Phase-field modelling for metals and colloids and nucleation therein—an overview

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Abstract

Phase-field modelling, as it is understood today, is still a young discipline in condensed matter physics, which established itself for that class of systems in condensed matter physics, which can be characterized by domains of different phases separated by a distinct interface. Driven out of equilibrium, their dynamics results in the evolution of those interfaces, during which those might develop into well-defined structures with characteristic length scales at the nano-, micro- or mesoscale. Since the material properties of such systems are, to a large extent, determined by those small-scale structures, acquiring a precise understanding of the mechanisms that drive the interfacial dynamics is a great challenge for scientists in this field. Phase-field modelling is an approach that allows us to tackle this challenge simulation-based. This overview summarizes briefly the essentials of the conceptual background of the phase-field method, as well as recent issues the phase-field community is focusing on, as far as they are related to nucleation. To that end a brief introduction to the basic understanding underlying the diffuse interface description, which is the conceptual backbone of phase-field modelling, is given at the beginning, followed by a detailed picture of its achievements so far in applications to nucleation phenomena in metals and colloids. Within the most relevant fields of condensed matter physics, approached by phase-field modelling until now, applications to metallic systems are a traditional domain of phase-field modelling and nucleation phenomena therein have been addressed by several groups. This paper provides an overview of these. Advances in the field of colloidal systems, on the other hand, are only more recent and are addressed here in the context of contributions to soft matter physics in general.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

This introduction to the phase-field part of this *Journal of Physics: Condensed Matter* special issue does not aim at a comprehensive review of phase-field modelling. For such recent reviews the reader is referred to [1–3] and references therein. Here the idea is rather to put together some basic concepts and some recent issues of phase-field modelling as far as they are relevant for the topic of this volume. To that end this overview paper starting the volume's phase-field part will focus on an overview of contributions based on phase-field modelling to nucleation as well as soft matter systems as the larger class of systems to which colloids belong.

This paper is organized as follows. First I briefly summarize some basic concepts underlying phase-field modelling. Afterwards I discuss recent issues in the phase-field community. Successively I will address contributions to nucleation and soft matter systems and I conclude with an outlook.

2. The basic concept of phase-field modelling

Many inhomogeneous systems involve domains of well-defined phases separated by a distinct interface. If they are driven out of equilibrium one phase will grow at the cost of the other. Examples are phase separation by spinodal

decomposition or nucleation and subsequent growth of the nucleus in the nourishing phase [4]. Another example which has often been discussed as a paradigmatic problem is that of dendritic solidification [5–7, 10]. The phenomenological description of these phenomena involves the definition of a precisely located interfacial surface on which boundary conditions are imposed. One of those boundary conditions typically yields a normal velocity at which the interface is moving. This is the so-called *sharp interface* approach, adopted both in analytical and numerical studies for a variety of contexts involving a moving boundary. The origin of such a description is often transparent, being obtained by symmetry arguments and common sense as well as mass and energy conservation considerations. Nevertheless the properties of sharp interface models can be quite subtle as in the case for dendritic growth. This is strongly coupled to the question of how to view the interfacial surface. Already when introducing the notion of a surface quantity Gibbs implicitly entertained the idea of a diffuse interface [8]: any density of an extensive quantity (e.g. the mass density) between two coexisting phases varies smoothly from its value in one phase to its value in the other. The existence of a transition zone, though microscopically of atomic extent, underlies this definition of surface quantities as given by Gibbs. In phase transition phenomena, this notion has been employed in the spirit of Landau and Khalatnikov [11], who were the first to introduce an additional parameter—i.e. a *phase field*—to label the different phases in their theory on the absorption of liquid helium. Essentially phase-field modelling, as it appeared subsequently in the literature in the context of phase transition phenomena [9, 12], is connected to such an additional order parameter. Clearly such models have advanced numerical treatment as well as understanding of interfacial growth phenomena since.

Even though quite a young approach to tackle such problems, phase-field models have been employed by different groups in quite different spirits. One might even be tempted to say that a variety of philosophies accompanying phase-field modelling have already emerged. One way to view this method to model interfacial growth is to understand it as a numerical technique, which helps to overcome the necessity of solving for the precise location of the interfacial surface explicitly in each time step of a numerical simulation as achieved by the introduction of one or several additional phase-field variables. In such an approach the phase-field variables are continuous fields which are functions of space **r** and time *t*. They are introduced to describe the different relevant phases. Typically these fields vary slowly in bulk regions and rapidly, on length scales of the order of the correlation length ξ, near interfaces. ξ is also a measure of the finite thickness of the interface. The free energy functional $\mathcal{A}$ determines the phase behaviour. Together with the equations of motion this yields a complete description of the evolution of the system. In other contexts, such as critical dynamics [13, 4, 14], the fields are order parameters distinguishing the different phases. In a binary alloy, for example, the local concentration or sub-lattice concentration can be described by such fields. The ideas involved in this approach have a long history, referring back to van der Waals [15, 16].

With this background the materials science community associates the use of continuum field models in particular with the work of Cahn and collaborators [17, 9, 18]. Within their contribution to the field, phase-field models are more than just a 'trick' to overcome numerical difficulties. Rather they are rigorously derived based on the variational principles of irreversible thermodynamics as founded by Onsager [19]. Then, ensuring *thermodynamic consistency* of the model equations can serve as a justification of a phase-field model. In this sense phase-field models can also be formulated for problems for which sharp interface equations are not yet available. Consequently it might be their analysis which yields a formerly unknown sharp interface formulation and helps to clarify the physics in the interfacial region.

One has to contrast this procedure with a very established second way to validate a phase-field model. This second approach assumes that a given sharp interface formulation of the growth problem is the correct description of the physics under consideration. On the basis of this assumption, a phase-field model can be justified by simply showing that it is asymptotic to the correct sharp interface description, i.e. that the latter arises as the *sharp interface limit* of the phase-field model when the interface width is taken to zero. Obviously this procedure works only for cases in which a well-established set of continuum equations describing the dynamics in the sharp interface formulation does exist. Moreover, employed in this way phase-field models do not seem to be much help to elucidate the physics of the interfacial region beyond what is captured within the sharp interface model equations.

However, the latter is only partially true and leads to a third philosophy appearing in the phase-field community lately. It is rooted in the understanding of the interfacial surface to be finite in the sense of Gibbs denoted above: if one assumes a phase-field model to be thermodynamically consistent and to describe a physical situation for which an established sharp interface formulation exists, as well, then, certainly, in the *sharp interface limit* the phase-field model should correspond precisely to that sharp interface formulation. However, keeping in mind that the interface can be understood to be of finite width, not only the *sharp interface limit* of a phase-field model is a meaningful physical limit, but also the so-called *thin interface limit* introduced by Karma and Rappel [20–22].

