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A phase field concept for multiphase systems

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Abstract

The phase field theory describing the evolution of a dual phase boundary is extended to multiphase problems: Each phase is identified with an individual phase field and the transformation between all pairs of phases is treated with its own characteristics. The governing differential equations for the evolution of the multiphase system are derived by minimizing the free energy functional. This free energy functional is expanded in a series over the pair energies between the different phases, where the local fluctuations of one phase are treated with respect to its counter-phase. The proposed generalized multiphase concept reproduces the dual phase system as a limiting case.

The relevance of the model for metallic systems is discussed with respect to eutectic and peritectic solidification and grain growth.

0. Introduction

The phase field method [1,2,4–7] has achieved a considerable interest in the recent years. Based on the Ginzburg–Landau theory of phase transitions, it shows a wide range of applications – especially in materials sciences – by now ranging from dendritic growth into an undercooled liquid [3,4], over faceted growth [5] to structural solid–solid phase transitions [7].

The basis of the theory is the functional of the local free energy density depending on the order parameter of the system and its spatial derivatives. The order parameter may be a scalar function like the fraction of solid f_s in solid–liquid phase change problems, that varies from 0 in the liquid to 1 in the

solid, or a vector function for anisotropic surfaces [8]. In general, however, a small volume of matter has different possible ordered states, like the properitectic and the peritectic state in the peritectic phase transformations. The peritectic and the properitectic phase cannot coexist, therefore only one of them can achieve a volume fraction of 1 within a small volume, if this volume is not intersected by a phase boundary.

Some order parameters, on the other hand, can coexist. One example is the structural order parameter and the order parameter of solutal demixing, that both describe the formation of coherent precipitations in metals [7].

In this paper we restrict ourselves to that type of order parameters p_i , which describe the local phase state of a system exclusively.

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In a system with n possible phase states, the $\binom{n}{2}$ interactions between these phases are described by a sum over the pairwise intercorrelations of the different order parameters.

Section 1 gives the formal definition of multiphase order parameters and the free energy functional. In Section 2, the equations of motion of the individual phases are derived by minimizing the free energy functional. Section 3 gives numerical results for some simple triple point problems. Finally the relevance of the theory for metallic systems is discussed.

1. The multiphase free energy density

According to the standard definition, an order parameter p in phase change problems represents a property of the system that is non-zero in a distinct region of the phase space and 0 otherwise.

In solid–liquid phase change problems, the order parameter p is casually identified with the fraction solid of a small volume of the material. It may also be identified with the angular intensity change of a Laue diffraction function showing a typical pattern for each solid system. These patterns vanish in the liquid state. Different metallic phases are to be identified by different patterns.

The order parameter, according to this definition, is not a characteristic of a single state, but the distinction between two different states. Within a system exhibiting three different phase states, for example α , β , and liquid phases of a peritectic system, the α pattern vanishes at the transition to liquid and it changes to the β pattern at the transition to the β phase. Thereby we might interpret β phase and liquid as “non α phase states”. We then define the set of phase fields p_i by the local fraction of a metallic phase i , that is non-zero if the diffraction pattern of the small volume reveals the pattern typical of phase i and 0 otherwise. If no pattern at all can be identified, the phase state is liquid, which is included as individual phase state in the set of phase fields p_i .

For n phases we get the constraint

$$\sum_{i=1}^n p_i(\mathbf{x}, t) = 1. \quad (1)$$

We then allow the phase fields p_i to vary between 0 and 1,

$$0 \leq p_i \leq 1, \quad (2)$$

as known from the standard phase field model.

We adapt here the interpretation given by Oxtoby [9], that the “smear out” of the order parameter corresponds physically to the decrease of the structural order in a solid–liquid interface on an atomic scale. Only within these interface regions more than one of the order parameters is greater than 0.

Let us now set up the free energy functional F of the system in its dependence on the local phase field variables p_i and their spatial derivatives ∇p_i ,

$$F\{p_1, \dots, p_n, \nabla p_1, \dots, \nabla p_n\} = \int \hat{f}(p_1, \dots, p_n, \nabla p_1, \dots, \nabla p_n) dV. \quad (3)$$

We expand the local free energy density

$$\hat{f} = \hat{f}^0 + \sum_i \hat{f}_i^1 + \sum_{i,k(i \neq k)} \hat{f}_{ik}^2 + \sum_{i,k,l(i \neq k \neq l)} \hat{f}_{ikl}^3 + \dots \quad (4)$$

\hat{f}^0 contains the part of the free energy, that is independent of the phase state; \hat{f}_i^1 contains the energy differences of bulk phase i ; \hat{f}_{ik}^2 is the energy part that is sensitive on the boundary between phases i and k ; \hat{f}_{ikl}^3 would contain the triple point energies and so on.

In the following we assume that the triple point energies and energies of higher order are negligible. This corresponds to the physical assumption that the triple point between three different phases adjusts according to the movement of the dual phase boundaries and possesses no, or negligible, dynamics of its own.

The potential part of the local free energy \hat{f} can be written as a direct extension of the standard double well function:

$$\hat{f}_{ik}^{\text{pot}} = \frac{1}{4a_{ik}} \left[p_i^2 \cdot p_k^2 - m_{ik} \left(\frac{1}{3} p_i^3 + p_i^2 p_k - \frac{1}{3} p_k^3 - p_k^2 p_i \right) \right], \quad (5)$$

where m_{ik} is the linear coefficient of deviation from thermodynamic equilibrium. In general, the contribu-

tions $(m_{ik}/12a_{ik})p_i^3$ or $(m_{ik}/12a_{ik})p_k^3$ respectively in (5) are part of the bulk free energy. Their difference accounts for the difference of the bulk energies \hat{f}_i^{pot} and \hat{f}_k^{pot} for small deviations from thermodynamic equilibrium.

The pair potential contributions $(m_{ik}/4a_{ik})(p_i^2 p_k - p_k^2 p_i)$ and $(1/4a_{ik})p_i^2 p_k^2$ in (5), contributing only at the interface, define the potential barrier between both phases in order to prevent a spontaneous phase transition. The given expression (5) combines both contributions in an analytical expression (Fig. 1). Other formulations that show the same properties to the lowest order $p_i p_k$ would be possible.

The kinetic term $\hat{f}_{ik}^{\text{kin}}(p_i, p_k, \nabla p_i, \nabla p_k)$ is expanded in a series over powers of $p_i, p_k, \nabla p_i$ and ∇p_k . Considering aspects of symmetry and theory of irreducible representation [10] the kinetic term obeys to lower order power series in p_i and ∇p_i :

$$\hat{f}_{ik}^{\text{kin}}(p_i, p_k, \nabla p_i, \nabla p_k) = \frac{1}{2}\varepsilon_{ik}^2 |p_k \nabla p_i - p_i \nabla p_k|^2, \quad (6)$$

where ε_{ik} is referred to as the gradient energy coefficient of the phases i and k .

