Phase field modelling of interfaces from first principles

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Abstract. Phase field modelling is a technique in (computational) material science that utilises diffuse interface constructions to simulate the dynamics of microstructural evolution. To date, phase field modelling of crystalline interfaces has been guided mainly by phenomenology and symmetry considerations, rather than microscopic physics. The central equation of motion minimises a free energy with respect to the phase field, which is considered as a space and time dependent, coarse-grained, continuous degree of freedom of the system. However, it is neither clear how to interpret the phase field microscopically, nor how to derive the equation of motion from atomic interactions. Based on the (classical) density functional theory by Haymet and Oxtoby, we derive the phase field model by Allen and Cahn, which is commonly used for modelling crystalline interfaces. In the present article, we summarise the physical implications of the various observables and parameters as well as the underlying approximations.

1. Introduction

Phase field modelling is a very successful method to study structural properties of condensed matter systems in time and space at coexistence [1]. Recently, it has been used to characterise grain boundaries, i.e. systems where the two phases in coexistence correspond to two different crystalline orientations [2, 3, 4]. A phase field model is an equation of motion for a phase field $\phi(\mathbf{r},t)$,

$$\dot{\phi}(\mathbf{r},t) = \mathcal{F}[\phi(\mathbf{r},t)] ,$$

where $\mathcal{F}$ is some (non-local) functional operating on $\phi(\mathbf{r},t)$. In practise, it is very hard to design phase field models that contain enough physics and remain analytically and/or computationally tractable. The phase field is a local degree of freedom or, more specifically, a local order parameter that indicates the local phase of the system. In the context of grain boundaries, it is also known as the crystallinity. Because the equation of motion is not usually derived from microscopic physics, its precise interpretation is a priori unclear. For the same reason, the couplings occurring in the functional $\mathcal{F}$ cannot be traced back or derived from experimental features of the system.

The Allen-Cahn equation

$$\dot{\phi}(\mathbf{r},t) = M \left( \epsilon^2 \nabla^2 \phi(\mathbf{r},t) - \frac{\partial}{\partial \phi} w(\phi) \right)$$

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is one specific realisation of a phase field model. It is a minimal model in the sense that it
displays most of the important physics based only on two terms: A square gradient term with
coupling $\varepsilon^2$ diffusively smoothen out rapid spatial variations of the field, while the term $w'(\phi)$,
which is local in the field gives some non-linear feedback. The whole right hand side is multiplied
by the mobility $M$, which effectively sets the time scale of the spatial relaxation of the system.

This equation of motion can be derived from a free energy functional that is constructed in
the spirit of Landau and Ginzburg, keeping only the leading order terms of a Taylor expansion
which respect the symmetries of the model. The aim of the work presented in the following is to
derive an equation of motion in the Allen-Cahn form from first principles. The key ingredient
is the direct correlation function $C^{(2)}(r)$, the Fourier transform $c(k)$ of which is closely related
to the structure factor $S(k)$ and therefore is directly accessible experimentally,

$$S(k) = (1 - \rho_0 V'' c(k))^{-1},$$

where $\rho_0 V''$ is the number of particles in the unit cell over which the Fourier transform has
been taken. The volume $V''$ is the range of the direct correlation function. Because the
direct correlation function of the liquid is isotropic, its Fourier transform depends only on the
magnitude of $k$, which suggests to introduce $\tilde{c}(|k|)$ so that $c(k) = \tilde{c}(|k|)$.

The entire derivation we discuss in the following is based on standard, grand canonical
thermodynamics: A full grand potential is approximated by considering the excess free energy,
which is the difference between the ideal free energy of the free problem (the non-interacting,
solvable system) and the fully interacting one. The excess free energy is then expanded
in terms of the direct correlation function using a functional Taylor series. The various
(systematic) approximations have been developed by Haymet and Oxtoby [5, 6] in the context
of classical density functional theory, which is based on the fundamental observation that the
(thermodynamic) external potential is a unique functional of the density profile in a system. At
the level of thermodynamics, the particle distribution is the only degree of freedom and standard
thermodynamics relates its average to the system parameters.

