

The Role of Microscopic Anisotropy in the Macroscopic Behavior of a Phase Boundary

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A Landau–Ginzburg approach is implemented to study the influence microscopic anisotropy on the interfacial boundary between two phases. The continuum limit for a lattice spin system with anisotropic interactions J_i and spacing a_i leads to the system of equations $\tau(\partial\phi/\partial t) = \sum_{i=1}^d \xi_i^2(\partial^2\phi/\partial x_i^2) + \frac{1}{2}(\phi - \phi^3) + 2u$, $\partial u/\partial t + (l/2)(\partial\phi/\partial t) = K\Delta u$. Here, ϕ is an order parameter, u is the temperature, τ is a relaxation time, ξ_i are related to J_i and a_i , l is the latent heat of fusion, and K is the diffusivity. Both equilibrium and non-equilibrium conditions are considered. A modified Gibbs–Thompson relation $\Delta s u(r, \theta) = -[\sigma(\theta) + \sigma''(\theta)] \kappa - \tau v \sigma(\theta) / \xi_A^2(\theta) + \mathcal{O}(\xi^2)$ is obtained, where s is entropy density, κ is curvature, v is normal velocity of the interface, and $\xi_A(\theta)$ is a measure of the thickness of the interface. © 1986 Academic Press, Inc.

1. INTRODUCTION

In this paper we study the influence of anisotropy on the interface between two phases of a material. This is a subject which has been studied in various contexts including the Wulff construction approach [1–13]. The questions we address here are the following: (i) How is the anisotropy in the molecular structure communicated to the macroscopic behavior of the interface? (ii) What is the relationship between the anisotropy of the material and other parameters (to be defined below) such as supercooling, surface tension, correlation length, relaxation time, curvature, and velocity of the interface?

Beginning with an anisotropic lattice spin system, we derive the continuum limit, and show that a mean field treatment (using a Landau–Ginzburg approximation) leads to a set of equations [14–24] for the temperature u and the phase of order parameter ϕ . A formal asymptotic analysis then suggests a modified Gibbs–Thompson relation (in two dimensions),

$$\Delta s u(r, \theta) = -[\sigma(\theta) + \sigma''(\theta)] \kappa(r, \theta) - \frac{\tau}{\xi_A^2(\theta)} v \sigma(\theta) + \mathcal{O}(\xi^2) \quad (1.1)$$

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where u has been scaled so that $u = 0$ is the equilibrium melting temperature. Here θ is the angle between the x axis and the normal to the interface, $\sigma(\theta)$ is the angle dependent surface tension, κ is the curvature, Δs is the change in entropy density difference between liquid and solid, ξ is a correlation length, τ is a relaxation time, v is the normal velocity of the interface [$v \equiv \pm |v|$, positive toward the liquid], and $\xi_A(\theta)$ is a measure of the thickness of the interface which is defined by (3.9). The relaxation time, τ , is assumed to be either a constant or a function of orientation angle, $\tau(\theta)$.

The basic ideas are identical for higher dimensions, with the main differences arising from the generalization of the curvature and the derivatives with respect to angle.

This approach to anisotropy has a number of advantages. First, it provides a clear connection between anisotropy of the microscopic and macroscopic levels. Second, it unifies the study of anisotropy in equilibrium and nonequilibrium. Thus, it is evident that the anisotropy in surface tension is always a factor whose importance depends on the magnitude of ξ , while the competitive importance of curvature and velocity depend strongly on the ratio τ/ξ^2 . Further development of these ideas may lead to a better understanding of the role of velocity in crystal growth.

On the other hand the basic limitation of this approach is that one must study higher order differential equations in order to retain more detailed anisotropy of the original lattice system. For example, in two dimensions, anisotropy along the two orthogonal directions leads to precisely the known equilibrium result. However, any anisotropy along the diagonals of a cubic lattice would be annihilated unless one retained the fourth order in wave numbers corresponding to fourth-order derivatives in the differential equation.

2. DERIVATION OF THE ANISOTROPIC LANDAU-GINZBURG HAMILTONIAN

We define a (Bravais) *lattice*, \mathcal{L} , in d -dimensional Euclidean space as an infinite set of points, or "sites," in a translationally invariant array, specified by the *lattice vectors*

$$\mathbf{R} = \sum_{j=1}^d n_j \mathbf{a}_j \quad (2.1)$$

where $\{\mathbf{a}_j\}$ ($j = 1, 2, \dots, d$) are a set of linearly independent (primitive) vectors and $\{n_j\} \in \mathbb{Z}^d$ are the indexing integer vectors.

The *reciprocal lattice* (in the terminology of solid state physics, e. g., p. 64 of [25]) corresponding to \mathcal{L} is defined as the set and vectors $\mathbf{K} \in \mathbb{R}^d$ such that

$$e^{i\mathbf{K} \cdot \mathbf{R}} = 1 \quad \text{for all } \mathbf{R} \in \mathcal{L}. \quad (2.2)$$

The reciprocal lattice is also a Bravais lattice (p. 86 of [25]). Hence, any \mathbf{K} in the reciprocal lattice may be expressed as

$$\mathbf{K} = \sum_{j=1}^d m_j \mathbf{b}_j \quad (2.3)$$

for some $\{m_j\} \in \mathbb{Z}^d$, $\mathbf{b}_j \in \mathbb{R}^d$. One can construct the \mathbf{b}_j from the a_j , e. g., for $d=3$ one has

$$\begin{aligned} \mathbf{b}_1 &= \frac{2\pi a_2 \times a_3}{a_1 \cdot (a_2 \times a_3)}; \\ \mathbf{b}_2 &= \frac{2\pi a_3 \times a_1}{a_1 \cdot (a_2 \times a_3)}; \\ \mathbf{b}_3 &= \frac{2\pi a_1 \times a_2}{a_1 \cdot (a_2 \times a_3)}, \end{aligned} \quad (2.4)$$

which have the property

$$b_i \cdot a_j = 2\pi \delta_{ij} \quad (2.5)$$

where δ_{ij} is the Kronecker delta function. The identity (2.5) implies for any R in the lattice and K in the reciprocal lattice,

$$\mathbf{K} \cdot \mathbf{R} = 2\pi \sum_{j=1}^d m_j n_j. \quad (2.6)$$

Given a lattice, \mathcal{L} , we define a finite subset of called the *lattice domain*, $\mathcal{L}_{N_1, \dots, N_d}$, as the set of vectors $\mathbf{x} \in \mathcal{L}$ such that

$$\mathbf{x} = \sum_{j=1}^d n_j \mathbf{a}_j, \quad |n_j| \leq N_j, \quad N_j = \text{positive integer}. \quad (2.7)$$

