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# An analytical study of the static state of multi-junctions in a multi-phase field model

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ABSTRACT

We investigate the properties of the multi-order parameter phase field model of Steinbach and Pezzolla [I. Steinbach, F. Pezzolla, A generalized field method for multi-phase transformations using interface fields, Physica D 134 (1999) 385–393] with respect to the behavior in triple and higher order junctions. From the structure of this model, it was speculated that "dynamical" solutions may exist in the triple junction, which could lead to a violation of Young's law. Here we confirm analytically recent numerical simulations showing that such dynamical states do not exist, and that an equilibrium solution therefore does indeed correspond to a minimum of the free energy; this implies that Young's law must be satisfied in the framework of the model. We show that Young's law is a consequence of the interface kinetic equilibrium and not due to a mechanical force balance, in agreement with earlier predictions [C. Caroli, C. Misbah, On static and dynamical Young's condition at a trijunction, J. Phys. I France 7 (1997) 1259–1265].



## 1. Introduction

The evolution of microstructures is of fundamental importance for material properties, and its simulation is therefore of highest priority for development of novel materials, as well as industrial and academic research activities. Nowadays, phase field models are considered as the method of choice for simulating interfacial pattern formation processes and the kinetics of moving boundary problems which are the basic processes that lead to the well-known and diverse microstructures. In these methods, the complicated tracking of interfaces is replaced by evolution equations for the "phase fields", which serve as order parameters for distinguishing between different phases and grains. A localized spatial change of the order parameters therefore determines the positions of interfaces, and e.g. at triple junctions three order parameters vary simultaneously rather rapidly in space. When a phase field model is applied to simulate the coarsening in multi-grain structures and grain growth, the corresponding sharp interface model should fulfill Young's law [1], which states that at a junction of multiple interfaces the sum of the surface tension induced forces sums up to zero. This implies that specific angles between the interfaces have to be established at these junctions, which are determined by the values of the interfacial energies. Physically, this equilibration can be considered as the result of minimization of the interfacial energy. Since the balance of forces at these multiple junctions is not contained explicitly in phase field formulations, the models have to be developed and checked with care to ensure that they do indeed satisfy this important and fundamental law. In particular for heterogeneous nucleation, where a new phase appears in contact with a third phase, the proper geometric adjustment of triple lines is important, and therefore it is essential to use consistent models.

A rather generic analysis for one class of phase field models based on a Lagrange multiplier formalism has been performed by Garcke and co-workers [2]. By a matched asymptotic analysis they show that Young's law is satisfied, and even the more general case of anisotropic materials is considered there. The underlying phase field model is based on a minimization of a functional that is defined via a "continuous" free energy density, i.e. the model is constructed such that pure phases, binary interfaces and multiple junctions are treated in the same framework. For practical purposes, however, it is often desirable to use models that are defined piecewise in space, since they are based on a so-called multi-obstacle potential. Literally, this implies that different evolution equations and equilibrium conditions have to be satisfied within the different regions mentioned above; this is a consequence of the fact that the obstacle potential, in contrast to a traditional Landau free energy functional, is defined piecewise. Together with the complication that these domains are changing their shape during

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the evolution and the nonsmooth transitions between them, an investigation in the spirit of a matched asymptotic analysis would be much more difficult.

A prominent model of this sort that is frequently used for various applications has been developed by Steinbach and Pezzolla [3]. As will be shown below, this model might exhibit through its structure other "nonequilibrium" solutions of the stationary phase field equations in a multiple junction, which means that in particular a ground state solution would not necessarily be unique. As a consequence, it seems to be possible that other interface conditions, which violate Young's law for isotropic materials, may exist. To show that the model does not suffer from such drawbacks, two of the present authors checked that such "dynamical solutions" are at least not found in their numerical simulations [4]. In three dimensions in particular, however, such numerical evidence is hard to obtain due to the difficulty of fixing appropriate boundary conditions. It is the purpose of the present paper to prove explicitly and analytically that these spurious dynamical solutions do not exist, and that therefore Young's law is indeed satisfied.

## 2. The multi-phase field model

In the multi-phase field model [3] the equations of motion are derived variationally from a free energy functional:

$$F = \int \left\{ \sum_{\alpha=1}^{N} \sum_{\beta>\alpha}^{N} \left( \frac{-4\eta_{\alpha\beta}\sigma_{\alpha\beta}}{\pi^2} \nabla\phi_\alpha \nabla\phi_\beta + \frac{4\sigma_{\alpha\beta}}{\eta_{\alpha\beta}} \phi_\alpha \phi_\beta \right) \right\} \mathrm{d}V. \quad (1)$$

The order parameters $\phi_\alpha$, which discriminate between the phases or grains, are constrained to the range 0–1. $\eta_{\alpha\beta} = \eta_{\beta\alpha}$ and $\sigma_{\alpha\beta} = \sigma_{\beta\alpha}$ are parameters characterizing the interface thickness and interfacial energy density between phases $\alpha$ and $\beta$, respectively. In the above functional, only interfacial terms are taken into account, and bulk driving forces are suppressed. This model is e.g. appropriate for describing the coarsening during polycrystalline grain growth. As we will see below, the specific choice of this functional is not critical, and therefore the following analysis applies also to similar models.