In the following, we will firstly introduce various parameters and observables of the system.
We will then trace out the gist of the classical density functional theory by Haymet and Oxtoby.
Based on these ideas, we will then sketch the derivation of a phase field model from the same
thermodynamic principles. In the course, we will be able to point out approximations and
limitations of the theory. By rejecting the notion of phase field modelling as only being an
effective theory and accepting density functional theory as its microscopic foundation, any
approximation, constraint or limitation is inherited by the resulting phase field model. In the
last part, we will discuss some of these issues further, focusing on the physical implications. The
technical details of the derivation will be published elsewhere [7].

2. The model

The grain boundary we are considering develops in a bicrystal, which is created by bringing two
ideal crystals of the same material in close contact.\footnote{In the following we will use “crystal” and “lattice” synonymously, which entails that the basis of the crystal is trivial.} In general there will be a misorientation
between the crystal lattices as well as a relative translation between them. Figure 1 shows
an example of a two-dimensional bicrystal with a misorientation angle $\alpha$.\footnote{A $\Sigma = 5$ boundary is generally regarded as a candidate for a very sharp boundary. We use it here to illustrate a diffusive interface nevertheless.} Between the two
misoriented lattices is a slab of atoms of the same species that can freely rearrange. The situation
is very similar to a liquid confined between to crystalline lattices. The liquid interpolates the
atomic structure between the two boundary conditions, which can, in principle, be moved out infinitely far.

While the temperature $T$ is fixed throughout the calculation and will enter only implicitly through the direct correlation function, the chemical potential $\mu$ with which the liquid layer is connected to an external reservoir is of crucial importance. Working in a grand canonical ensemble rather than a canonical one has a dramatic effect on the ground state of the system [9].

The most interesting observable is the density profile $\rho_i(r)$ across the interface (subscript $i$), in particular its width which can, of course, be derived from the profile. If the two lattices have the same orientation, the equilibrium structure of the atoms in the gap is solely determined by the relative translation of the constraining lattices. If they have the same translation, then one expects a continuation of the boundary lattices, i.e. a reconstruction of a single crystal. A non-vanishing phase-factor (i.e. a relative translation) can lead to some tension across the interface and the density profile contains information about the elasticity of the system.

Other relevant observables include the grand potential itself, steric forces, the effective pressure preventing the interfacial width from increasing without limit etc. For simplicity, in the following we will focus solely on the density profile.

2.1. Density functional theory
It is a matter of straightforward thermodynamics to derive a self-consistency equation which is the starting point for the classical density functional theory in the flavour of Haymet and Oxtoby:

$$\ln \left( \frac{\rho_i(r)}{\rho_0} \right) = \int_\Omega d^d r' C^{(2)}(r - r') (\rho_i(r') - \rho_0),$$

which runs over the entire volume $\Omega$ of the system. This equation is a second order (functional) perturbation theory of the full density function $\rho_i(r)$ about a homogeneous liquid with density $\rho_0$, which can be extended and therefore improved systematically.
Figure 2. Cartoon of a local Fourier transform. The full black line shows the density \( \rho_i(\mathbf{r}) \) which varies strongly throughout the system of size \( \Omega \). However, within a (small) volume \( V(\vec{r}) \) located around \( \vec{r} \), all variation of \( \rho_i(\mathbf{r}) \) can be captured in a Fourier sum. Representing fast changes in Fourier space and leaving the slow changes in real-space, amounts to a separation of length scales. The cartoon shows the value of a coefficient \( \mu_n(\vec{r}) \) throughout the system as the envelope of the density profile (dotted). By taking the Fourier transform within the small volume \( V(\vec{r}) \), one arrives at a density profile which can be periodically continued throughout the system (gray, thinner line), see Eq. (9). This is the profile considered by Haymet and Oxtoby to argue that there are physical systems corresponding to those encountered by the separation of length scales.