We will abbreviate $\mathcal{L}_{N_1, \dots, N_d}$ by \mathcal{L}_N , [$N \equiv \prod_{j=1}^d (2N_j + 1)$]. The boundary of a lattice domain will be denoted by ∂_N . The dual lattice domain, $\mathcal{L}_{N_1, \dots, N_d}^*$ or \mathcal{L}_N^* , is defined as the set of (wave) vectors $\mathbf{q} \in \mathbb{R}^d$ such that

$$\mathbf{q} = \sum_{j=1}^d \frac{m_j \mathbf{b}_j}{2N_j + 1}, \quad |m_j| \leq N_j \quad (2.8)$$

and \mathbf{b}_j are the vectors defined in (2.3) [i.e., the primitive vectors of the reciprocal lattice]. Thus, for three dimensions, given the primitive vectors \mathbf{a}_j , the dual lattice domain is specified upon substitution of (2.4) into (2.8). For any $\mathbf{x} \in \mathcal{L}_N$, $\mathbf{q} \in \mathcal{L}_N^*$ one has the relation:

$$\mathbf{x} \cdot \mathbf{q} = 2\pi \sum_{j=1}^d \frac{m_j n_j}{2N_j + 1}, \quad |m_j| \leq N_j, \quad |n_j| \leq N_j. \quad (2.9)$$

The basic property we need is

PROPOSITION 2.1. *For any $x \in \mathcal{L}_N$, one has the identity*

$$\sum_{q \in \mathcal{L}_N^*} e^{iq \cdot x} = N\delta(x). \quad (2.10)$$

Proof. For $x=0$ the result is clear. If $x \neq 0$, then at least one of the n_j , say n_α , in (2.7) is nonzero. Using (2.9) one obtains

$$\begin{aligned} \sum_{q \in \mathcal{L}_N^*} e^{iq \cdot x} &= \sum_{\substack{m_1, \dots, m_d \\ |m_j| \leq N_j}} \exp i \left[\frac{2\pi m_1 n_1}{2N_1 + 1} + \dots + \frac{2\pi m_d n_d}{2N_d + 1} \right] \\ &= \sum_{m_j \neq m_\alpha, j \neq \alpha} \prod e^{i(2\pi m_j n_j / (2N_j + 1))} \sum_{m_\alpha = -N_\alpha}^{N_\alpha} e^{i(2\pi m_\alpha n_\alpha / (2N_\alpha + 1))}. \end{aligned} \quad (2.11)$$

The last sum is a geometric series which can be written as

$$\begin{aligned} &\sum_{m_\alpha = -N_\alpha}^{N_\alpha} e^{i(2\pi m_\alpha n_\alpha / (2N_\alpha + 1))} \\ &= e^{-i2\pi n_\alpha (N_\alpha / (2N_\alpha + 1))} \frac{1 - e^{i2\pi n_\alpha}}{1 - e^{i2\pi n_\alpha / (2N_\alpha + 1)}}. \end{aligned} \quad (2.12)$$

Since n_α is an integer, the numerator on the right-hand side vanishes, while the denominator remains finite since $|n_\alpha| \leq N_\alpha$.

We note that the lattice geometry can be treated more generally by defining a lattice which labels points which are the corners of translationally invariant *cells* that contain a number of sites. Furthermore, the geometry of the lattice domains may also be treated more generally than that implied by (2.7). Both of these issues are discussed in [26, 27].

An important class of Bravais lattices is the *hyperrectangular lattice*, $\mathcal{L}^{(d)}$, specified by the primitive lattice vectors

$$\mathbf{a}_j = a_j \hat{e}_j, \quad j = 1, \dots, d \quad (2.13)$$

where the $\{\hat{e}_j\}$ are unit vectors in \mathbb{R}^d , and the $\{a_j\}$ are positive real numbers. The lattice domain $\mathcal{L}_{N_1, \dots, N_d} = \mathcal{L}_N^{(d)}$ consists of vectors $\mathbf{x} = (n_1 a_1, \dots, n_d a_d)$ where $|n_j| \leq N_j$, $N = \prod_{j=1}^d (2N_j + 1)$. The dual lattice domain $\mathcal{L}_N^{(d)*}$ then consists of vectors $\mathbf{q} \in \mathbb{R}^d$, specified by

$$\mathbf{q} = \left(\frac{2\pi m_1}{L_1}, \dots, \frac{2\pi m_d}{L_d} \right), \quad L_j \equiv (2N_j + 1) a_j, \quad (2.14)$$

where m_j are integers such that $|m_j| \leq N_j$.

For any lattice \mathcal{L} , we define a set of spin variables, $\phi(\mathbf{x})$, ($\mathbf{x} \in \mathcal{L}$), which will have

values in an appropriate set. The energy level of each configuration $\{\phi(\mathbf{x})\}$ is given by the (reduced) Hamiltonian

$$\bar{\mathcal{H}} \equiv -\beta E = \frac{1}{2}\beta \sum_{\mathbf{x}, \mathbf{x}'} J(\mathbf{x} - \mathbf{x}') \phi(\mathbf{x}) \phi(\mathbf{x}') \quad (2.15)$$

in terms of the interaction or coupling function, $J(x - x')$, where $\beta \equiv 1/k_B T$, $k_B \equiv$ Boltzmann's constant, T is temperature in absolute units, and the summation is over all \mathbf{x} and \mathbf{x}' in a lattice domain \mathcal{L}_N .

The boundary conditions on $\phi(x)$ are the values imposed on $\phi(\mathbf{x})$ for $\mathbf{x} \in \partial\mathcal{L}_N$. We will assume the boundary conditions ensure $|\phi(x)| \leq M$ for some $M > 0$. One may consider other possibilities, such as free boundary conditions, which are attained by summing over boundary spins without additional restrictions, or periodic boundary conditions, attained by identifying the first spin with the $(2N_j + 1)$ the spin in each direction. In general, conditions which ensure the existence of the surface free energy [26, 27] will be more than adequate for our purposes in this section.

If $\phi(\mathbf{x})$ is restricted to the set $\{\pm 1\}$, then (2.15) is an Ising system. Although the Ising model is often stated in the language of magnetic systems, i. e., $\phi(\mathbf{x}) = \pm 1$, the simple transformation, $n(\mathbf{x}) \equiv \frac{1}{2}[\phi(\mathbf{x}) + 1]$, adapts the model to a lattice-gas with $n(\mathbf{x}) \in \{0, 1\}$ as an occupation variable.

A related model is obtained by allowing the spins to vary over all real numbers [$\phi(\mathbf{x}) \in \mathbb{R}$] while imposing a probability measure which maintains a finite internal energy. Incorporating this measure into the Hamiltonian, one may consider

$$\bar{\mathcal{H}} = \frac{1}{2}\beta \sum_{\mathbf{x}, \mathbf{x}'} J(\mathbf{x} - \mathbf{x}') \phi(\mathbf{x}) \phi(\mathbf{x}') - \sum_{\mathbf{x}} w[\phi(\mathbf{x})] \quad (2.16)$$

where w is generally assumed to be an even fourth-order polynomial with extrema at ± 1 . This model, which is often called the ϕ^4 model, converges in an appropriate limit to an Ising model [28–29].