To clarify the difference between the *sharp interface limit* and this *thin interface limit* here I will consider the growth of a dendrite with tip radius R into an undercooled melt [23]. Under more general circumstances, R might be representative of a typical macroscopic length scale such as the container size. For dendritic solidification at large undercoolings the growth is rapid and the radius of curvature of the dendritic tip is relatively small. As a consequence effects of capillary action and kinetics on the local interfacial temperature can be significant. In this regime, sharp interface limits of the phase-field equations have been performed [24–29], which assume that the dimensionless interfacial temperature u is of the order of the small parameter ξ/R. Contributions from capillary effects and kinetics can be regarded to be of the same order. In this limit one also considers ξ to be small compared to the capillary length l_c, which presents a stringent resolution

requirement for a numerical computation that aspires to describe this limiting case. At low undercoolings, on the other hand, dendrites grow more slowly and have a larger radius of curvature, so that it is reasonable to model capillary effects and kinetics as small corrections. Karma and Rappel refer to the corresponding analysis as the *thin interface limit*. For this thin interface limit one assumes $\xi \ll R$ but allows $\xi \sim l_c$. Almgren [30] has described this analysis as *isothermal asymptotics*, since to leading order in ξ/R the temperature is isothermal throughout the interfacial region with $u = O(\xi/R)$. An extension to general non-isothermal multicomponent alloy systems allowing for arbitrary phase diagrams with two phases was achieved in [31] only recently based on a second-order asymptotics.

Now again one interest in employing such an isothermal asymptotics or thin interface limit can be understood to be of numerical origin: it can serve to legitimize a choice of model parameters which ensures an improved numerical performance. On the other hand, isothermal asymptotics can also be used to obtain first-order generalizations of the well-known Gibbs–Thompson relation, which usually yields the temperature value locally at the interface. In turn, such a generalization can facilitate subsequent stability analysis of the model.

Thus currently phase-field modelling is a field in which numerical efforts as well as an intense focus on thermodynamic backgrounds and asymptotic behaviour of the models drive the development of this approach. It is this symbiosis which opens up new perspectives to gain further understanding about interfacial growth problems, if one extends the paradigmatic, purely diffusion-limited, dendritic growth problem step by step to further physical mechanisms such as, for example, additional hydrodynamical or mechanical driving forces. Moreover, this allows us to also tackle the behaviour of other material systems such as soft matter systems with the perspective, on the one hand, to investigate at least paradigmatic features of fundamental problems of condensed matter physics related to interfacial and phase dynamics on a general, system-independent level for the easiest accessible material systems.

3. Recent issues in phase-field modelling

The efforts described in this paper so far have resulted in very elaborate model formulations as well as very elaborate numerical implementations (see, e.g., [33]), which by now allow us to simulate, for example, the growth of a single dendritic microstructure by taking into account at the same time long-range transport fields in reasonable time and high spatial resolution. Thereby such approaches constitute an important contribution to carry out the relevant parameter studies to identify the mechanisms determining the coupled phase and micro- or nanostructure dynamics in a condensed matter systems. In computational materials design, for example, this allows us to investigate the relation between processing parameters and microstructure evolution and—at best—also successively the materials properties at the macroscale of a material systems via phase-field model parameter studies.
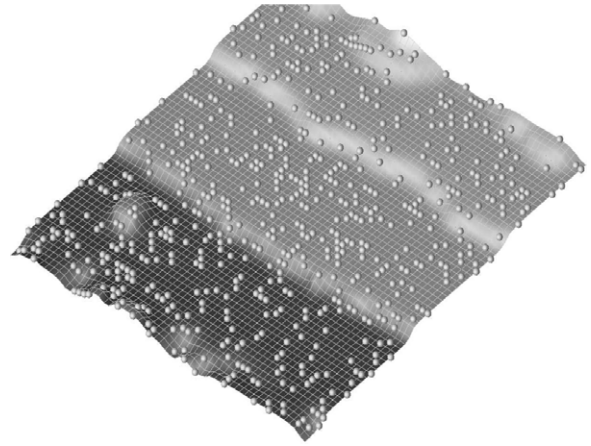

Figure 1. The result of a simulation where the phase-field approach has been coupled to a Monte Carlo scheme. The coupled approach has been applied to epitaxial growth of a vicinal surface. As depicted in the figure, the microscopic structure of the vicinal steps is captured via the phase-field function, whereas the deposited atoms are resolved as single atoms via the Monte Carlo scheme. The precise coupling algorithm is described in [36]. Figure courtesy of M Radke de Cuba.

3.1. Designing multi-scale models based on the phase-field approach

The above reveals that there is an inherent challenge to the simulation-based study of coupled phase and structure evolution problems in condensed matter physics, to which phase-field models can be applied: the latter is essentially a multi-scale dynamics, i.e. a dynamics where different evolution paths occurring at different length and timescales are strongly coupled to each other. On this background it is quite easy to understand that, in the further development of the phase-field method in the context of computational materials design, a lot of activities are concerned with this 'scale-bridging' issue. Basically three ways have emerged in the community to do so. The first is to design innovative algorithms which couple different computational techniques originally designed for complementary scales such as, for example, DLA (diffusion-limited aggregation) [32], LBA (lattice Boltzmann automata) [34] or MC (Monte Carlo) [36] (see figure 1) schemes to a phase-field model. The second is to use advanced numerical techniques, such as multi-grid, adaptivity and parallelization, to do fast computations for several scales based on a single model approach [38, 37, 33]. A third possibility arises from analytics, i.e. rigorous homogenization methods where one identifies the most relevant dynamical processes at each scale and develops a scale-bridging model based on these via expansion techniques [35]. With respect to the first way, i.e. the coupling of different computational techniques originally designed for complementary scales, one has to distinguish between two approaches to do so: the first is to couple the different techniques dynamically, such that in every time step of the overall algorithm calculations with both methods are carried out and well-defined quantities are continuously evaluated and exchanged across the scales. The examples above [32, 34, 36] fall
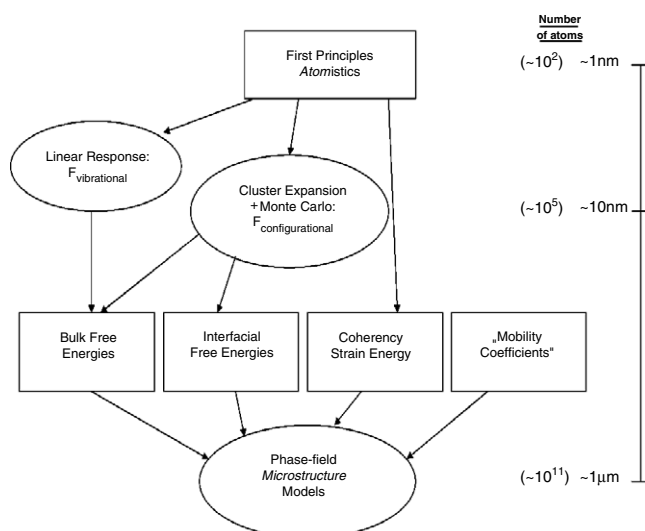
Figure 2. Illustration of the general multi-scale first-principles/phase-field method following a *weak coupling* coupling concept describe in [39]. Redrawn from [39] with permission of the authors.

into this category. From a computational point of view this is still very demanding and possible only for carefully selected problems. Certainly homogenization methods can help to establish more model approaches of this kind in the future. A second approach is the calculation of physical quantities, which are determined at lower scales of the overall simulation and can be assumed to be constant during the simulation at the larger scales, *a priori* to insert them into the upper scale simulations as fixed parameters. Whereas the latter has sometimes been termed *weak coupling*, the former is often referred to as *hard* or *full dynamic coupling*. A very general multi-scale first-principles/phase-field method following a *weak coupling* concept has recently been developed in [39]. It can be pictured as depicted in figure 2.