Haymet and Oxtoby separated length scales by reparameterising the density \( \rho_i(\mathbf{r}) \) in the form

\[
\rho_i(\mathbf{r}) = \rho_0 \left( 1 + \sum_n \mu_n(\mathbf{r}) e^{-i\mathbf{k}_n \cdot \mathbf{r}} \right). \tag{5}
\]

This is not (quite) a Fourier series, because the coefficients \( \mu_n(\mathbf{r}) \) are themselves space dependent. While the right hand side of Eq. (5) is certainly capable of representing any density profile \( \rho_i(\mathbf{r}) \) in many different ways, the coefficients \( \mu_n(\mathbf{r}) \) are in the present form under-determined. Haymet and Oxtoby provide a good physical argument [6], why a parametrisation \( \mu_n(\mathbf{r}) \) exists which corresponds to a separation of length scales, so that, for example,

\[
\mu_n(\vec{r}) \rho_0 = V^{-1} \int_{V(\vec{r})} d^d r \rho_i(\mathbf{r}) e^{-i\mathbf{k}_n \cdot \mathbf{r}}, \tag{6}
\]

for \( \mathbf{k}_n \neq \mathbf{0} \) and \( (1 + \mu_0(\mathbf{r})) \rho_0 = V^{-1} \int_{V(\vec{r})} d^d r \rho_i(\mathbf{r}) \). The integral in Eq. (6) takes the Fourier transform of \( \rho_i(\mathbf{r}) \) over a (small) volume \( V \) centred at \( \vec{r} \). As illustrated in Figure 2, this amounts to a separation of length scales: If the \( \mu_n \) in Eq. (5) obey Eq. (6), they change very little over the volume \( V \). Within this volume all structure must be captured by the representation in reciprocal space.

It is instructive to consider the effect of the reparameterisation of \( \rho_i \), Eq. (5), on the self-consistency equation (4) without the separation of length scales. After expanding the \( \mu_n(\mathbf{r} + \mathbf{r}') \) in a Taylor series about \( \mathbf{r} \) one arrives at

\[
\ln \left( 1 + \sum_n \mu_n(\mathbf{r}) e^{i\mathbf{k}_n \cdot \mathbf{r}} \right) = \sum_n e^{i\mathbf{k}_n \cdot \mathbf{r}} \rho_0 \left( \mathbf{c}(\mathbf{k}_n) \mu_n(\mathbf{r}) - \tau \nabla \mathbf{k} \mathbf{c}(\mathbf{k}_n) \nabla \mu_n(\mathbf{r}) + \ldots \right) \tag{7}
\]
where \( \hat{c}(|\mathbf{k}_n|) \) are the Fourier coefficients of the direct correlation function \( C^{(2)} \) taken over the domain \( V'' \) for \( \mathbf{k}_n \), see Eq. (3). Since \( C^{(2)} \) is a property of the liquid phase, it can safely be assumed to be isotropic. The volume \( V'' \) is to be chosen so large, that the direct correlation function \( C^{(2)} \) is negligibly small outside. The smaller the volume \( V'' \), the fewer terms are needed in a faithful Taylor expansion of the coefficients \( \mu_n(\mathbf{r}) \).

Without the separation of length scales, Eq. (7) is intractable, because of the \( \mathbf{r} \)-dependence of the Fourier coefficients \( \mu_n(\mathbf{r}) \) on the right hand side, which makes it impossible to use the orthogonality of \( \exp(i\mathbf{k}_n \mathbf{r}) \) to project out Fourier coefficients by integration.

Using the separation of length scales allows precisely that: If one considers \( \mathbf{r} \) only within a small volume \( V(\mathbf{r}) \) then one can rewrite

\[
\ln \left( 1 + \sum_n \mu_n(\mathbf{r}) e^{i\mathbf{k}_n \mathbf{r}} \right) = \sum_n e^{i\mathbf{k}_n \mathbf{r}} V'' \rho_0 \left( \hat{c}(|\mathbf{k}_n|) \mu_n(\mathbf{r}) - i\nabla_k \hat{c}(|\mathbf{k}_n|) \nabla_r \mu_n(\mathbf{r}) + \ldots \right)
\]

and derive a set of integro-differential equations for \( \mu_n(\mathbf{r}) \) by Fourier transforming on both sides. This is the path taken in [6].