From the functional one can derive equations of motion for the "interfacial fields" $\psi_{\alpha\beta}$:

$$\dot{\psi}_{\alpha\beta} = -\left( \frac{\delta}{\delta\phi_\alpha} - \frac{\delta}{\delta\phi_\beta} \right) F \quad (2)$$

which are used to express the time evolution of the phase fields:

$$\dot{\phi}_\alpha = \frac{1}{\tilde{N}} \sum_{\beta\neq\alpha} \mu_{\alpha\beta} \dot{\psi}_{\alpha\beta} \quad (3)$$

with kinetic coefficients $\mu_{\alpha\beta} = \mu_{\beta\alpha}$. Here we mention that $\tilde{N}$ is not the number of order parameters but the number of nontrivial order parameters, i.e. with $0 < \phi_\alpha < 1$, at the present point of interest. Therefore, the evolution equations look different in bulk phases (where no evolution takes place), binary interfaces and triple and higher order junctions. For example in a binary interface, where only two fields differ from the values 0 and 1, we have $\tilde{N} = 2$; no time evolution takes place in the bulk, where $\tilde{N} = 0$. These piecewise definitions lead to complications in analytical investigations like asymptotic analyses. In a numerical realization, however, where the phase fields are only defined on a discrete lattice, the dynamical evolution also has to be applied to points directly adjacent to an interface, because otherwise the motion is pinned. Furthermore, we note that the model is equivalent to descriptions using a Lagrange multiplier in the special case of equal mobilities.

For the particular case of the triple-junction region between phases 1, 2 and 3 we therefore get

$$\dot{\phi}_1 = \frac{1}{3} \left( \mu_{12}\dot{\psi}_{12} + \mu_{13}\dot{\psi}_{13} \right), \quad (4)$$

$$\dot{\phi}_2 = \frac{1}{3} \left( -\mu_{12}\dot{\psi}_{12} + \mu_{23}\dot{\psi}_{23} \right), \quad (5)$$

$$\dot{\phi}_3 = \frac{1}{3} \left( -\mu_{13}\dot{\psi}_{13} - \mu_{23}\dot{\psi}_{23} \right). \quad (6)$$

When the system reaches a stationary state, all time derivatives of the phase fields are zero and we have

$$0 = \frac{1}{3} \left( \mu_{12}\dot{\psi}_{12} + \mu_{13}\dot{\psi}_{13} \right), \quad (7)$$

$$0 = \frac{1}{3} \left( -\mu_{12}\dot{\psi}_{12} + \mu_{23}\dot{\psi}_{23} \right), \quad (8)$$

$$0 = \frac{1}{3} \left( -\mu_{13}\dot{\psi}_{13} - \mu_{23}\dot{\psi}_{23} \right). \quad (9)$$

This set of three linear equations for the interface fields $\psi_{12}$, $\psi_{13}$, $\psi_{23}$ is of rank 2, and therefore the general static solution is

$$\dot{\psi}_{12}(\vec{r}) = \frac{a}{\mu_{12}}, \qquad \dot{\psi}_{13}(\vec{r}) = \frac{-a}{\mu_{13}}, \qquad \dot{\psi}_{23}(\vec{r}) = \frac{a}{\mu_{23}}, \quad (10)$$

where $a$ is a constant which can have arbitrary values and, in general, may vary in space. For $a$ not equal to zero all $\dot{\psi}_{\alpha\beta}$ are nonzero and depend on the interface mobilities. At this first glance, without reference to the definition of the interfacial fields as derived from the functional $F$, there appears no reason to assume that $a$ should be zero, and that would mean that an equilibrium configuration depends explicitly on kinetic properties, which is counterintuitive for purely dissipative processes. In fact, a nonvanishing value of $\dot{\psi}_{\alpha\beta}$ indicates a "motion" between phases $\alpha$ and $\beta$.

The physical meaning of the nonzero solutions Eq. (10) is that the system is in a stationary state, but the interface motion between any two phases is still going on as a "circular flux", which transforms phase 1 into phase 2 and phase 3 such that the net flux is zero. We denote such a solution, where the phase fields are stationary, $\dot{\phi}_\alpha = 0$, but with nonvanishing time derivatives of at least some interface fields, $\dot{\psi}_{\alpha\beta} \neq 0$, as a "dynamical equilibrium". Because the nontrivial solutions Eq. (10) depend on interface mobilities, the angles between different interfaces will in general also depend on the interface mobilities in such a dynamical equilibrium state. That would imply that Young's law is a kinetic law in the framework of the multi-phase model rather than a thermodynamic equilibrium condition that depends on the interfacial energy densities only; the possibility of such solutions would raise severe doubts as regards the phase field model, which should be able to reflect basic and well accepted thermodynamic properties. Therefore, it was checked numerically in [4] that such "dynamical solutions" do not exist. Intuitively, such solutions are hard to imagine, since the existence of a circular flux in one direction should not be favorable to an opposite counterflux, and there is no obvious reason for a breaking of the symmetry. Nevertheless, the existence of such dynamical equilibria is well known e.g. in the context of probability fluxes in master equations, which are conceptually similar to the above evolution equations (4)–(6) [5].

We note that this spurious degree of freedom in equilibrium interfaces is a property of triple and higher order junctions. For a binary interface, the corresponding equilibrium equations read

$$0 = \frac{1}{2}\mu_{12}\dot{\psi}_{12}, \quad (11)$$

$$0 = -\frac{1}{2}\mu_{12}\dot{\psi}_{12}, \quad (12)$$

and therefore the only interface field must be stationary, $\dot{\psi}_{12} = 0$; thus a dynamical equilibrium cannot exist in these regions.

