, R^* is such that for $R < R^*$ there exists a solution of the eigenvalue problem (4.8) with $\text{Pe}>0$ and $T_2 = T_0$, but for $R > R^*$ all solutions with $\text{Pe}>0$ require that $T_2 < T_0$.

In the case of a small, but finite Pe, one can obtain the asymptotic solution of the problem (4.8): the temperature gradient in the transition region is small and can be found from Eq. (4.14) conserving two terms of the series; the temperature in this region is almost constant and equal to T_2 (now $T_2 \nrightarrow T_0$); and, finally, $\xi(u)$ can be obtained from Eq. (4.8b) with $T=T_2$. Then from the solvability condition (4.11) we obtain a quadratic equation with respect to V,

$$\Delta\varphi(\xi_2,T_2) + \frac{\sigma}{\gamma\kappa}V - \frac{1}{\lambda}J_1 V + \frac{C_1}{\lambda^2}J_2 V^2 + \cdots = 0, \tag{4.17a}$$

$$\sigma = \kappa\int_{-\infty}^{+\infty}\left(\frac{d\xi}{du}\right)^2 du, \tag{4.17b}$$

$$J_1 = \int_{-\infty}^{+\infty}\frac{\partial\Delta\varphi}{\partial T}[\xi(u),T_2]\,U[\xi(u),T_2]\,du, \tag{4.17c}$$

$$J_2 = \int_{-\infty}^{+\infty}\frac{\partial\Delta\varphi}{\partial T}[\xi(u),T_2]\int_{-\infty}^{u}U[\xi(\tilde{u}),T_2]\,d\tilde{u}\,du, \tag{4.17d}$$

where σ is the surface energy (the Gibbs free energy of a transition region[4]) and J_1,J_2 are weak functions of T_2 and the type of the potential used.

Nonstationary 1D solutions of Eqs. (4.4) and (4.6) with boundary conditions (4.8c) can also be obtained in the small-Pe limit. Equation (4.14) still is the inner solution of the nonstationary problem where now $u = x - \int^t V(t)\,dt$, and Eq. (4.17) is the correct inner relation between temperature and velocity of the transition region. However, Eq. (4.13) is no more the outer solution of the problem. Instead, the outer solution of Eq. (4.4) can be obtained with the aid of the Green's function of the heat equation. Utilizing Laplace's theorem on asymptotic expansion of an integral,[15] one can get the relation between temperature of the transition region and its velocity in the form [instead of Eq. (4.10)]

$$T_2 = T_1 + \frac{L}{C}\left(1 + \alpha\frac{V'}{V^3} + \cdots\right). \tag{4.18}$$

Here prime denotes differentiation with respect to time.

To study all properties of the transition kinetics, the Gibbs free energy (3.1) has been introduced in Sec. III. The 1D *isothermal* transition from ξ_1 to ξ_2 at $T < T_0$ for this potential is described by the solution of Eq. (4.8b)

$$\frac{d\xi}{du} = -\sqrt{\frac{a(T)}{\kappa}}\,\omega(\xi), \tag{4.19}$$

which has the form of a solitary wave of the same structure as in equilibrium (3.16) with a characteristic width δ differing by $\sqrt{[a(T_0)/a(T)]}$ times the equilibrium value. [Note that for the potential (3.1) δ is independent of $f(T)$]. From Eq. (4.11) one can see that the velocity of motion of such a wave is unique and equal to $V = -(\gamma\delta/\Omega)f(T)$. If $f(T)$ is linear in temperature (3.12), the latter yields

$$V=\mu(T_0 - T), \quad \mu=\gamma\kappa L_0/\sigma T_0, \quad \sigma=\Omega\sqrt{(\kappa a_0)}. \tag{4.20}$$

Here μ is called a kinetic coefficient.

In the *adiabatic* case, the velocity of the 1D stationary transition obeys Eq. (4.17), which, for the generator (3.9), takes the form,

$$\theta=(rR - j_1)\,\mathrm{Pe} + j_2\,\mathrm{Pe}^2, \quad r=\frac{E}{Q}, \tag{4.21a}$$

$$j_1 = \frac{T_0}{L_0^2\delta}J_1 = \int_0^1 \frac{\nu(\xi)[1-\nu(\xi)]}{\omega(\xi)}\,d\xi = \frac{19}{30}\approx 0.633, \tag{4.21b}$$

$$j_2 = \frac{T_0}{L_0^2\delta^2}J_2 = \int_0^1 \frac{\nu(\xi)}{\omega(\xi)}\int_\xi^1 \frac{1-\nu(\tilde\xi)}{\omega(\tilde\xi)}\,d\tilde\xi\,d\xi = \frac{\pi^2}{6} - 1 \approx 0.645, \tag{4.21c}$$

$$\theta=\frac{C_1(T_0 - T_1)}{L_0} - 1, \tag{4.21d}$$

where θ is the reduced temperature of the initial phase. Positive θ is the measure of a hypercooling of the initial phase, while negative θ corresponds to the superheating of the final one (4.10).

