

Higher-order phase field models and detailed anisotropy

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An interface between two phases is considered. A set of differential equations of arbitrary order is derived from a Landau-Ginzburg approach. The higher-order equations reveal more detailed structure of the interface. In particular, any anisotropy of the interactions is exhibited in the equations and the modified Gibbs-Thompson relation at the interface.

In this paper we derive a set of differential equations of arbitrary order from a Landau-Ginzburg^{1,2} approach and show that this has various physical implications for phase boundaries in both equilibrium and nonequilibrium problems. The ideas are a further development of those considered in previous work.³⁻¹²

The physical situation of interest consists of a material (occupying a region Ω) which may be in either of two phases, e.g., solid or liquid, which are separated by an interface Γ . A small but finite correlation length $C\xi$ implies that the thickness of Γ , the interfacial tension σ , across Γ , and the deviation from the planar equilibrium melting temperature on Γ are all nonzero quantities.^{3,9} A key aspect to understanding the behavior of the interface, particularly questions of shape, stability, and pattern formation, is the relationship between the temperature at the interface and other variables such as the interfacial tension, curvatures, normal velocity, anisotropy, and orientation angles. In particular, an important problem is the implication of the microscopic information, particularly anisotropy, for the macroscopic equations and the consequent behavior of the interface. We find that for any even integer m , the m -fold anisotropy is communicated through the m th power of q , the wave number, which leads to the appropriate m th-order differential of the order parameter. The effect on the shape and motion of the interface is most clearly manifested in Eq. (29), for sixfold anisotropy.

The model we consider is the continuum limit of a spin system on a hyperrectangular lattice \mathcal{L} in d -dimensional space. Given spin variables $\phi(x)$ for x in \mathcal{L} , which may assume all real values, a double-well potential $w(\phi(x))$, which maintains a finite energy, and a set of interactions $J(x-x')$, one may write a (reduced) Hamiltonian as

$$\overline{\mathcal{H}} \equiv \frac{1}{2} \sum_{x,x' \in \mathcal{L}} J(x-x')\phi(x)\phi(x') - \sum_{x \in \mathcal{L}} w(\phi(x)) . \quad (1)$$

$$\mathcal{F}\{\phi\} \equiv \int F dx_1 \dots dx_d ,$$

$$F = \frac{1}{2} \sum_{n=1}^{\infty} \sum'_{p_1+\dots+p_d=2n} (-1)^{n+1} \xi^{2n} b(2n; p_1, \dots, p_d) (D_1^{p_1/2} \dots D_d^{p_d/2} \phi)^2 + G(\phi) - 2u\phi , \quad (5)$$

where the primed sum is over all sets of positive, even numbers $\{p_1, \dots, p_d\}$ whose sum is $2n$. The coefficients may be

Using the discrete Fourier transforms

$$\hat{\phi}(q) \equiv \sum_{x \in \mathcal{L}} e^{iq \cdot x} \phi(x), \quad \hat{J}(q) \equiv \sum_{x \in \mathcal{L}} e^{-iq \cdot x} J(x) , \quad (2)$$

the interaction term of (1) may be written as

$$\sum_{x,x' \in \mathcal{L}} J(x-x')\phi(x)\phi(x') = N^{-1} \sum_q \hat{J}(q) \hat{\phi}(q) \hat{\phi}(-q) , \quad (3)$$

where N is the number of spins in the lattice.

The Hamiltonian is then rewritten by (i) expressing $\hat{J}(q)$ in a power series in $(q \cdot x)^n$ by expanding $e^{-i(q \cdot x)}$ (later to be truncated), (ii) defining the discrete derivatives (in the j th direction)

$$D_j f(x) \equiv \frac{f(x+a_j) - f(x)}{a_j} , \quad (4)$$

where a_j is the lattice spacing, and (iii) using a discrete integration by parts in order to convert the $q^j e^{-iq \cdot x}$ terms into discrete derivatives of $\phi(x)$. For convenience, we make the assumption that $J(x)$ is symmetric in reflection about any axis (hence, about the origin). This assumption means that odd powers of q , and thereby odd-order derivatives, will vanish due to symmetry. The analysis proceeds similarly without this assumption. A length scale ξ emerges (see Ref. 13, chapter 3) from the scaling of the sums $\sum_x J(x) x_1^{p_1} \dots x_d^{p_d}$. We pass to a formal continuum limit, letting $a_j \rightarrow 0$. Then the discrete derivatives become the analogous continuum derivatives, which we also denote by $D_j f(x)$. A free energy is obtained by adding $-2u\phi$ to the Hamiltonian (u is the temperature, scaled so that $u=0$ is the usual melting temperature). Combining the double-well potential w with the $\phi(x)$ terms which have not been differentiated, one obtains the free energy