Following the presentation in [30], we introduce the discrete Fourier transforms $\hat{\phi}$ and \hat{J} defined on the dual lattice domain \mathcal{L}_N^* by

$$\begin{aligned} \hat{\phi}(\mathbf{q}) &= \sum_{\mathbf{x} \in \mathcal{L}_N} e^{i\mathbf{q} \cdot \mathbf{x}} \phi(\mathbf{x}); \\ \hat{J}(\mathbf{q}) &= \sum_{\mathbf{x} \in \mathcal{L}_N} e^{-i\mathbf{q} \cdot \mathbf{x}} J(\mathbf{x}). \end{aligned} \quad (2.17)$$

As a consequence of Proposition 2.1, one has the inverse transforms

$$\begin{aligned} \phi(\mathbf{x}) &= N^{-1} \sum_{\mathbf{q} \in \mathcal{L}_N^*} e^{-i\mathbf{q} \cdot \mathbf{x}} \hat{\phi}(\mathbf{q}); \\ J(\mathbf{x}) &= N^{-1} \sum_{\mathbf{q} \in \mathcal{L}_N^*} e^{i\mathbf{q} \cdot \mathbf{x}} \hat{J}(\mathbf{q}). \end{aligned} \quad (2.18)$$

A key idea [30] in the development is to reexpress the interaction term, i. e., the double sum in (2.15) or (2.16), as follows.

PROPOSITION 2.2. *If \mathcal{L}_N is a lattice domain and \mathcal{L}_N^* is the corresponding dual then one has the identity*

$$\sum_{\mathbf{x}, \mathbf{x}' \in \mathcal{L}_N} J(\mathbf{x} - \mathbf{x}') \phi(\mathbf{x}) \phi(\mathbf{x}') = N^{-1} \cdot \sum_{\mathbf{q} \in \mathcal{L}_N^*} \hat{J}(\mathbf{q}) \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q}). \tag{2.19}$$

Proof. Using definitions (2.17) in the right-hand side of (2.19) one obtains

$$\begin{aligned} \sum_{\mathbf{q}} \hat{J}(\mathbf{q}) \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q}) &= \sum_{\mathbf{x}, \mathbf{x}', \mathbf{x}''} \left\{ \sum_{\mathbf{q}} e^{-i\mathbf{q} \cdot (\mathbf{x} - \mathbf{x}' + \mathbf{x}'')} \right\} J(\mathbf{x}) \phi(\mathbf{x}') \phi(\mathbf{x}'') \\ &= \sum_{\mathbf{x}, \mathbf{x}', \mathbf{x}''} N \delta(\mathbf{x} - \mathbf{x}' + \mathbf{x}'') J(\mathbf{x}) \phi(\mathbf{x}') \phi(\mathbf{x}'') \\ &= \sum_{\mathbf{x}', \mathbf{x}''} J(\mathbf{x}'' - \mathbf{x}') \phi(\mathbf{x}') \phi(\mathbf{x}'') \end{aligned} \tag{2.20}$$

upon using Proposition 2.1 in the second equality.

We now proceed with the derivation for a Hamiltonian which may be anisotropic. To simplify the analysis we specialize to hyperrectangular lattices defined by (2.13). The general case may be treated similarly; the main difference is in the definition of the discretized derivatives defined below, and in taking the “continuum limit.”

We define the “discretized derivative” in the j th direction by

$$D_j f(x) \equiv \frac{f(x + a_j) - f(x)}{a_j}. \tag{2.21}$$

We shall use the notation $g(t) = \mathcal{O}(t^p)$ to indicate that for some positive constants t_0 and c , one has

$$|g(t)| \leq c|t|^p \quad \text{if } |t| \leq t_0. \tag{2.22}$$

The discretized derivative for $e^{i\mathbf{q} \cdot \mathbf{x}}$ is

$$D_j e^{i\mathbf{q} \cdot \mathbf{x}} = \frac{e^{i\mathbf{q} \cdot \mathbf{x}}}{a_j} [e^{i\mathbf{q} \cdot \mathbf{a}_j} - 1] = i q_j e^{i\mathbf{q} \cdot \mathbf{x}} + \mathcal{O}(q_j^2 a_j). \tag{2.23}$$

PROPOSITION 2.3. *For the hyperrectangular lattice domain $\mathcal{L}_N^{(d)}$ and its dual $\mathcal{L}_N^{(d)*}$, one has the identities*

$$(i) \quad N^{-1} \sum_{\mathbf{q} \in \mathcal{L}_N^{(d)*}} \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q}) = \sum_{x \in \mathcal{L}_N^{(d)}} [\phi(x)]^2; \tag{2.24}$$

$$\begin{aligned}
(ii) \quad & N^{-1} \sum_{\mathbf{q} \in \mathcal{L}_N^{(d)*}} q_j^2 \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q}) \\
& = \sum_{x \in \mathcal{L}_N^{(d)}} [D_j \phi(x)]^2 + \mathcal{O} \left[N^{-1} a_j \sum_{\mathbf{q}} \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q}) q_j^3 \right] \\
& \quad + \mathcal{O} \left(N_j^{-1} \left| \sum_x D_j \phi(x) \right| \right). \tag{2.25}
\end{aligned}$$

Proof. Identity (2.24) follows from the definition (2.17) and Proposition 2.1. Rewriting the left-hand side of (2.25) we have

$$N^{-1} \sum_{\mathbf{q}} q_j^2 \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q}) = N^{-1} \sum_{q_k (k \neq j)} \sum_{q_j} q_j^2 \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q}). \tag{2.26}$$

The inner sum can be written, using (2.17) and (2.23), as

$$N^{-1} \sum_{q_j} q_j^2 \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q}) = N^{-1} \sum_{q_j} \sum_{\mathbf{x}} q_j e^{i\mathbf{q} \cdot \mathbf{x}} \phi(\mathbf{x}) \sum_{\mathbf{x}'} q_j e^{-i\mathbf{q} \cdot \mathbf{x}'} \phi(\mathbf{x}') \tag{2.27}$$

$$\begin{aligned}
& = N^{-1} \sum_{q_j} \sum_{\mathbf{x}} [D_j e^{i\mathbf{q} \cdot \mathbf{x}} + \mathcal{O}(q_j^2 a_j) e^{i\mathbf{q} \cdot \mathbf{x}}] \phi(\mathbf{x}) \\
& \quad \times \sum_{\mathbf{x}'} [D_j' e^{-i\mathbf{q} \cdot \mathbf{x}'} + \mathcal{O}(q_j^2 a_j) e^{-i\mathbf{q} \cdot \mathbf{x}'}] \phi(\mathbf{x}'). \tag{2.28}
\end{aligned}$$

We use (2.23) again for the $\mathcal{O}(q_j^2 a_j)$ terms

$$\begin{aligned}
& N^{-1} \sum_{\mathbf{q}} \sum_{\mathbf{x}} \mathcal{O}(q_j^2 a_j) e^{i\mathbf{q} \cdot \mathbf{x}} \phi(\mathbf{x}) \sum_{\mathbf{x}'} q_j e^{-i\mathbf{q} \cdot \mathbf{x}'} \phi(\mathbf{x}') \\
& = N^{-1} a_j \sum_{\mathbf{q}} \mathcal{O}(q_j^2) q_j \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q}). \tag{2.29}
\end{aligned}$$

Next, we implement “discrete integration by parts” on the leading order terms using the identity,

$$\begin{aligned}
\sum_{n=-M}^M [f(n+1)g(n) - f(n)g(n)] & = - \sum_{n=-M}^M [f(n+1)g(n+1) - f(n+1)g(n)] \\
& \quad + [f(M+1)g(M+1) - f(-M)g(-M)]
\end{aligned}$$

which implies

$$\begin{aligned}
& \left| N^{-1} \sum_{\mathbf{x}} (D_j e^{i\mathbf{q} \cdot \mathbf{x}}) \phi(\mathbf{x}) + N^{-1} \sum_{\mathbf{x}} e^{i\mathbf{q} \cdot (\mathbf{x} + \mathbf{a}_j)} D_j \phi(\mathbf{x}) \right| \\
& \leq \sup_{\mathbf{x} \in \mathcal{L}_N^{(d)}} |\phi(\mathbf{x})| \frac{1}{2N_j + 1}. \tag{2.31}
\end{aligned}$$

Using a similar bound for the sum over x' and then summing over $q \in \mathcal{L}_N^{(d)*}$, one obtains (2.25).