## 3. Theoretical analysis

To show that the aforementioned dynamical equilibrium solutions do not exist, we consider the general case with an arbitrary number of phases $\tilde{N}$ in the junction of interest and arbitrary mobilities. From Eq. (2) the following relation can be deduced:

$$\dot{\psi}_{\alpha\beta} = -\dot{\psi}_{\gamma\alpha} + \dot{\psi}_{\gamma\beta}, \tag{13}$$

where $\gamma$ can be any value among 1 to $\tilde{N}$ (in the following we assume that, by proper relabeling, in the $\tilde{N}$-junction of interest the phase fields $\phi_1$ to $\phi_{\tilde{N}}$ are different from zero). In the following we use $\gamma = 1$ without loss of generality (if phase 1 is not present in the multi-junction, another value of $\gamma$ should be used). Plugging Eq. (13) into Eq. (3) with $\gamma = 1$ we derive

$$\dot{\phi}_\alpha = \frac{1}{\tilde{N}} \left( -\sum_{\beta=1}^{\tilde{N}} \mu_{\alpha\beta} \dot{\psi}_{1\alpha} + \sum_{\beta=1}^{\tilde{N}} \mu_{\alpha\beta} \dot{\psi}_{1\beta} \right) \tag{14}$$

for $\alpha = 1, \ldots, \tilde{N}$. Because

$$\sum_{\alpha=1}^{\tilde{N}} \dot{\phi}_\alpha = \frac{1}{\tilde{N}} \left( -\sum_{\alpha=1}^{\tilde{N}} \sum_{\beta=1}^{\tilde{N}} \mu_{\alpha\beta} \dot{\psi}_{1\alpha} + \sum_{\alpha=1}^{\tilde{N}} \sum_{\beta=1}^{\tilde{N}} \mu_{\alpha\beta} \dot{\psi}_{1\beta} \right) = 0 \tag{15}$$

the number of independent equations in Eq. (14) is less than or equal to $\tilde{N} - 1$. This relation expresses that at each point the sum of all phase fields has to be equal to 1; therefore they are not all independent. Consequently, only $\tilde{N} - 1$ equations with $\alpha$ being 2 to $\tilde{N}$ are considered in the following. The above equations can be transformed into a matrix form which is easier for further consideration:

$$\dot{\Phi} = \frac{1}{\tilde{N}} \mathbf{A} \dot{\Psi} \tag{16}$$

with

$$\Phi = \begin{pmatrix} \phi_2 \\ \vdots \\ \phi_m \\ \vdots \\ \phi_{\tilde{N}} \end{pmatrix}, \qquad \dot{\Psi} = \begin{pmatrix} \dot{\psi}_{12} \\ \vdots \\ \dot{\psi}_{1\tilde{N}} \end{pmatrix} \tag{17}$$

and the matrix **A** given in Box I.

For the derivation of above matrix form we have used the following relations:

$$\mu_{\alpha\alpha} = 0, \tag{19}$$

$$\mu_{\alpha\beta} = \mu_{\beta\alpha}, \tag{20}$$

$$\dot{\psi}_{\alpha\alpha} = 0, \tag{21}$$

$$\dot{\psi}_{\alpha\beta} = -\dot{\psi}_{\beta\alpha}. \tag{22}$$

**A** is a real and symmetric $(\tilde{N} - 1) \times (\tilde{N} - 1)$ matrix, and therefore it has real eigenvalues. The remaining step is now to show that **A** is invertible, because then

$$\dot{\Psi} = \tilde{N} \mathbf{A}^{-1} \dot{\Phi}. \tag{23}$$

Then, for a stationary state $\dot{\Phi} = 0$, and therefore also the interface fields vanish, $\dot{\Psi} = 0$, which excludes the existence of dynamic equilibria.

To prove the remaining step, i.e. the invertibility of the matrix **A**, we make use of Gershgorin's theorem. It states that the eigenvalues of **A** must lie within the so called Gershgorin discs in the complex plane with centres $A_{\alpha\alpha}$ (no sum convention) and radii $R_\alpha = \sum_{\beta \neq \alpha} |A_{\alpha\beta}|$ for all $\alpha$. (Notice that in our case we have the additional knowledge that the eigenvalues are real.) Because the mobilities $\mu_{\alpha\beta}$ with $\alpha \neq \beta$ are assumed to be all bigger than 0, according to Eq. (18), $A_{\alpha\alpha} + R_\alpha = -\mu_{\alpha 1} < 0$ (see Fig. 1). This means that the value 0 is not within the Gershgorin discs of **A** and all hence the eigenvalues of **A** are nonzero. Consequently, the matrix **A** can be inverted, which concludes the proof.

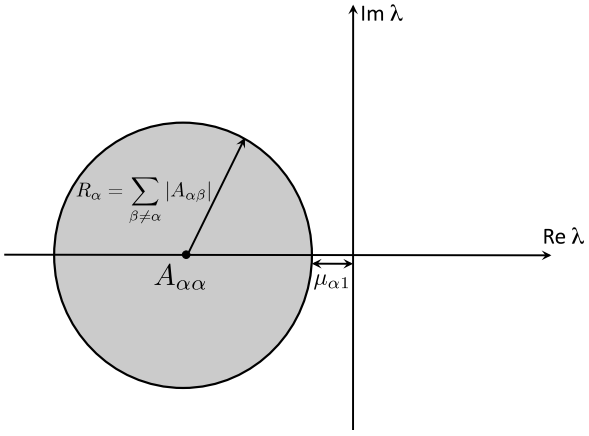


**Fig. 1.** The eigenvalues λ of the matrix **A** are located within the union of the $\tilde{N}$ Gershgorin discs. Since all circles lie in the left half-plane and do not contain the origin, all eigenvalues must be negative, i.e. **A** is negative definite and in particular invertible.