Apart from these 'scale-bridging' efforts, likewise noteworthy broader directions of further development of the phase-field method have emerged.

3.2. Simulating nanoscale interfacial dynamics in condensed matter physics

What's remarkable about this point is that, due to the continuum field nature of the phase-field approach, one would claim that it should not be valid in the nanoscale region. However, due to the successes of continuum approaches in nanofluidics it appears to be justifiable to proceed with phase-field models for phase transition problems of a similar physical nature at this scale, as well. Indeed quite successful studies have been carried out already [41]. Also the idea of employing phase-field models to investigate heterogeneous nucleation dynamics as reviewed in section 4 is based upon this underlying physical picture.

3.3. Dynamics in soft matter systems at the micro- and nanoscale

The application of phase-field modelling to soft matter systems is still more recent than its application to metallic alloys, which corresponds to the fact that soft matter physics as such is certainly still more of an emergent scientific field than the classical metal physics. Nevertheless there is a relation between the two in the following sense: colloids— displaying a structural length scale between several nanometres and one micrometre—have started to establish themselves as model systems to investigate fundamental questions that concern the phase and structure dynamics of metallic alloys. The reason is that, from an experimental point of view, the parameters which quantify the nucleation and growth kinetics of these material systems can be measured more easily than in, for example, metallic melts. This concerns, among others, the nucleation rate, the interfacial energies as well as the kinetic and capillary anisotropies of a phase interface. For this reason the investigation of nucleation and initial growth dynamics in an interdisciplinary effort, spanning colloidal and traditional metallic material systems, seems promising to yield new insights also for the latter. It comes along with the fundamental question of condensed matter physics also underlying the priority programme 1296 [40] and thus the papers of this volume: can the analogy between different condensed matter systems be taken that far so that the investigation of experimentally and theoretically simpler-to-handle systems can answer questions of interfacial and phase dynamics in a system-independent general manner?

Another prominent soft matter model system is that of a liquid capsule enclosed by a thin elastic shell. Looking at this model problem one realizes that modelling its small-scale dynamics shares again a lot of challenges with today's problems to obtain reliable, quantitative micro-mechanical models for the dynamics in material systems. For liquid capsules these problems have recently received considerable attention in cellular biology, bioengineering, and micro-encapsulation technology (see, e.g., [135] and references therein). Lately also in this field phase-field models have been successfully applied, e.g. to the dynamics of microscopic vesicle membranes as red blood cell membranes.

Sharing a lot of the challenges of today's problems in materials science applies to further soft matter systems such as polymer systems and liquid crystals as well. Also in these fields contributions by phase-field modelling could be achieved, which will be reviewed in the following.

In all of the examples of this section the further development of phase-field modelling benefits largely from strong collaborations with experimental partners to verify models but also to get a better feeling for the accuracy of model parameters and basic mechanisms essential to grasp in any model description. Certainly the above survey cannot claim completeness due to the starting popularity of phase-field modelling in quite different communities. However, it reflects to a large extent the content of 'phase-field-dominated' sessions at related conferences such as the national physics conferences in Europe and the APS spring meeting.

4. Nanoscale simulations of nucleation in multicomponent and multi-phase alloys

The application of phase-field modelling to nucleation as a phenomenon at the nanoscale is justified, if one takes into account the great success of continuum approaches in nanofluidics as proven by vast comparison to experiments. Employed in this manner it provides an approach allowing us to account for effects of the physical diffuseness of a nucleus interface and thereby go beyond classical nucleation theory[1]. To put the development of phase-field modelling for nucleation phenomena in context, I will first provide a brief review of the classical concepts of nucleation theory to which I refer later in the remainder of the introduction to this section, before I discuss the more recent phase-field-based contributions to this field.

Nucleation is a complex fluctuation phenomenon. Atomistic simulations performed by Swope and Andersen [48] and Wolde and Frenkel [49] reveal that, even during homogeneous crystal nucleation in a single-component liquid, several local atomic arrangements (bcc, fcc, hcp, icosahedral) compete, of which ofttimes a metastable phase becomes dominant. For multicomponent and multi-phase alloys the complexity increases, as the composition of nuclei enters as an extra state variable. Nevertheless, the development of approaches towards multicomponent nucleation is still based on the classical kinetic theory of nucleation, which had first been formulated by Farkas [50] and Becker and Döring for homogeneous nucleation, and was successively adopted for general first-order phase transformations in condensed matter physics by Turnbull and Fisher [51]. The approach relies on a set of master equations that consider only single-molecule attachment and detachment processes (a good approximation at the early stages of solidification). Analytical as well as numerical treatment of the problem indicates that, after a transient period, steady-state conditions are established, under which the nucleation rate, i.e. the net volumetric formation rate of critical fluctuations, can be expressed as

$$I = I_0 \exp\left(\frac{\Delta F^\star}{k_B T}\right). \qquad (1)$$

Here I_0 is the nucleation prefactor, $F^\star$ is the free energy of critical fluctuations, while k_B and T are the Boltzmann factor and the temperature, respectively. In determining the free energy of the heterophase fluctuations, the classical nucleation theory relies on the droplet model (introduced by Gibbs for studying phase stability), which views the heterophase fluctuations as spherical crystals, whose free energy is expressed in terms of their radius R and the volumetric free energy difference $\Delta g(<0)$ between bulk and crystal and the undercooled liquid, as well as the interfacial free energy γ:

$$F = \left(\frac{4\pi}{3}\right) R^3 \Delta g + 4\pi R^2 \gamma. \qquad (2)$$

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[1] Note that, in this context, essentially the width over which the phase-field variable varies gains a physical interpretation.
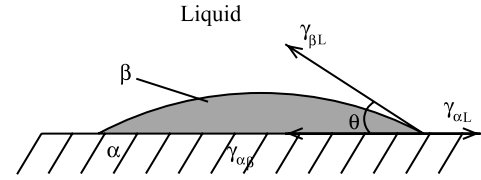

Figure 3. Heterogeneous nucleation of a 'spherical cap'-shaped second phase β on a planar initial phase α according to the 'spherical cap' model. This figure, just as for further figures in this section, courtesy of R Siquieri following [84].