To proceed further we list two conditions on $J(\mathbf{x})$ for arbitrary \mathcal{L} which will be used in discussing $\hat{J}(\mathbf{q})$:

A. Reflection through the origin. For any $x \in \mathcal{L}$, one has

$$J(\mathbf{x}) = J(-\mathbf{x}).$$

B. Reflection through an axis. If $\mathbf{x} = \sum_{j=1}^d n_j \mathbf{a}_j$ and $\mathbf{x}' = \sum_{j=1}^d n'_j \mathbf{a}_j$, where for some k_0 ,

$$n'_j = \begin{cases} n_j, & j \neq k_0, \\ -n_j, & j = k_0, \end{cases} \tag{2.32}$$

then one has

$$J(\mathbf{x}) = J(\mathbf{x}'). \tag{2.33}$$

The basic Landau–Ginzburg approximation [30–32] consists of formally expanding the Fourier transform, $J(q)$, of the interaction function as follows:

$$\begin{aligned} \hat{J}(\mathbf{q}) = \sum_{\mathbf{x} \in \mathcal{L}_N} J(\mathbf{x}) e^{-i\mathbf{q} \cdot \mathbf{x}} &= \sum_{\mathbf{x}} J(\mathbf{x}) - i \sum_{\mathbf{x}} \mathbf{q} \cdot \mathbf{x} J(\mathbf{x}) \\ &\quad - \frac{1}{2} \sum_{\mathbf{x}} (\mathbf{q} \cdot \mathbf{x})^2 J(\mathbf{x}) + \dots \end{aligned} \tag{2.34}$$

The second term vanishes if condition A is valid (as do all odd terms). If condition B (which implies A) is valid then the cross terms in $(\mathbf{q} \cdot \mathbf{x})^2$ will cancel as a consequence of (2.9). For the hyperrectangular lattice domain, we summarize the result as

PROPOSITION 2.4. *If $J(\mathbf{x})$ is an interaction function defined on $\mathcal{L}_N^{(d)}$ and satisfies conditions A and B then*

$$\hat{J}(q) = \hat{J}(0) - \frac{1}{2} \sum_{\mathbf{x}} J(\mathbf{x}) [q_1^2 x_1^2 + \dots + q_d^2 x_d^2] + \mathcal{O}(|q|^4) \tag{2.35}$$

with $\hat{J}(0) \equiv \sum_{\mathbf{x}} J(\mathbf{x})$.

We consider two important special cases of $J(\mathbf{x})$.

Case I. Isotropic nearest-neighbor model. We assume the hypercubic lattice $\mathcal{L}_N^{(d)}$ with $a_j \equiv a$ in (2.13). The interaction function

$$\begin{aligned} J(\mathbf{x}) &= J && \text{if } |\mathbf{x}| = a \\ &= 0 && \text{otherwise} \end{aligned} \tag{2.36}$$

then has the Fourier transform

$$\hat{J}(\mathbf{q}) = 2dJ - a^2 J^2 |\mathbf{q}|^2 + \mathcal{O}(|\mathbf{q}|^4). \quad (2.37)$$

This means that the interaction part of the Hamiltonian may be expressed through Proposition 2.2 as

$$\begin{aligned} & \frac{1}{2} \sum_{\mathbf{x}, \mathbf{x}'} J(\mathbf{x} - \mathbf{x}') \phi(\mathbf{x}) \phi(\mathbf{x}') \\ &= \frac{1}{2N} \sum_{\mathbf{q}} J(\mathbf{q}) \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q}) \\ &= \frac{1}{2N} \sum_{\mathbf{q}} \{2dJ - a^2 J \mathbf{q} \cdot \mathbf{q}\} \phi(\mathbf{q}) \hat{\phi}(-\mathbf{q}) + \mathcal{O} \left[\sum_{\mathbf{q}} |\mathbf{q}|^4 \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q}) \right] \quad (2.38) \\ &= dJ \sum_{\mathbf{x}} [\phi(\mathbf{x})]^2 - \frac{a^2 J}{2} \sum_{\mathbf{x}} \sum_{j=1}^d [D_j \phi(\mathbf{x})]^2 \\ & \quad + \mathcal{O} \left[\sum_{\mathbf{q}} |\mathbf{q}|^4 \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q}) \right] + \left[N^{1/d} \sum_{\mathbf{x}} D_j \phi(\mathbf{x}) \right] \quad (2.39) \end{aligned}$$

using Proposition 2.3.

Case II. Anisotropic nearest-neighbor model. Now consider the general lattice $\mathcal{L}_N^{(d)}$ with

$$\begin{aligned} J(\mathbf{x}) &= J_i & \text{if } |\mathbf{x}| = |\mathbf{a}_i|, \quad i = 1, \dots, d. \\ &= 0 & \text{otherwise.} \end{aligned} \quad (2.40)$$

Using Proposition 2.4 in this case, we obtain

$$J(q) = 2 \sum_{i=1}^d J_i - \frac{1}{2} \sum_{i=1}^d J_i a_i^2 q_i^2 + \mathcal{O}(|\mathbf{q}|^4). \quad (2.41)$$

Hence, Propositions 2.2 and 2.3 imply

$$\begin{aligned} & \frac{1}{2} \sum_{\mathbf{x}, \mathbf{x}'} J(\mathbf{x} - \mathbf{x}') \phi(\mathbf{x}) \phi(\mathbf{x}') \\ &= d\bar{J} \sum_{\mathbf{x}} [\phi(\mathbf{x})]^2 - \frac{1}{2} \sum_{\mathbf{x}} \sum_{j=1}^d a_j^2 J_j [D_j \phi(\mathbf{x})]^2 + (\text{higher order}) \quad (2.42) \end{aligned}$$

where the higher order terms are the same as in (2.39), and $d\bar{J} = \sum_1^d J_i$.

For this anisotropic case, the Hamiltonian (2.16) is

$$\begin{aligned} \bar{\mathcal{H}} = & \frac{\beta}{2} \sum_{x \in \mathcal{L}_N^{(d)}} \sum_{j=1}^d a_j^2 J_j [D_j \phi(\mathbf{x})]^2 - \beta d \bar{J} \sum_{x \in \mathcal{L}_N^{(d)}} [\phi(\mathbf{x})]^2 \\ & - \sum_{x \in \mathcal{L}_N^{(d)}} w[\phi(\mathbf{x})] + (\text{higher order}) \end{aligned} \tag{2.43}$$

where the higher order terms are listed in (2.39). We note that the $\mathcal{O}[\sum_{\mathbf{q}} |\mathbf{q}|^4 \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q})]$ term is representative for the entire sum of similar terms with $|\mathbf{q}|^{2k}$ ($k \geq 2$) replacing $|\mathbf{q}|^4$.