For $R\to\infty$ (e.g., $\gamma\to 0$), Eq. (4.21a) becomes $\mathrm{Pe}=\theta/rR$ which is equivalent to Eq. (4.20) with $T = T_2$, i.e., positive solutions are possible only for $\theta > 0$. For finite $R \geqslant j_1/r$ positive solutions of Eq. (4.17a) exist also for $\theta > 0$ only. But for $R < j_1/r$ positive solutions of Eq. (4.21a) are possible for $\theta_l < \theta < 0$, where

$$\theta_l \equiv \inf\{\theta : \mathrm{Pe}(\theta,R) > 0\} \tag{4.22}$$

is the limiting value of the parameter θ. Then the critical value of R (4.16) is

$$R^* = \frac{j_1}{r}. \tag{4.23}$$

For the limiting value of θ (4.22) from Eq. (4.21a) (the small-Pe limit) one can obtain, i.e.,

$$\theta_l = \begin{cases} -\dfrac{(rR - j_1)^2}{4j_2}, & \text{for } R < R^* \\ 0, & \text{for } R \geqslant R^* \end{cases}. \tag{4.24}$$

Excluding R from Eqs. (4.21a) and (4.24) results in

$$\theta_l = -j_2\,\mathrm{Pe}^2. \tag{4.25}$$

As $R \geqslant 0$, Eq. (4.24) yields the "maximum possible" superheating of the final phase

$$\tilde\theta_l = -\frac{j_1^2}{4j_2} \approx -0.1553. \tag{4.26}$$

In fact, the last estimate is not exact because Eq. (4.21a) has been obtained in the small-Pe limit. The exact value of the maximum possible superheating comes from the temperature of the final phase in the ITES (3.20c)

$$\bar\theta = -\frac{\exp Q}{\exp Q - 1} + \frac{1}{Q}. \tag{4.27}$$

Thus if the initial phase of the system with $R < R^*$ has the temperature in the domain $T_0 - L_0/C_1 < T_1 < T_0 - L_0(\theta_l + 1)/C_1$, then it will be replaced by a new one with the temperature $T_2 = T_1 + L_0/C_1 > T_0$. Herewith T_1 cannot exceed T_0 because $-1 < \bar\theta < -1/2$ for $Q > 0$. Utilizing the isothermal terminology (which should be applied to the adiabatic case with great caution) one can say that the heat, released at the transition from the metastable (supercooled) initial phase, appears to be engulfed by the growing phase, which is metastable (superheated) also. This effect can be called *heat trapping*.

In the 1D nonstationary adiabatic case, matching the inner (4.17) and outer (4.18) solutions we obtain the equation

$$\frac{\delta^2}{\alpha}\frac{\mathrm{Pe}'}{\mathrm{Pe}^3} + (rR - j_1)\,\mathrm{Pe} + j_2\,\mathrm{Pe}^2 = \theta, \tag{4.28}$$

which has stationary solutions (4.21a) and also time-decaying solutions of the Stefan type

$$\mathrm{Pe}\sim\frac{\delta}{\sqrt{-2\alpha\theta t}}, \quad \theta<0. \tag{4.29}$$

The 1D stability analysis of Eq. (4.28) shows that Stefan's solutions (4.29) are always stable (uniformly). However, out of two roots of the Eq. (4.21a) with $\theta_l < \theta < 0$ only the largest corresponds to the stable stationary solution. It means that the limiting values θ_l (4.22) constitute the stability boundary (instability inside the boundary) for the solutions of the eigenvalue problem (4.8)

Thus velocity of a transition must obey the condition of uniform or kinetic stability

$$\frac{dV}{dT_1} < 0, \tag{4.30}$$

which is physically obvious because otherwise velocity would decrease if we cool the system down. The solvability condition (4.11) together with (4.30), constitute the selection criterion for our problem.

Summarizing results in terms of the bifurcation theory, one can say that $\theta = 0$ is always the bifurcation point of the eigenvalue problem (4.8), but its type changes with the value of the parameter R: above the critical point ($R > R^*$) a bifurcation is stable transcritical, at the critical point ($R = R^*$) it is supercritical of codimension two, and below ($R < R^*$) it is unstable transcritical with the stable branch of a finite amplitude.

The classical analysis of the interface with an infinitesimal thickness corresponds to the limit $\kappa\to 0$ for the constant surface energy σ and relaxation diffusivity d (i.e., $a_0\to\infty$ and $\gamma\to\infty$). In this limit, $\delta\to 0$ and Eq. (4.17) becomes equivalent to Eq. (4.20) with $T = T_2$. It means that the classical limit of the adiabatic problem corresponds to the quasiisothermal boundary condition. The essentially nonisothermal boundary condition (4.17) can be utilized in the free-boundary problem if T_2 is substituted by a temperature of the boundary. The outer solution (4.13) at $u=0$ may serve as the second boundary condition. In Sec. VI they will also be used to discuss the morphological stability of 1D stationary solutions of the original problem (4.4) and (4.6).