Equation (2) reveals that a maximum of $F^\star = (16\pi/3)\gamma^3/\Delta g^2$ is reached at the critical radius $R^\star = -2\gamma/\Delta g$.

The adaptation of this classical droplet model to heterogeneous nucleation has been reviewed by Christian [52]. The most commonly discussed model in this context is the spherical cap model, taking into account the free energy reduction due to the creation of a triple junction line between the nucleating solid, the liquid and a pre-existing solid phase (container wall, foreign particle, primary phase), which acts as substrate (see figure 3). Under such conditions only a fraction of the homogeneous nucleus needs to be formed by random fluctuations, a phenomenon that reduces the height of the nucleation barrier. For a planar interface, the critical fluctuation is a spherical cap, whose size is determined by the contact angle θ between the solid–substrate and liquid–solid interfaces. This accounts for the case where heterogeneous nucleation comes along with partial wetting of the seed nucleus. A still different nucleation mechanism, which is not discussed in the following, is based on complete wetting. Details on this mechanism can be found in [164], and in relation to heterogeneous nucleation in [165].

In the above partial wetting scenario the contact angle is fully determined by the free energies of the solid–liquid, solid–substrate and liquid–substrate interfaces. Under such conditions, the ratio of the free energies of the heterogeneous and homogeneous nuclei is given by the catalytic potency factor:

$$f(\theta) = (2 + \theta)(1 - \cos\theta)^2/4. \qquad (3)$$

The drawbacks of classical nucleation theory emerge from those of the droplet model, which rely on the thermodynamic properties of the macroscopic bulk phase, when calculating the free energy of near-critical clusters. According to the experiments by Howe [53] and Huisman *et al* [54] and computer simulations, as reviewed by Laird and Haymet [55], the crystal–liquid and crystal–glass interfaces are diffuse on the molecular scale, extending over several molecular layers, with an interface thickness comparable to the size of critical fluctuations. This invalidates the main assumption of the droplet model, that the interface thickness is negligible with respect to the size of the fluctuations. As a consequence two new challenges emerge:

(i) To derive a kinetic theory that incorporates the differences in the diffusion of the individual species.

 (ii) To develop models that include the dependence of the Gibbs free energy and interface free energy on cluster composition and cluster size for multicomponent alloys.

Reviews by Gunton [56], Granasy and James [57] and Oxtoby [58] give a survey of these new developments. Here I only focus on theories that address nucleation in binary and multicomponent alloys, in particular the contribution of phase-field modelling with respect to the two upper issues, to clarify the kind of contribution that can be expected by phase-field theory in this context.

Even if the application of phase-field modelling to nucleation can be justified as discussed in section 3.2, any kind of field theoretical approach to nucleation needs to be validated carefully by comparison to molecular simulation models and density functional theory predictions as well as experiments (see figure 9). Since the molecular modelling addressing fundamental nucleation-related issues has quite often been done for the easiest accessible model systems, this is also a field where the interdisciplinary research for fundamental new insights into the mechanisms of heterogeneous nucleation naturally becomes a material systems spanning approach. In the following I will therefore briefly review the basic steps in theory development for homogeneous and heterogeneous nucleation, independent of the material system underlying for validation. This comprises molecular simulation and DFT results to demonstrate how phase-field modelling is generally embedded in these nucleation-related investigations.

The classical kinetic model has been extended to nucleation in binary and multicomponent systems by several authors: Kozisek and Demo [59], Wilemski and Wyslouzil [60], Slezov *et al* [61], Kozisek *et al* [62], Slezov and Schmelzer [63] and Schmelzer *et al* [64]. A general theory for phase separation, which includes coagulation/splitting, has been developed by Binder and Stauffer [65]. An essential finding in this context was that, for significantly different diffusivities of the constituents, the nucleation pathway may avoid the saddle point of the free energy surface as shown by Greer *et al* [66]. Recent work by Kelton [67] takes into account the coupled fluxes of interfacial attachment and long-range diffusion. The numerical solution of his model reveals that the time-dependent nucleation rate scales with the smaller mobility and that the steady-state rates and induction times differ significantly from values predicted by the classical theory. The kinetics of formation of phases with arbitrary stoichiometric compositions in multicomponent solid solutions has been addressed by Slezov and Schmelzer, successively [63]. More recently, a new theoretical approach for nucleation and growth in multicomponent systems has been proposed by Schmelzer *et al* [64], which relies on an improved cluster model that considers non-bulk local states. In the spirit of such improved cluster models Granasy used a phenomenological diffuse interface theory [68], which can be understood as a first step towards a phase-field model for nucleation. Doing so he took into account the finite thickness of the nucleus interface. This allowed him to remove the several orders of magnitude difference seen between theory and experiment for vapour condensation [69] and crystal nucleation in [70]. This model has been

generalized by Volkman *et al* [71] and Moire and Herlach [72] for nucleation in ternary alloys and by Kvamme [73] for multicomponent alloys. In a recent model of *binary* nucleation, Schmelzer [74] determines the optimum composition of nuclei via a minimization of the sharp interface cluster free energy with respect to cluster composition, while relying on a composition-dependent interface free energy and regular solution thermodynamics. This approach leads, much like the field theoretical models, to a diminishing nucleation barrier when approaching the spinodal. A multicomponent version of the theory has been presented in [64]. While the application of models for condensation and phase separation has been developed in detail, its generalization for crystallization in liquids and glasses is less straightforward, as it requires a knowledge of the interfacial free energy as a function of temperature and composition. This requires further theoretical considerations and modelling. Recent developments of the theory for heterogeneous nucleation include the analysis of the role played by impurities and adsorbed layers by Cantor [75] and Greer [76], and a refined description of the kinetics which controls the mechanisms of phase selection in solidification of atomized droplets by Perepezko [77].

Generally, two contributions of phase-field theory to develop the above understanding further are possible: the first concerns only the energetics of the nucleation event, while the second applies to studies of simultaneous crystal nucleation and growth, which contains the additional challenge of a proper statistical mechanical treatment of the nucleation process. They are discussed in sections 4.1 and 4.2, respectively. Moreover, section 4.3 reports a study where the statistical part has been treated by a Monte Carlo model, which has been coupled to a phase-field model formulation for the phase transition dynamics. The capacity of the resulting numerically very efficient overall model is demonstrated for inoculation.

4.1. Nucleation energetics in binary alloys

Realizing that the solid–liquid interface is known to extend to several molecular layers, in modelling nucleation it becomes a challenge to pay particular attention to the diffuseness of a nucleus interface as successively enforced by experiments [78], computer simulations [79] and statistical mechanical treatments based on the density functional theory [80]. As a consequence Granasy *et al* continued their above approach [68] and were the first to employ a phase-field model to determine the energetic nucleation barrier of nuclei in homogeneous nucleation [70, 81], followed by Roy [82].

In [47] this work was extended to study energy barriers for heterogeneous nucleation events as well. In this work a special emphasis was put on the nucleation event of one phase on top of another as found, for example, in a peritectic material system. For a more detailed understanding of the phase-field approach to describe this, we review it in the following paragraphs.