Eq. (6) can be interpreted as follows: The gradient of one order parameter ∇p_k measures the interface energy to all the rest of the possible order parameters or phases. The contribution of one specific interface type $p_i \rightarrow p_k$, therefore, is weighted by the density of these states. ∇p_i has no contribution to the phase transformation $p_i \rightarrow p_l$, if $p_l = 0$ in the local volume, i.e. if no phase p_l is present. The operator $p_k \nabla p_i - p_i \nabla p_k$ fulfils this requirement to the lowest order p_i and ∇p_i .

It is easy to see that in the case of a dual phase system,

$$p_i = 1 - p_k; \quad p_l = 0 \quad \text{for all } l \neq k, l \neq i, \quad (7)$$

the multiphase kinetic functional reduces to the standard phase field function [3].

Summarizing, we postulate the following form for the free energy functional:

$$\hat{f} = \sum_{i,k (i < k)}^n \hat{f}_{ik}$$

$$\begin{aligned} &= \sum_{i,k (i < k)}^n \left(\hat{f}_{ik}^{\text{kin}}(p_i, p_k, \nabla p_i, \nabla p_k) + \hat{f}_{ik}^{\text{pot}}(p_i, p_k) \right) \\ &= \sum_{i,k (i < k)}^n \left(\frac{\varepsilon_{ik}^2}{2} |p_k \nabla p_i - p_i \nabla p_k|^2 + \frac{1}{4a_{ik}} \left[p_i^2 p_k^2 \right. \right. \\ &\quad \left. \left. - m_{ik} \left(\frac{1}{3} p_i^3 + p_i^2 p_k - \frac{1}{3} p_k^3 - p_k^2 p_i \right) \right] \right), \quad (8) \end{aligned}$$

where the ‘‘thermophysical’’ data ε_{ik} and a_{ik} are to be defined for each type of interface individually.

This functional is a direct extension of the dual phase field functional. It is sensitive on triple- or multiple-phase points, where one individual phase is in contact with different counter-phases. This will be demonstrated in Sections 2 and 3.

2. The equations of motion for the phase fields

As stated in Section 1, the phase fields p_i cannot be identified with order parameters as used in conventional phase change problems. At the triple point of the phases (p_i, p_k, p_l) , the change of p_i can be affected by the phase changes $i \rightarrow k$ and $i \rightarrow l$ simultaneously. In general, we have to sum up all possible phase change contributions for the change of the phase field p_i :

$$\dot{p}_i = \sum_{k (k \neq i)} q_{ik}, \quad (9)$$

where the q_{ik} are the sources (respectively sinks) for the phase field p_i , that correspond to the particular phase transformation between phases i and k .

These q_{ik} now may be derived by the minimization of the local free energy of the system

$$\begin{aligned} \tau_{ik} q_{ik} &= \left(\nabla \frac{\partial}{\partial \nabla p_i} - \frac{\partial}{\partial p_i} \right) \hat{f}_{ik}; \\ p_l &= \text{constant}, \quad \text{for } l \neq i, k. \end{aligned} \quad (10)$$

It must be noted that the p_i and ∇p_i do not span an independent set of variables of the system. This is illustrated in Fig. 2. Due to the smear out of the phase field variables p_i , at the triple point all three phase fields have non-zero values, while at the dual phase lines only two phase fields interact.

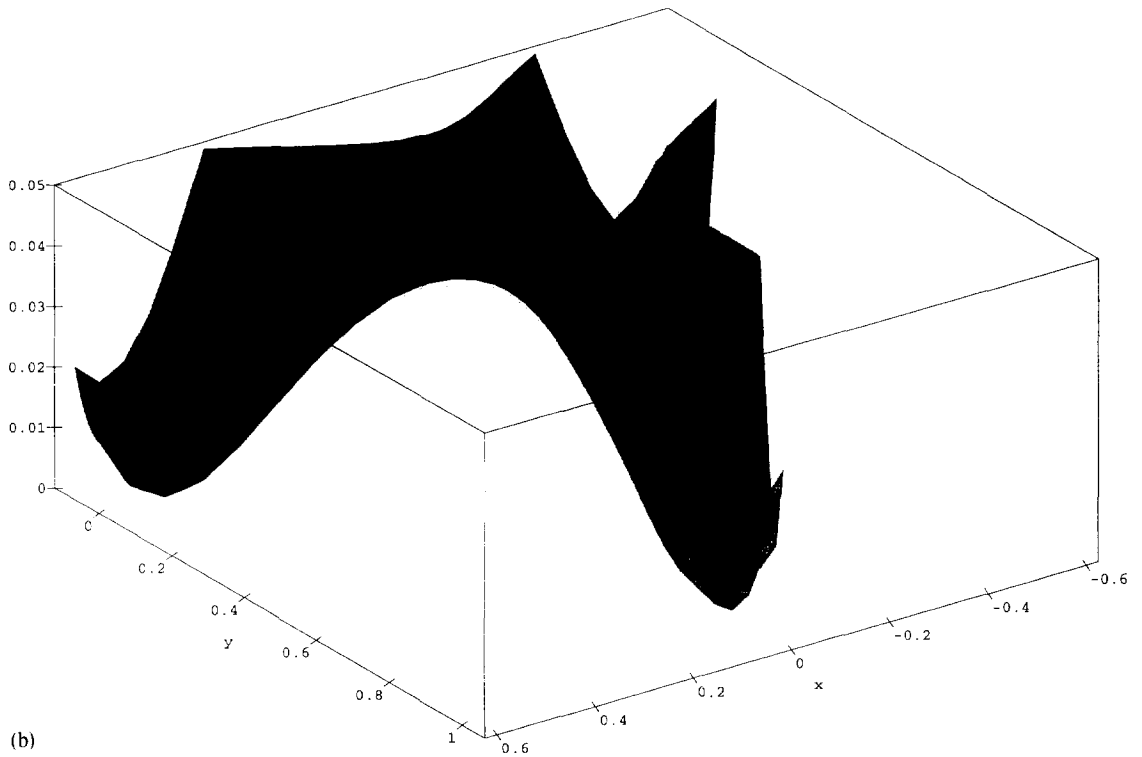
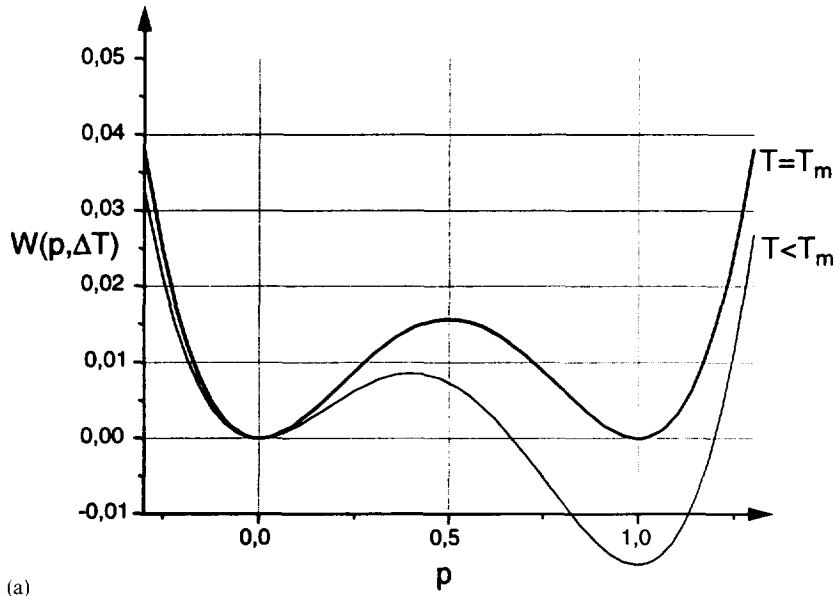