2.2. Approximations

Instead of following this route further, we list the assumptions and approximations made so far and, in the next section, apply them directly to the free energy in order to derive a phase field model.

- The first approximation is the functional Taylor expansion of the excess free energy about a homogeneous, uniform liquid, which leads to the direct correlation function \( C^{(2)}(\mathbf{r}) \), see Eq. (4). At first sight, it is surprising to expand the free energy of a solid about a liquid. This discussion appears very prominently in the literature [10]. In particular, it has been pointed out that the extrema of the liquid structure factor coincide with the peaks in the solid structure factor. In that sense the liquid “knows” about its solid phase. However, the two phases are separated by a transition and therefore by a singularity in the free energy. In cases where the (average) coordination numbers for liquid and solid phase differ strongly one might question the validity of the approximation.

On the other hand, the full direct (two-point) correlation functional \( C^{(2)}(\mathbf{r}, \mathbf{r}', [\rho_i]) \), which is a functional of the density \( \rho_i(\mathbf{r}) \), contains all information about all correlations in the system at any density \( \rho_i(\mathbf{r}) \). It is therefore not surprising that a single object \( C^{(2)} \) can contain all information about the liquid and the solid phase. What is surprising is much rather that it is possible to expand the free energy of an arbitrary profile \( \rho_i(\mathbf{r}) \) about the direct correlation functional evaluated only at \( \rho_i(\mathbf{r}) \equiv \rho_0 \).

The functional Taylor expansion can be improved systematically by including higher functional derivatives, corresponding to higher order direct correlation functions, \( C^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \), \( C^{(4)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') \), \ldots . Although the resulting equations are not bilinear anymore, they do not change qualitatively and the scheme remains valid.

- The second approximation is the Taylor expansion of the coefficients \( \mu_n(\mathbf{r}) \) which resulted in Eqs. (7) and (8). Improving this approximation means including higher order derivatives of \( \mu_n(\mathbf{r}) \) and \( \hat{c}(|\mathbf{k}_n|) \). The quality of the expansion is controlled by the volume \( V'' \), the range of the direct correlation function. If it falls off sufficiently quickly, only very few derivatives of the coefficients \( \mu_n(\mathbf{r}) \) are needed for a satisfactory approximation.

- The separation of length scales is less an approximation than a constraint on the parametrisation. Haymet and Oxtoby were able to identify physical systems with periodic
external potentials which would produce the periodically continued density profiles

$$\rho(\mathbf{r}; \mathbf{r}) = \rho_0 \left( 1 + \sum_n \mu_n(\mathbf{r}) e^{i\mathbf{k}_n} \right), \quad (9)$$

see also Figure 2. Alternatively, one can regard Eq. (8) as the generalised problem Eq. (7). If there is a solution \( \{ \mu_n(\mathbf{r}) \} \) of Eq. (8) then it will also solve Eq. (7) by setting \( \mathbf{r} = \mathbf{r} \).

The separation of length scales breaks down when the \( \mu_n(\mathbf{r}) \) vary too strongly over the volume \( V(\mathbf{r}) \). Because \( V \) corresponds to \( \Sigma \) or is a multiple thereof, large \( \Sigma \)-boundaries are less reliably handled by the present method, although it can be improved systematically. It is not trivial to take the limit \( \Sigma \rightarrow \infty \) in a way that makes arbitrary misorientation angles accessible.

- The specific choice of the reciprocal lattice vectors introduced in Eq. (5) seems to be arbitrary but turns out to be crucial to the theory. The choice for the set \( \{ \mathbf{k}_n \} \) is limited to those sets which allow the density profile in both boundaries to be representable. Because these boundary lattices are anisotropic, the volume \( V(\mathbf{r}) \) is oriented. However, since there are two boundary lattices, the set must be chosen as to accommodate both lattices simultaneously. It is not possible to choose two distinct sets, because of the required orthogonality of \( \exp(-i\mathbf{k}_n\mathbf{r}) \).