In a peritectic material system it is particularly relevant to understand the nucleation of the peritectic phase on top of the properitectic phase, since this is the nucleation process yielding the stationary growth morphology. For this specific nucleation
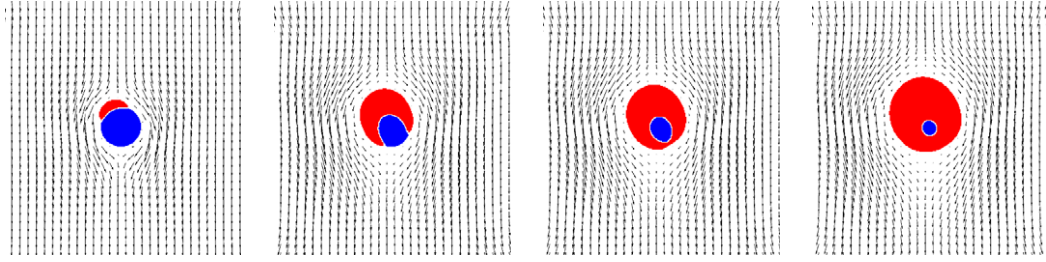
Figure 4. Investigation of the peritectic transformation under the influence of convection. The dark circle indicates the properitectic phase and the light structure the peritectic phase, which is nucleating on top of the properitectic one. Arrows are vectors indicating the velocity of the hydrodynamic field in the molten phase. Figures courtesy of R Siquieri.

process the precise configuration of the properitectic phase, i.e. its free energy on the one hand and its morphology on the other [83], should contribute to the precise nucleation rate.

Nevertheless the spherical cap model for the nucleation of a second phase β on an initial phase α assumes the initial phase as a planar front as depicted in figure 3. In this picture the interfacial tensions $\gamma_{\alpha L}$, $\gamma_{\alpha \beta}$ and $\gamma_{\beta L}$ balance each other enclosing a contact angle θ, if the following condition is fulfilled:

$$\gamma_{\alpha L} = \gamma_{\alpha \beta} + \gamma_{\beta L} \cos \theta. \qquad (4)$$

ΔF^* of equation (1), determining the activation energy of the respective heterogeneous nucleation event, is then given, respectively, in two and three dimensions by

$$\Delta F^* = \begin{cases} \dfrac{\gamma_{\beta L}^2}{\Delta F_B} \times \dfrac{\theta^2}{\theta - (1/2)\sin 2\theta}, & \text{2D} \\[2ex] \dfrac{\gamma_{\beta L}^3}{\Delta F_B^2} \times \dfrac{16\pi(2+\cos\theta)(1-\cos\theta)^2}{12}, & \text{3D.} \end{cases} \qquad (5)$$

Here ΔF_B is the difference between the bulk free energy of the peritectic phase and of the liquid phase.

The starting point of the phase-field approach given in [47] to go beyond this is the free energy functional of a representative volume of the investigated material system. This free energy functional is given by the volume integral:

$$\mathcal{F} = \int_V f \, \mathrm{d}V, \qquad (6)$$

with the free energy density defined as

$$f = \frac{W(\theta)^2}{2} \sum_i (\nabla p_i)^2 + \sum_i p_i^2 (1-p_i)^2$$
$$+ \tilde{\lambda} \left[\frac{1}{2} \left[c - \sum_i A_i(T) g_i(\mathbf{p}) \right]^2 + \sum_i B_i(T) g_i(\mathbf{p}) \right] \qquad (7)$$

where $W(\theta) = W_0(1 + \epsilon_4 \cos 4\theta)$ depends on the orientation of the interface, with $\theta = \arctan \partial_y p_i / \partial_x p_i$, ϵ_4 being the measure of the anisotropy and $\tilde{\lambda}$ being a constant. The function g_i couples the phase fields to the concentration and the temperature:

$$g_i = \frac{p_i^2}{4} \{ 15(1-p_i)[1+p_i-(p_k-p_j)^2] + p_i(9p_i^2-5) \}.$$

The coefficients $A_i(T)$ and $B_i(T)$ define the equilibrium phase diagram [46]:

$$A_i(T) = c_i \mp (k_i - 1)U, \qquad A_L = 0,$$

$$B_i(T) = \mp A_i U \qquad B_L = 0,$$

where $U = (T_p - T)/(|m_i|\Delta C)$ is the dimensionless undercooling, k_i are the partition coefficients, and A_L and B_L are the corresponding liquid coefficients.

Three phase fields $p_i \in [0, 1]$, where $\sum_{i=1}^3 p_i = 1$, are employed in this phase-field approach. These p_i label the properitectic, the peritectic and the liquid phase, respectively, i.e. $i = \alpha$ (for the properitectic phase), $i = \beta$ (for the peritectic phase) and $i = L$ (for the liquid phase) compose $\mathbf{p} \equiv (p_\alpha, p_\beta, p_L)$. Their dynamical evolution is derived from the free energy functional $\mathcal{F}$:

$$\frac{\partial p_i}{\partial t} = \frac{1}{\tau} \frac{\delta \mathcal{F}}{\delta p_i},$$

where τ is a relaxation time. The concentration field is given by

$$\frac{\partial c}{\partial t} + p_L \mathbf{v} \cdot \nabla c - \nabla \cdot \left(M(p_i) \nabla \frac{\delta \mathcal{F}}{\delta c} - \mathbf{J}_{AT} \right) = 0. \qquad (8)$$

Here $M(p_i)$ denotes the mobility and $\mathbf{J}_{AT}$ an anti-trapping term. The basic form of these model equations has been derived initially in [46]. Their extension to anisotropy effects based on the term $W(\theta)$ was developed in [47], just as well as their extension for an additional hydrodynamic field equation in the liquid phase realized as follows:

$$\frac{\partial p_L \mathbf{v}}{\partial t} = -p_L \mathbf{v} \cdot \nabla \mathbf{v} - p_L \nabla \mathbf{p} + \frac{1}{Re} \nabla^2 p_L \mathbf{v} + M_1^2. \qquad (9)$$

Equation (9) is a modified Navier–Stokes equation, where $Re = \frac{\rho U}{\nu}$. M_1^2 is a dissipative interfacial force per unit volume and is modelled as in [85].

A representative evolution according to the full set of model equations (6)–(9) is depicted in figure 4, where time runs from the upper left picture to the upper right and lower left to lower right. The light circle indicates the properitectic phase and the dark structure the peritectic phase, which is nucleating on top of the properitectic one. Comparing peritectic growth with and without convection one finds that hydrodynamic
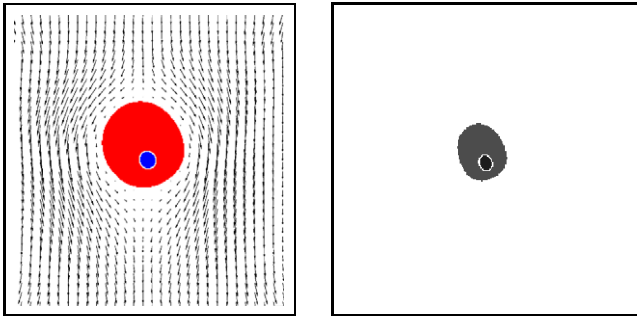
Figure 5. Comparison of peritectic growth with and without convection. Figures courtesy of R Siquieri.

