CONTINUUM METHODS
IN THE
KINETIC THEORY OF PHASE TRANSFORMATIONS

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Abstract.

In this paper the author tries to show benefits of using mean field theory for the study of dynamics of phase transformations utilizing both theoretical and computer simulation methods. This theory combines the fundamental approach with the variety of applications that can be analyzed. In such theory, it is assumed that the state of a system away from equilibrium, in addition to temperature and pressure, must be characterized by one more thermodynamic variable responsible for relaxation in the material. For the solid-to-solid transformation such a variable is the order parameter field, whose evolution can be described by the time-dependent-Ginzburg-Landau-type equation. In this paper the accent is made on thermal effects of transformations such as surface creation and dissipation, mechanism of metastable-phase production, and period-doubling regime in coarsening. Relevance to the transformations in binary alloys is also discussed.

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**Introduction.** Any phase transformation necessarily involves an interface separating two phases. The first continuum ideas about the structure of an interface can be attributed to Gibbs [1] and Van der Waals [2]. However, modern development of continuum or field theory of phase transformations originates from the works of Landau [3]. He introduced an order parameter as a variable which, in addition to temperature and pressure, characterizes the state of a system undergoing ordering. The same year Landau [4] introduced the "gradient energy" contribution which allowed him to write the free energy of an inhomogeneous system, i.e. the coarse-grained free-energy, in the form of the functional:

\[ G(T,P) = \int \left[ g_0(T,P,\xi) + \Delta g(T,P,\xi) + (\kappa/2)(\nabla \xi)^2 \right] d^3x \]  

(1)

where integration is over the whole volume occupied by the system. Here \( \Delta g \) has a typical double-well form as a function of the degree of order \( \xi \) and is reckoned from the level \( g_0(T,P) \) of a completely disordered homogeneous phase \( \alpha \) characterized by the vanishing order parameter \( (\xi=0) \). The same approach is applicable to the study of phase transitions of the first order (FOT) and second order (SOT) with different functional dependence of \( \Delta g \) on the order parameter, e.g.:

\[ \Delta g = \begin{cases} \frac{1}{2}a\xi^2 \left[ h - \frac{3}{2}(h+2)\xi + \xi^2 \right], & h = 6\lambda(T-T_\alpha)/aT_\beta, \text{ FOT} \\ \frac{1}{2}a\xi^2 \left[ \tau + \frac{1}{2}\xi^2 \right], & \tau = (T-T_\gamma)/T_C, \text{ SOT} \end{cases} \]  

(2)

where \( a \) is the scale of the energy increment, \( T_\alpha(P) \) and \( L \) are respectively the equilibrium temperature of the ordered and disordered phases and the latent heat of the FOT, \( T_C(P) \) is the critical temperature for the SOT. From the double-well form of \( \Delta g(T,\xi) \) for FOT one can immediately reveal the existence of the states \( \xi_\alpha \) and \( \xi_\beta \), that correspond to the free energy minima (may be local) and intermediate state \( \xi_\gamma \), that corresponds to the free energy maximum and separates the states \( \alpha \) from \( \beta \) (\( \xi_\alpha > \xi_\gamma > \xi_\beta \)). The free energy increment of this state \( \Delta g_\gamma \) is known as the activation barrier (Fig. 1).

![Figure 1](image)

**Figure 1.** Sketches of the order-parameter variations with temperature for the first- (FOT) and second-order (SOT) transformations.

Another mechanism of phase separation may occur in a mixture of two or more species when quenched into a thermodynamically unstable region. Such a system undergoes spinodal decomposition and, as it was introduced by Cahn and Hilliard [5], can be described by the same coarse-grained free energy functional (1) with the composition of one of the species being the order parameter. The most important difference comes from the fact that the order parameter, i.e. composition, exhibits the conservation law: \( \int \xi d^3x = \text{const} \). Because of that, the decomposition is controlled by relatively slow diffusive transport.

Another model which will be of interest for us is Cahn's model of crystallization [6], which stressed that different mechanism of crystallization may appear as a result of different diffuseness of the interface. There is a number of other physical examples which can be described by this type of theory. In the case of a displasive structural transformation the order parameter is strain [7]. The problem of interest is also relevant to magnetic transitions with magnetization as the order parameter.

**Equilibrium properties of interfaces.** From these simple ideas many important properties of an equilibrium interface represented as a layer of rapid variation of the order parameter may be derived as follows.
interatomic distance. In fact, it suffices to have \( l_i \) only two or three times greater than \( d \), because all of the thermodynamic functions, e.g. surface energy, depend upon the exponential of the ratio \( (l_i/d) \) [6]. However, Eq.(8) may imply another, kinetic, criterion of validity for the continuum theory of phase transformations: diffuse interface approach is applicable if an interface exhibits a linear kinetic law, because no other mechanism of interface motion is capable of exhibiting such kinetics.