To describe the kinetics of phase transitions in the vicinity of the ITES it is more convenient to use Eq. (4.2) instead of Eq. (4.3). In the stationary 1D case for a medium with constant $\gamma,\kappa,\lambda,C_1,L$ this equation has the form

$$VT\frac{ds}{du}+\lambda\frac{d^2T}{du^2}+\frac{V^2}{\gamma}\left(\frac{d\xi}{du}\right)^2=0.$$

If we integrate this equation over $(-\infty,+\infty)$ taking into account Eq. (4.8d) and evaluating the enthalpy in the ITES we obtain the following relation for V:

$$\int_{\xi_1}^{\xi_2}T\,ds+\frac{2\lambda L}{\gamma\kappa C_1}=\frac{V}{\gamma}\sqrt{\frac{2}{\kappa}}\int_{\xi_1}^{\xi_2}\sqrt{w(\bar{\xi},\bar{T})-w(\bar{\xi}_1,\bar{T}_1)}\,d\xi. \quad (4.31)$$

V. QUALITATIVE AND NUMERICAL ANALYSIS OF PHASE TRANSITION KINETICS

To study different regimes of the transition kinetics, we shall analyze solutions of the eigenvalue problem (4.8) with the potential (3.1), (3.9), and (3.12) and no restrictions on the value of the Peclet number (4.15). If we introduce dimensionless variables

$$\tau=u/\delta_0,\quad q=1-\xi,\quad p=-\delta_0\frac{d\xi}{du},$$
$$g=C_1(T_2-T)/L_0, \quad (5.1)$$

Eqs. (4.8b) and (4.8d) assume the form of a set of three first-order ordinary differential equations,

$$\frac{dq}{d\tau}=p, \quad (5.2a)$$
$$\frac{dp}{d\tau}=\omega(q)\left(1-2q+\frac{\theta+g}{r}\right)-2vp, \quad (5.2b)$$
$$\frac{dg}{d\tau}=\mathrm{Pe}\left[\nu(q)+\frac{e}{2}(\omega^2-p^2)-g\right]. \quad (5.2c)$$

Further parameters will obey the restrictions,

$$e<1/\Omega, \quad (5.3a)$$
$$r>1/2, \quad (5.3b)$$
$$-r<\theta<r-1, \quad (5.3c)$$
$$r>1/8\Omega+e/12\sqrt{3}, \quad (5.3d)$$

where the first denotes that $T_1^*>0$, the second-that $T_2^*-T_1^*>L_0/C_1$, the third-that $T_1^*<T_1$ and $T_2<T_2^*$, and the fourth, which is opposite to condition (3.14), guarantees absence of the adiabatic states.

The set (5.2) can be considered a dynamical system, describing a motion of a nonlinear damped oscillator of the unit mass with the Hamiltonian

$$H=\tfrac{1}{2}p^2+\Pi(q,g),\quad \Pi=-\tfrac{1}{2}\omega^2(q)-\frac{\theta+g}{r}\nu(q), \quad (5.4a)$$

where the double-hump potential $\Pi(q,g)$ is not bounded from below and parametrically depends upon "dynamical time τ" which is opposite to the "physical time t" of the evolution of a thermodynamic system. For the variation of the Hamiltonian we have

$$\frac{dH}{d\tau}=-2vp^2+\frac{\partial\Pi}{\partial g}\frac{dg}{d\tau}, \quad (5.4b)$$
$$\frac{1}{\mathrm{Pe}}\frac{dg}{d\tau}+g+e\left[H+\left(\frac{1}{Q}-\theta-g\right)\frac{\partial\Pi}{\partial g}\right]=0. \quad (5.4c)$$

This shows that the energy of physically interesting solutions ($0\leqslant q\leqslant 1, dg/d\tau\geqslant 0$) dissipates in time, if the damping coefficient

$$v\equiv\tfrac{1}{2}R\,\mathrm{Pe}, \quad (5.5)$$

which is the dimensionless velocity of the transition, is positive.

The set (5.2) can be studied by methods of the qualitative theory of dynamical systems. Singular points $\{q,p,g\}$ of this system satisfy the conditions,

$$p=0, \quad (5.6a)$$
$$-\Pi_q=\omega(q)[1-2q+(\theta+g)/r]=0, \quad (5.6b)$$
$$g=\nu(q)+e\omega^2(q)/2, \quad (5.6c)$$

where (5.6b) is the equation of equilibrium states (2.5) and (5.6c) is the equation of the states with equal enthalpy (3.17b). Except for initial $\{1,0,1\}$ and final $\{0,0,0\}$ phases, these conditions are satisfied by the intermediate state $(q^*,0,g^*)$, which has $0<q^*<1$, $0<g^*<1$, if θ,E,Q satisfy (5.3).