written as

$$b(2n; p_1, \dots, p_d) \equiv \frac{1}{p_1! \dots p_d!} \int J(x) x_1^{p_1} \dots x_d^{p_d} \times dx_1 \dots dx_d \quad (6)$$

The function ϕ must satisfy $\tau\phi_t = \delta\mathcal{F}/\delta\phi$ where τ is a relaxation time. Truncating (5) to order M and applying the Euler-Lagrange equations to it, one obtains the equation, in the domain $\Omega \subset \mathbb{R}^d$,

$$\tau\phi_t = \sum_{n=1}^M \sum'_{p_1+\dots+p_d=2n} \xi^{2n} b(2n; p_1, \dots, p_d) \times D_1^{p_1} \dots D_d^{p_d} \phi - G'(\phi) + 2u \quad (7)$$

To avoid ill-posed mathematical problems, we must restrict M to be odd. This equation is coupled with the heat diffusion equation

$$u_t + \frac{l}{2} \phi_t = K \Delta u \quad (8)$$

where l is the latent heat of fusion (per unit mass) and K is the thermal diffusivity (the heat capacity per unit volume has been set equal to unity). A prototype $G(\phi)$ is $\frac{1}{4}(\phi^2 - 1)^2$ so that $-G'(\phi) = \phi - \phi^3$. For $M=1$, these equations reduce to second-order equations previously studied³⁻¹² (see also the recent review article in Ref. 14). A complete mathematical problem is specified by imposing appropriate initial and boundary conditions (which depend on the nature of the container material and physical considerations extraneous to the present discussion), e.g.,

$$u(0, x) = u_0(x), \quad \phi(0, x) = \phi_0(x) \quad x \in \Omega \quad (9)$$

$$u(t, x) = u_\pm(t, x), \quad \phi(t, x) = \phi_\pm \quad (10)$$

$$\frac{\partial^j}{\partial v^j} \phi(t, x) = 0 \quad x \in \partial\Omega \quad (10)$$

where ϕ_\pm are the roots of $-G'(\phi) + 2u = 0$ with $+$ denoting the liquid and $-$ the solid, and v is the normal to the boundary. The interface Γ between the two phases is then the set of points in Ω on which the order parameter ϕ vanishes.

The interfacial tension σ across Γ can be calculated by using (5) in a logical local interpretation of the usual definition

$$\sigma \equiv \frac{\mathcal{F}\{\phi\} - \frac{1}{2}\mathcal{F}\{\phi_+\} - \frac{1}{2}\mathcal{F}\{\phi_-\}}{A} \quad (11)$$

where A is the area of the interface. See Ref. 3 for details.

In the isotropic case, the calculations are simplified so that σ may be determined to all orders in n . In this case, (7) may be written as

$$\tau\phi_t = \sum_{n=1}^M \xi^{2n} \frac{J_{2n}}{(2n)!} (D_{11} + \dots + D_{dd})^n \phi - G'(\phi) + 2u \quad (12)$$

$$J_{2n} \equiv \int J(x) (x_1^2 + \dots + x_d^2)^n dx$$

The leading-order transition layer solution for [small ξ and $\tau = O(\xi^2)$] must be $\phi^0(t, r) = \psi(\rho)$, $\rho \equiv r/\xi$, where r is defined as the coordinate normal to Γ (positive toward the

liquid) and ψ satisfies

$$\sum_{n=1}^M \frac{J_{2n}}{(2n)!} \frac{\partial^{2n} \psi}{\partial \rho^{2n}} - G'(\psi) = 0 \quad (13)$$