In the regime where this approximation is valid, we consider the ‘‘continuum limit,’’ i. e., the limit as $N \rightarrow \infty$ with other parameters scaled in a meaningful way. For the hyperrectangular lattice we adjust the a_i so that the volume of the lattice domain is constant, i. e., for some fixed set of $\{C_j\}_{j=1, \dots, d}$:

$$N_j |a_j| = C_j. \tag{2.44}$$

To ensure boundedness of the ground state energy, we scale the interaction function $J(x)$ (which we assume positive) so that

$$\sum_{\mathbf{x}} J(\mathbf{x}) = C_0 \tag{2.45}$$

for some constant C_0 which is independent of N .

Let $\bar{\mathcal{H}}_N$ be the Hamiltonian for the hyperrectangular domain $\mathcal{L}_N^{(d)}$, given by (2.16), in the anisotropic case (given by (2.40)). If the error terms expressed in (2.39) or (2.41) are neglected and the continuum limit $N \rightarrow \infty$ is taken in accordance with (2.44), (2.45) then $\lim_{N \rightarrow \infty} \bar{\mathcal{H}}_N = \bar{\mathcal{H}}_{\text{cont}}$ where

$$\bar{\mathcal{H}}_{\text{cont}} = \int d\mathbf{x} \left\{ \sum_{i=1}^d \frac{\xi_i^2}{2} \left(\frac{\partial \phi(x)}{\partial x_i} \right)^2 - d \bar{J} [\phi(\mathbf{x})]^2 - w[\phi(\mathbf{x})] \right\} \tag{2.46}$$

and the $\{\xi_i\}$ depend on $\{J_i\}$, $\{C_i\}$, and $\{a_i\}$, and are a measure of the correlation lengths in the respective directions.

Combining the $\phi^2(\mathbf{x})$ term with the $w[\phi(\mathbf{x})]$ into the prototype double-well potential

$$w[\phi(\mathbf{x})] = \frac{1}{8} [\phi^2(\mathbf{x}) - 1]^2 \tag{2.47}$$

and adding a term $-2u\phi(\mathbf{x})$ which is the temperature multiplied by entropy change, we obtain the free energy (with the subscripts denoting partial derivatives):

$$\begin{aligned} \mathcal{F}[\mathbf{x}, \phi(\mathbf{x}), \phi_{x_1}(\mathbf{x}), \dots, \phi_{x_d}(\mathbf{x})] = & \int d\mathbf{x} F[\mathbf{x}, \phi(\mathbf{x}), \phi_{x_1}(\mathbf{x}), \dots, \phi_{x_d}(\mathbf{x})]. \\ F = & \sum_{i=1}^d \left[\frac{\xi_i^2}{2} \left(\frac{\partial \phi(x)}{\partial x_i} \right)^2 + \frac{1}{8} [\phi(\mathbf{x})^2 - 1]^2 - 2u\phi(\mathbf{x}) \right]. \end{aligned} \tag{2.48}$$

3. AN ANISOTROPIC PHASE FIELD MODEL AND A FORMAL ASYMPTOTIC ANALYSIS

The free energy given by (2.48) is now a function of a single variable, $\phi(\mathbf{x})$, whose domain is a subset $\Omega \subset \mathbb{R}^d$. Thus, the spins on the lattice have been replaced by a continuum variable. From the nature of (2.48) it is clear that for small values of u , $\phi(x)$ near ± 1 are preferred equilibrium values, while very large values of $|\phi(x)|$ correspond to high energy levels and are consequently excluded on a probabilistic basis in the free energy functional, which has a weighting $e^{-\mathcal{F}}$. The variable $\phi(x)$ may now be regarded as a phase variable or order parameter. Recalling the simple shift by a constant which transforms the magnetism language to lattice gas language (see comments preceding (2.16)), we may regard $\phi = +1$ as the liquid phase while $\phi = -1$ is the solid phase.

The next physical ansatz entails the assumption, common to mean field theories (e. g., see pp. 1070–1072 of [30]), that in equilibrium, the function $\phi(\mathbf{x})$ will be an extremum of \mathcal{F} . In particular, if $\phi(\mathbf{x})$ is perturbed by a smooth function $\eta(\mathbf{x})$, i. e., $\phi(\mathbf{x}) \rightarrow \phi(\mathbf{x}) + \varepsilon\eta(\mathbf{x})$, which vanishes on the boundary, $\partial\Omega$, then differentiating with respect to ε , one has

$$\frac{d\mathcal{F}}{d\varepsilon} = \int dx \left\{ \frac{\partial}{\partial\phi} \eta + \frac{\partial}{\partial\phi_{x_1}} \eta_{x_1} + \cdots + \frac{\partial}{\partial\phi_{x_d}} \eta_{x_d} \right\} = 0. \quad (3.1)$$

Using Gauss' theorem with $\mathbf{f}_i \equiv \partial\mathcal{F}/\partial\phi_{x_i}$, i. e.,

$$\int \eta \nabla \cdot \mathbf{f} \, dx + \int \mathbf{f} \cdot \nabla \eta \, dx = \int \nabla \cdot (\eta \mathbf{f}) \, dx = \int (\eta \mathbf{f})_n \, d\sigma = 0$$

where the last integral $\int d\sigma$ is over the boundary $\partial\Omega$ and $(\eta \mathbf{f})_n$ is the normal component to the boundary, we obtain

$$0 = \int d\mathbf{x} \left\{ \frac{\partial}{\partial\phi} - \frac{\partial}{\partial x_1} \frac{\partial}{\partial\phi_{x_1}} - \cdots - \frac{\partial}{\partial x_d} \frac{\partial}{\partial\phi_{x_d}} \right\} \eta \quad (3.2)$$

for all smooth η which vanish on the boundary. Thus, in equilibrium one has the phase field equation:

$$0 = \sum_{i=1}^d \xi_i^2 \frac{\partial^2 \phi(\mathbf{x})}{\partial x_i^2} + \frac{1}{2} [\phi(\mathbf{x}) - \phi(\mathbf{x})^3] + 2u(\mathbf{x}). \quad (3.3)$$

If the system is not in equilibrium, one may modify (3.1) and (3.3) by introducing [16, 17] a relaxation time, τ , and using the Landau–Ginzburg Model A equation (symbolically written $\tau\phi_t = \delta\mathcal{F}/\delta\phi$ [31]):

$$\tau \frac{\partial\phi}{\partial t} = \sum_{i=1}^d \xi_i^2 \frac{\partial^2 \phi}{\partial x_i^2} + \frac{1}{2} (\phi - \phi^3) + 2u. \quad (3.4)$$

As discussed in [16], the phase field must also satisfy the heat equation

$$\frac{\partial u}{\partial t} + \frac{1}{2} \frac{\partial \phi}{\partial t} = K \Lambda u. \tag{3.5}$$

Thus, if ϕ is near +1 and $u = T - T_M$ is negative then the material is said to be supercooled.