To analyze the stability of singular points we find the Jacobian matrix of the set (5.2)

$$D=\frac{\partial(\dot{q},\dot{p},\dot{g})}{\partial(q,p,g)}.$$

The Routh–Hurwitz criterion of stability of singular points (5.6) has the form of the three inequalities,

$$SpD=-\mathrm{Pe}(1+R)<0, \quad (5.7a)$$
$$\det D=e\,\mathrm{Pe}(Q^{-1}-\theta-g)\Pi_{qg}^2-\mathrm{Pe}\,\Pi_{qq}<0, \quad (5.7b)$$
$$\mathrm{Pe}^2R(1+R)+\mathrm{Pe}\,R\Pi_{qq}+e\,\mathrm{Pe}(Q^{-1}-\theta-g)\Pi_{qg}^2>0. \quad (5.7c)$$

The first condition (5.7a) is satisfied not only for singular points, but everywhere in the phase space, $\{q,p,g\}$, which means that the dynamical system (5.2) is a dissipative one. The second condition (5.7b) is opposite to the condition of stability of the equilibrium states in the adiabatic system (2.10). It is not true for initial and final phases but is true for the intermediate state, unless it is an adiabatic one. Below we shall study thermodynamical systems without adiabatic states, which is the case if Eq. (5.3d) is satisfied. The third condition (5.7c) is achieved for the intermediate state as $\Pi_{qq}(q^*,g^*)>0$. Thus the singular point $(q^*,0,g^*)$ is a stable spiral point and $(q_i,0,g_i)$ are unstable points of the saddle type.

We shall now examine the phase space of the dynamical system (5.2) with parameters θ,E,Q that satisfy conditions (5.3). Because of the energy dissipation by the oscillator, the dynamical system does not execute periodic motions. Depending upon the parameter values and initial conditions, a trajectory $\{q(\tau),p(\tau),g(\tau)\}$ may escape to infinity or approach the attractor $\{q^*,0,g^*\}$. The solution of the eigenvalue problem (4.8) now may be considered a trajectory $\{q(\tau),p(\tau),g(\tau)\}$ from the saddle point $\{0,0,0\}$ (final phase) to the saddle point $\{1,0,1\}$ (initial phase)—a heteroclinic trajectory. As is known from the qualitative theory of dynamical systems in a plane,[16-18] structurally stable or "coarse" dynamical systems cannot have such trajectories. A heteroclinic trajectory can appear only through the structural bifurcation and the parameters, which give us the desired trajectory, constitute the bifurcation set $\mathrm{Bi} = [\theta,E,Q,R,v]$. Notice, that the original problem (4.8) has seven internal parameters $(L_0,T_0,C_1,a_0,\kappa,\lambda,\gamma)$, one input—$T_1$, and two output parameters T_2 and V, while the nondimensional system (5.2) has only three internal (E,Q,R), one input—θ, and one output parameter v or Pe.

For quantitative determination of parameters from the Bi set, numerical calculations of trajectories (5.2) were carried out by the standard Runge–Kutta method of the fourth order. Because numerical calculations cannot be done at the point $\{0,0,0\}$ they were started, instead, at the point $\{\tilde q,\tilde p,\tilde g\}$ at instant $\tau = 0$. Linearizing the system (5.2) we can obtain that

$$\tilde p = A\tilde q, \quad A = \sqrt{1+\theta/r+v^2} - v,$$

$$\tilde g = B\tilde q^2, \quad B = \mathrm{Pe}\,\frac{6+e(1-A^2)}{2(\mathrm{Pe}+2A)}.$$

The value $\tilde q = 0.01$ was chosen for the calculations.

The Bi-set search was carried out for fixed values of $E,Q,R,$Pe by varying the parameter θ until the behavior of the separatrix from the saddle $\{0,0,0\}$ changed qualitatively: for increasing time τ it either entered the basin of the attractor $\{q^*,0,g^*\}$ or left the domain $0<q<1, 0<g<1$ (Fig. 2). The domain (θ_1,θ_2) with boundaries corresponding to different qualitative behavior of the separatrix was iterated several times by the bisectional method in order to obtain a more accurate value of the parameter θ from the Bi set. The dynamical system with $E = 0.5$, $Q = 0.25$, and different values of R has been studied and the results are discussed below.

Projections of the Bi set to the plane (Pe,θ) for Pe$\leqslant$0.1 are represented in Fig. 3. Solid lines correspond to Eq. (4.21a). Deviation of numerical results from analytical ones along the θ axis did not exceed 0.004. For $R \geqslant 0.317$ we always got $\theta > 0$ for all positive values of Pe, while for $R < 0.317$ negative values of θ are permitted, which means that the superheated final phase appears. For $R = 0.317$ the plot Pe(θ) has the square-root singularity near $\theta = 0$, that is well described by Eq. (4.21a).