That implies that the present method applies only to \( \Sigma \)-boundaries, where the two boundary lattices have a common sub-lattice, the coincidence site lattice (CSL) \(^6\). The Fourier transform of the CSL is the DSC lattice \(^6\) in reciprocal space, which provides the coarsest regular lattice that contains both reciprocal lattices as sub-lattices.

Because the very existence of a Fourier domain, that is the oriented volume \( V(\mathbf{r}) \), breaks rotational invariance in space, certain crystalline orientations across the boundary cannot be realised. For example, the gap in Figure 1 cannot be filled with a crystal that has a misorientation angle \( \alpha/2 \) and \(-\alpha/2 \) with respect to the two boundary lattice, because it would not be periodic with respect to the Fourier domain. In other words, by parameterising \( \rho_i(\mathbf{r}) \) in terms of Fourier coefficients, that are determined in an integral over a finite, oriented volume, one implicitly suppresses certain degrees of freedom.

With these precautions in mind, it is shown in the next section how to derive an Allen-Cahn type free energy from DFT by applying directly to the free energy the approximations that have been used above to simplify the self-consistency equation Eq. (4).

### 3. Derivation of a phase field model

The functional Taylor expansion used above in the self-consistency equation for the density \( \rho_i(\mathbf{r}) \), Eq. (4), can also be used directly to approximate the free energy \( \mathcal{F}[\rho_i] \) of the system. Because this is a thermodynamic potential, the local potential \( u(\mathbf{r}) \) is given by its functional derivative with respect to the density \( \rho_i \). This observation allows the construction of a “pseudo grand potential”

\[
\mathcal{W}(\rho_i, [u]) = \mathcal{F}[\rho_i] - \int_\Omega d^3r u(\mathbf{r}) \rho_i(\mathbf{r})
\quad (10)
\]

which reduces to the grand potential \( \mathcal{W}[u] \), if evaluated for the density \( \rho_i(\mathbf{r}) \) that minimises it. The minimisation procedure can be turned into an equation of motion of \( \rho_i \), and later for the phase field, by imposing

\[
\rho_i(\mathbf{r}, t) = -M \frac{\delta}{\delta \rho_i(\mathbf{r}, t)} \mathcal{W}(\rho_i, [u])
\quad (11)
\]

\(^6\) DSC stands for “displacement shift complete”, but this expansion is not in wide use.
with some mobility $M$ which can be absorbed into the definition of time. Considering the grand canonical ensemble means that $\rho_i$ is not a conserved, which is in line with the recent result on the effect of the different ensembles on the groundstate of a crystalline interface [9]. Parameterising $\rho_i$ in terms of the coefficients $\mu_n(\overline{r})$, all non-conservation will be conveniently encapsulated in the evolution of $\mu_0(\overline{r})$.

We will now sketch how to derive $\tilde{W}$ as a functional of $\mu_n(\overline{r})$ and derive an Allen-Cahn type equation by imposing the basic dynamics Eq. (11).

As mentioned above, the first step is to use the functional Taylor expansion to express the free energy $\mathcal{F}$ in a perturbation theory over a homogeneous liquid. Next, $\rho_i$ is replaced by its Fourier representation Eq. (5) and the coefficients $\mu_n(\overline{r})$ are expanded in a Taylor expansion as in Eq. (7). This expansion is truncated at second order.

At this stage, the pseudo free energy $\tilde{W}$ still depends on the entire set of coefficients $\{\mu_n\}$. One can use this expression to derive an equation of motion for every $\mu_n(\overline{r})$ according to Eq. (11). However, the aim of the present considerations is to find an expression for a (single) phase field $\phi$ which then gives rise to an equation of motion of Allen-Cahn form.

To reduce the number of degrees of freedom, we introduce a common amplitude $\phi(r)$ which enters in the form

$$\mu_n(\overline{r}) = (1 - \phi(\overline{r})) \mu^l_n + \phi(\overline{r}) \mu^r_n,$$

(12)

where $\mu^l_n$ are the coefficients characterising the left boundary crystal and $\mu^r_n$ are the corresponding coefficients on the right. The boundary conditions of the field $\phi$ are therefore $\phi = 0$ on the far left and $\phi = 1$ on the far right. The field $\phi$ modulates the strength of the Bragg reflections and therefore is the phase field or “crystallinity” in the true sense of the word.