Mathematically, the coupled nonlinear parabolic system (3.4), (3.5) may be considered subject to initial conditions and suitable boundary conditions, e. g., Dirichlet or Neumann, as in the isotropic case [16, 22]. In equilibrium, (3.5) reduces to Laplace's equation, so that $u(\mathbf{x})$ is determined uniquely by the boundary condition on u .

We consider now the asymptotic solutions (for small ξ) to the equilibrium problem (3.3) with the aim of obtaining a generalized Gibbs–Thompson relation [34, 12, 13, 2, 3, 35, 36]. The methods involved are similar to the isotropic case (see, e. g., [16, 17]) although we do not make the arguments rigorous here. The technique is most easily illustrated in two dimensions although the same analysis can be performed in arbitrary dimension.

We formulate the problem as follows. Let $x = (x, y)$ be in R^2 . If the interaction function $J(\mathbf{x})$ is nearest neighbor anisotropic as in Case II, i. e. (2.40), then our derivation leads to Eq. (3.3) in Ω :

$$\xi^2 \Delta \phi + (\xi_1^2 - \xi^2) \phi_{xx} + \frac{1}{2}(\phi - \phi^3) + 2u = 0 \tag{3.6}$$

where we assume that the interactions are stronger in the x direction, and $|\xi_1/\xi|$ is bounded as we take ξ, ξ_1 to zero. If the interface is given by

$$\Gamma \equiv \{(x, y) \in R^2: \phi(x, y) = 0\} \tag{3.7}$$

and ξ_1, ξ are small, then we formulate the question: For which functions $u(x, y)$ will the interface Γ be a circle of radius R_0 ?

With polar coordinates

$$x = r \cos \theta, \quad y = r \sin \theta \tag{3.8}$$

and redefined parameters

$$\begin{aligned} \xi_A^2(\theta) &\equiv \xi^2 + (\xi_1^2 - \xi^2) \cos^2 \theta, \\ \xi_B^2(\theta) &\equiv \xi^2 + (\xi_1^2 - \xi^2) \sin^2 \theta \end{aligned} \tag{3.9}$$

Eq. (3.6) transforms to

$$\begin{aligned} \xi_A^2 \frac{\partial^2 \phi}{\partial r^2} + \xi_B^2 \frac{1}{r} \frac{\partial \phi}{\partial r} - 2(\xi_1^2 - \xi^2) \frac{1}{r} \sin \theta \cos \theta \frac{\partial \phi}{\partial r \partial \theta} \\ + \left[\frac{\partial^2 \phi}{\partial \theta^2} \text{ terms} \right] + \frac{1}{2} (\phi - \phi^3) + 2u = 0 \end{aligned} \tag{3.10}$$

The $\partial\phi^2/\partial\theta^2$ terms are formally always $\mathcal{O}(\xi^2)$. Since we know (by assumption) that the function ϕ will cross the axis at R_0 we define

$$\bar{r} = r - R_0, \quad \bar{\rho} = \frac{r - R_0}{\xi_A(\theta)}. \tag{3.11}$$

The first order in the asymptotic analysis consists of matching ‘‘inner’’ and ‘‘outer’’ solutions [16] which are $\mathcal{O}(1)$ solutions with respect to the variables defined in (3.11). In particular, for each θ , one has the solution

$$\phi_0(r, \theta) \equiv \tanh \frac{r - R_0}{2\xi_A(\theta)} \tag{3.12}$$

to the equation

$$\xi_A^2 \frac{\partial^2 \phi_0}{\partial \bar{r}^2} + \frac{1}{2} (\phi_0 - \phi_0^3) = 0. \tag{3.13}$$

Defining ϕ_1 by $\phi \equiv \phi_0 + \xi_A \phi_1$ and subtracting (3.13) from (3.10), we see that ϕ_1 must satisfy

$$\xi_A^2 \frac{\partial^2 \phi_1}{\partial \bar{r}^2} + \frac{1}{2} [1 - 3\phi_0^2] \phi_1 = \frac{1}{\xi_A} G + (\text{higher order terms}) \tag{3.14}$$

$$G(r, \theta) \equiv -2u + 2(\xi_1^2 - \xi^2) \frac{1}{\bar{r} + R_0} \sin \theta \cos \theta \frac{\partial^2 \phi_0}{\partial \theta \partial \bar{r}} - \xi_B^2 \frac{1}{\bar{r} + R_0} \frac{\partial \phi_0}{\partial \bar{r}}$$

where the higher order terms are formally $\mathcal{O}(\xi^2)$ in both the r and ρ variables (i. e., inner and outer solutions). As in the isotropic case, the derivative of the first-order solution is itself a solution to the homogeneous equation obtained from the functional differentiation of (3.13). That is, $\partial\phi_0/\partial r$ solves

$$L\Psi \equiv \xi_A^2 \frac{\partial^2 \Psi}{\partial \bar{r}^2} + \frac{1}{2} [1 - 3\phi_0^2] \Psi = 0. \tag{3.15}$$

Thus, ϕ_1 can be a solution to (3.14) [$L\phi_1 = \xi_A^{-1}G$], if and only if, ϕ_0 is \mathcal{L}_2 orthogonal to G . That is, if we multiply (3.14) by $\partial\phi_0/\partial r$, (3.15) by ϕ_1 , use integration by parts and the boundary conditions, we obtain the necessary and sufficient condition (to leading order)

$$\int_{-\infty}^{\infty} G(r, \theta) \frac{\partial \phi_0}{\partial \bar{r}} d\bar{r} = 0. \tag{3.16}$$

We consider each term in (3.16) separately. The function u must be of order ξ for R_0 to be $\mathcal{O}(1)$. Hence, we may assume $u = \xi\bar{u}$ where \bar{u} is independent of ξ (see

[16, 22] for further discussion). Thus $\partial\bar{u}/\partial\bar{r}$ is bounded independently of ξ , i. e., u varies slowly in comparison with ϕ_0 . Hence,

$$\int_{-\infty}^{\infty} -2u \frac{\partial\phi_0}{\partial\bar{r}} d\bar{r} = -4u + \mathcal{O}(\xi^2) \quad (3.17)$$

the second term in (3.16) is evaluated (in anticipation of its relationship to surface tension) using

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{\partial^2\phi_0}{\partial\theta\partial\bar{r}} \frac{\partial\phi_0}{\partial\bar{r}} d\bar{r} &= \frac{1}{2} \frac{\partial}{\partial\theta} \int_{-\infty}^{\infty} \left(\frac{\partial\phi_0}{\partial\bar{r}} \right)^2 d\bar{r} \\ &= \frac{1}{2} \left[\frac{\partial}{\partial\theta} \frac{1}{2\xi_A(\theta)} \right] \int_{-\infty}^{\infty} \left(\frac{\partial\phi_0}{\partial(\rho/2)} \right)^2 d(\rho/2) \\ &= \frac{1}{2} \left[\left(\frac{\partial}{\partial\theta} \frac{1}{2\xi_A(\theta)} \right) \right] \cdot \frac{2}{3}. \end{aligned} \quad (3.18)$$

The third term is simply

$$\begin{aligned} \int_{-\infty}^{\infty} \left(\frac{\partial\phi_0}{\partial r} \right)^2 dr &= \frac{1}{2\xi_A(\theta)} \int_{-\infty}^{\infty} \frac{\partial\phi_0}{\partial(\rho/2)} d(\rho/2) \\ &= \frac{1}{2\xi_A(\theta)} \frac{2}{3}. \end{aligned} \quad (3.19)$$