Fig. 1. Double well potential as used in standard phase field computations (a). Extending to more than two phase states leads to higher dimensional functions of the potential (b), (c). Note each of the binary subsystems reproduces a standard double well potential.

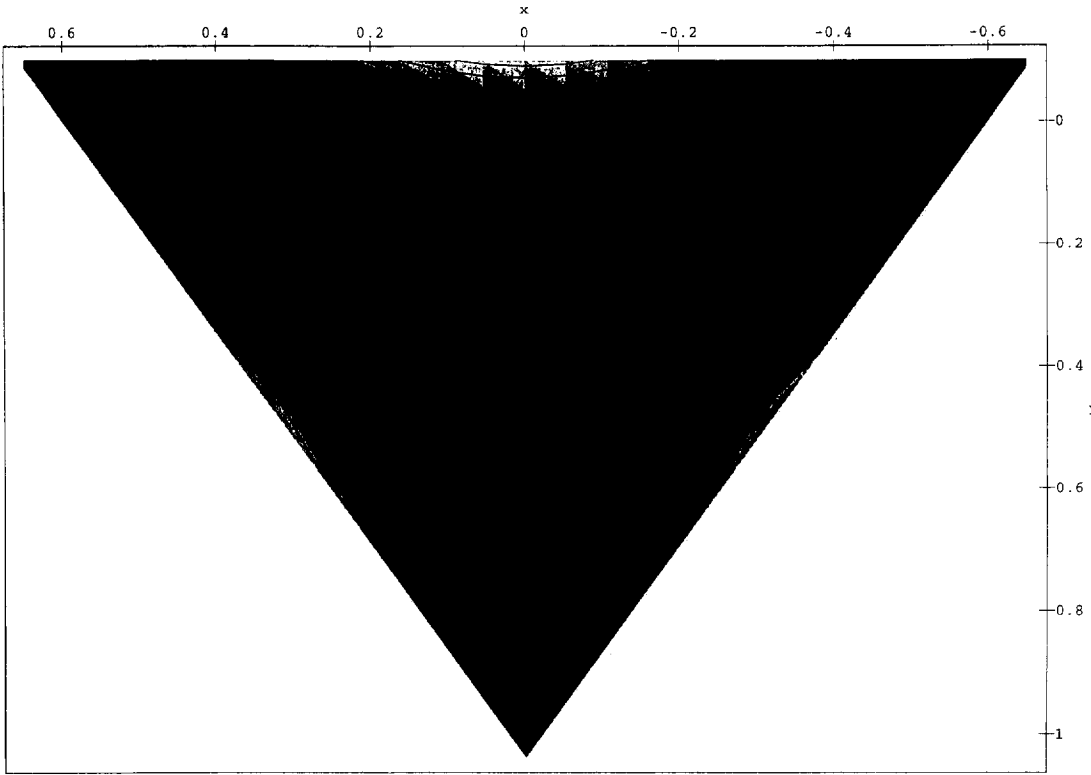


Fig. 1. (continued).

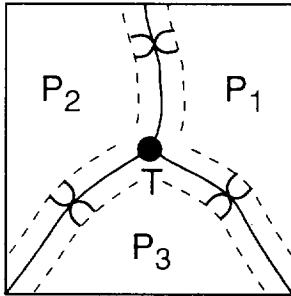


Fig. 2. Triple point between three different phases p_1, p_2, p_3 . Due to the smear out of the phase field variables non-zero values of all three phase fields are observed simultaneously only at the triple point.

Using the constraint (1) we find

$$\frac{\partial p_i}{\partial p_j} = -1 - \sum_{k \ (k \neq i, k \neq j)}^n \frac{\partial p_k}{\partial p_j}, \quad i \neq j, \quad (11)$$

where the functional dependences $\partial p_k / \partial p_j$ are unknown in general. These contributions, however, are

dependent on the coexistence of at least three phases i, j, k and therefore constitute contributions of the order of the triple point energies. Neglecting these contributions as before we find

$$\frac{\partial p_i}{\partial p_j} = -1, \quad i \neq j \quad (12)$$

and accordingly

$$\frac{\partial (\partial_{x_l} p_i)}{\partial (\partial_{x_l} p_j)} = -1, \quad i \neq j, \quad l = 1, 2, 3 \quad (13)$$

for derivatives in all spatial directions x_l .

Inserting the definition of the pair energy \hat{f} (8) into (10) and using (12) and (13) we derive (see Appendix A)

$$\tau_{ik} q_{ik} = \varepsilon_{ik}^2 (p_k \nabla^2 p_i - p_i \nabla^2 p_k) - \frac{1}{2a_{ik}} p_i p_k [p_k - p_i - 2m_{ik}(\Delta T_{ik})], \quad (14)$$

where m_{ik} is the local driving force, dependent on the mobility of the interface and the thermal local undercooling ΔT_{ik} of the interface with respect to the local equilibrium conditions between the phases i and k . Constitutional deviations from equilibrium might also be considered in this context.