**Heat-balance equation.** Apparently that a considerable emission or absorption of latent heat associated with the motion of an interface affects the rate of transformation. A number of challenging questions arise with regard to this problem: What is the distribution of heat sources within the interface? How does it influence the transformation? Are there any sinks possible in the transition region if the net effect corresponds to the release of latent heat? The last question is not easy to answer if one recalls that the homogeneous part of the free energy goes up and down as the order parameter varies inside the interface. However, one should not forget that heat sources are determined by energy (enthalpy) variations but not the free energy. All these questions can be answered by deriving an equation for the energy evolution which would take into consideration variation of the order parameter and its gradients inside the interface. The heat equation as represented below was derived by Roylburd and the present author [12] from the first law of thermodynamics and is based on a calculation of a small variation of the internal energy density as a result of a small inhomogeneous variation of the order parameter:

\[
C_P \frac{dT}{dt} = \nabla (\lambda \nabla T) + Q(x,t), \quad Q = -\left( \frac{\delta W}{\delta \xi} \right)_T \frac{d\xi}{dt} = -T \left( \frac{\delta S}{\delta \xi} \right)_T \frac{d\xi}{dt} - \left( \frac{\delta G}{\delta \xi} \right)_T \frac{d\xi}{dt}
\]

(9)

Here \( Q \) is the density of instantaneous heat sources, \( W \) and \( S \) are functionals of the internal energy and entropy respectively; \( C_P \) and \( \lambda \) are specific heat and thermal conductivity. The heat source, Eq.(9) consists of the entropy contribution which may be either positive or negative depending upon the direction of the reaction and the dissipation which, due to Eq.(7), is proportional to the velocity squared and hence always positive. The application of the second law to our system yields a constraint on the evolution equation for the order parameter

\[
\left( \frac{\delta G}{\delta \xi} \right)_T \frac{d\xi}{dt} \leq 0
\]

(10)

which shows that the linear Onsager-type equation is a good, but not a unique, choice for this purpose. The heat source can also be expressed through the homogeneous part of the internal energy density \( w \):

\[
Q = -\left( \frac{\delta w}{\delta \xi} \right)_T + \left( \kappa - T \frac{d\kappa}{dT} \right) \nabla^2 \xi \frac{d\xi}{dt}
\]

(11)

This topic was recently a subject of extensive study [13]. However all of these works suffer from one major problem which stems from the fact that the gradient energy contribution was not accounted for in the internal energy functional of the system. That did not allow the authors to derive the full expression for the heat source, Eq.(11), where the inhomogeneous part in brackets is responsible for the surface creation and dissipation effect.

Before looking at the dynamic analysis of the system undergoing FOT whose evolution is governed by Eqs. (7,9), we should look at the variance of the system or full set of materials parameters on the mesoscopic level of description that emerge in the system. There are seven of these parameters: \( C_p, T_{eq}, L, \Delta g_p, \kappa, \lambda, \gamma \) where \( C_p \) characterizes an untransformed system; \( T_{eq}, L, \) and \( \Delta g_p \), are bulk properties of the transformation; \( \kappa \) is the range of interactions in the system; \( \lambda \) and \( \gamma \) are kinetic coefficients that set up the time of thermal and relaxation processes. In the ideal situation, all of these parameters should be derived from the microscopic theory of the system in question. This is especially important for \( \Delta g_p, \kappa, \) and \( \gamma \). To the best knowledge of the author this has not yet been done. Therefore, these parameters must be determined by matching the relevant theoretical and experimental quantities: \( \Delta g_p \) and \( \kappa \) can be found from the interfacial energy and thickness measurements, Eqs.(5,6), and \( \gamma \) from the kinetic coefficient of growth, Eq.(8). The latter naturally arises from measurements of the interface motion during growth or dissolution of the second phase, and the former from the coarsening kinetics.

In addition to the interfacial thickness \( l_i \), two other length scales, capillary \( l_c = \gamma T_{eq} / \sigma / L^2 \) and kinetic \( l_p = \lambda / \mu L \), appear for FOT. It is interesting to note that results of the analysis of the dynamical system of
Eqs. (1,7,9) can be classified with regard to only two dimensionless parameters:

\[ U = \frac{l_c}{2l_t} = \frac{C_p T_e \Delta g_{\beta}}{L^2}, \quad R = \frac{l_c}{l_t} = \frac{\lambda T}{C_p \gamma K} \]  \hspace{1cm} (12)

The first parameter in (12) is the ratio of the energy scales and characterizes the thermodynamic coupling between thermal and ordering modes. The second parameter in (12) is the ratio of the thermal diffusivity \( \alpha = \frac{\lambda}{C_p} \) to the interfacial mobility \( M = \gamma K \) and represents dynamic properties of the system. All different evolution regimes of the adiabatic system can be understood as interplay of the two parameters \( U \) and \( R \).