Combining (3.16)–(3.19) we have the relation

$$\begin{aligned} 4u &= \left\{ (\xi_1^2 - \xi^2) \sin\theta \cos\theta \frac{\partial}{\partial\theta} \left(\frac{1}{2\xi_A(\theta)} \right) - \frac{\xi_B^2(\theta)}{2\xi_A(\theta)} \right\} \\ &\quad \times \frac{1}{R_0} \int_{-\infty}^{\infty} \left(\frac{\partial\phi_0}{\partial(\rho/2)} \right)^2 d(\rho/2). \end{aligned} \quad (3.20)$$

4. A MODIFIED GIBBS–THOMPSON RELATION FOR AN EQUILIBRIUM SYSTEM WITH ANISOTROPY

In this section we reexpress (3.20) in terms of the surface tension and entropy for this model. The surface tension is defined in general by [16]

$$\sigma \equiv \frac{\mathcal{F}\{\phi\} - (1/2)\mathcal{F}\{\phi_+\} - (1/2)\mathcal{F}\{\phi_-\}}{A} \quad (4.1)$$

where ϕ_{\pm} are the liquid and solid solutions (without an interface) which solve $\frac{1}{2}(\phi - \phi) + 2u = 0$, while ϕ is a solution with an interface as discussed in Section 3. To first order in ξ , we may replace ϕ by ϕ_0 (defined by (3.12)) in $\{\phi\}$. Integrating

across the interface so that $\phi = \text{constant}$, and using integration by parts, we obtain from (3.13)

$$\begin{aligned} \text{Const.} &= \int \left[\xi_A^2 \frac{\partial^2 \phi_0}{\partial \bar{r}^2} + \frac{1}{2} (\phi_0 - \phi_0^3) \right] \frac{\partial \phi_0}{\partial \bar{r}} d\bar{r} + \mathcal{O}(\xi^2) \\ &= \int \left[\xi_A^2 \frac{1}{2} \frac{\partial}{\partial \bar{r}} \left(\frac{\partial \phi_0}{\partial \bar{r}} \right)^2 + \frac{1}{2} (\phi_0 - \phi_0^3) \frac{\partial \phi_0}{\partial \bar{r}} \right] d\bar{r} + \mathcal{O}(\xi^2). \end{aligned} \quad (4.2)$$

The integral may then be evaluated to yield (the constant must be zero)

$$\frac{\xi_A^2}{2} \left(\frac{\partial \phi_0}{\partial \bar{r}} \right)^2 = \frac{1}{8} (\phi_0^2 - 1)^2 + \mathcal{O}(\xi). \quad (4.3)$$

Using (4.3) in $\mathcal{F}\{\phi_0\}$ one has

$$\begin{aligned} \mathcal{F}\{\phi_0\} &= A \int_{-\infty}^{\infty} d\bar{r} \left\{ \frac{\xi_A^2}{2} \left(\frac{\partial \phi_0}{\partial \bar{r}} \right)^2 + \frac{1}{8} (\phi_0^2 - 1)^2 - 2u\phi_0 \right\} + \mathcal{O}(\xi^2) \\ &= A \int_{-\infty}^{\infty} d\bar{r} \left\{ \xi_A^2 \left(\frac{\partial \phi_0}{\partial \bar{r}} \right)^2 - 2u\phi_0 \right\} + \mathcal{O}(\xi^2). \end{aligned} \quad (4.4)$$

Using the argument leading to (3.17) to obtain

$$\int_{-\infty}^{\infty} 2u\phi_0 = \mathcal{O}(\xi^2) \quad (4.5)$$

$$\mathcal{F}\{\phi_+\} + \mathcal{F}\{\phi_-\} = 0 \quad (4.6)$$

on has from the definition of surface tension, (4.1),

$$\begin{aligned} \sigma(\theta) &= \xi_A^2(\theta) \frac{1}{2\xi_A(\theta)} \int_{-\infty}^{\infty} \left(\frac{\partial \phi_0}{\partial \bar{\rho}/2} \right)^2 d\bar{\rho}/2 = \xi_A^2(\theta) \frac{1}{\xi_A(\theta)} \frac{2}{3} \\ &= \frac{\xi_A(\theta)}{\xi} \sigma_{\text{iso}}, \end{aligned} \quad (4.7)$$

where σ_{iso} is the isotropic surface tension (i.e., $\xi_1 = \xi$ and $\sigma_{\text{iso}} = \frac{2}{3}\xi$).

The second derivative with respect to angle is

$$\sigma''(\theta) = \frac{\xi_A''(\theta)}{\xi} \sigma_{\text{iso}} \quad (4.8)$$

$$\begin{aligned} \xi_A''(\theta) &= \frac{-(\xi_1^2 - \xi^2)}{\xi_A(\theta)} [\cos^2 \theta - \sin^2 \theta] \\ &= (\xi_1^2 - \xi^2) \cos \theta \sin \theta \frac{d}{d\theta} \left(\frac{1}{\xi_A(\theta)} \right). \end{aligned} \quad (4.9)$$

Noting that the entropy difference between the pure liquid (ϕ_+) and pure solid (ϕ_-) is 4, we obtain from (3.20), the modified Gibbs–Thompson relation:

$$\Delta s u(r, \theta) = -[\sigma(\theta) + \sigma''(\theta)] \kappa(r, \theta) + \mathcal{O}(\xi^2) \quad \text{on } \Gamma, \quad (4.10)$$

where κ is the curvature. This identity is consistent with classical results based on balance of free energies (e. g., see p. 39 of [10]).

This relation has been obtained as the temperature at the interface of a circle. A local analysis of an arbitrary interface with the same curvature, κ , also leads formally to (4.10). Figure 1 [set $v = 0$] illustrates a typical situation with the curvature at (x_0, y_0) equal to $1/R_0$. We let C_0 be the osculating circle at the point (x_0, y_0) ; i. e., it has the same curvature and normal as the interface at this point. Translating to new coordinates with origin at the center of C_0 , we obtain (4.10) for an arbitrary smooth interface. The definition of the angle θ remains the same, i. e., the angle between the normal to the interface and a horizontal axis. A more technical version of this idea may be found in [16] (Sect. 4).