Notice that we did not have to make assumptions on the form of the free energy functional, and therefore the statement concerning the nonexistence of dynamical equilibria is generic.

With the same formalism, we can investigate the time evolution of the phase field model and its relation to the functional derivatives. According to Eqs. (2) and (3) the kinetic equation of phase fields can be expressed in a matrix form:

$$\dot{\Phi} = -\mathbf{M} \cdot \frac{\delta F}{\delta \Phi} \tag{24}$$

where

$$\dot{\Phi} = \begin{pmatrix} \dot{\phi}_1 \\ \vdots \\ \dot{\phi}_{\tilde{N}} \end{pmatrix} \tag{25}$$

and

$$\frac{\delta F}{\delta \Phi} = \begin{pmatrix} \dfrac{\delta F}{\delta \phi_1} \\ \vdots \\ \dfrac{\delta F}{\delta \phi_{\tilde{N}}} \end{pmatrix}. \tag{26}$$

Notice that we keep here all phase fields, although they are not independent by the argument above. The mobility matrix **M** of size $\tilde{N} \times \tilde{N}$ is then real and symmetric and has the structure shown in Box II.

According to Gershgorin's theorem, the eigenvalues of the matrix **M** are bigger than or equal to 0. This means that **M** is a positive semidefinite matrix, which implies that the motion of each phase field is indeed driven by the *decay* of the free energy, as should be expected. We note that at least one eigenvalue has to be zero, because of the mutual dependence of the phase fields due to the sum constraint.

$$\mathbf{A} = \begin{pmatrix} \sum_{\beta=1,\beta\neq 2}^{\tilde{N}} \left(-\mu_{2\beta}\right) & \mu_{23} & \cdots & \cdots & \cdots & \cdots & \mu_{2\tilde{N}} \\ & & & \vdots & & & \\ \mu_{m2} & \cdots & \mu_{m(m-1)} & \sum_{\beta=1,\beta\neq m}^{\tilde{N}} \left(-\mu_{m\beta}\right) & \mu_{m(m+1)} & \cdots & \mu_{m\tilde{N}} \\ & & & \vdots & & & \\ \mu_{\tilde{N}2} & \mu_{\tilde{N}3} & & \cdots & & \mu_{\tilde{N}(\tilde{N}-1)} & \sum_{\beta=1,\beta\neq m}^{\tilde{N}} \left(-\mu_{m\beta}\right) \end{pmatrix} \tag{18}$$

**Box I.**

$$M = \begin{pmatrix} \mu_{12}+\mu_{13}+\cdots+\mu_{1\tilde{N}} & -\mu_{12} & -\mu_{13} & \cdots & -\mu_{1\tilde{N}} \\ -\mu_{21} & \mu_{21}+\mu_{23}+\cdots+\mu_{2\tilde{N}} & -\mu_{23} & \cdots & -\mu_{2\tilde{N}} \\ -\mu_{31} & -\mu_{32} & \ddots & & \vdots \\ \vdots & \vdots & & \ddots & -\mu_{(\tilde{N}-1)\tilde{N}} \\ -\mu_{\tilde{N}1} & -\mu_{\tilde{N}2} & \cdots & -\mu_{\tilde{N}(\tilde{N}-1)} & \mu_{\tilde{N}1}+\mu_{\tilde{N}2}+\cdots+\mu_{\tilde{N}(\tilde{N}-1)} \end{pmatrix} \tag{27}$$

**Box II.**

## 4. The relation to Young's law

So far, we have shown that in equilibrium, i.e. for $\dot{\phi}_\alpha = 0$, also the time derivatives of the interfacial fields vanish, $\psi_{\alpha\beta} = 0$. In this section we discuss how this result is related to the formation of contact angles at multi-junctions.

First we prove that the free energy of the system decreases in the multi-phase field model, i.e. $F$ is a Lyapunov function. This property is important for phase field models in general and related to the analysis at the end of the previous section. However, in the formulation of the model using the antisymmetric interface fields this characteristic is not directly visible. Hence we calculate