It must also approach appropriate distinct limits as $\rho \rightarrow \pm\infty$. An important identity needed to evaluate (11) is obtained by multiplying (13) by $\partial\psi/\partial\rho$ and computing the integral from $-\infty$ to ρ . Using the notation

$$\psi_j \equiv \frac{\partial^j \psi}{\partial \rho^j}, \quad ||g||^2 \equiv \int_{-\infty}^{\rho} g^2(\rho) d\rho \quad (14)$$

one may write this identity as

$$\sum_{n=1}^M \frac{J_{2n}}{(2n)!} \int_{-\infty}^{\rho} \psi_j \psi_1 - \int_{-\infty}^{\rho} G'(\psi) \psi_1 = 0 \quad (15)$$

The second integrand is clearly an exact differential. To see that the first is also exact, one may apply the general identity (subscripts again denoting derivatives),

$$\phi_{2n} \phi_1 = \frac{d}{dr} \left[\sum_{k=1}^{n-1} (-1)^{k+1} \phi_{2n-k} \phi_k + \frac{(-1)^{n-1}}{2} \phi_n^2 \right] \quad (16)$$

which may be verified by induction. Combining (15) and (16) results in the identity

$$||[G(\psi)]^{1/2}||^2 = \sum_{n=1}^M (-1)^{n+1} \frac{J_{2n}}{(2n)!} (n - \frac{1}{2}) ||\psi_n||^2 \quad (17)$$

The interfacial tension σ can now be evaluated to leading order by noting that the $2u\phi$ term vanishes in (11) and that the integration in the tangential directions cancels with the area in the denominator. One then has

$$\begin{aligned} \sigma &= \frac{1}{2} \sum_{n=1}^M (-1)^n \frac{J_{2n}}{(2n)!} ||\psi_n||^2 + ||[G(\psi)]^{1/2}||^2 \\ &= \sum_{n=1}^M (-1)^{n+1} \frac{J_{2n}}{(2n)!} n ||\psi_n||^2 \end{aligned} \quad (18)$$

where the second equality follows from (17).

Next, we consider the question of determining the temperature at a developed interface. Suppose the surface is moving with a (normal) velocity v at the point x_0 , and has principal curvatures summing to κ [e.g., $\kappa = (d-1)/R_0$ for a d -dimensional sphere of radius R_0]. Asymptotic analysis shows that the interfacial structure is (to dominant order) independent of t . With ρ defined as above, but now also depending on t through the location of the interface, and v defined as $\pm|v|$ (plus sign if motion is toward the liquid), we may write

$$\tau\phi_t = \frac{-v\tau}{\xi} \phi_\rho \quad (19)$$

$$\xi^{2n} (D_{11} + \dots + D_{dd})^n \phi = \frac{\partial^{2n} \phi}{\partial \rho^{2n}} + \xi n \kappa \frac{\partial^{2n-1} \phi}{\partial \rho^{2n-1}} + O(\xi^2)$$

Thus, in the isotropic case, one may write (12) to $O(\xi)$ as

$$\sum_{n=1}^M \frac{J_{2n}}{(2n)!} \left[\frac{\partial^{2n} \phi}{\partial \rho^{2n}} + n \kappa \xi \frac{\partial^{2n-1} \phi}{\partial \rho^{2n-1}} \right] - G'(\phi) + 2u = -\frac{v\tau}{\xi} \frac{\partial \phi}{\partial \rho} \quad (20)$$

Assuming a solution of the form $\phi = \phi^0 + \xi\phi^1$ (where $\phi^0 = \psi$) solves (13), we note that ϕ^1 must solve (to leading order)

$$\begin{aligned} \xi L\phi^1 &\equiv \xi \sum_{n=1}^M \frac{J_{2n}}{(2n)!} \frac{\partial^{2n}\phi^1}{\partial\rho^{2n}} - G''(\psi)\phi^1 \\ &= -2u - \frac{v\tau}{\xi} \frac{\partial\psi}{\partial\rho} - \sum_{n=1}^{\infty} \xi \frac{J_{2n}}{(2n)!} n\kappa \frac{\partial^{2n-1}\psi}{\partial\rho^{2n-1}} \equiv F. \end{aligned} \quad (21)$$