To determine the critical value of R^* more accurately, the Bi-set parameter search was carried out for fixed values of $E,Q,\theta,$Pe, and varying of R. Projections of the Bi set on the (Pe,R) plane for θ close and equal to zero are shown in Fig. 4. The critical number R^* is the intersection of the curve Pe($\theta = 0,R$) with the abscissa and is close to the analytical result 0.3165··· which was obtained from Eq. (4.23).

The family of curves Pe vs hypercooling θ for different values of R without restrictions on Pe is shown in Fig. 5. Kinetically unstable branches of Pe(θ,R) curves, i.e., those which do not satisfy condition (4.30), are depicted by dashed lines

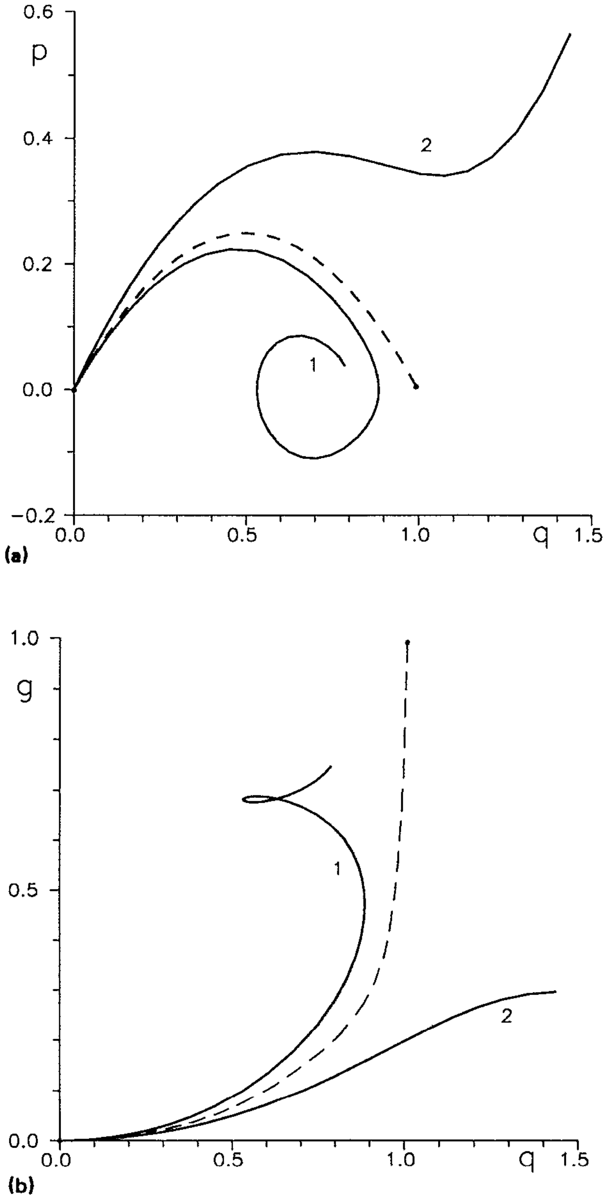

FIG. 2. Projections of the phase portrait of the dynamical system (5.2) with $E = 0.5$, $Q = 0.25$, $R = 0.5$ on planes (p,q)—(a) and (g,q)—(b). 1: convergent integral trajectories, $\theta = \theta_1$; 2: divergent integral trajectories, $\theta = \theta_2$. Dashed line: heteroclinic trajectory.

In Fig. 6 the family of curves is represented in the plane (v,θ). For $R \geqslant 10$ the velocity v almost completely ceases to depend upon R and approximates the limit $v = \theta/2r$ [compare with Eq. (4.21a)]. For $R = 0.317$ the function $v(\theta)$ has the square-root singularity near $\theta = 0$ as the function Pe(θ) does, and for $R < 0.317$ the values $\theta < 0$ are allowed. This picture corresponds to the bifurcational analysis of Eq. (4.21a). The heavy line in Fig. 6 is the kinetic stability boundary θ_l (instability inside). The dashed line is the analytical expression (small-Pe limit) of the kinetic stability

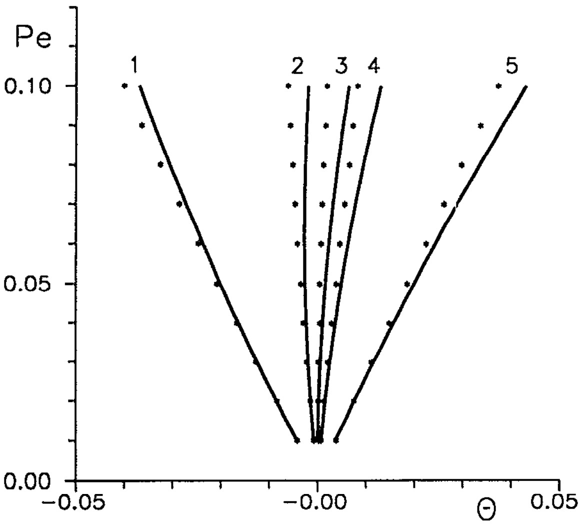

FIG. 3. Plots of the Peclet number Pe vs hypercooling θ for small Pe and different ratio R: 0.1(1); 0.275(2); 0.317(3); 0.35(4); 0.5(5). Solid lines—analytical curves.