Figure 6. Comparison of the nucleation rate on top of a facetted nucleus to the one on top of an unfacetted nucleus. Figure courtesy of R Siquieri.

Figure 7. Comparison of the nucleation rate on unfacetted nuclei of different radii. Figure courtesy of R Siquieri.

transport in the melt enhances the growth process considerably. This relation between melt flow and solidification dynamics is summarized in figure 5, where two pictures of growing microstructures are given at the same set of parameters except that the right microstructure is subject to flow whereas to the left growth proceeds purely diffusion-limited. These results are in qualitative agreement with experimental investigations of such peritectic material systems (see, e.g., [86]).

In order to employ (6)–(9) to investigate the heterogeneous nucleation event of a peritectic material system it is essential to realize that such a nucleation event arises as a critical fluctuation, which is a non-trivial time-independent solution of the above governing equations[2]. Solving (6)–(9) numerically under boundary conditions that prescribe bulk liquid properties far from the fluctuations ($p_i \rightarrow 1$ and $c \rightarrow c_\infty$ at the outer domain boundaries) and zero field gradients at the centre of the respective phases, one obtains the free energy of the nucleation event as

$$\Delta F^* = F - F_0. \tag{10}$$

Here, zero field gradients arise naturally due to the stationarity of the problem if the 'seed' phase is chosen large enough[3]. Moreover, F is obtained by numerically evaluating the integration over F after having the time-independent solutions inserted, while F_0 is the free energy of the initial liquid. Based on (10) the nucleation rate is then calculated as given by (1), where the nucleation prefactor I_0 of the classical kinetic approach is used, which proved consistent with experiments [89]. Note that, due to this at this point phase-field theory does not cast more light on the question of whether equation (1) is an appropriate formulation for the nucleation rate or not. Rather it contributes to an illustration of the influence of the underlying morphology of a properitectic nucleus (or seed nucleus in general) on the energetic barrier for the nucleation of the peritectic on top of it (respectively a second phase in general). Based on (1)—regardless

of indications that there is a demand to reinvestigate the latter, as well—the respective findings can be visualized by the nucleation rates obtained for different morphologies of different underlying seed phases as depicted in figures 6 and 7. One can take from figure 6 that the less facetted the properitectic phase, the larger the nucleation probability for a peritectic nucleation on top of it. For this result it is important to understand that the second phase was nucleated in the corner of the first. For the contribution resulting from the radius of the properitectic phase a similar relation is true: the larger the radius of the properitectic phase, the larger the probability of a peritectic nucleation on top of it. Both findings are in qualitative agreement with atomistic simulations. However, the new features the phase-field approach to heterogeneous nucleation inherently includes are (I) the notion of a diffuse interface, as well as (II) long-range interaction effects due to our continuum field approaching towards the problem. Thereby it meets the open issues (i) and (ii) stated below equation (3). In this sense it poses a valuable new approach towards heterogeneous nucleation in general, taking into account kinetic and thermodynamic as well as long-

---

[2] Obtained following the standard variational procedure of phase-field theory (see, e.g., [87, 88, 38]).

[3] Thermodynamically this is always possible. The functioning of the underneath relaxation procedure does not depend on the volume of the properitectic phase as such, but on the relative volume of the properitectic phase to volume which we chose as initialization for the peritectic phase. This has to be tuned close to a ratio to be expected from the position in the phase diagram to ensure convergence within the limit of a reasonable number of variations.
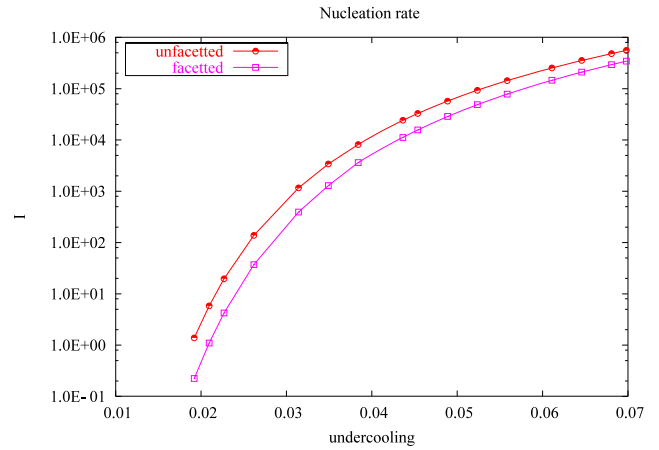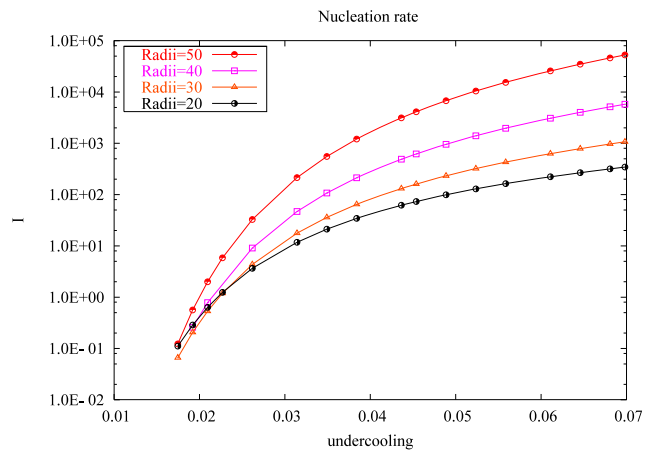
range interaction effects and differences in the diffusion of the individual species plus the dependence of the Gibbs free energy and interface free energy on the nucleus composition at the same time.