But since $\partial\psi/\partial\rho \equiv \chi$ is a solution to the homogeneous equation $L\chi = 0$, a necessary and sufficient condition for the solvability of (21) is the orthogonality of F and χ , i.e., $\int_{-\infty}^{\infty} F\chi d\rho = 0$. One has then the necessary solvability condition

$$\begin{aligned} \int_{-\infty}^{\infty} 2u\chi(\rho)d\rho &= -\xi \sum_{n=1}^M \frac{J_{2n}}{(2n)!} n\kappa \int_{-\infty}^{\infty} \frac{\partial^{2n-1}\phi^0}{\partial\rho^{2n-1}} \chi d\rho \\ &\quad - \frac{v\tau}{\xi} \int_{-\infty}^{\infty} \chi^2 d\rho. \end{aligned} \quad (22)$$

It can be shown that the left-hand side of (22) is $4u|_{\rho=0} + O(\xi^2)$ (details to appear in a subsequent paper). Using the notation defined above, one has, upon integrating by parts $(n-1)$ times and using the boundary conditions (10), the result

$$-4u = \xi \sum_{n=1}^M (-1)^{n-1} n ||\psi_n|| \kappa - \frac{v\tau}{\xi} ||\psi_1||. \quad (23)$$

Using the identity (18) for the interfacial tension and the fact that the change in entropy Δs between the two phases is four for this free energy, one obtains the following extension of the Gibbs-Thompson relation:

$$\Delta su = -\sigma\kappa - \frac{v\tau}{\xi} ||\psi_1||. \quad (24)$$

This has the same form as the relation derived from the second-order equation [$M=1$ in (7)] which has been made rigorous in that context under various equilibrium conditions.^{3,8,9,11,12} The main difference is that ϕ^0 is now a solution to a more complicated equation comprising more detailed information about the interface. Similar remarks apply to the interfacial tension σ .

An important manifestation of the inner structure of the interface is in the question of anisotropy. Retaining the $2M$ and lower-order derivatives in Eq. (7) means that the $2M$ -form (and lower) anisotropy is incorporated into the coefficients $b(2n; p_1, \dots, p_d)$ ($n=1, \dots, M$). The thickness of the interface and the interfacial tension are modified accordingly in these directions. Anisotropy which is greater than $2M$ -form is averaged by these coefficients. For example, a snowflake with sixfold symmetry would be described best by a sixth-order equation ($M=3$) and partially by a fourth-order equation ($M=2$). In the second-order equation ($M=1$), the anisotropy would be “washed out” entirely for the usual symmetric snowflake.

We illustrate these ideas explicitly with the sixth-order equation in two dimensions. In this case, Eq. (7) can be

written in polar coordinates as

$$\begin{aligned} \tau\phi_i &= C_6 \left[(1+d_1)\phi_{6\rho} + \xi \left(\frac{6+d_2}{r} \right) \phi_{5\rho} + \xi \frac{d_3}{r} \phi_{5\rho,\theta} \right] \\ &\quad \times C_4 \left[(1+a_1)\phi_{4\rho} + \xi \left(\frac{4+a_2}{r} \right) \phi_{3\rho} + \xi \frac{a_3}{r} \phi_{3\rho,\theta} \right] \\ &\quad + C_2 \left[\phi_{2\rho} + \frac{\xi}{r} \phi_\rho \right] - G'(\phi) + 2u + O(\xi^2), \end{aligned} \quad (25)$$

where the C_i positive constants are independent of θ and $\phi_{5\rho,\theta}$ denotes $\partial^5\phi/\partial\theta\partial\rho^5$, etc. The coefficients a_i, d_i (as well as the C_i) are calculated from (6) with the result

$$\begin{aligned} d_1(\theta) &\equiv \sin^2\theta \cos^2\theta, \\ d_1(\theta) &\equiv \sin^6\theta = -2\sin^2\theta \cos^2\theta + \cos^6\theta, \\ d_3(\theta) &\equiv 2\sin\theta \cos\theta (\cos^4\theta - \sin^4\theta), \\ a_1(\theta) &\equiv d_1(\theta), \\ a_2(\theta) &\equiv \sin^4\theta - 4\sin^2\theta \cos^2\theta + \cos^4\theta, \\ a_3(\theta) &\equiv 2\sin\theta \cos\theta (\cos^2\theta - \sin^2\theta). \end{aligned} \quad (26)$$