It is worth noting that in the present parametrisation, the entire system is a superposition of both crystalline lattices weighted by the phase field. The parametrisation Eq. (12) does not allow for complete disorder.

Using Eq. (12) in the expression for the pseudo grand potential at first leads to a considerably more complicated equation. The key problem is that the $\mu^l_n$ and the $\mu^r_n$ do not all “light up” (i.e. are non-zero) for the same $k_n$. The two lattices share some $k$-vectors, namely those that belong to the CSL in reciprocal space. On the other hand, many $\mu_n$ that are populated on one side, are not populated on the other. As will be shown below, common $k$-vectors tend to reduce the interfacial energy and this effect is typically stronger the smaller the common $k$-vectors, so that (typically) small $\Sigma$ are energetically favourable over large $\Sigma$.

At first sight, the situation simplifies considerably, if one assumes that if both $\mu^l_n$ and $\mu^r_n$ are non-zero for a given $n$, then they coincide. In this case, $\mu_n(\overline{r})$ as defined in Eq. (12) does not vary in space, if $\mu_n$ is populated on both sides. The remaining analysis would then focus on those $\mu_n$ which are populated on only one side. It turns out, however, that handling this special case, or handling the more general case, not subject to the extra condition of equality, is equally complicated.

The key simplification has a group theoretic origin: All $k$-vectors are grouped in stars which fulfil the symmetry of the underlying lattice on the right or on the left. Moreover, all $\mu_n$ within a star have the same value. This step effectively suppresses phase shifts throughout the system.\footnote{Allowing the phase field to be complex might be one way to overcome this limitation.}

An example for a star of $k$-vectors in a reciprocal BCC lattice is 111, 11T, 1T1, ... TTT. The group theoretic identity used in the simplification is derived from the Great Orthogonality Theorem [11]:

$$\sum_{\{k\}} k(a \cdot k) = \int d^d |k_0| a'$$

(13)

for any vector $a \in \mathbb{R}^d$. The vector $a'$ is the projection of $a$ on the $d'$-dimensional subspace.
spanned by the k-vectors, which might not be the entire \( \mathbb{R}^d \). The sum runs over an entire star which contains \( q \) vectors, all having the same magnitude \( |k_0| \). In the example mentioned above \( q = 8 \), \( d = d' = 3 \) and therefore \( a' = a \). For simplicity, we restrict the discussion to two-dimensional square lattices and three-dimensional lattices with cubic symmetry.

To use the theorem, the \( k \)-vectors are grouped into stars. Considering one such set of reciprocal lattice vectors on the left, \( \mathbb{K}_l \), and the corresponding set on the right, \( \mathbb{K}_r \), then produces the isotropic coupling

\[
\epsilon_i = -\left[ \mu_0^{1/2} + \mu_0^{2/2} \right] \left( \frac{q(d - 1)}{|k_0|d} c'(|k_0|) + \frac{q}{d} c''(|k_0|) \right) + 2\mu_0^{1/2} \mu_0^{2/2} \left( \frac{q_1}{|k_0|} c'(|k_0|) \right) \tag{14}
\]

where \( \mu_0^0 \) is the value of the \( \mu_n^0 \) for the reciprocal lattice vectors of the left star and \( \mu_0^r \) the value of the \( \mu_n^r \) within the right star. Within a star, all \( k \)-vectors have the same magnitude \( |k_0| \), which is where the derivatives of the Fourier transforms of the direct correlation function, \( c'(|k_0|) \) and \( c''(|k_0|) \) are evaluated at. The cardinality of the two stars \( \mathbb{K}_l \) and \( \mathbb{K}_r \), i.e. the number of elements in these sets, is \( q \). The dimension \( d \) is the dimension of the irreducible representation of the underlying symmetry group, which coincides with the dimension of the vector space the vectors in the stars span.