$$\begin{aligned} \frac{\mathrm{d}F}{\mathrm{d}t} &= \sum_{\alpha=1}^{\tilde{N}} \int \frac{\delta F}{\delta \phi_\alpha} \dot{\phi}_\alpha \mathrm{d}V \\ &= \sum_{\alpha,\beta=1}^{\tilde{N}} \int \frac{\delta F}{\delta \phi_\alpha} \mu_{\alpha\beta} \dot{\psi}_{\alpha\beta} \mathrm{d}V \\ &= \frac{1}{2} \sum_{\alpha,\beta=1}^{\tilde{N}} \int \left( \frac{\delta F}{\delta \phi_\alpha} \mu_{\alpha\beta} \dot{\psi}_{\alpha\beta} + \frac{\delta F}{\delta \phi_\beta} \mu_{\beta\alpha} \dot{\psi}_{\beta\alpha} \right) \mathrm{d}V \\ &= \frac{1}{2} \sum_{\alpha,\beta=1}^{\tilde{N}} \int \left( \frac{\delta F}{\delta \phi_\alpha} \mu_{\alpha\beta} \dot{\psi}_{\alpha\beta} - \frac{\delta F}{\delta \phi_\beta} \mu_{\alpha\beta} \dot{\psi}_{\alpha\beta} \right) \mathrm{d}V \\ &= \frac{1}{2} \sum_{\alpha,\beta=1}^{\tilde{N}} \int \left( \left( \frac{\delta F}{\delta \phi_\alpha} - \frac{\delta F}{\delta \phi_\beta} \right) \mu_{\alpha\beta} \dot{\psi}_{\alpha\beta} \right) \mathrm{d}V \\ &= -\frac{1}{2} \sum_{\alpha,\beta=1}^{\tilde{N}} \int \mu_{\alpha\beta} \dot{\psi}_{\alpha\beta} \dot{\psi}_{\alpha\beta} \mathrm{d}V \\ &= -\frac{1}{2} \sum_{\alpha,\beta=1}^{\tilde{N}} \int \mu_{\alpha\beta} \dot{\psi}_{\alpha\beta}^2 \mathrm{d}V \leq 0. \end{aligned} \tag{28}$$

Therefore the free energy of the system decreases until it reaches a minimum, where the time evolution stops.

In the following, we consider the special case of a triple junction formed by the phases 1, 2 and 3. According to Eq. (2) and the result of the preceding section that in equilibrium also the interface fields are stationary, we have

$$\frac{\delta F}{\delta \phi_1} = \frac{\delta F}{\delta \phi_2} = \frac{\delta F}{\delta \phi_3} =: \lambda'(\vec{r}), \tag{29}$$

which suggests interpreting the right hand side as a Lagrange multiplier; or, in another form,

$$\frac{\delta F}{\delta \phi_\alpha} - \lambda'(\vec{r}) = 0. \tag{30}$$

At the same time the sum constraint $\phi_1(\vec{r}) + \phi_2(\vec{r}) + \phi_3(\vec{r}) = 1$ has to be obeyed. Physically, we expect that in equilibrium the free energy has to be minimized. With the constraint, this can be expressed as the minimization of another functional $\tilde{F}$ which is defined as

$$\tilde{F} = F - \int \lambda(\vec{r}) \left( \phi_1(\vec{r}) + \phi_2(\vec{r}) + \phi_3(\vec{r}) - 1 \right) \mathrm{d}\vec{r} \tag{31}$$

where $\lambda(\vec{r})$ is a Lagrange multiplier. When $\tilde{F}$ has reached the constrained minimum then

$$\frac{\delta \tilde{F}}{\delta \phi_\alpha(\vec{r})} = \frac{\delta F}{\delta \phi_\alpha(\vec{r})} - \lambda(\vec{r}) = 0, \quad \alpha = 1, 2, 3. \tag{32}$$

Obviously, Eq. (32) is the same as Eq. (30) if we make the identification $\lambda = \lambda'$. Therefore, when the system reaches the static state, the constrained minimization conditions (Eq. (32)) are fulfilled and the system's free energy is minimized. Since Young's law is nothing else than the minimization of the interfacial energy, as will also be illustrated below, this law must be fulfilled when the system has reached the ground state. Here we point out that we consider only the case of isotropic surface energy, and therefore Herring torque terms do not appear [6].

In a phase field model the dihedral angles can only be defined accurately if the lengths of the binary interfaces coming together at a triple junction are large in comparison to the interface thickness and the core size of the triple junction, i.e. in the sharp interface limit; see Fig. 2. In this limit, when the interface width $\eta$ is much smaller than the size of the system, the (finite) core energy of the triple junction can be neglected in comparison to the binary

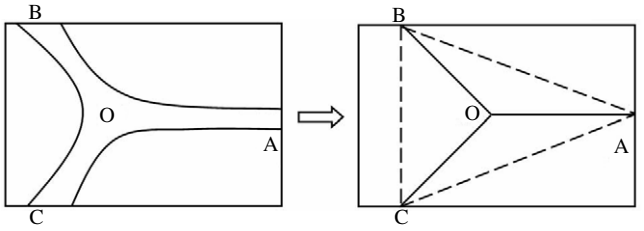


**Fig. 2.** The effect of the assumption that the interface width $\eta$ is much smaller than the system size. Under this assumption the sharp interface view can be applied. Since all of the interface energy is within the triangle ABC, only this area is considered for the energy minimization.

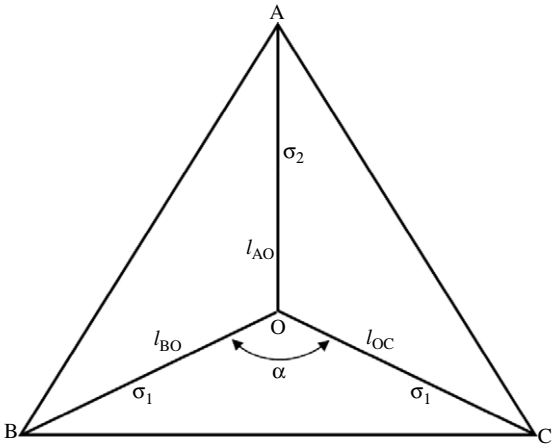


**Fig. 3.** Triangle ABC is an equilateral triangle with edge length 1. The interfacial energies of AO, BO and CO are $\sigma_2$, $\sigma_1$ and $\sigma_1$ respectively. BOC is denoted as $\alpha$. $l_{AO}$, $l_{BO}$ and $l_{OC}$ indicate the lengths of AO, BO and CO respectively.