A physical understanding of (4.10) may be attained as follows. If the coupling $J(\mathbf{x})$ is stronger in the x direction, then (4.7) implies that the surface tension is also larger in the x direction as one would expect. On the other hand, the thickness of

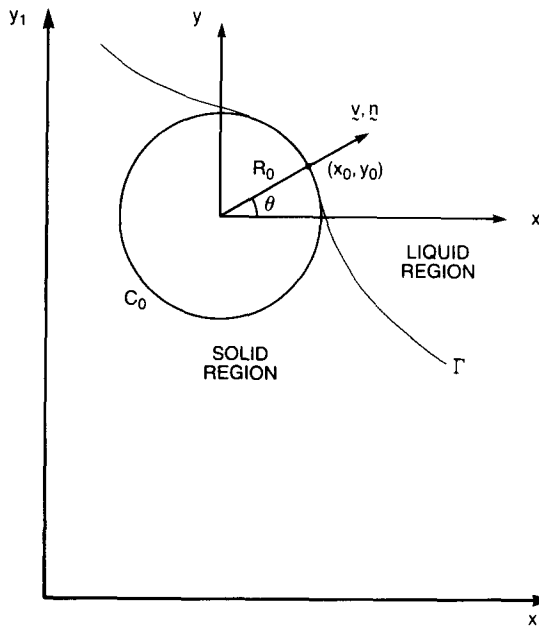


FIG. 1. The osculating circle has the same normal and curvature as Γ at the point (x_0, y_0) . Polar coordinates (r, θ) are defined with respect to the center of C_0 .

the interface (3.12) is also greater in the x direction. Suppose the entire material is in equilibrium at constant temperature. The surface tension has the effect of seeking to minimize curvature. Thus, it would attempt to adjust Γ so it has minimum curvature in the x direction, i. e., oblong in the y direction. However, the fact that the surface is considerably thicker in the x direction results in much too large a cost in energy as indicated in (4.10). Thus, the issue of the thickness dominates this competition and a curve Γ which is oblong in the x direction is the consequence (that is, the interfacial "volume" multiplied by surface tension is reduced).

5. NONEQUILIBRIUM ANISOTROPIC SYSTEMS AND GENERAL DISCUSSION

For a moving interface, the time-dependent terms in (3.4), (3.5) are nonzero, and some additional assumptions must be made. In considering the limits $\tau, \xi \rightarrow 0$, one must ensure

$$0 < m < \tau/\xi^2 < M < \infty \quad (5.1)$$

in order that the parabolic system (3.4), (3.5) does not approach a degenerate limit (see Sect. 2 of [16]). If (5.1) is satisfied and suitable, initial and boundary conditions are chosen, then one may prove the existence of unique solutions to the system for arbitrary large time.

The question of the temperature at the moving interface for the isotropic model has been considered in p. 8 of [19]. We now address this issue for the anisotropic model derived in Section 2, using the asymptotic methods of [16, 19] and Section 3. Suppose the normal velocity of the interface (see Fig. 1) is v at (x_0, y_0) . As in Section 4, we consider new radial coordinates, (r, θ) , with respect to the center of the osculating circle. If the normal velocity is constant in time (to leading order in ξ) and ϕ is locally independent of time in the moving coordinates, i. e., $r = R_0(t) = R_0(0) + vt$ represents the interface near the point of interest and ϕ is a function of $r - R_0(t)$ to leading order. Then we may write the left hand side of (3.4) as

$$\tau\phi_t = \frac{-v\tau}{\xi_A(\theta)} \frac{\partial\phi}{\partial\rho} + (\text{higher order}) \quad \bar{\rho} \equiv \frac{r - R_0(t)}{\xi_A(\theta)}. \quad (5.2)$$

We note that the terms which involve θ -derivatives will be $\mathcal{O}(\xi^2)$ and can be neglected. Thus we may write (3.4) in the form

$$\begin{aligned} \xi_A^2 \frac{\partial^2\phi}{\partial r^2} + \xi_B^2 \frac{1}{r} \frac{\partial\phi}{\partial r} - 2(\xi_1^2 - \xi^2) \frac{1}{r} \sin\theta \cos\theta \frac{\partial\phi}{\partial r \partial\theta} \\ + \frac{\tau v}{\xi_A(\theta)} \frac{\partial\phi}{\partial\rho} + \frac{1}{2} (\phi - \phi^3) + 2u + \mathcal{O}(\xi^2) = 0 \end{aligned} \quad (5.3)$$

For v which is $\mathcal{O}(1)$, we see that the contribution of the velocity term is of the same order as the curvature-surface tension contribution. The formal analysis is similar to that of Section 3. The main difference is that $G(r, \theta)$ must be replaced by

$$G(r, \theta, \mathbf{v}) \equiv G(r, \theta) - \frac{\tau v}{\xi_A(\theta)} \frac{\partial \phi_0}{\partial \bar{\rho}}. \quad (5.4)$$

Thus, (3.15) is again satisfied and a necessary and sufficient condition for the formal expansion is

$$\int_{-\infty}^{\infty} G(r, \theta, v) \frac{\partial \phi_0}{\partial \bar{r}} d\bar{r} = 0. \quad (5.5)$$

Thus, the additional term in (5.4) involves a contribution which may be evaluated using (3.19) and (4.87) with the result,

$$\Delta s u(x, y) = -[\sigma(\theta) + \sigma''(\theta)] \kappa - \frac{\tau}{\xi_A^2(\theta)} v \sigma(\theta) + \mathcal{O}(\xi^2). \quad (5.6)$$

Without anisotropy, the velocity term reduces to the result obtained in [19]. Note that $v \equiv -|v|$ if motion is toward the solid. The calculations leading to (4.10) and (5.76) are formal in that the following mathematical issues have not been completely resolved at this stage:

(A) In the formal expansion $\phi = \phi_0 + \xi_A \phi_1$, ϕ_1 and its derivatives are assumed to be bounded independently of ξ .

(B) The behavior near a point on a circular interface is assumed to be similar to that of an arbitrary interface having identical curvature.

(C) In the derivation of (5.6) it is assumed that there is a solution (u, ϕ) such that the interface Γ (defined by (3.7)) has constant velocity and ϕ is stationary in the moving coordinates (to leading order in ξ).

In order to resolve the issues in (A), one can presumably use the methods of [16] and consider Γ fixed as $\xi \rightarrow 0$, or the mathematically more satisfying treatment given in [22, 23] for a truly free boundary in the mathematical sense. Either of these methods seem to be adaptable to this problem, although the analysis involved in controlling the higher order terms has not yet been performed.

In (B) the central issue is that of using a local analysis for a global problem. This is reasonable for this type of problem and has been implicitly assumed in the derivation of the isotropic Gibbs-Thompson relation in all work prior to [16, 22]. In fact, the existence of a curve whose curvature $\kappa(x, y)$ is $cu(x, y)$ with $u(x, y)$ prescribed, is itself a nonlinear problem which was resolved in [22].

The most serious mathematical question is raised in (C). Even in the simplest

case of a plane wave the assumption of a constant velocity solution would mean proving the existence of a solution to the system of ordinary differential equations:

$$-\tau v \phi_x = \xi^2 \phi_{xx} + \frac{1}{2} (\phi - \phi^3) + 2u, \quad (5.7)$$

$$-v u_x + \frac{l}{2} v \phi_x = K u_{xx} \quad (5.8)$$

subject to appropriate boundary conditions on ϕ and u . These and related questions are currently being studied in collaboration with Paul Fife.

Physically, this derivation is a unified perspective into equilibrium and non-equilibrium anisotropy. The key physical assumption involved in tracing the anisotropic behavior from its microscopic origin to its macroscopic manifestation is in neglecting the higher order Fourier modes.

Our conjecture is that the exact equilibrium result for 4-fold symmetry can be obtained by retaining order q^4 and similarly for higher orders. In principle, then, one may hope to obtain a modified Gibbs–Thompson relation (including the velocity term) for arbitrary symmetry in arbitrary dimension. The preferred direction of growth would then be evident, as it is in (5.6).

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