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# Thermal Effects of Interfacial Dynamics

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### **Thermal Effects of Interfacial Dynamics**

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**Abstract.** Dynamical Ginzburg-Landau theory is applied to the study of thermal effects of motion of interfaces that appear after different phase transitions. These effects stem from the existence of the surface internal energy, entropy and temperature gradients in the interfacial transition region. Evolution equations for the interfacial motion are derived. For the experimental verification of the thermal effects the expression is derived for the amplitude of temperature waves during continuous ordering.

**Keywords:** dynamics of interfaces, APB motion, thermal effects

#### **1. Introduction**

An interface is an important paradigm in science that helps understand many, seemingly unrelated, physical situations. Commonly interfaces appear whenever a system undergoes some kind of a phase transition, which may be encountered in condensed matter, soft matter (biology) and even cosmology. Interfaces comprise layers of rapid variations of material's properties. They constitute structural defects and, because of the global disequilibrium of a defective system, a network of interfaces exhibits structural coarsening or time evolution of the interface density.

Three distinctly different types of boundaries may be identified in the above described examples: homophase boundaries, which separate two bulk pieces of the same phase and same composition, e.g. grain boundaries, Bloch domain walls, antiphase and Higgs field boundaries; isomorphous boundaries between phases of the same crystalline structure but significantly different composition, e.g. polymeric interfaces, they occur commonly via spinodal decomposition; and heterophase boundaries, which appear as a result of different first-order (discontinuous) phase transformations in materials and separate phases of different crystalline symmetry. A first-order phase transition is manifested by a finite discontinuity in the first derivatives of the appropriate thermodynamic potential. Unlike the first-order, continuous transitions correspond to singularities in the second derivative. This type of transitions is generally characterized by a loss of orientational or translational symmetry elements when different structural variants are possible in a transformed material, for example, order-disorder and magnetic transitions.

Arguably, the most convenient way of addressing such problem is the paradigm of the Landau theory of phase transitions [1] where one assumes that the Gibbs free energy in addition to temperature, pressure and composition is a continuous function of the long-range order parameter. This paradigm will be used here to study different thermal effects of motion of interfaces. In order to study thermal effects, naturally, we need a heat equation compatible with the dynamics of phase transitions that take place in the system. Such equation was derived in Ref. [2].

All cases of interfaces presented in this paper will be treated here on the common grounds of the dynamical Ginzburg-Landau theory where different transitions correspond to different order parameters in the free energy functional. In the present paper, however, we will not be concerned with specific model systems or types of transitions. Rather, we will concentrate on the general features of interfacial dynamics and thermal effects that may manifest in completely unrelated situations. A detailed treatment of the described problem will be published elsewhere [3].

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#### **2. Dynamics of Interface**

#### *2.1. Dynamical Ginzburg-Landau Theory of Phase Transitions*

In the framework of the Landau theory of phase transitions different states of a thermodynamic system, in addition to temperature *T* and pressure *P*, are characterized by a set of internal parameters  $\{\eta_i\}$  associated with the symmetry changes, which are usually called the order parameters (OP). The concept of an order parameter helps define a phase as a locally stable state of matter homogeneous in the order parameter. Different transitions may be laid out into the same framework if proper physical interpretations of order parameters are found. We restrict the present paper to the case of a scalar OP  $\eta$ . As a continuous function of its variables the Gibbs free energy density  $g(T, P, \eta)$  can be expanded in powers of the OP where only terms compatible with the symmetry of the system are included [1]:

$$
g(T, P, \eta) = g(T, P, 0) + \frac{1}{2}a(T, P)\eta^{2} + \frac{1}{3}b(T, P)\eta^{3} + \frac{1}{4}c(T, P)\eta^{4}
$$
 (1)

Commonly, the coefficients *a*, *b*, *c* are taken in the Landau form where the first one is linearly proportional to temperature,  $a(T) = a_0(T - T_c)$ , and *b*, *c* are temperature independent.