The complete set of equations using (14) and (9) reads:

$$\dot{p}_i = \sum_{k (k \neq i)}^n \frac{1}{\tau_{ik}} \left[\varepsilon_{ik}^2 (p_k \nabla^2 p_i - p_i \nabla^2 p_k) - \frac{p_i p_k}{2a_{ik}} (p_k - p_i - 2m_{ik}(\Delta T_{ik})) \right]. \quad (15)$$

This system of n partial differential equations, the n -phase field equations, can be reduced to a system of $(n - 1)$ independent partial differential equations by inserting relation (1). The numerical solution of this set of differential equations on the first look seems to require a substantial computational effort. In a specific computation, it will depend on the local phase state, which of the equations (15) has to be solved. A closer look upon the phase field equation (15) reveals that the time derivative $\dot{p}_i(\mathbf{x}, t)$ vanishes aside from interface regions with

$$\begin{aligned} p_i(\mathbf{x}, t) \cdot p_k(\mathbf{x}, t) &> 0, \\ p_k \nabla^2 p_i &\neq 0 \quad p_i \nabla^2 p_k \neq 0. \end{aligned} \quad (16)$$

Thus in a simulation of a growing microstructure the solution of the phase field equation for each phase i is required only in its interface region. This simple observation reduces drastically the computational effort for the solution of the phase field equations.

In Section 3, the physical significance of the parameters τ_{ik} , ε_{ik} , a_{ik} and m_{ik} is briefly reviewed and some numerical examples are given.

3. Numerical examples

The set of differential equations (15) is solved using a standard Finite Difference algorithm on a rectangular grid. The physical meaning of the coefficients of the equation τ , ε , a , m , is treated elsewhere in detail for the dual phase model [5].

In the multiphase model, these relations must be fulfilled for each pair parameters τ_{ik} , ε_{ik} , a_{ik} , m_{ik} separately, since the dual phase model must be reproduced as a limiting case. It must be noted that only a complete set of parameters τ_{ik} , ε_{ik} , a_{ik} , m_{ik} defines the characteristics of a specific dual boundary and that the differences between two boundaries $i \leftrightarrow k$, $i \leftrightarrow l$ are in general not given by the difference of only a single parameter like ε_{ik} respectively ε_{il} for example.

The parameters τ_{ik} , ε_{ik} , a_{ik} , m_{ik} may be related to the measurable quantities μ_{ik} —mobility, σ_{ik} —surface energy and λ_{ik} —thickness of the interface by the well-known relations [e.g. 1]:

$$\tau_{ik} = \frac{L_{ik} \lambda_{ik}}{T_{ik} \mu_{ik}}, \quad (17)$$

$$\varepsilon_{ik}^2 = \lambda_{ik} \sigma_{ik}, \quad (18)$$

$$a_{ik} = \frac{\lambda_{ik}}{72 \sigma_{ik}}, \quad (19)$$

$$m_{ik} = \frac{6a_{ik} L_{ik} (T_{ik} - T)}{T_{ik}}, \quad (20)$$

where T_{ik} is defined as equilibrium temperature for phase change $i \rightarrow k$ (e.g. melting temperature T_m in solidification problems). L_{ik} is defined as the heat released during phase change $i \rightarrow k$ (e.g. heat of fusion in solidification problems). m_{ik} is defined as the driving force for phase change $i \rightarrow k$ depending on deviation from equilibrium. Note that $m_{ik} = -m_{ki}$ is antisymmetric due to the fact that the release of heat $+L_{ik}$ during the phase change $i \rightarrow k$ is equivalent to the consumption of heat $-L_{ik} = L_{ki}$ during the phase change $k \rightarrow i$. The same argument accounts for the mobility $\mu_{ik} = -\mu_{ki}$. The remaining coefficients are positive and symmetric.

In the following we will present some of our numerical results for single- and multiphase systems:

- Single phase isotropic systems have mainly been investigated to check the performance of the software, but there might also be some interest in such systems with respect to e.g. condensation and growth of liquid droplets in gaseous atmospheres (e.g. in combustion phenomena).

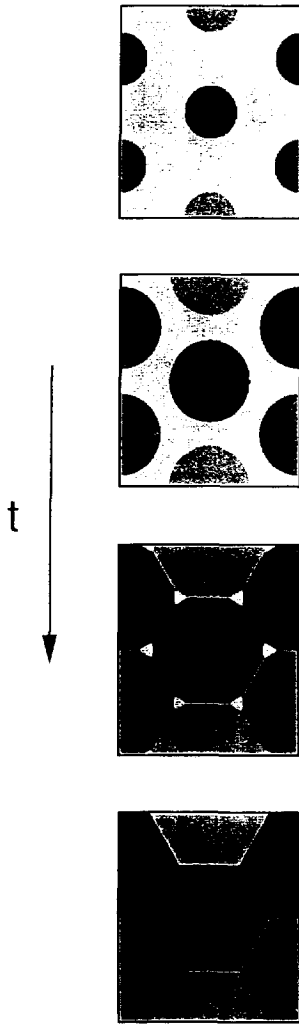


Fig. 3. Evolution of objects of a single isotropically growing phase (e.g. droplets of a liquid growing from a gas-phase). The mutual interaction between the individual droplets leads to the formation of 120° angles at the triple point as to be expected.

Fig. 3 shows the result of a computer simulation of the growth of an array of droplets in a homogeneous undercooled ambient. As initial condition we have introduced four spherical nuclei that were arrayed in a hexagonal lattice with periodic boundary conditions in the two dimensions in order to avoid the effects evoked by the influence of the boundary conditions on the growth and ripening of the droplets. The droplets collide at the same time with each other and the 120° angles at the triple

points that naturally appear after the collision stay exactly at this value on a longer time-scale.

In the case of multiphase systems, triple points between the individual phases may occur, e.g. at the solid–liquid–gas triple point. The different interfacial energies σ_{ik} between solid and liquid (σ_{sl}), solid and vapour (σ_{sv}) and liquid and vapour (σ_{lv}) in this case vary significantly as known from wetting experiments being most important for welding and brazing technology. Taking $\sigma_{ik} \neq \sigma_{il}$ leads to triple points with angles between the individual phases differing from 120° following the well-known relation for the angles at a triple junction in a situation of local mechanical equilibrium [11]:

$$\frac{\sin \alpha_{ij}}{\sigma_{ij}} = \text{constant}. \quad (21)$$

For the given surface energy ratio of e.g.

$$k = \frac{\sigma_{12}}{\sigma_{13}} = \frac{\sigma_{12}}{\sigma_{23}} = 0.5, \quad (22)$$

the angle α_{12} in equilibrium has to be equal to $\alpha_{12} = 2 \arccos(\frac{1}{2}k) = 151^\circ$.