The rightmost term in Eq. (14) contains properties of the star generated by the intersection \( \mathbb{I} = \mathbb{K}_l \cap \mathbb{K}_r \), which has cardinality \( q_1 \) and spans a space of dimension \( d_1 \). In addition to the isotropic coupling \( \epsilon_i \), a second coupling is produced if \( \mathbb{I} \) is non-empty, \( q_1 > 0 \). In two dimensions, \( \mathbb{I} \) is either empty or coincides with \( \mathbb{K}_l \) and \( \mathbb{K}_r \), so that \( q_1 = 0 \) or \( q_1 = q \). If \( \mathbb{I} = \mathbb{K}_l = \mathbb{K}_r \) the star picked belongs to the CSL in reciprocal space.

The situation is slightly more complicated in three-dimensional, cubic systems, which we want to discuss now. A star might belong to the CSL, so that \( \mathbb{I} = \mathbb{K}_l = \mathbb{K}_r \) and again \( q_1 = q \). Alternatively, the intersection might be empty. Finally, the two boundary lattices might be there are some \( \mathbb{I} \) that are neither empty nor identical to the stars chosen in the boundary. These intersections then have dimension \( d_1 = 1 \). In three-dimensional cubic crystal systems, it is impossible that the two boundary lattices have two common directions without having the third direction in common as well.

Therefore, whenever \( q_1 \) is neither 0 (empty intersection) nor \( q \) (identity), then \( d_1 = 1 \) and the star \( \mathbb{I} \) spans the vector space corresponding to that particular common direction. One can always choose a coordinate system so that this direction is \( e_z \), which, however, can have any orientation relative to the interface.

The anisotropic coupling reads

\[
\epsilon_a = 2\mu_0^{1/2} \mu_0^{2/2} \left( -\frac{q_1}{|k_0|d_1} c'(|k_0|) + \frac{q_1}{d_1} c''(|k_0|) \right). \tag{15}
\]

The couplings \( \epsilon_i \) and \( \epsilon_a \) enter the grand potential in the form

\[
\epsilon_i (\nabla_r v_r(r))^2 + \epsilon_a \nabla_r v_r(r) P_1 \nabla_r v_r(r) \tag{16}
\]

where the matrix \( P_1 \) projects any vector to the subspace spanned by \( \mathbb{I} \).

As suggested earlier, one would normally expect that \( c' \) and \( c'' \) are evaluated where the structure factor peaks, so that \( c' = 0 \) and \( c'' < 0 \). In this case, \( \epsilon_i \) and \( \epsilon_a \) have opposite signs, which leads to the observation that common reciprocal lattice vectors reduce the interfacial energy and the interfacial width; in fact \( \epsilon_i \) and \( \epsilon_a \) have the dimension of a length squared. Since the peaks in the structure factor typically sharpen with decreasing \( k \), the reduction of the interfacial energy and width by common lattice vectors is stronger the shorter the common vectors.
It is worth going through the different cases in \( d = 3 \): If \( I = I_l = I_r \) then \( P_l = 1 \) is just an identity, \( d_l = d \) and \( q_l = q \). In this case, the two couplings \( \epsilon_l \) and \( \epsilon_a \) can be added so that Eq. (16) becomes

\[
- \left[ \mu_0^l - \mu_0^r \right]^2 \left[ q(d-1) \frac{e^\prime(|k_0|)}{|k_0|d} + \frac{q}{d} e^\prime(|k_0|) \right] (\nabla_\nu \phi(r))^2
\]

which means, in particular, that this contribution vanishes if \( \mu_0^l = \mu_0^r \) as discussed earlier: if \( I = I_l = I_r \) and \( \mu_0^l = \mu_0^r \) then none of the Fourier coefficients associated with the star actually varies in space, see Eq. (12).