Coexistence of two phases at equilibrium entails a transition region between them, called an *interface*. The presence of interfaces makes the system essentially inhomogeneous even at equilibrium that is, there appear gradients of OP. There is a certain penalty on the inhomogeneous system in the form of the "gradient energy" contribution into the free energy, which is represented here in the standard Ginzburg-Landau-Cahn-Hilliard form [4, 5]. Since an interface comprises the spatial variation of the OP, the Gibbs free energy of the entire system should be written in the functional form:

$$
G = \int \left( g(T, P, \eta) + \frac{1}{2} \kappa (\nabla \eta)^2 \right) d^3 x \qquad (2)
$$

Being away from equilibrium the thermodynamic system relaxes back to an equilibrium state and an evolution equation for the OP takes the form of the time-dependent Ginzburg-Landau equation (TDGLE)

$$
\frac{d\eta}{dt} = -\gamma \left(\frac{\delta G}{\delta \eta}\right)_{T,P} \tag{3}
$$

Motion of an interface is accompanied by energy redistribution and heat propagation in the system. A thermodynamically rigorous general heat equation (GHE) was derived in Ref. [2]:

$$
C\frac{dT}{dt} = \nabla(\lambda \nabla T) + Q(\mathbf{x}, t)
$$
  
\n
$$
Q(\mathbf{x}, t) = -\left(\frac{\delta E}{\delta \eta}\right)_{V,T} \frac{d\eta}{dt}
$$
  
\n
$$
= -\left[\left(\frac{\partial e}{\partial \eta}\right)_{V,T} - \kappa_E \nabla^2 \eta\right] \frac{d\eta}{dt} \qquad (4)
$$
  
\n
$$
\kappa_E = \kappa - T \frac{d\kappa}{dT}
$$

Here  $Q(\mathbf{x}, t)$  is the density of instantaneous heat sources and  $\lambda$  is the thermal conductivity. The system of coupling TDGLE (3) and GHE (4) describes creation and subsequent evolution of an interface in a medium. Both equations, are of diffusion type and are characterized by diffusivities, the thermal diffusivity  $\alpha = \lambda/C$ for the latter and the ordering diffusivity  $m = \gamma \kappa$  for the former. The ratio of these diffusivities  $R$  is an important parameter, which determines different regimes of interfacial dynamics:

$$
R \equiv \frac{\alpha}{m}
$$

#### *2.2. Interfaces at Equilibrium*

At equilibrium the internal parameters relax to specific values which are functions of temperature and pressure,  $\eta^E = \Xi(T, P)$ , and can be found by minimization of the Gibbs free energy (1). The latter takes the form of the Euler-Lagrange equation:

$$
\frac{\delta G}{\delta \eta} \equiv \frac{\partial g}{\partial \eta} - \kappa \nabla^2 \eta = 0 \tag{5}
$$

Equation (5) is known to have many different solutions with different symmetries. However, only onedimensional translationary invariant solutions, which represent flat interfaces, possess thermodynamic stability at constant temperature and pressure.

As known [6, 7], all properties of an interface at equilibrium are completely determined by just one intensive quantity, the surface tension or *surface energy* σ. The equilibrium surface tension in a one-component medium is the excess Gibbs free energy of the system with an interface, per unit area of the interface, compared to that of the homogeneous bulk ordered or disordered phase occupying the same volume. Then, utilizing Eqs. (2) and (5), one can obtain an expression for the surface energy [5, 8]:

$$
\sigma = \int_{-\infty}^{+\infty} \kappa \left(\frac{d\eta}{du}\right)^2 du \tag{6}
$$

To characterize an interfacial thickness we adopt the definition introduced in [5]:

$$
l_I \equiv \frac{[\eta]}{\max|\nabla \eta|} \approx \frac{\kappa[\eta]^2}{\sigma}; \quad [\varphi] \equiv \varphi|_{x = +\infty} - \varphi|_{x = -\infty}
$$
(7)

It is advantageous to introduce following surface quantity [8]:

$$
\Gamma_s \equiv \int_{-\infty}^{+\infty} \delta s \, dx, \quad \delta s = \left\{ \hat{s} - s_+ - (\eta - \eta_+) \frac{[s]}{[\eta]} \right\}.
$$
\n(8)

The quantity  $\Gamma$ , does not diverge and, in the spirit of Gibbs [6], may be called the relative surface entropy with respect to the OP. The quantities in square brackets are the jump quantities.

The formula for the equilibrium surface energy, Eq. (6), coincides with that away from equilibrium, which allows us to introduce the surface entropy  $\chi$  and internal energy  $\varepsilon$  as follows:

$$
\chi \equiv -\frac{d\sigma}{dT}; \quad \varepsilon \equiv \sigma + T\chi \tag{9}
$$

If at equilibrium an interface exists at a specific temperature only, as is the case for a first order transition, differentiation in Eq. (9) is understood in the sense of disequilibrium. Likewise, the equilibrium definition of the interfacial thickness, Eq. (7), may be extended on nonequilibrium situations of moving boundaries.