The $O(1)$ equation with solution $\psi(\rho, \theta)$ is given by

$$O = C_6(1+d_1)\psi_{6\rho} + C_4(1+a_1)\psi_{4\rho} + C_2\psi_{2\rho} + G'(\phi^0). \quad (27)$$

Employing the reasoning which led to (23) we see that a solution of the form $\phi = \psi + \xi\phi^1$ is possible only if $\xi\phi^1$ solves

$$\begin{aligned} L\phi^1 &\equiv C_6(1+d_1)\phi_{6\rho}^1 + C_4(1+a_1)\phi_{4\rho}^1 + C_2\phi_{2\rho}^1 - G''(\phi^0)\phi^1 \\ &= \frac{-2u}{\xi} - \frac{C_2}{r} \psi_\rho - \frac{(4+a_2)}{r} \psi_{3\rho} - \frac{a_3}{r} \psi_{3\rho,\theta} \\ &\quad - \frac{(6+d_2)}{r} \psi_{5\rho} - \frac{d_3}{r} \psi_{5\rho,\theta} \equiv F. \end{aligned} \quad (28)$$

Once again, $\partial\psi/\partial\rho$ solves the homogeneous equation for (23), and so the solvability condition $\int_{-\infty}^{\infty} F\partial\psi/\partial\rho d\rho = 0$ implies the interfacial temperature condition

$$\begin{aligned} -\frac{\Delta su}{\kappa} &= C_2 ||\psi_1|| \\ &\quad + C_4 \left[-(4+a_2) ||\psi_2|| - \frac{a_3}{2} \frac{d}{2\theta} ||\psi_2|| \right] \\ &\quad + C_6 \left[(6+d_2) ||\psi_3|| + \frac{d_3}{2} \frac{d}{d\theta} ||\psi_3|| \right]. \end{aligned} \quad (29)$$

Thus the question of evaluating the temperature at the interface is reduced to solving the sixth-order ordinary differential equation (27) for any orientation angle θ . Given a particular set of principal curvatures and temperature of a point on the interface, Eq. (29) then determines the normal velocity of the interface. More detailed anisotropy and higher dimensions may be considered using the same methods.

A physical interpretation of the phenomenon exhibited by (29) is that anisotropy in $J(x)$ is inherited by the correlation length, which is proportional to ξ in the isotropic case. The anisotropy in the correlation length is mani-

fested in the interfacial tension and width. In an appropriate limit in which these quantities vanish and the interface becomes sharp (i.e., $\xi \rightarrow 0$) this anisotropy must also disappear. This, of course, is the Stefan problem limit which consists of the physics of heat diffusion in both phases along with the latent heat of fusion at a sharp interface on which $u = 0$ by definition. The nature of the double-well potential $G(\phi)$ plays a part in this limit since it is a measure of the extent to which the material prefers to be in a distinct phase. In fact, the $\delta(\phi^2 - 1)$ limit of $G(\phi)$ is analogous to the Ising limit of the ϕ^4 model.^{15,16} If we write, for example, $G(\phi) \equiv aH(\phi)$, where a is a small parameter, then one obtains a relation analogous to (23) in which ξ is replaced by $\xi a^{1/n}$ in the sum and u by au . Assuming τ to be proportional³ to ξ^2 , the coefficient of $|\psi_1|$ is $(-a^{1/2}v\tau)/\xi$. If ξ and a approach zero with $\xi a^{1/n-1} \rightarrow 0$ then the relation (23) approaches $u = 0$ which is the Stefan limit. It is evident, formally, that in

this limit the interface approaches zero thickness and that one attains the heat diffusion equation on both sides of the interface. The latent heat, or Stefan condition, is also obtained from (8). The situation is analogous for any of the anisotropic cases, thus indicating that this type of anisotropy is a direct consequence of the orientation dependence of the correlation length and interfacial thickness.

Finally, we note that a number of mathematical assumptions have been made in the formal derivations which lead to (23) and (29). Unlike the second-order equations these derivations have not yet been made rigorous. In fact, the existence of solutions to (13) for small ξ is itself a non-trivial problem. The lack of a maximum principle for equations greater than second order is a central difficulty.

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