boundary in the plane (v,θ) that comes out of Eqs. (4.21a), (4.24), (4.25), and (5.5).

$$v=\frac{1}{r}\sqrt{-\theta}\,(\sqrt{-\tilde{\theta}_l}-\sqrt{-\theta}\,), \tag{5.8}$$

and for small θ is close to the real stability boundary θ_l. The intersection of the heavy line with the abscissa would give the minimum value of θ which corresponds to the ITES $(R=0,v=0)$. This value is close to the analytical result $\bar{\theta}=-0.5211\cdots$ obtained from Eq. (4.27) but differs strongly from $\tilde{\theta}_l=-0.1553$ [see Eq. (4.26)]. This is quite natural as the small-Pe approximation is not legitimate for the ITES.

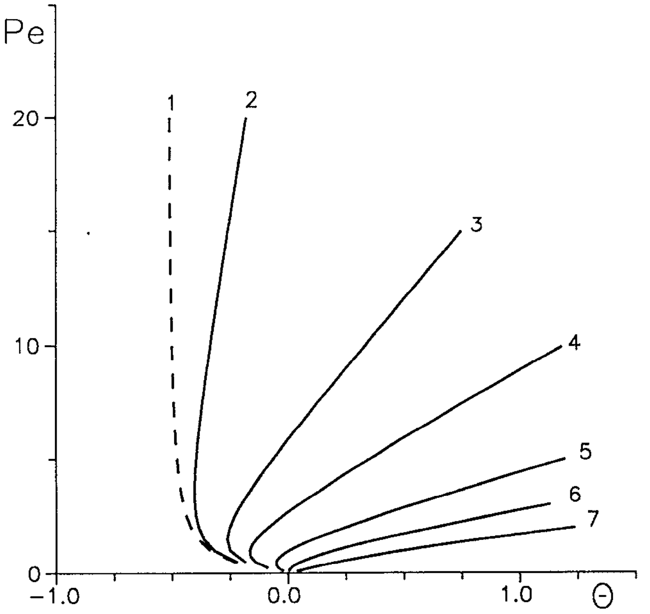

FIG. 5. Plots of the Peclet number Pe vs hypercooling θ for different ratio R: 10^{-5}(1); 10^{-2}(2); 0.05(3); 0.1(4); 0.2(5); 0.317(6); 0.5(7). Dashed regions represent kinetically unstable solutions.

The ITES cannot be achieved by the present numerical method but can be approached by decreasing R. The projections of the integral trajectory of our dynamical system on planes (p,q) and (g,q) for small values of R and v $(R=10^{-3}, v=6.25\times10^{-3}, \theta=-0.483)$ which are quite close to the ITES (3.18) (solid curves) are shown in Fig. 7: $g(q)$ decreases significantly, but $p(q)$ differs little from the equilibrium distribution. Thus despite the thermodynamic instability, the ITES is a very important dynamic characteristic of the system with low heat conductivity.

Distributions $q(\tau)$ and $g(\tau)$ for the same parameter values are shown in Fig. 8. One can see that temperature and

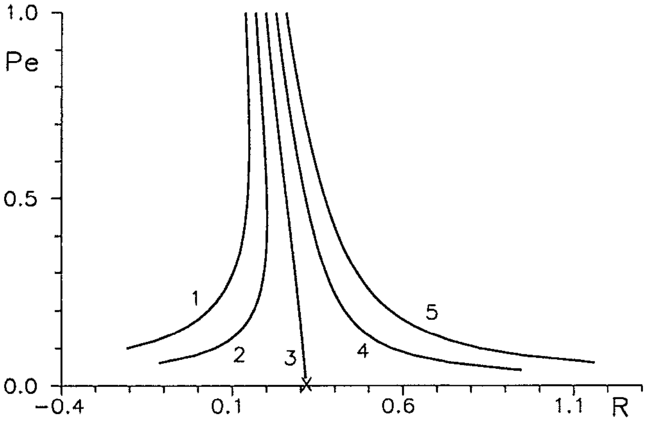

FIG. 4. Plots of the Peclet number Pe vs the ratio R for different hypercoolings θ: −0.1(1); −0.05(2); 0(3); 0.05(4); 0.1(5). X—the analytical value of the critical number R^*.