4.2. Nucleation and subsequent growth

To extend the phase-field approach described in section 4.1 such that it simulates nucleation events together with subsequent growth processes, a proper statistical mechanical treatment of the nucleation process is essential. This requires the introduction of uncorrelated Langevin noises into the governing equations, with amplitudes that are determined by the fluctuation–dissipation theorem as shown by Pavlik and Sekerka [90, 91]. In this context the development of phase-field models has been embedded in the general development of field theoretical models for homogeneous and heterogeneous nucleation, after the realization that the nanometre-sized heterophase fluctuations, that form on typical experimental timescales, can naturally be handled in the framework of continuum or field theoretic models that are able to address local states, which differ from the bulk crystal or liquid states. In general, these local physical states are characterized by the locally averaged (coarse-grained) order parameters of these models. The free energy of the inhomogeneous system then becomes naturally a functional of the order parameter field. In direct analogy to the case of the classical droplet model, where the critical fluctuation represents a maximum of the free energy function, here the critical fluctuation is given by the extremum of the free energy functional. In the past decades various field theoretic models have been developed for crystal nucleation. Many of them are direct descendants of the single-order-parameter-gradient theories by van der Waals [15, 16] and Cahn and Hilliard [18]. In the classical field theories of nucleation the free energy of the inhomogeneous system (liquid and critical fluctuation) is approximated by local functionals of the type

$$\mathcal{F} = \int_V f[m(\mathbf{r})] + \kappa (\nabla m)^2 \, dV, \qquad (11)$$

where m is a structural order parameter, which can be viewed as the amplitude of the dominant Fourier component of the crystal singlet density and κ is a constant, while the free energy density f has a double-well form, which is asymmetric in the undercooled state. The square-gradient term of the order parameter accounts for the diffuse interface itself. The simple square term limits the application of equation (11) to systems where the interface itself is characterized by a single length scale. This is classically assumed in the phase-field community, where the order parameter has originally been introduced to tackle the dynamical evolution of the interface with respect to that of the nanoscopic or microscopic structure it surrounds. Consequently the main attributes required for the length scale of the diffuse interface width is that it is smaller than any of the characteristic length scales of the simulated condensed matter structures and that it corresponds to the correlation length directly at the critical point [38]. However, a functional of form (11) has, for several

years, also been employed to derive Ginzburg–Landau-type continuum descriptions of, for example, polymer blends, see for example [162]. In this context the interface between different domains might be characterized by two length scales: in a binary polymer blend at strong segregation there is the intrinsic width describing the slope of the concentration profile at the centre of the interface. Moreover, there is the bulk correlation length, which quantifies how the wings of the concentration profile approach the coexistence value of the composition in the bulk. In this case equation (11) is limited to the early stages of phase separation and weak segregation. For the case, where this can no longer be assumed, different gradient expansions have been devised, e.g. for diblock copolymers [162, 163].

In the context of nucleation it is exactly the saddle point of the free energy functional (11) which describes the critical fluctuation (nucleus). The respective term $m(\mathbf{r})$ emerges as a non-trivial solution of the Euler–Lagrange equation:

$$\frac{\delta F}{\delta m} = \frac{\partial F}{\partial m} - 2\kappa \nabla^2 m = 0 \qquad (12)$$

under boundary conditions $m \rightarrow m_0$ for $\|\mathbf{r}\| \rightarrow \infty$ and $\Delta m \rightarrow 0$ for $\|\mathbf{r}\| \rightarrow 0$, where $\delta F/\delta m$ is the functional derivative of the free energy with respect to the order parameter field, while $m_0 = 0$ is the order parameter of the undercooled liquid.

Assuming spherical symmetry—a reasonable approximation considering the weak anisotropy of the interface free energy—the Euler–Lagrange equation reduces to an ordinary differential equation. If the free energy density is of piecewise parabolic form, the Euler–Lagrange equation is linearized and the solution can be found analytically. This method has been used to address such problems as crystal nucleation and growth in one-component liquids by Bagdassarian and Oxtoby [92] and Granasy and Oxtoby [93], hard-sphere crystallization by Wild and Harrowell [94] and crystallization in the presence of metastable phases by Granasy and Oxtoby [95]. A more complex single-order-parameter Cahn–Hilliard model relying on a quadratic free energy density has more recently been introduced by Granasy *et al* [96] to evaluate interfacial properties from nucleation experiments.

An extension of the Cahn–Hilliard theory to nucleation in multicomponent phase-separating systems is due to Hoyt [97]. Other important generalizations of the Cahn–Hilliard theory are the Hohenberg–Halperin [14] C-type field theoretic models in which the time evolution of the non-conserved structural order parameter is coupled to other fields of conserved dynamics. Models of this type are the first field theoretical approaches for this scientific context, which can be termed phase-field models. The first to actually introduce Langevin noise in such model formulations were Elder *et al* [98] followed by Drolet *et al* [99]. Subsequently Granasy *et al* used a similar technique to simulate the nucleation of primary dendritic particles with different crystallographic orientations. To describe differences in the crystallographic orientation, they introduced a non-conserved orientational field following earlier attempts by Kobayashi *et al* [100, 101]. However, other than Kobayashi, they extended the orientational field to

the liquid, where it fluctuates in time and space, a feature reflecting the short-range order of the liquid. Such simulations permitted the determination of the Kolmogorov exponent, which describes the time evolution of the crystalline fraction for multi-grain dendritic solidification and for anisotropically growing particles interacting via diffusion fields (so-called *soft impinging*). The results are consistent with devitrification experiments in metallic glasses and have successively been extended by Pusztai and Granasy [43] to solidification.

Technically the extension of the phase-field approach for nucleation to nucleation *and* subsequent growth in multicomponent alloys involves—besides the introduction of Langevin noise—the introduction of further field variables for composition and orientation, which increase the number of coupled Euler–Lagrange equations that define the fluctuation [102]. This poses computational restrictions, in particular since the simulation of the Langevin-noise term in the governing stiff partial differential equations is often prohibitively time-consuming. One remedy is to simply increase the amplitude with noise. This, however, raises the possibility that the fluctuations, which initiate solidification, will differ from the real fluctuations significantly. To avoid practical difficulties associated with modelling noise-induced nucleation, crystallization in simulations is often initiated by randomly placing supercritical particles into the simulation domain (see, e.g., Simmons [103] or Lo *et al*, who merely mimicked the nucleation event in peritectic alloys using such a procedure [44, 45]). An alternative method has been proposed by Granasy *et al* [81] who first calculated properties of the critical fluctuations and then placed the latter randomly in the simulation domain, while at the same time also adding a Langevin-noise term, which determines whether these nuclei grow and dissolve.

An alternative way to proceed, which has been proven to be numerically very efficient, consists in the coupling of the phase-field model approach to a Monte Carlo approach for the statistical aspects involved. The resulting model scheme is described in section 4.3.

Moreover, focusing on the heterogeneous nucleation event tied to the nucleation of a new nucleus on the surrounding system's wall, first steps were set by Castro [104] and Granasy *et al* [105]. Castro [104] introduced walls into a single-order-parameter model (one-component case) by assuming a no-flux boundary condition at the interface ($\mathbf{n}\nabla\phi = 0$, where $\mathbf{n}$ is the normal vector of the wall), which results in a contact angle of 90° at the wall–solid–liquid triple junction. Subsequently Langevin noise is introduced to model nucleation. Following a similar route, Granasy *et al* [105] introduced chemically inert surfaces ($\mathbf{n}\nabla\phi = 0$ and $\mathbf{n}\nabla c = 0$ at the wall perimeter) into a binary phase-field theory while incorporating an orientation field, and performed simulations to address heterogeneous nucleation on foreign particles, at rough surfaces and in confined space (porous matter and channels). This work has recently been extended by the author and others in [160, 161].