#### *2.3. Interfaces Away from Equilibrium*

To describe motion of an interface away from equilibrium, we shall use to our advantage the fact that the OP changes very rapidly inside the interfacial transition zone while remaining practically constant or changing very slowly outside the zone, see Fig. 1. Here  $\eta_{\pm} \equiv \eta(x = \pm \infty) = \Xi(T_E, P_E)$  are the equilibrium bulk-phase OP values. Instead of the Cartesean coordinate system  $\mathbf{x} = (x, y, z)$ , let's introduce new *curvilinear time-dependent coordinates*  $\{u =$  $U(\mathbf{x}, t), v = V(\mathbf{x}, t), w = W(\mathbf{x}, t)$  such that OP is a



*Figure 1.* Curvilinear coordinate system  $(u, v, w)$  associated with a moving interface.

function of one coordinate *only*:  $\eta = \eta(u)$  [2, 9–11]. One may introduce the velocity of motion  $V_n(v, w, t)$ of the surface  $U = \text{const.}$  The  $U = \text{const.}$  surfaces are equidistant and the radius of curvature of these surfaces is  $r = r_0(v, w, t) + u$ , where  $r_0(v, w, t)$  is the radius of curvature of the surface  $U = 0$ , see Fig. 1.

In the curvilinear coordinates TDGLE (3) transforms into an "ODE" as follows [2, 9–11]:

$$
\kappa \left( \frac{d^2 \eta}{du^2} + k_\eta \frac{d\eta}{du} \right) - \frac{\partial g(T, \eta)}{\partial \eta} = 0; \quad k_\eta = 2K + \frac{V_n}{m}.
$$
\n(10)

Here *K* is the curvature of the surface  $U = \text{const}$  and the number  $k_n$  may be called the dynamic curvature of an interface. Introduction of the time-dependent curvilinear coordinates has an advantage in that the evolution of the OP field may be described now by the motion of one surface  $U = 0$  in space and time. If the geometric number of the interface is small enough:

$$
Ge \equiv 2K_0 l_I \ll 1 \tag{11}
$$

the free energy change may be separated into volumetric and interfacial contributions

#### *2.4. Local Evolution Equation of Interfacial Dynamics*

Consider a transition from one state to another when the OP changes its bulk-phase value form  $\eta_+$  to  $\eta_-,$ see Fig. 1. In order to derive the evolution equation

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for a piece of interface we transform TDGLE (3) and GHE (4) to the time-dependent curvilinear coordinates where  $\eta = \eta(u)$  and  $T = T(u, v, w)$  and average these equations over the thickness of the interface. That is why we multiply all the terms of Eq. (10) by *d*η/*du* and integrate them over the interval  $(u_-, u_+)$ . Taking into account that  $d\eta/du$  vanishes at *u*<sub>−</sub> and u<sub>+</sub> and utilizing the relation:

$$
dg = \frac{\partial g}{\partial \eta} d\eta + \frac{\partial g}{\partial T} dT \tag{12}
$$

we obtain an equation for the motion of a phase separating interface:

$$
\sigma\left(2K_0 + \frac{V_n}{m}\right) = L\frac{T_E - T_-}{T_E} + F_{GD} + \frac{1}{2}C\frac{[T]^2}{T_-} + O\left([T]^3, l_I^3 K_0^3\right)
$$
(13a)

$$
F_{\rm GD} \equiv \int_{u-}^{u+} (s - s_+) \frac{\partial T}{\partial u} \, du \tag{13b}
$$

Equation (13) reveals the driving forces for the interfacial motion and is the principal result of the present paper. According to Eq. (13a), an interface is driven not only by its curvature  $(-2K_0)$  and the free energy difference on both sides of the interface  $\{L(T_E - T_-)/T_E\}$ , but also by another force,  $F_{GD}$ , which vanishes if the temperature is uniform in the transition zone or the thickness of the latter is zero, see Eq. (13b). Such force may be called *Gibbs-Duhem force.* Notice that the driving forces in Eq. (13a) have units of pressure because they act on a unit area of the interface.