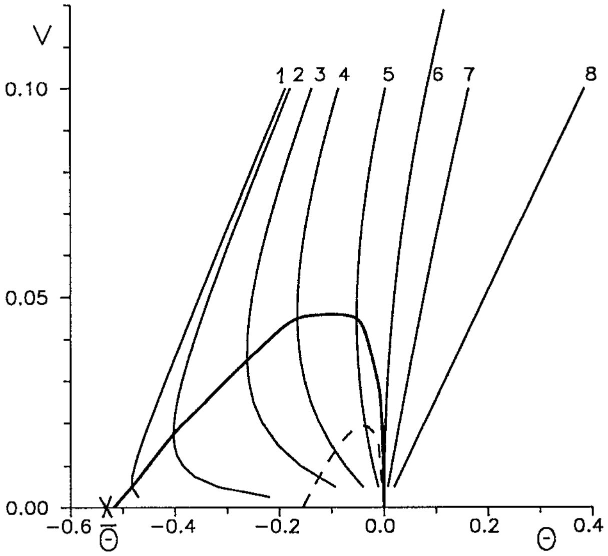

FIG. 6. Plots of the velocity v vs hypercooling θ for different ratio R: 10^{-3}(1); 10^{-2}(2); 0.05(3); 0.1(4); 0.2(5); 0.317(6); 0.5(7); 10(8). The heavy line represents the kinetic stability boundary, the dashed line—the analytic expression (5.8). X—denotes $\bar{\theta}$ (4.27).

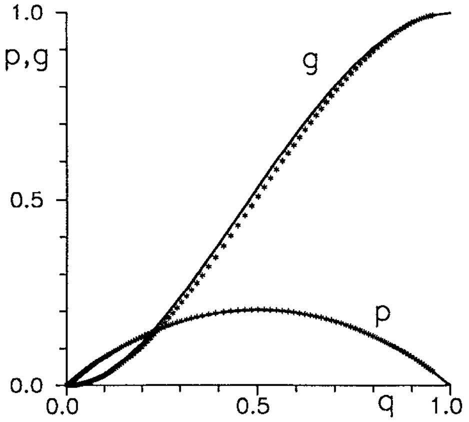

FIG. 7. The phase portrait of the dynamical system (5.2) with $R = 10^{-3}$, $v = 6.25\times 10^{-3}$ ($\theta = -0.483$). Solid lines represent the ITES (3.18).

ordering fields have the same length scale and that the ITES is not only a structural kink but a thermal kink as well. Thus near the ITES temperature might appear as a possible substitute for an ordering field.

To characterize temperature and ordering field distributions in space we introduce thermal (l_g) and structural (l_q) characteristic lengths of a transition region

$$l_g = \left[\max \frac{dg(\tau)}{d\tau}\right]^{-1}, \quad l_q = \left[\max \frac{dq(\tau)}{d\tau}\right]^{-1}.$$

The characteristic lengths as functions of dimensionless velocity of a process v for $R = 0.5$ are shown in Fig. 9 together with the inverse Peclet number. For small velocities $l_q \ll l_g \approx \mathrm{Pe}^{-1}$. With an increase in speed the structural length increases slightly, the thermal length decreases strongly, approaching the former value and for $v \to \infty$: $\mathrm{Pe}^{-1} \ll l_g < l_q$. Thus with a process rate increase, which may be caused by the change of external conditions, the transient region structure does not vary essentially, but the thermal distribution reduces drastically so that for high velocities a regular estimate of the thermal length as a ratio of the thermal diffusivity to the velocity of a process is no longer valid. A similar situation takes place also for values $R < R^*$. The latter follows also from the expansion of the analytic solution (4.12) in case of $\mathrm{Pe} \gg 1$ where $T \approx T_2 - U(u)/C_1$.

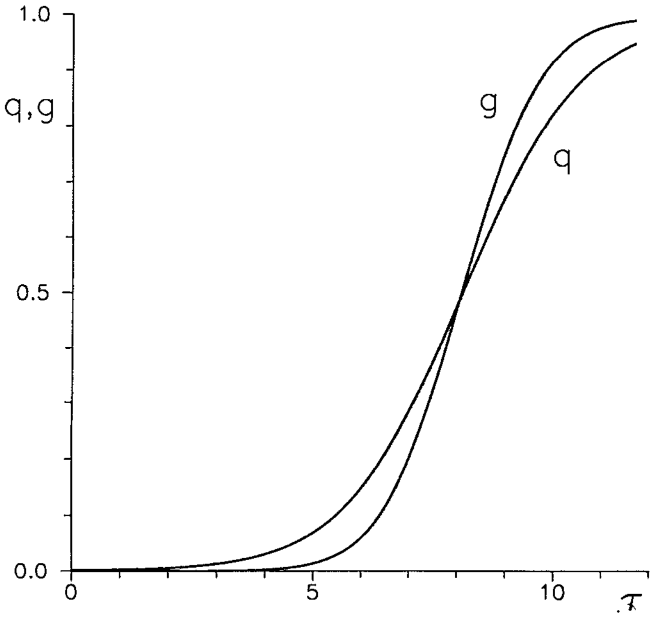

FIG. 8. Distributions of the dimensionless ordering $q(\tau)$ and temperature $g(\tau)$ fields for $R = 10^{-3}$, $v = 6.25\times 10^{-3}$.