interface energies, and the sharp interface picture can be used. First, we note that in a phase field model that is based on a multi-obstacle potential the support of any multi-junction, i.e. the region where at least one phase field differs from the bulk values 0 or 1, is finite; in contrast, for a multi-well potential, all fields decay only exponentially. Second, as pointed out in [7], Young's law only makes sense in the sharp interface limit (or, in other words, on outer length scales much bigger than the interface thickness). In this limit, however, the core energy scales according to Eq. (1) as $\sigma\eta L$ ($L$ is proportional to the system size), whereas the binary interface energy scales as $\sigma L^2$. In the limit of sharp interfaces (or large systems), $\eta/L \ll 1$, the core energy contribution is therefore negligible.

Because all the interfacial energy of the system is within the triangle ABC we focus on this region (see Fig. 3). For simplicity, the triangle ABC is assumed to be an equilateral triangle with edge length 1 and equal interfacial energies $\sigma_1$ of interfaces BO and CO, and the interfacial energy density of the segment AO is $\sigma_2$. The angle $\angle$BOC is denoted as $\alpha$. Then the total interfacial energy of the system is

$$\begin{aligned} F_{int} &= l_{BO}\sigma_1 + l_{CO}\sigma_1 + l_{AO}\sigma_2 \\ &= \frac{\sigma_1}{2\sin(\alpha/2)} + \frac{\sigma_1}{2\sin(\alpha/2)} + \left(\frac{\sqrt{3}}{2} - \frac{1}{2}\cot(\alpha/2)\right)\sigma_2, \end{aligned}$$

where $l_{BO}$, $l_{CO}$ and $l_{AO}$ are the interface lengths of the (straight) segments. Minimization with respect to the only degree of freedom, $\alpha$, requires

$$\frac{dF_{int}}{d\alpha} = \frac{1}{4}\left(\sigma_2 - 2\sigma_1\cos(\alpha/2)\right)\csc^2(\alpha/2) = 0. \tag{33}$$

The solution is $\cos(\alpha/2) = \sigma_2/\sigma_1$, which is the well-known force balance condition of Young's law.

So far, we have discussed only equilibrium situations, and it is conceivable that the behavior changes during growth. An example would be provided by lamellar eutectic solidification, and such a situation has been investigated in [7]. The conclusion was that Young's law is strictly valid only in equilibrium, and the next order correction to the dihedral angle scales as $v^2$, where $v$ is the growth velocity. Furthermore, it was concluded that Young's law is a consequence of chemical equilibrium instead of a mechanical balance of forces. This implies that for nonequilibrium situations the velocity dependent correction of the contact angle depends on the molecular attachment rate instead of the speed of sound. In fact, the inclusion of mechanical effects has to be done separately and is not included in the description [7], and the same holds for our model. If elastic effects are taken into account, stress singularities at a triple junction also enter into the expression for the chemical potential. This singularity is however weaker than the singularity due to the interface curvature as long as the geometry at the triple junction is not crack-like, and therefore the nominal contact angles are unchanged even in the presence of elastic effects [8].

An analysis of moving interfaces and triple junctions is performed in Appendix. A moving interface is stretched by a "relativistic dilatation" factor $[1 - (v/v_0)^2]^{-1/2}$, where the characteristic velocity $v_0$ scales as $v_0 \sim \sigma\mu$, which is the velocity scale that describes the rate of atomic attachment at interfaces and is not related to the sound speed. Therefore we conclude that also in the multi-order parameter phase field model Young's law has to be considered as a result of interface kinetic equilibrium instead of a mechanical force balance, in agreement with the analysis in [7]. Deviations from Young's law – if any – can therefore only be expected if the interface speed is of the order of the velocity scale $v_0$. For solidification with characteristic values $\sigma \sim 10^{-1}$ J/m$^2$ and $\mu \sim 10^{-1}$ m$^3$ J$^{-1}$ s$^{-1}$ the characteristic velocity scale for the interface kinetics is therefore about $v_0 \sim \mu\sigma \sim 10^{-2}$ m s$^{-1}$. In contrast, for solid-state transformations, we obtain for $\sigma \sim 10^{-1}$ J/m$^2$ and $\mu \sim 10^{-7}$ m$^3$ J$^{-1}$ s$^{-1}$ the much lower characteristic velocity $v_0 \sim \mu\sigma \sim 10^{-8}$ m s$^{-1}$, which is still above the experimental austenite grain growth velocity [9] of about $v \sim 10^{-9}$ m s$^{-1}$, but of course far below the front velocity in martensitic transformations, and therefore deviations from Young's law are likely to be observed in such cases.

Finally, we note that Eq. (23) continues to hold also for moving trijunctions, e.g. due to undercooling of one phase. Then, however $\dot{\Phi} \neq 0$, and therefore of course also $\dot{\Psi} \neq 0$. Nevertheless, due to the invertibility of the matrix **A**, which does not depend on the free energy functional, the time derivatives of the interface fields are uniquely related to the interface motion described through $\dot{\Phi}$, and no additional degrees of freedom appear.

## 5. Summary

According to the theoretical consideration it is proven that dynamic equilibria, which were hypothesized for the multi-order parameter phase field model [3], do not exist. As a consequence, Young's law is satisfied and is indeed a thermodynamic law rather than a kinetic law also in the framework of this model, and this is due to the equilibration of interface kinetics and not a mechanical force balance. The results are consistent with the numerical simulation carried out in Ref. [4].