The temperature gradient in the integrand of  $F_{GD}$ and the temperature jump [*T* ] should be found from GHE, Eq. (4), which in the new curvilinear coordinates  $(u, v, w)$  transforms as follows:

$$
C\frac{\partial T}{\partial t} = \lambda \left(\frac{\partial^2 T}{\partial u^2} + k_T \frac{\partial T}{\partial u}\right) + Q\left(T, \eta, \frac{d\eta}{du}\right);
$$
  
\n
$$
k_T = 2K + \frac{V_n C}{\lambda}
$$
\n
$$
Q(u) = V_n \frac{d\eta}{du} \left[ \left(\frac{\partial e}{\partial \eta}\right)_{V,T} - \kappa_E \left(\frac{d^2 \eta}{du^2} + 2K_0 \frac{d\eta}{du}\right) \right]
$$
\n(14)

Here  $k_T$  is the thermal curvature of the interface.

To elucidate the physical meaning of  $F_{GD}$  we solve the stationary GHE (14) ( $\partial T/\partial t = 0$ ) inside the interface using a method of asymptotic expansion. First, we obtain integral representations of the temperature gradient when the temperature gradient in the final phase

at  $u = u_$  is zero. Then we integrate this expression by parts in order to expand it in increasing powers of  $k_T$  and we retain the terms of the order not higher than  $(l_1k_T)$ . Such an expansion may be considered an expansion into "powers of disequilibrium" and is possible if  $l_I k_T \ll 1$ , which, in addition to the condition (11), requires the generalized Peclet number to be small:

$$
Pe \equiv l_I V_n C / \lambda \ll 1 \tag{15}
$$

Then the temperature gradient and the entropy difference in Eq. (13b) may be calculated using the equilibrium structure of the OP  $\eta_I(u)$ , Eq. (5). This gives us the expression for the Gibbs-Duhem force:

$$
F_{\rm GD} = -\frac{V_n}{\lambda} \bigg( J_1 - \frac{C}{\lambda} V_n J_2 - 2K_0 J_3 \bigg) \tag{16}
$$

The coefficients *J* 's represent different moments of the entropy density. Exact expressions for the quantities *Ji*'s for different types of interfaces may be found in Ref. [3]. It is instructive, however, to elucidate the physical nature of the terms in Eq. (16) using only measurable quantities such as the latent heat *L* and the relative surface entropy  $\Gamma_s$ , Eq. (8). Taking into account that  $[s]_{T_E} = L/T_E$  we obtain:

$$
J_1 \approx \frac{T_E}{l_I} \Gamma_s^2 - \frac{l_I}{6T_E} L^2 \tag{17}
$$

The type of transition affects the relative magnitudes of  $\Gamma_s$  and *L*, which in turn dramatically affects the magnitude of  $J_1$  in Eq. (17), being negative for a typical first order transition and positive for a continuous transition. It means that  $F_{GD}$  propels the motion of interfaces that appear after first order transitions serving as a driving force and opposes motion of interfaces after continuous transitions manifesting a drag force. Substituting Eqs.  $(16)$  and  $(17)$  into Eq.  $(13)$  we arrive at the linear approximation of the local evolution equation:

$$
L\frac{T_E - T_-}{T_E} = 2\sigma K_0 + \left(\frac{\sigma}{m} - \frac{l_I}{6\lambda T_E}L^2 + \frac{T_E}{\lambda l_I}\Gamma_s^2\right)V_n\tag{18}
$$

The most important consequence of the temperature gradient inside the interface is the alteration of the term proportional to the interfacial velocity in the evolution equation (18). An advantage of this equation is that it is expressed through measurable quantities and appropriate thermodynamic parameters of a system only and still is applicable to many different situations.

#### *2.5. Heat Balance Equation*

To find the equation for the temperature jump for a curved interface we average the stationary GHE (14)  $(\partial T/\partial t = 0)$  in the interval  $(u_-, u_+)$  and obtain the heat balance equation:

$$
\lambda \left\{ \left[ \frac{\partial T}{\partial u} \right] + [T]k_T(0) \right\} + V_n(L - 2\varepsilon K_0) = 0 \quad (19)
$$

Equation (19) differs from the regular heat-balance (Stefan) boundary condition in the term proportional to the curvature of the interface  $K_0$ , which vanishes for a flat or immobile interface when the interfacial area does not vary. This term constitutes the *surface creation and dissipation effect*.