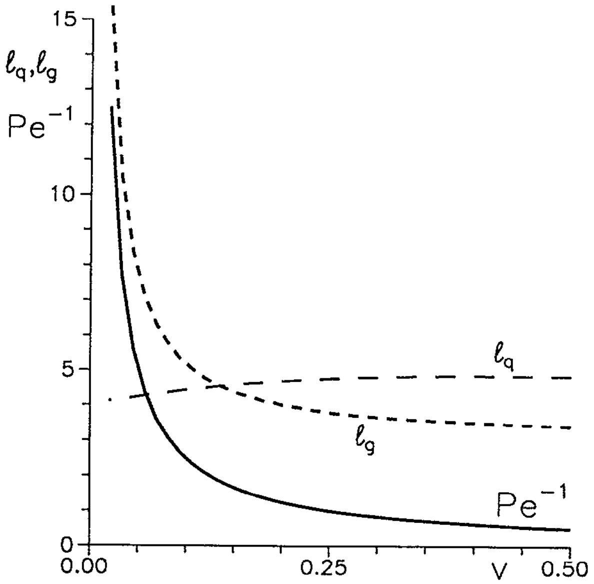

FIG. 9. Plots of the characteristic thermal l_g and structural l_q lengths and the inverse Peclet number vs velocity v of the process.

VI. DISCUSSION

We have considered phase states and the first-order phase transition kinetics under adiabatic conditions for different system parameters and found the features that distinguish such systems from isothermal ones.

(1) Homogeneous and inhomogeneous states of equilibrium which are thermodynamically unstable under isothermal conditions can be stable under adiabatic conditions. For instance, the critical nucleus or a periodic solution can be adiabatically stable, at least with respect to small static perturbations.

(2) A new type of nonuniform state of equilibrium may exist which is inhomogeneous in temperature as well as in the ordering field. This is an unstable state of the saddle type but a dynamical trajectory of a transition from one phase to the other in the system with low heat conductivity may pass very close to it.

(3) An exothermal transition with the temperature of the final phase higher than the equilibrium transition point (metastable phase) is possible in adiabatic systems with a small ratio of the thermal diffusivity to the relaxation one. This criterion is independent of the velocity of a transition and qualitatively independent of the type of potential used.

In this paper, various equilibrium states have been analyzed for thermodynamic stability. Kinetics of phase transitions must be analyzed for stability as well. In the small-Pe limit the stability analysis can be carried out in the framework of a free-boundary problem where one must solve the heat equation (4.4) in the bulk with boundary conditions at the front, which determine the temperature and its normal gradient. Taking into consideration the effect of dissipation or creation of surface[4] equations (4.13) and (4.17) for the nonisothermal interface yield the conditions (in the 2D one-sided model)

$$T_f = T_0 - T_0 \frac{\sigma}{L} K - \mu V_n + \frac{L}{C_l}\left(j_1 \frac{\delta}{\alpha} V_n - j_2 \frac{\delta^2}{\alpha^2} V_n^2\right), \tag{6.1a}$$

$$\lambda \frac{\partial T}{\partial n_f} = - V_n (L - \sigma K), \tag{6.1b}$$

where V_n is the normal to the front component of the growth velocity and K is the local curvature. The classical solutions of our problem are absolutely stable for deep supercoolings $\theta \geqslant R/(1-Q)$. Herewith the temperature of the final phase is much less than the equilibrium point. The geometrical approach developed by Umantsev and Davis[19] may help to analyze the morphological stability of the 1D nonclassical transitions. To do this one ought to represent V_n in the form of the first approximation to the basic state velocity V (4.21a)

$$V_n = V + MK + \cdots, \tag{6.2}$$

where the number M depends upon parameters of the basic state. This representation shows that all perturbations of a plane front grow if $M > 0$ and decay if $M < 0$. It turns out that

$$M = \alpha \frac{1 - r\,\mathrm{Pe}(1-Q)}{(rR - j_1)\,\mathrm{Pe} + 2 j_2\,\mathrm{Pe}^2}, \tag{6.3}$$

where Pe is the solution of Eq. (4.21a). Analysis of formulas (4.21a), (4.30), and (6.3) shows that kinetically stable solutions are morphologically unstable and vice versa. However, this corollary does not exclude the possibility of the formation of the metastable phase. A 2D computer simulation of the free-boundary problem with the boundary conditions (6.1) yields the formation of superheated final phase (heat trapping). The above described mechanism of metastable phase formation may be relevant to the solute trapping effect which can be reached more easily than the heat trapping because the solute diffusivity is much less than the thermal one.

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