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## Appendix. Stationary and moving interfaces and triple junctions

The behavior in interfaces can also be investigated in more detail both for stationary and for evolving systems. Here we make use of the linearity of the phase field equations that are given by Eqs. (1)–(3). For a triple junction the evolution equations are explicitly

$$\dot{\phi}_1 = \frac{4\sigma\mu}{3\eta}(2\phi_1 - \phi_2 - \phi_3) + \frac{4\eta\sigma\mu}{3\pi^2}(2\nabla^2\phi_1 - \nabla^2\phi_2 - \nabla^2\phi_3), \tag{A.1}$$

$$\dot{\phi}_2 = \frac{4\sigma\mu}{3\eta}(-\phi_1 + 2\phi_2 - \phi_3) + \frac{4\eta\sigma\mu}{3\pi^2}(-\nabla^2\phi_1 + 2\nabla^2\phi_2 - \nabla^2\phi_3), \tag{A.2}$$

$$\dot{\phi}_3 = \frac{4\sigma\mu}{3\eta}(-\phi_1 - \phi_2 + 2\phi_3) + \frac{4\eta\sigma\mu}{3\pi^2}(-\nabla^2\phi_1 - \nabla^2\phi_2 + 2\nabla^2\phi_3), \tag{A.3}$$

where we have assumed for simplicity that all interfacial energies $\sigma_{\alpha\beta} = \sigma$, thicknesses $\eta_{\alpha\beta} = \eta$ and mobilities $\mu_{\alpha\beta} = \mu$ are equal. The same analysis can be carried out for arbitrary choices of these parameters.

By Fourier transformation,

$$f(\vec{r}) = \int_{-\infty}^{+\infty} \hat{f}(\vec{k}) \mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{r}} \mathrm{d}\vec{k} \tag{A.4}$$

we obtain after a dimensionless rescaling of the length by $\tilde{x} = \pi x/\eta$ and time according to $\tilde{t} = 4\sigma\mu t/3\eta$,

$$\dot{\hat{\phi}}_1 = 2y\hat{\phi}_1 - y\hat{\phi}_2 - y\hat{\phi}_3, \tag{A.5}$$

$$\dot{\hat{\phi}}_2 = -y\hat{\phi}_1 + 2y\hat{\phi}_2 - y\hat{\phi}_3, \tag{A.6}$$

$$\dot{\hat{\phi}}_1 = -y\hat{\phi}_1 - y\hat{\phi}_2 + 2y\hat{\phi}_3. \tag{A.7}$$

with $y = 1 - \tilde{\vec{k}} \cdot \tilde{\vec{k}}$. Rewritten as a matrix equation,

$$\dot{\hat{\Phi}} = \mathbf{A}\hat{\Phi}, \tag{A.8}$$

where the entries of the vector $\hat{\Phi}$ are the Fourier transforms of the phase fields, we obtain the eigenvalues and eigenvectors of **A**:

$$\lambda_1 = 0, \qquad \vec{v}_1 = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \tag{A.9}$$

$$\lambda_2 = 3y, \qquad \vec{v}_2 = \begin{pmatrix} -1 \\ 0 \\ 1 \end{pmatrix}, \tag{A.10}$$

$$\lambda_3 = 3y, \qquad \vec{v}_3 = \begin{pmatrix} -1 \\ 1 \\ 0 \end{pmatrix}. \tag{A.11}$$

Eigenvector 1 describes the metastable equilibrium state $\phi_1 = \phi_2 = \phi_3 = 1/3$, whereas the states 2 and 3 describe a binary interface between phases 1 and 3, and one between phases 1 and 2, respectively. Notice that the two last eigenvalues are equal, and therefore the linear combination, which describes an interface between phases 2 and 3, is also an eigenstate.

The general time dependent solution is (in reciprocal space)

$$\Phi(\tilde{\vec{k}}, t) = c_1(\tilde{\vec{k}})\vec{v}_1 + c_2(\tilde{\vec{k}}) \exp(3y\tilde{t})\vec{v}_2 + c_3(\tilde{\vec{k}}) \exp(3y\tilde{t})\vec{v}_3. \tag{A.12}$$

For a stationary triple junction only those $k$-modes which lead to a vanishing eigenvalue can contribute, which means that for the second and third eigenvalues only modes with $\tilde{\vec{k}} \cdot \tilde{\vec{k}} = 1$ are admitted. Additionally, the order parameters need to be real, i.e. $c_i(\tilde{\vec{k}}) = c_i(-\tilde{\vec{k}})^*$. Hence a stationary triple junction can be considered as a superposition of the metastable equilibrium state (first eigenvector) and a superposition of planar binary interfaces, which are described by sine functions (second and third eigenvectors). One can directly check that this solution also has vanishing time derivatives of the interface fields. We also note that the constraint that the sum of all phase fields has to be 1 everywhere demands that $c_1(\tilde{\vec{k}}) = \delta(\vec{k})/3$.

For a moving triple junction, the selected $k$-vector becomes complex, and therefore binary interfaces have both an oscillating and an exponential contribution. Since the constant mode for the first eigenvector is translationally invariant, only the other two eigenvectors need to be considered. A steady state solution with triple-junction velocity $\tilde{\vec{v}}$ requires a complex $k$-vector with

$$1 = \tilde{\vec{k}} \cdot \left( \tilde{\vec{k}} - \frac{\mathrm{i}}{3}\tilde{\vec{v}} \right), \tag{A.13}$$

which can have nonvanishing Fourier amplitudes. The imaginary contribution to the eigenvector implies that the spatial dependence of this mode is a product of a trigonometric function with a velocity dependent exponential, and therefore the profile of a moving interface is changed.