#### **3. Thermal Effects of Interfacial Dynamics**

#### *3.1. Homophase Interfaces*

Homophase interfaces (HOI) appear after a continuous transition, when on both sides of the interface are different variants of the same phase. Antiphase domain boundaries and magnetic domain walls are examples of HOI's. Motion of HOI has been addressed in numerous studies, which go back to Lifshitz's seminal paper [12] where he conjectured a linear proportionality between the speed and curvature of a moving antiphase domain boundary. Allen and Cahn [10] used a continuum approach, similar to that of the present paper, and, on the premise of the invariable interfacial profile of the moving isothermal HOI in the direction of its motion, showed that a small piece of a gently curved interface, condition (11), will move with the velocity  $V_n = -2mK_0$ . Umantsev [13] considered the influence of the internal energy excess on the dynamics of HOI in the framework of the Onsager theory of linear response and showed that such excess causes *thermal drag effect* on the motion of HOI. The drag alters the kinetics and the effective interfacial mobility becomes  $m/(1+D_0)$ . In the denotations of the present paper the drag coefficient is  $D_0 = m \chi \varepsilon / \lambda \sigma l_I$ , which shows that the interfacial dynamics is limited not only by the mobility of an interface but also by the thermal conduction with the drag coefficient  $D_0$  measuring the relative role of these processes.

A number of questions, however, remained unanswered by the simplified Onsager-type formulation in Ref. [13]. For instance, what is the temperature distribution around the interface? What is the mechanism of thermal drag? What will happen if the energy transfer mechanism (thermal conduction) is turned off? In order to answer these questions we shall carry out a Ginzburg-Landau analysis of HOI motion.

The free energy *g* for a system undergoing continuous transition must be an even function of OP because states with  $\pm n$  are indistinguishable. This makes the coefficient  $b$  in Eq. (1) vanish. The homogeneous equilibrium set  $\eta_E = \Xi(T)$  for such free energy consists of a totally disordered  $\alpha$ -state with  $\eta_{\alpha} = 0$  and two ordered variants of the same phase,  $\beta$  and  $\gamma$ , with  $\eta_p^{\beta} = \pm \sqrt{-\tau}$ ,  $\tau = (T/T_C - 1)$ . Above the critical temperature  $T_C$  ( $\tau > 0$ ) this set is reduced to only one completely disordered α-state. Below  $T_C$  (τ < 0) this set consist of homogeneous ordered states  $\eta_\beta$  and  $\eta_{\nu}$  with the disordered  $\alpha$ -state being unstable. Stable heterogeneous isothermal solutions of Eq. (5),  $\eta_I(x)$ , exist at any  $T_E < T_C$  and represent transition layers (HOI) where OP changes from  $\eta_{\gamma}$  to  $\eta_{\beta}$  over the dis-(HOI) where OP changes from  $\eta_{\gamma}$  to  $\eta_{\beta}$  over the distance  $l_I = 2\sqrt{-2\kappa/a_0\tau}$ . The surface energy of HOI is  $\sigma = 2/3\sqrt{-2\kappa a_0\tau^3}$ ,  $\Gamma_s$  equals the surface entropy  $\chi$ , Eq. (9),  $[s] = 0$  and  $\varepsilon \cong T_{E} \chi$  because  $\chi \gg \sigma / T_{E}$ . Then  $F_{GD} \sim V_n$  (drag force) and there is a thermal correction of the order  $DV_n$  to the velocity of HOI motion  $V_n$  even for slightly curved and thus slowly moving pieces of interface. The mean-field drag coefficient *D* may be easily recovered from Eq. (18):

$$
D = \frac{ma_0(1+\tau)}{2\lambda T_c}.
$$
 (20)

To explain the drag effect we propose a borrowreturn mechanism, see Fig. 2. Both variants on either side of the interface are characterized by the same amount of internal energy density. Transformation inside the interface from one variant to the other, however, requires crossing the internal energy barrier (maximum), which corresponds to the disordered phase with  $\eta_{\alpha} = 0$ . So, a small volume of substance must borrow a certain amount of energy proportional to  $\Delta e$  from the neighboring volumes while moving uphill on the internal energy diagram, Fig. 2, and return it later on the downhill stage of the transformation. The borrowreturn mechanism entails the internal energy flux vector, which requires a transport mechanism, served here by the heat conduction. The drag effect is due to finite rate of such mechanism measured by the conductivity λ.