Thermal Effects of Transformations. Thermal effects are important to transformations in many different situations even where the boundary of a sample is maintained under isothermal conditions. This happens because one cannot fully control the inner regions of a sample that undergoes a phase transformation. One such example, APB motion will be considered below. However, the majority of the examples will be taken from adiabatic, i.e. thermally insulated, systems undergoing FOT. The thermodynamic condition of equilibrium of such systems corresponds to the maximum entropy under a constraint of constant energy (or enthalpy). Adiabatic and isothermal systems have the same homogeneous equilibrium states. But the degree of local stability is different in the two systems: isothermal stability is assessed by the sign of the modulus \( G_{65} \), while for adiabatic stability positivity of the modulus \( [G_{65} - (G_{17})^2/G_{11}] \) is needed [14].

The dynamic criterion of linear stability for an adiabatic system, i.e. reaction of a system on arbitrarily small fluctuations (normal modes), differs from the local thermodynamic one, but coincides with that for an isothermal system. The discrepancy between the local thermodynamic and linear dynamic criteria of stability happens because the dynamic analysis determines a reaction of a system on all fluctuations, even those which do not conserve energy completely (microcanonical ensemble) [15]. The most "dangerous" for stability wavenumbers turn out to be nearly isothermal.

The initial stages of FOT from unstable homogeneous equilibrium states (\( G_{65} < 0 \)) can be studied analytically [15]. To more fully examine the formation of microstructure on later stages, a method of numerical simulations was applied to the disintegration of an unstable \( \alpha \)-state in the 1D adiabatic system (path w in Fig.1), [16]. Simulations start from the parent state supercooled below its critical temperature of instability \( T \), plus "thermal fluctuations" superimposed on it. They revealed three mechanisms of the creation of interfaces in early stages of transformation. Different regimes of linear and nonlinear behavior are summarized in the plane of parameters \( U \) and \( R \) (Fig. 2).

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**Figure 2.**— Different regimes of the early stages of the microstructure formation during FOT.
Nonclassical nucleation (case a). If parameter $U$ is large enough, $U > R+1$ (the adiabatic modulus is strongly negative) the uniform mode ($k=0$) is the fastest growing wave mode. This is similar to the isothermal system with the only difference that rate of growth of the uniform mode is determined by the adiabatic modulus instead of the isothermal one. An isothermal mechanism of correlation of initial fluctuations prevails on early stages and creates inhomogeneities on the scale of the cutoff wavelength of instability. This mechanism is analogous to nonclassical nucleation which is effective for metastable states just above the instability point and consists in the creation of a diffuse heterophase fluctuation with an amplitude of transformation far below that of the product phase $\varepsilon_p$.

Continuous modulation (case c). If parameter $U$ is small enough, $U < 1$ (the adiabatic modulus is positive), the wave number of the fastest mode is finite, but the uniform mode is neutral. Thus over this range of conditions the system is unstable with respect to the order parameter modulation. In case of the strong coupling, $U << 1$ (hatched region of Fig. 2), growing modes obey the nonlinear Cahn-Hilliard equation, so that the order parameter changes its global type and exhibits the conservation law. The mobility of this regime $\left(\lambda / \Delta g_{ct}^2 T\right)$ is large and independent of the relaxation constant $\gamma$ of Eq. (7), which means that such a decomposition is totally controlled by heat transfer. Modulations, which emerge from the finite wavelength instability of the $\gamma$-state, create an almost perfect periodic domain structure in early stages of decomposition. Hence, for systems with a nonconserved order parameter, decomposition of an unstable state can follow a path of finite-wavelength modulation governed by energy conservation. This behavior is directly analogous to the spinodal decomposition of a system with a conserved order parameter. The difference is that for the conserved order-parameter modulations start immediately from the beginning of the process while, in the present case, transformation at first reaches the intermediate equilibrium state in a uniform fashion and only then commences exhibiting modulations of the order-parameter field. For a weakly metastable system, such a mechanism of first-order transformation represents an alternative to nucleation and growth. Achieving the conditions necessary for this mechanism in a specific system will of course depend on the ability to suppress competing nucleation during preceding cooling.

Hybrid transformation (case b). For a case where $1 < U < R+1$ (the adiabatic modulus is still negative), the fastest mode has a finite wave number and the uniform mode grows also. During the growth stage in such systems, additional domains and their boundaries may appear as the result of a front-splitting instability and a kinetic transition from the stationary to the Stefan regime. Careful study of the equilibrium state diagram of the system shows that front splitting is also a result of the continuous modulation mechanism.