Fig. 4 shows the grain boundary of the same simulation as before, but $\epsilon_{12}^2/\epsilon_{13}^2 = 0.5$. We found an asymptotic approach to $\alpha_{12} = 135^\circ$, but the position does not reach the predicted equilibrium angle at the triple junction. The position versus time is shown in Fig. 4(c). We suppose that the angle has locally already reached its equilibrium value although the corresponding phase boundaries are still curved due to the fact that the entire interface has to adjust.

- Solids in general reveal crystallographic structures. The different crystallographic orientations are related to an anisotropic behaviour, which still has residual symmetries. Describing phase transitions from an isotropic liquid to an anisotropic solid accordingly requires the implementation of anisotropy into the phase field equations. This can be done either by taking the kinetic factor τ_{ik} or the diffusivity of the phase field ϵ_{ik} dependent on the phase boundary orientation relative to the crystallographic orientations of the neighbouring grains/phases ($\tau_{ik} = \tau_{ik}(\theta_i, \theta_k)$; $\epsilon_{ik} = \epsilon_{ik}(\theta_i, \theta_k)$).

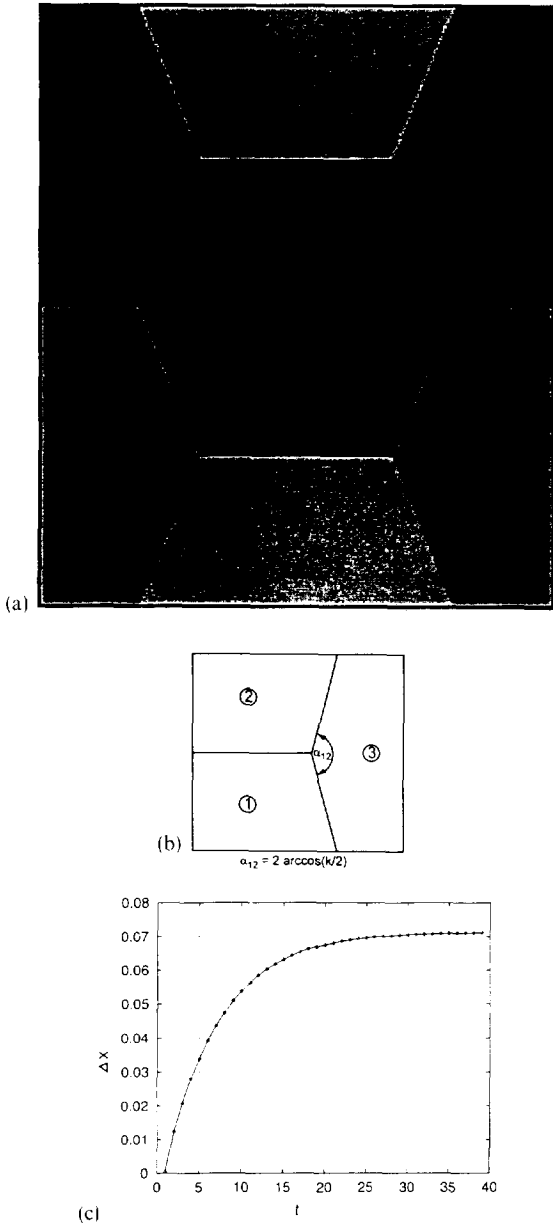


Fig. 4. The difference in interfacial tension between two different phases results in deviation from the 120° symmetry of the triple point (a). The simulation reveals a relaxation of the triple point coordinate (b). The asymptotic value, however, does not correspond to the equilibrium value predicted from analytical considerations (c). Reasons for this behaviour are discussed in the text.

We confine ourselves to formulate the anisotropy of the system by taking an anisotropic relaxation

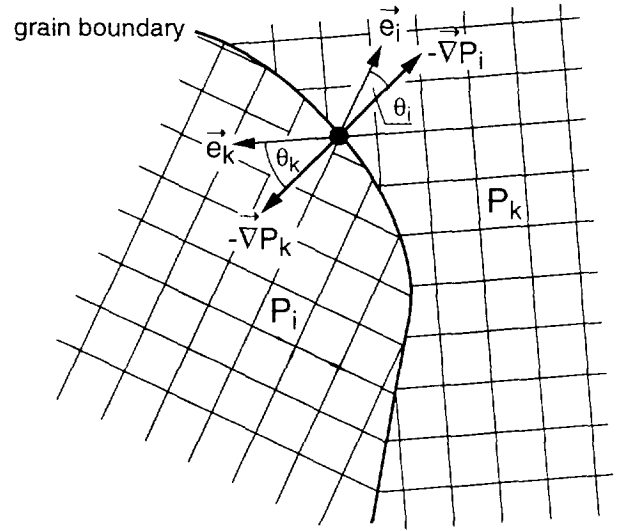


Fig. 5. Definition of the angles θ_i, θ_k being used to describe anisotropic growth of solids. The angle θ_i corresponds to the angle between the normal of the phase boundary determined by ∇p_i and the crystallographic orientation given by the e_i vectors.

rate τ_{ik} :

$$\tau_{ik} = \tau_{ik}(\theta_i, \theta_k), \tag{23}$$

where θ_i, θ_k are related to the crystallographic orientations of the phases i and k , see Fig. 5. In case of solid-liquid boundaries the value τ_{ik} only depends on the crystallographic orientation of the solid phase i , $\tau_{ik} = \tau_{ik}(\theta_i)$. Depending on the choice of these functional relationships the description of diffuse, metallic growth corresponding to a small degree of anisotropy is as well possible as modelling of faceted growth [5].

The multiphase concept in this context can be used to treat different grains of a single phase exhibiting various orientations in space. For this purpose all orientations are divided into ten orientation classes (Pott's model) and each class is identified with one order parameter.

Fig. 6(a) shows the competitive growth of 100 initial nuclei in two dimensions. In Fig. 6(b) a three-dimensional computer simulation of 36 grains with different crystallographic orientation can be seen. Both simulations reveal the grain selection-behaviour of directionally solidified material.