The energy flux through the interface is manifested in the temperature waves of amplitude  $[T]$ , which can be



*Figure 2*. Borrow-return mechanism. Internal energy of a substance as a function of an order parameter.

calculated from Eq. (19) assuming that  $\left[ dT/du \right] = 0$ :

$$
[T] = -\frac{2\varepsilon K_0}{C(R - 1 + RD)} \approx -2T_E \chi \frac{m}{\lambda} K_0 \propto (-\tau)^{1/2}
$$
\n(21)

Notice that the surface energy  $\varepsilon$  and entropy  $\chi$  have the critical temperature dependence, which yields the critically dependent temperature jump  $[T] \propto (-\tau)^{1/2}$ .

According to Eq. (20), as  $\lambda \rightarrow 0$  HOI slows down and stops completely if  $\lambda = 0$ , implying that in a poorly conducting material HOI motion is totally controlled by the heat transfer. Vanishing of the velocity of motion of a curved HOI in an ideal insulator (a material with  $\lambda = 0$ , if such material exists, is a striking result. Mathematically this means that the system of Eqs. (3) and (4) has an equilibrium non-onedimensional solution for  $\lambda = 0$ . This solution represents a *temperature double layer*  $\Delta \tau$  in the transition zone.

#### *3.2. Heterophase Interfaces*

Heterophase interfaces (HTI) separate contiguous phases of the same medium, but different symmetries and appear as a result of a first order (discontinuous) transition. Isothermal effects of interfacial dynamics have been thoroughly investigated in Ref. [9]. In one of the earlier papers [14] we have developed a model for analytical study of thermal effects. According to this model a high symmetry phase corresponds to  $\eta_{\alpha} = 0$ , while a low symmetry phase has the value of  $\eta_{\beta} = 1$  at

all temperatures. They are separated by an equilibrium state with the temperature independent value of OP  $\eta_{\gamma} = 1/2h(T)$ , which corresponds to an unstable state above  $T_c$ , but gains thermodynamic stability below  $T_c$ . In accordance with the Gibbs phase rule, the thermodynamic equilibrium between  $β$  and  $α$  phases is achieved at the specific temperature:  $T_E = T_c/(1 - a_0/6L)$ . A first order transition from  $\alpha$  to  $\beta$  phase is accompanied by the release of the latent heat *L* in the same amount at all temperatures. In this model the relative surface entropy vanishes, the thickness and the surface energy are temperature independent and, hence, remain unchanged even away from equilibrium. The coefficients *J* of the Gibbs-Dihem force, Eq. (16), are calculated in Ref. [14].

To reveal different thermal effects during first order transitions we shall consider a typical problem of growth of a spherical particle of the  $\beta$ -phase from the α-phase matrix. The *u*-axis is directed from β-phase to  $\alpha$ -phase, Fig. 1, so that the center of curvature is in the  $\beta$ -phase and the growth of the particle corresponds to positive values of  $V_n$ . Thermal effects do not change the critical nucleus radius,  $r_{cr} = 2\sigma T_E/L(T_E - T_-),$ unless  $\lambda \rightarrow 0$ , see Eq. (18). The rate of transformation, however, is different from the isothermal value. The most dramatic thermal effect, as can be seen from Eq. (18), manifests a possibility to have  $\beta$ -phase growing  $(V_n > 0)$  even when its temperature after transformation is above the equilibrium value ( $T_{-} > T_{E}$ ). This means that the low symmetry  $\beta$ -phase grows at the expense of the high symmetry  $α$ -phase at a temperature above the equilibrium point. In case of crystallization of water this would have meant the growth of superheated ice from supercooled water. This effect has been called *heat trapping* and was studied in detail in Ref.  $[2, 14]$ . As one can see from Eq.  $(18)$ , for the heat trapping to occur the coefficient in front of the term linear in  $V_n$  must be negative and, as  $\Gamma_s = 0$ , the following criterion must be fulfilled:

$$
\frac{l_I L^2}{\sigma T_E} > 6 \frac{\lambda}{m} \tag{22}
$$

Criterion (22) should be considered as the low limit on the thickness of the interface or the upper limit on the rate of thermal conduction in the system for the heat trapping to occur. It is not the case for crystallization of ice but is quite feasible for crystallization of other substances. The heat trapping becomes possible when the Gibbs-Duhem force becomes large enough to propel an interface against the negative bulk driving force.