There is a discrepancy between the final state of the system and the fine-grained structure which appears in the early stages of transformation. Two mechanisms help the system to attain a stable equilibrium: growth and coarsening. Growth is a fast mechanism which occurs usually far from equilibrium and, depending upon the kinetic properties of the system, may be accompanied by an overshooting with subsequent recovery of the parent phase and achievement of the globally stable structure or even metastable product phase formation (locally stable, but unstable globally). This means that the $\beta$ phase, appearing as a result of such transformation, is superheated above the equilibrium temperature. This effect, called heat-trapping, consists of adiabatic absorption by the front of the heat released by the transition from the unstable or metastable $\alpha$ state so that the product phase appears to be metastable (in the isothermal sense). It exists only in a bounded interval of supercoolings $\Delta T^* < \Delta T < L/C$, with the low limit $\Delta T^*$ depending upon the kinetic parameter $R$ and is absent if this parameter is above the critical value: $R^* = j/\Omega$ (Fig. 2), where $j$ is a number of the order of one which depends upon the free energy potential used $[12, 14]$. The heat-trapping regime is due to heat diffusion inside the interfacial transition region and is analogous to the partitionless solidification of alloys, solute trapping, which results in the appearance of crystalline alloys with solute in excess of equilibrium solubility $[17]$.

Coarsening is a slow mechanism of the establishment of global, two-phase, equilibrium with a complete phase separation. It is customary to view coarsening as a curvature-driven motion. In this case, there would be no coarsening in the 1D system where all boundaries are flat. In fact, coarsening is driven by the reduction of surface energy which acts to reduce the number of domain walls in our system. When the volume fraction of coarsening particles is rather high the coarsening process is a result of strong short-range interaction between close particles through the order-parameter field (hard impingement) and takes the form of the sequential doubling of the structural period (spacing). Two types of coarsening may occur: dissolution of a particle accompanied by a local temperature dip, or coalescence of two neighboring particles accompanied by the creation and growth of an interconnecting neck and strong local elevation of temperature. Both types eventually lead to a new equilibrium state with the double period $[16]$.

Surface creation and dissipation effect (SCDE). Another example of thermal effects can be found in
creation/destruction of an interface or its portions during the transformation [18]. The surface energy which accompanies appearance/disappearance of pieces of an interface must be manifested in the form of a negative/positive addition to the latent heat of transformation, where the latter is the result of the chemical driving force in the system. To assess the SCDE, one should derive the proper heat-balance interface condition from the full Eq. (11). The analysis shows [12] that such a condition takes the form:

$$\lambda \phi_n T_\beta - \lambda \phi_n T_\alpha = V_n [L(T) - 2K(\sigma - T(d\sigma/dT))]$$

(13)

where $\phi_n$ is the derivative in the direction normal to the front and $K$ is the curvature of the interface. This condition differs from the regular Stefan boundary condition in the second term in the RHS, which is solely responsible for variations of the interfacial area. Davis and the present author [19] studied the influence of this effect on the absolute stability of the solidification front during crystal growth from a hypercooled melt (FO), i.e. the condition when the front looses dendritic or cellular structure and restores completely the morphological stability. If the SCDE is not considered the absolute stability is achieved when the thermal length $l_c = \alpha/V_n$ becomes equal to the capillary length $l_c$ [20]. Consistent account for the SCDE shows that stabilization occurs when $l_c$ becomes equal to $l_c(1 - L/CT)$, that is for larger front speeds and initial hypercoolings. This means that the SCDE works "against" the regular Gibbs-Thompson effect and retards stabilization.

The most interesting example of the SCDE comes from the study of the APB motion during an order-disorder transition (SOT). It is customary to view this type of transformation totally as a curvature-driven motion [21] because the chemical driving force between antiphase domains is absent and the latent heat vanishes (path 1 in Fig. 1). However, the SCDE yields the heat release and temperature increase of those regions where previously the interface was (path 2 in Fig. 1). This effect can be estimated by considering a minority variant sphere of the initial radius $R_0$, shrinking in a large majority variant matrix at the initial temperature $T_0$ because this problem constitutes the basis for the APB motion. Equilibration of the surfacial internal energy of the sphere before shrinking $4\pi R_0^2(\sigma - Td\sigma/dT)$ and the thermal energy of the material after the dissolution of the minority variant $(4\pi/3)R_0^3C_p(T - T_0)$ yields the criterion of attainability of the critical point after the dissolution:

$$\tau_0 = 18\alpha a/(C_pT_0R_0^2)$$

(14)

Thus the SCDE will affect the dynamics of the coarse graining and change the transformation path because it goes extremely slow when temperature approaches the critical point (critical slowing down).

References
2. J.D. van der Waals, Z. Physik. Chem. (Leipzig) 13, 657 (1894)
4. L.D. Landau, Phys. Zs. Sowjet, 12, 123 (1937); ibid, p. 236