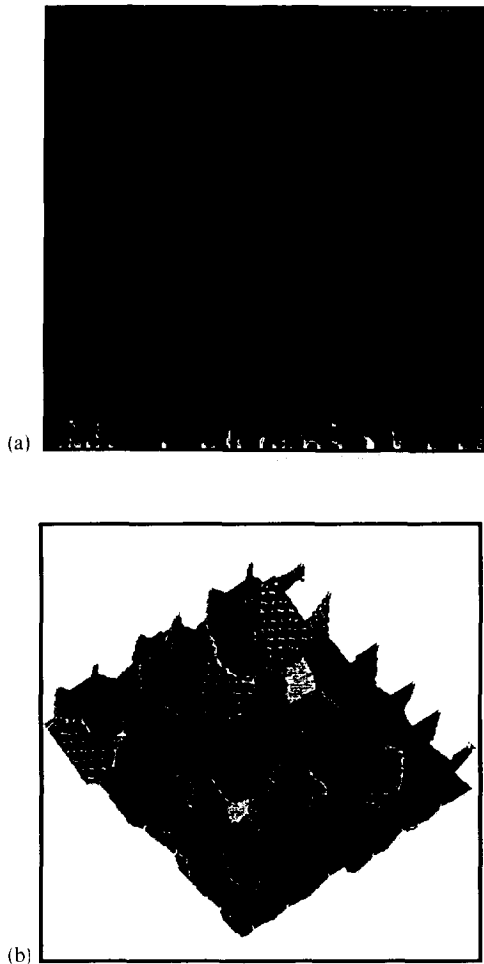


Fig. 6. Competitive growth of anisotropically growing, faceted crystals into an isothermal undercooled melt. The given example shows grain selection phenomena being calculated for solidifying silicon in two (a) and three (b) dimensions.

– Coupling the phase field equations to both thermal and solutal fields allows modelling of microstructure formation in real multiphase alloys such as eutectic (e.g. Fe–C, Al–Si), monotectic (e.g. Al–Pb) and peritectic systems (e.g. TiAl, YBaCuO [12]).

Fig. 7 shows a computer simulation of three different time steps of a growth/dissolution process of a peritectic system. The growth of the faceted peritectic phase p is coupled to the dissolution of the properitectic phase.

In the liquid phase the properitectic particles dissolve corresponding to their particle diameter

(surface curvature). Hence, the local concentration $c(x, T)$ in the liquid arises around the dissolving particles.

It can be observed that the microstructure of the growing material is not planar, but exhibits bridges between the solidifying interface and the properitectic particles as has been proposed and experimentally observed [13].

4. Conclusions and outlook

A phase field model has been proposed allowing the treatment of several thermodynamic phases in global non-equilibrium, where on a local scale pairwise interactions between two phases near thermodynamic equilibrium are considered.

Superposition of these pairwise interactions issues the characteristics of triple point (multiphase equilibria) situations. The solution of the multiphase field equation thereby reveals the kinetics of phase transitions, that is related to the limited diffusion of solute or energy respectively.

The applications of this concept reach from multi-grain systems to eutectic or peritectic transformations in solidification problems. Extensions to other phase transformation problems are possible.

The equilibrium conditions of the interface can be taken from existing thermodynamic data bases. Looking at the variety of existing phase diagrams for metallic alloys or ceramics reveals the potential applications of our method for the prediction of microstructure evolution. Besides implementing existing thermodynamic data, however, many physical properties, especially those of interfacial energies, have to be determined or at least to be estimated.

Our future work will focus on streamlining of the software code in order to calculate microstructures with some hundreds of different objects corresponding to differently oriented grains of various phases. The algorithms will be tested and verified using transparent organic analogues allowing for a quantitative check of the phase evolution dynamics during solidification.

Simultaneously, qualitative studies especially on peritectically growing, technologically important

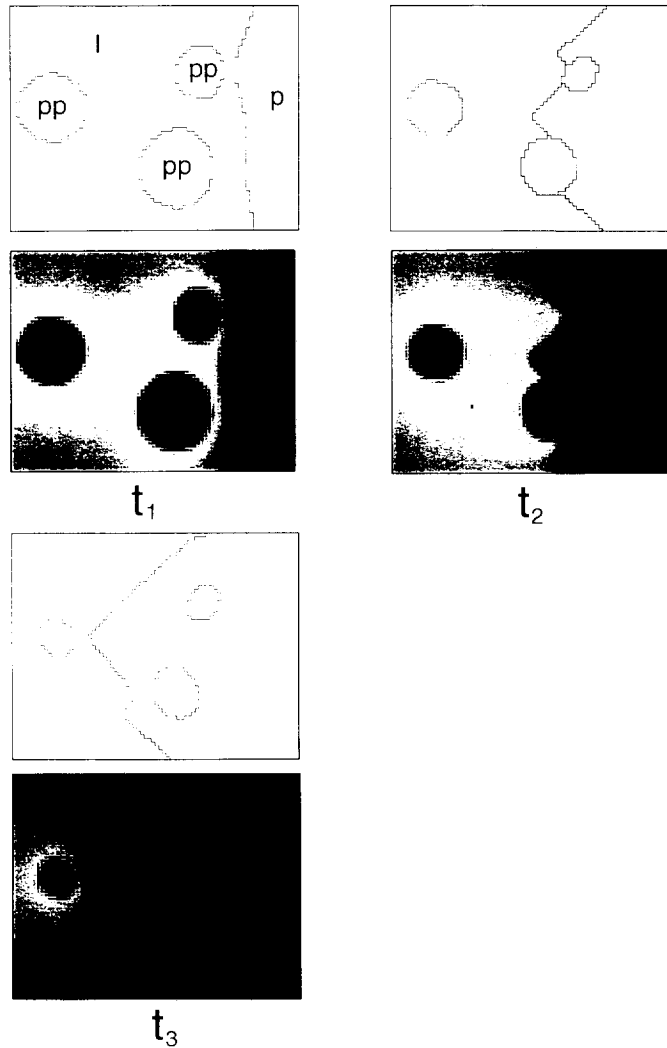


Fig. 7. Computer simulation of three different time steps of a growth/dissolution process of a peritectic system. The growth of the faceted peritectic phase p is coupled to the dissolution of the properitectic phase. The lower figures show the corresponding concentration field with sinks and sources: where light grey describes high, dark grey low concentration of solute in liquid. Black areas denote solid phases.

systems, e.g. Ti–Al or the Y–Ba–Cu–O high T_c superconducting system will be performed and other possible application areas will be identified.