We note that no bulk driving force terms have been added in the description so far; therefore all interface motion is driven by a reduction of the interfacial energy only. Driving force terms are usually added via a strongly nonlinear contribution [10] to the free energy functional, and then a simple treatment in reciprocal space is not possible.

The same analysis can be carried out for a moving binary interface. This case has the advantage that only two antiparallel $k$-vectors appear which point in the interface normal direction. For a motion in the $x$ direction with velocity $v$ the real and imaginary parts of the reciprocal vector $\tilde{\vec{k}} = (\tilde{k}_r + \mathrm{i}\tilde{k}_i)\vec{e}_x$ are

$$\tilde{k}_r = \pm\sqrt{1 - \tilde{v}^2/16}, \qquad \tilde{k}_i = \tilde{v}/4, \tag{A.14}$$

where the dimensionless time scale is now $\tilde{t} = 2\sigma\mu t/\eta$. In these rescaled units the steady state equation for the interface profile moving in the positive $x$ direction becomes in the inner region

$$\phi_1'' + \phi_1 - \frac{1}{2} + \frac{1}{2}\tilde{v}\phi_1' = 0, \tag{A.15}$$

which is equivalent to the motion of a damped pendulum around the origin $\phi_1 = 1/2$ if we identify the phase field with the coordinate and position with time. Then the deformed interface profile becomes

$$\phi_1 = 1 - \phi_2 = \frac{1}{2} - \frac{\alpha}{2} \exp\left( -\frac{\tilde{v}}{4}(\tilde{x} - \tilde{v}\tilde{t}) \right) \sin\left( \sqrt{1 - \frac{\tilde{v}^2}{16}}(\tilde{x} - \tilde{v}\tilde{t}) \right) \tag{A.16}$$

with a matching constant $\alpha$. At points where the phase field acquires the values 0 and 1 it has to be matched to the "outer" solutions $\phi_1 \equiv 0; 1$. Due to the damping it is not possible that at both matching points the slope of the phase field profile vanishes, which implies that $\phi_1$ has a kink at one, at least, of the edges, in contrast to the static case $\tilde{v} = 0$, and therefore the profile becomes asymmetric. Since all solutions (A.16) for arbitrary values of $\alpha$ solve the phase field equations, additional conditions have to be invoked to determine the value of this constant. We checked numerically that the free energy is minimized if the phase field profile is smooth at the leading edge in the growth direction (and therefore it has a kink at the trailing edge); for large values of $\alpha \gg 1$ and small

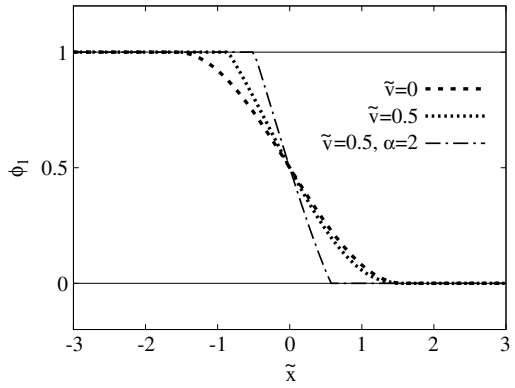


**Fig. A.4.** Stationary and moving interface profiles. For $\tilde{v} = 0.5$ the dotted curve has vanishing slope at the leading edge, whereas the dash–dotted line also has a kink there; the latter is energetically unfavorable.

velocities, $\tilde{v} \ll 1$, the free energy density $\tilde{f} = \phi_1'^2/2 + \phi_1(1-\phi_1)/2$ is dominated by the gradient square term, $\phi_1'^2/2 \simeq \alpha^2/8$ and the interface thickness becomes $\eta \simeq 1/\alpha$, and therefore the free energy scales as $F \simeq \alpha/8$, which is a monotonically increasing function of $\alpha$; it reaches its global minimum for a choice of $\alpha$ that leads to a smooth profile at the leading edge, where the phase field becomes constant. Therefore the proper value of $\alpha$ is determined by the condition $\phi_1'(x_1) = 0$, where $x_1$ is the point where $\phi_1(x_1) = 0$. Interface profiles for different velocities are shown in Fig. A.4. Obviously, for $\tilde{v} = 0$ we recover the static value $\alpha = 1$.

The important point is now that the motion leads to an interface profile stretching with the factor $(1-\tilde{v}^2/16)^{-1/2}$, which introduces a characteristic velocity scale; see Eq. (A.16). Converting back to real units, $\tilde{v} = v\pi/2\sigma\mu$, the "dilatation" factor becomes $(1 - (v/v_0)^2)^{-1/2}$. The relevant velocity scale, $v_0 = 8\sigma\mu/\pi$, depends only on interfacial properties, in particular the kinetic coefficient $\mu$, which describes the rate of molecular attachment at the interface, and is not related to the speed of sound. Deviations from Young's law, if any, are expected to become relevant only on interface speeds of the order of this velocity scale. In agreement with the model in [7], this shows that the equilibrium at triple junctions is the result of a "chemical" and not a mechanical equilibrium, which would lead to the appearance of the speed of sound.

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