If \( I \) is empty, then \( q_l = 0 \), so that Eq. (16) contains only terms proportional to \( q_l \):

\[
- \left[ \mu_0^l + \mu_0^r \right]^2 \left[ q(d-1) \frac{e^\prime(|k_0|)}{|k_0|d} + \frac{q}{d} e^\prime(|k_0|) \right] (\nabla_\nu \phi(r))^2
\]

Finally, if \( I \) is not empty but also not identical to \( I_l \) or \( I_r \), then the common reciprocal lattice vectors can be chosen to belong to the \( e_z \) subspace, so that \( \nabla_\nu \phi(r) P_l \nabla_\nu \phi(r) = (\nabla_\nu \phi(r))^2 \) and Eq. (16) becomes:

\[
\left[ - \left[ \mu_0^l + \mu_0^r \right]^2 \left[ q(d-1) \frac{e^\prime(|k_0|)}{|k_0|d} + \frac{q}{d} e^\prime(|k_0|) \right] + 2 \mu_0^l \mu_0^r \left( \frac{q_l}{|k_0|d} e^\prime(|k_0|) \right) \right] (\nabla_\nu \phi(r))^2
\]

\[ + 2 \mu_0^l \mu_0^r \left( \frac{q_l}{|k_0|d} e^\prime(|k_0|) + \frac{q_l}{d} e^\prime(|k_0|) \right) (\nabla_\nu \phi(r))^2 \]

All contributions apart from the second term in Eq. (19) are isotropic. In general, a star contributes to the isotropic term \( (\nabla_\nu \phi)^2 \) and possibly in addition to \( (\nabla_\nu \phi)^2 \). Summing over all contributions from a large number of stars then leads to a grand potential of the form

\[
\bar{\mathcal{W}}_{AC}(\phi) = \int_{\Omega} \text{d}^dr \left[ w(\phi(r)) + \frac{1}{4} \rho_0^2 V'' \left( \mathcal{E}_i (\nabla_\nu \phi(r))^2 + \mathcal{E}_a (\nabla_\nu \phi(r))^2 \right) \right],
\]

which contains an integral over the density \( w(\phi(r)) \) which collects all contributions to the free energy that are local in \( \phi(r) \). This form of a pseudo grand potential gives rise to the dynamics

\[
M^{-1} \dot{\phi} = - \frac{\delta \bar{\mathcal{W}}}{\delta \phi} = - \frac{d}{d\phi} w(\phi(r)) + \frac{1}{2} \rho_0^2 V'' \left( \mathcal{E}_i \nabla_\nu^2 \phi(r) + \mathcal{E}_a \partial_\nu^2 \phi(r) \right)
\]

which is precisely the form proposed by Allen and Cahn, Eq. (2).

4. Discussion and outlook

Most of the approximations and limitations have been discussed already. The introduction of a phase field, which reduces the many local degrees of freedom (namely all fields \( \mu_n(r) \)) to a single one, is the most significant step in the derivation of the phase field model. There is some degree of arbitrariness in the definition of \( \phi \), see Eq. (12). For example, the alternative definition

\[
\mu_n(r) = \frac{1}{2} \phi(r) \left( (\phi(r) - 1) \mu_n^l + (\phi(r) + 1) \mu_n^r \right)
\]

also allows for two distinct boundary configurations with \( \phi = -1 \) on the left and \( \phi = 1 \) on the right, but forces, by continuity, the system to be completely disordered at some point across the interface where \( \phi = 0 \). Every parametrisation by a single common amplitude \( \phi(r) \) introduces
constraints of this form. This is a consequence of the reduction to a single degree of freedom rather than a feature of the present derivation.

Because the exact definition of the field $\phi$ is somewhat arbitrary, one might argue that the Allen-Cahn form found in Eq. (21) is merely a consequence of keeping the lowest non-trivial terms, such as the two-point direct correlation function in Eq. (4) and the second order of the $\mu_n$ in the derivations in Section 3.

The present work therefore provides only one method of deriving a phase field model and its couplings from first principles. There might be alternative paths, which require fewer approximations or that manage to include higher order couplings as effective lower order couplings. The quality and practicability of different schemes has to be decided in a comparative study.

Further research is also needed to adapt the present method to multiple species, in which case the direct correlation functions become tensors and the Fourier coefficients $\mu_n$ vectors.

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