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Appendix A

The aim of this appendix is the derivation of the phase field equation (15) from the free energy density (8), i.e.:

$$\begin{aligned}
F\{p_1, \dots, p_n, \nabla p_1, \dots, \nabla p_n\} \\
= \int \hat{f}(p_1(\mathbf{x}, t), \dots, p_n(\mathbf{x}, t), \\
\nabla p_1(\mathbf{x}, t), \dots, \nabla p_n(\mathbf{x}, t)) dV, \quad (\text{A.1})
\end{aligned}$$

$$\begin{aligned}
\hat{f} &= \hat{f}^{\text{kin}}(p_1(\mathbf{x}, t), \dots, p_n(\mathbf{x}, t), \\
&\nabla p_1(\mathbf{x}, t), \dots, \nabla p_n(\mathbf{x}, t)) \\
&+ \hat{f}^{\text{pot}}(p_1(\mathbf{x}, t), \dots, p_n(\mathbf{x}, t)), \\
\hat{f}^{\text{kin}} &= \sum_{i,k}^n \hat{f}_{ik}^{\text{kin}}, \quad (\text{A.2})
\end{aligned}$$

$$\hat{f}^{\text{pot}} = \sum_{i,k}^n \hat{f}_{ik}^{\text{pot}}, \quad (\text{A.3})$$

$$\hat{f}_{ik}^{\text{kin}} = \frac{1}{2} \varepsilon_{ik}^2 |p_k \nabla p_i - p_i \nabla p_k|^2, \quad (\text{A.4})$$

$$\begin{aligned}
\hat{f}_{ik}^{\text{pot}} &= \frac{1}{4a_{ik}} p_i^2 p_k^2 \\
&- \frac{m_{ik}}{4a_{ik}} \left(\frac{p_i^3}{3} + p_i^2 p_k - \frac{p_k^3}{3} - p_i p_k^2 \right). \quad (\text{A.5})
\end{aligned}$$

The derivation of phase field equations requires the minimization of the free energy F , given in Eq. (A.1).

The phase change rate q_{jk} for the phase change of $p_j \rightarrow p_k$ is given by the variational derivative of the free energy functional F :

$$\tau_{jk} q_{jk} = -\frac{\delta F}{\delta p_j} = \left(\nabla \frac{\partial}{\partial \nabla p_j} - \frac{\partial}{\partial p_j} \right) \hat{f}, \quad (\text{A.6})$$

where we use the notation

$$\nabla \frac{\partial}{\partial \nabla p_j} := \sum_{i=1}^3 \frac{\partial}{\partial x_i} \frac{\partial}{\partial (\partial_{x_i} p_j)}. \quad (\text{A.7})$$

Inserting (A.1) in (A.6) yields

$$\tau_{jk} q_{jk} = \left(\nabla \frac{\partial}{\partial \nabla p_j} - \frac{\partial}{\partial p_j} \right) \sum_{r,s}^n \left\{ \hat{f}_{rs}^{\text{kin}} + \hat{f}_{rs}^{\text{pot}} \right\}. \quad (\text{A.8})$$

Neglecting contributions of the order of triple point energy to the phase change rate of phases j and k , only terms with indices j and k are considered. This way, the sum reduces to

$$\tau_{jk} q_{jk} = \left(\nabla \frac{\partial}{\partial \nabla p_j} - \frac{\partial}{\partial p_j} \right) \left\{ \hat{f}_{jk}^{\text{kin}} + \hat{f}_{jk}^{\text{pot}} \right\} \quad (\text{A.9})$$

$$\begin{aligned}
&= \nabla \frac{\partial}{\partial \nabla p_j} \left(\hat{f}_{jk}^{\text{kin}} \right) + \nabla \frac{\partial}{\partial \nabla p_j} \left(\hat{f}_{jk}^{\text{pot}} \right) \\
&- \frac{\partial}{\partial p_j} \left(\hat{f}_{jk}^{\text{kin}} \right) - \frac{\partial}{\partial p_j} \left(\hat{f}_{jk}^{\text{pot}} \right) \quad (\text{A.10}) \\
&= (\text{a}) + (\text{b}) - (\text{c}) - (\text{d}).
\end{aligned}$$

The different contributions are treated separately:

Contribution (b) obviously vanishes due to the fact that $\hat{f}_{jk}^{\text{pot}}$ does not depend on ∇p_j .

In the following we deal with term (a). For this purpose we define

$$\partial_{x_i} p_j := \frac{\partial p_j}{\partial x_i}, \quad (\text{A.11})$$

and

$$\partial_{x_i}^2 p_j := \frac{\partial^2 p_j}{\partial x_i^2}. \quad (\text{A.12})$$

Using Eq. (A.4) yields:

$$\begin{aligned}
(\text{a}) &= \nabla \frac{\partial}{\partial \nabla p_j} \hat{f}_{jk}^{\text{kin}} \\
&= \nabla \frac{\partial}{\partial \nabla p_j} \frac{\varepsilon_{jk}^2}{2} |p_k \nabla p_j - p_j \nabla p_k|^2 \\
&= \frac{\varepsilon_{jk}^2}{2} \sum_{i=1}^3 \frac{\partial}{\partial x_i} \left\{ \frac{\partial}{\partial (\partial_{x_i} p_j)} |p_k \nabla p_j - p_j \nabla p_k|^2 \right\}. \quad (\text{A.13})
\end{aligned}$$

The term in braces may be written as

$$\begin{aligned}
&\frac{\partial}{\partial (\partial_{x_i} p_j)} |p_k \nabla p_j - p_j \nabla p_k|^2 \\
&= \frac{\partial}{\partial (\partial_{x_i} p_j)} \left| p_k \begin{pmatrix} \partial_{x_1} p_j \\ \partial_{x_2} p_j \\ \partial_{x_3} p_j \end{pmatrix} - p_j \begin{pmatrix} \partial_{x_1} p_k \\ \partial_{x_2} p_k \\ \partial_{x_3} p_k \end{pmatrix} \right|^2 \quad (\text{A.14}) \\
&= \frac{\partial}{\partial (\partial_{x_i} p_j)} \left[(p_k \partial_{x_1} p_j - p_j \partial_{x_1} p_k)^2 \right. \\
&\quad \left. + (p_k \partial_{x_2} p_j - p_j \partial_{x_2} p_k)^2 + (p_k \partial_{x_3} p_j - p_j \partial_{x_3} p_k)^2 \right] \quad (\text{A.15}) \\
&= 2(p_k \partial_{x_i} p_j - p_j \partial_{x_i} p_k) \left(p_k - p_j \frac{\partial_{x_i} p_k}{\partial_{x_i} p_j} \right) \\
&= 2(p_k \partial_{x_i} p_j - p_j \partial_{x_i} p_k)(p_k + p_j) \quad (\text{by Eq. (13)}). \quad (\text{A.16})
\end{aligned}$$

The term $(p_k + p_j)$ is a finite constant between 0 and 1 and – considering no third phase coexisting – it takes the value 1.