Equation (18) also point at another situation when the growing phase may be observed at a temperature above equilibrium one that is around regions in materials where the curvature is negative (the center of curvature is in the parent phase). The difference with the heat trapping effect is that the latter is possible even for flat interfaces.

Another example of thermal effects can be revealed in the analysis of the heat balance before and after a HTI sweeps material during a first order transformation. The amount of heat released is called the heat of transformation. It is commonly attributed to the product of the latent heat and the transformed volume. However, as Eq. (19) demonstrates, if the moving interface is curved, the heat of transformation will differ from the above described amount by the amount of the surface internal energy times the surface area created or destroyed. This effect, which may be called the *surface creation and dissipation effect*, has been notice by Wollkind in reference [15] and used in the form of a boundary condition in one of his later papers. Tiller discussed the surface creation or destruction effect in reference [16]. The theoretical description of this effect in [16], however, was not appropriate because the author attributed it to the evolution equation, similar to Eq. (18), instead of the heat-balance condition, Eq. (19). The rigorous derivation of the surface creation and dissipation effect has been given by Roytburd and the present author in reference [2], and used by Davis and the present author in reference [17] to study the influence of this effect on the absolute stability of the solidification front during crystal growth from a hypercooled melt, i.e. the condition when the front looses dendritic or cellular structure and restores completely the morphological stability.

#### **4. Discussion**

In summary, we have presented theoretical description of a few thermal effects in interface motion. These effects are robust and conceivably independent of the method employed for analysis. Eqs. (18) and (19) identify the local interfacial variables  $V_n$ ,  $K_0$ ,  $T_$ ,  $[T]$ ,  $[dT/du]$ , and relate them to the kinetic properties of the medium like  $\alpha$ , *m* and thermodynamic interfacial quantities,  $L, \sigma, \varepsilon, \Gamma_s, l_I$ . These equations are local in the sense that they are independent of the history of the process and may be used as boundary conditions in a global problem of structural evolution like that of dendritic growth

in crystallization or domain growth after continuous ordering.

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There are two distinctly different sets of thermal effects considered in this paper. One set originates from the existence of the Gibbs-Duhem thermodynamic force on the interface, which is one of the principal results of the present paper. In the cases of continuous and discontinuous transitions this force has opposite directions compared to the velocity of the interface, resulting in heat trapping effect for the latter and drag effect for the former. Interestingly to note that thermal drag exists despite of the vanishing latent heat of the transition, which causes thermal effects during first order transformations, e.g. solidification. Thermal drag occurs because the conversion of one variant into another is accompanied by the transmission of energy between neighboring pieces of a material, which cannot occur infinitely fast. HOI moves towards the center of its curvature with a speed which is lower than that predicted by the Lifshitz-Allen-Cahn theory [12, 10]. The Gibbs-Duhem force is antiparallel to the boundary velocity and has the meaning of a drag force. Such slowing down should be taken into account in experimental verification of the theory of coarsening of HOI structure albeit thermal effects do not change time exponents of the latter.

The present treatment convincingly demonstrated that the thermal conductivity of a material is vital for the coarsening of the HOI structure. If the thermal conductivity vanishes ( $\lambda = 0$ ) that is the energy-transfer mechanism is "turned off", curved HOI's become stable. Stability of a spherical particle of a minority variant in a majority matrix is quite surprising and needs a physical explanation inasmuch as critical nuclei in the theory of the first order transformation are equilibrium but *unstable* states of the system. "Dissolution" of a minorityvariant spherical particle is caused by Laplacian pressure from the curved interface (Gibbs-Thompson effect, see Eq. (18)). At the same time the Gibbs-Duhem force generates an additional (thermal) pressure in the particle that neutralizes Laplacian pressure.

Another set of thermal effects stems from the existence of the surface internal energy and necessity to carry it over together with the moving interface. In the case of a discontinuous transition this entails the surface creation and dissipation effect, which consists in altering the heat of transformation on the amount of the internal energy of the surface area created or destroyed by the moving curved interface. In the case of a continuous transition the surface internal energy entails

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thermal waves around a moving interface. Temperature waves must accompany motion of any antiphase domain boundary and can be revealed by different imaging techniques and serve as experimental verification of the thermal drag effect. One possibility is in situ observation in infrared light. Another possibility is the Mirage technique measurement, which utilizes the gradients in the index of refraction of air arising from the temperature gradients induced by the temperature waves on the specimen surface [18].

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