These calculations lead to

$$\begin{aligned}
 \text{(a)} &= \frac{\varepsilon_{jk}^2}{2} \sum_{i=1}^3 \frac{\partial}{\partial x_i} \{2(p_k \partial_{x_i} p_j - p_j \partial_{x_i} p_k)\} \\
 &= \varepsilon_{jk}^2 \sum_{i=1}^3 \left\{ (\partial_{x_i} p_k) (\partial_{x_i} p_j) + p_k \left(\partial_{x_i}^2 p_j \right) \right. \\
 &\quad \left. - (\partial_{x_i} p_j) (\partial_{x_i} p_k) - p_j \left(\partial_{x_i}^2 p_k \right) \right\} \\
 &= \varepsilon_{jk}^2 \sum_{i=1}^3 p_k \partial_{x_i}^2 p_j - p_j \partial_{x_i}^2 p_k \\
 &= \varepsilon_{jk}^2 (p_k \nabla^2 p_j - p_j \nabla^2 p_k). \quad \text{(A.17)}
 \end{aligned}$$

Next it is shown that contribution (c) vanishes. For this purpose we write:

$$\text{(c)} = \frac{\partial}{\partial p_j} \hat{f}_{jk}^{\text{kin}} \quad \text{(A.18)}$$

$$= \frac{\partial}{\partial p_j} \frac{\varepsilon_{jk}^2}{2} |p_k \nabla p_j - p_j \nabla p_k|^2 \quad \text{(A.19)}$$

$$= \varepsilon_{jk}^2 (p_k \nabla p_j - p_j \nabla p_k) \frac{\partial}{\partial p_j} (p_k \nabla p_j - p_j \nabla p_k) \quad \text{(A.20)}$$

$$= \varepsilon_{jk}^2 (p_k \nabla p_j - p_j \nabla p_k) \left(\left(\frac{\partial p_k}{\partial p_j} \right) \nabla p_j - \nabla p_k \right). \quad \text{(A.21)}$$

Use of Eq. (12) yields

$$\text{(c)} = \varepsilon_{jk}^2 (p_k \nabla p_j - p_j \nabla p_k) (-\nabla p_j - \nabla p_k). \quad \text{(A.22)}$$

Under the assumption that only the phases j and k are present at j - k boundary, i.e. $\nabla p_j = -\nabla p_k$, the term (c) is equal to zero.

Finally we treat contribution (d) and consider Eq. (12):

$$\begin{aligned}
 \text{(d)} &= \frac{\partial}{\partial p_j} \hat{f}_{jk}^{\text{pot}} \\
 &= \frac{\partial}{\partial p_j} \left\{ \frac{1}{4a_{jk}} p_j^2 p_k^2 \right. \\
 &\quad \left. - \frac{m_{jk}}{4a_{jk}} \left(\frac{p_j^3}{3} + p_j^2 p_k - \frac{p_k^3}{3} - p_j p_k^2 \right) \right\} \quad \text{(A.23)}
 \end{aligned}$$

$$\begin{aligned}
 &= \frac{1}{4a_{jk}} \left\{ 2p_j p_k^2 + 2p_j^2 p_k \frac{\partial p_k}{\partial p_j} - m_{jk} \left(p_j^2 + 2p_j p_k \right. \right. \\
 &\quad \left. \left. + p_j^2 \frac{\partial p_k}{\partial p_j} - p_k^2 \frac{\partial p_k}{\partial p_j} - p_k^2 - 2p_j p_k \frac{\partial p_k}{\partial p_j} \right) \right\} \\
 &= \frac{1}{4a_{jk}} \{2p_j p_k (p_k - p_j) - 4m_{jk} p_j p_k\} \quad \text{(A.24)}
 \end{aligned}$$

$$= \frac{1}{4a_{jk}} \{2p_j p_k (p_k - p_j) - 4m_{jk} p_j p_k\} \quad \text{(A.25)}$$

$$= \frac{1}{2a_{jk}} p_j p_k (p_k - p_j) - \frac{m_{jk}}{a_{jk}} p_j p_k. \quad \text{(A.26)}$$

Inserting these results in Eq. (A.10) we get

$$\begin{aligned}
 \tau_{jk} q_{jk} &= \varepsilon_{jk}^2 (p_k \nabla^2 p_j - p_j \nabla^2 p_k) \\
 &\quad - \frac{1}{2a_{jk}} p_j p_k (p_k - p_j) + \frac{m_{jk}}{a_{jk}} p_j p_k. \quad \text{(A.27)}
 \end{aligned}$$

Finally, the phase field equation (15) is obtained by summing up all possible phase change contributions. According to Eq. (9) one obtains:

$$\begin{aligned}
 \dot{p}_j &= \sum_{k (k \neq j)}^n q_{jk} \\
 &= \sum_{k (k \neq j)}^n \frac{1}{\tau_{jk}} \left\{ \varepsilon_{jk}^2 (p_k \nabla^2 p_j - p_j \nabla^2 p_k) \right. \\
 &\quad \left. - \frac{1}{2a_{jk}} p_j p_k (p_k - p_j) + \frac{m_{jk}}{a_{jk}} p_j p_k \right\}, \quad \text{(A.28)}
 \end{aligned}$$

which we set out to deduce.

Finally, let us ensure that the sum $\sum_{j=1}^n p_j(\mathbf{x}, t)$ is conserved. This is equivalent to deriving from the phase field equations that $\sum_{j=1}^n \dot{p}_j = 0$ is valid.

Bearing in mind that $\tau_{jk} = \tau_{kj}$, $\varepsilon_{jk}^2 = \varepsilon_{kj}^2$, $a_{jk} = a_{kj}$ and $m_{jk} = -m_{kj}$, it is easily seen from (31) that $q_{jk} = -q_{kj}$ is valid. Thus the sum $\sum_{j=1}^n \dot{p}_j$ can be written as:

$$\begin{aligned}
 \sum_{j=1}^n \dot{p}_j &= \sum_{j=1}^n \sum_{k (k \neq j)}^n q_{jk} \\
 &= \sum_{j=2}^n \sum_{k=1}^{j-1} q_{jk} + \sum_{j=1}^{n-1} \sum_{k=2}^n q_{jk} \quad \text{(A.29)}
 \end{aligned}$$

$$= \sum_{j=2}^n \sum_{k=1}^{j-1} q_{jk} - \sum_{j=1}^{n-1} \sum_{k=2}^n q_{kj} \quad \text{(A.30)}$$

$$\begin{aligned}
&= \sum_{j=2}^n \sum_{k=1}^{n-1} (k < j) q_{jk} - \sum_{k=1}^{n-1} \sum_{j=2}^n (j > k) q_{jk} \\
&= \sum_{j=2}^n \sum_{k=1}^{n-1} (k < j) q_{jk} - \sum_{j=2}^n \sum_{k=1}^{n-1} (k < j) q_{jk} \\
&= \sum_{j=2}^n \sum_{k=1}^{n-1} (q_{jk} - q_{jk}) = 0
\end{aligned} \tag{A.31}$$

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