4.3. Phase-field simulations of inoculation

Formation of nanocrystalline microstructures from highly undercooled liquids is associated with extremely high
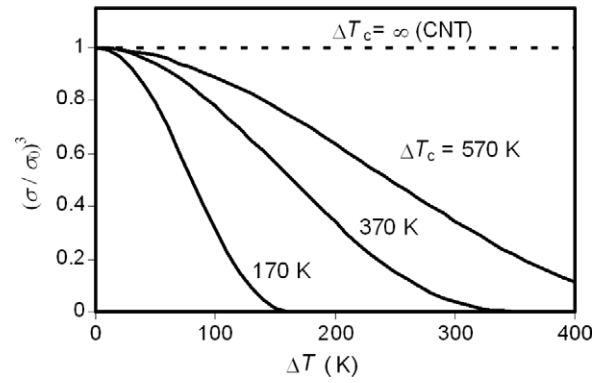

Figure 8. Variation of the normalized interfacial energy with undercooling, calculated based on a diffuse interface model of nucleation [108]. The dashed line corresponds to the classical nucleation theory. According to non-classical theories of nucleation, the interfacial energy decreases with increasing undercooling and can vanish at a non-zero critical temperature. Figure reprinted with permission from [108]. Copyright 2002 by Elsevier.

nucleation rates, often orders of magnitudes larger than those predicted from the classical nucleation theory [106]. Diffuse interface models of nucleation provide an explanation for this nucleation behaviour, in terms of the variation of the solid/liquid interfacial energy with temperature [107]. Figure 8 shows an example of such variations [108]. In [108] copious nucleation and subsequent nanocrystallization have been simulated based on one overall approach. To do so, the merits of standard phase-field and the so-called Potts method [111] were combined. The resulting model was extended by Hubert *et al* for surface diffusion effects [112]. In that form the model consists of two state parameters—the phase field ϕ and the temperature T—as well as the orientation order parameter θ.

The differential equations for φ and T can be derived from the free energy functional [112, 38]:

$$\mathcal{F} = \int [g(\phi, T) + \tfrac{1}{2}\epsilon^2|\nabla\phi|^2 + \tfrac{1}{2}\nu^2\phi^2 G(|\nabla\theta|)]\,dV,$$

where ϵ is the diffusion constant for the phase-field variable. They are given by

$$
\begin{aligned}
\frac{\partial \varphi}{\partial t} = M_\varphi \Bigg[& \bar{\epsilon}^2\eta^2\nabla^2\varphi + \bar{\epsilon}^2\nabla \\
& \times \left(\frac{8}{\pi} D_S\nabla\left[\eta^2\frac{2}{\pi}\left(-\frac{1}{\bar{\epsilon}^2}\nabla^2\varphi + \bar{\epsilon}^2\varphi'(t) \right) \right] \right) \Bigg] \\
& + \epsilon^2\eta\eta'[\sin(2\theta)(\varphi_{YY} - \varphi_{XX}) + 2\cos(2\theta)\varphi_{XY}] \\
& - \tfrac{1}{2}\bar{\epsilon}^2[\eta'^2 + \eta\eta''][2\sin(2\theta)\varphi_{XY} - \nabla^2\varphi - \cos(2\theta) \\
& \times (\varphi_{YY} - \varphi_{XX})] \\
& + \epsilon^2\Gamma \\
& + 6(1-\varphi)\varphi\frac{L}{T_\mathrm{m}}(dt_c(2\varphi - 1) + \Delta T) + E_\mathrm{mis}, \quad (13)
\end{aligned}
$$

with an anisotropy factor $\eta = 1 + \epsilon_{as}\cos(2\theta)$, Γ a random number in the range of $[-0.5; 0.5]$ and

$$\frac{\partial T}{\partial t} = \Delta T\frac{\partial \varphi}{\partial t} + \alpha\nabla^2 T. \quad (14)$$
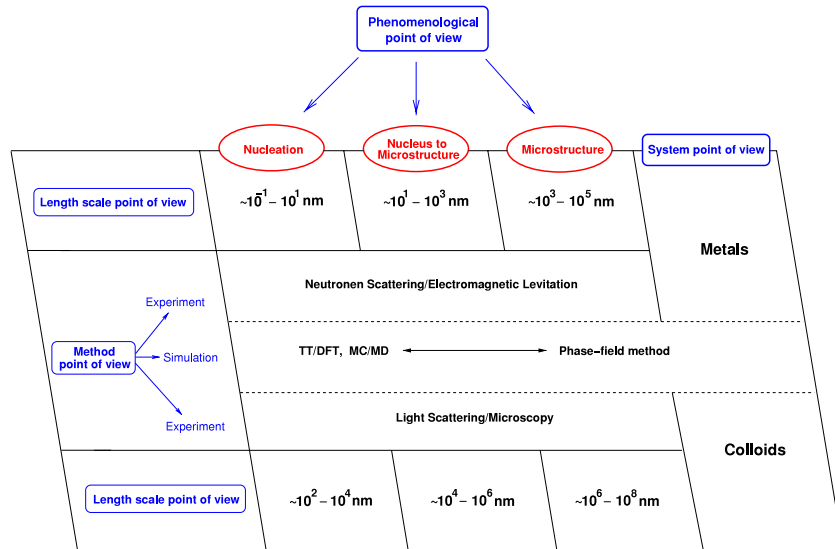
Figure 9. Illustration of the interdisciplinary approach in the research priority programme Nucleation and growth kinetics in colloids and metals—steps towards a scale- and system-bridging understanding [40]: to advance towards a system- and scale-bridging detailed understanding of the energetics and kinetics of heterogeneous nucleation and microstructure formation, two different experimental (binary colloids and binary metallic alloys) model systems are investigated jointly by experimental scientists working with different experimental techniques together with theoreticians, whose expertise is likewise diverse, ranging from density functional theory (DFT) over molecular simulations (MC/MD) to the phase-field method and who, at the same time, aim at a rigorous connection of these methods. Phase-field modelling is an integral part of this research priority programme. Here this sketch serves as an example to demonstrate the different 'dimensions' of the interdisciplinary research setting, in which the phase-field method was able to develop itself over the last two decades by, at the same time, contributing to more and more fundamental problems of condensed matter physics.

The first line of equation (13) represents the general phase-field diffusion dynamics, the second surface diffusion. The third and fourth lines yield terms accounting for the anisotropy of the crystal [110]. Moreover, the fourth line contains a term which models thermal fluctuations.

The mismatch energy E_{mis} is given by

$$E_{mis} = \sum_n (F(\theta) - F(\theta_n)). \tag{15}$$

This energy difference is determined by the sum over neighbouring cells of the involved Monte Carlo algorithm. During each step a new random orientation is determined for each cell of that Monte Carlo scheme. There is a probability p that the orientation switches from the old to a new one given by

$$p = 1 - \exp\left(\frac{E_{mis}(\theta_{new}) - E_{mis}(\theta_{old})}{kT} + \xi\right), \tag{16}$$

with ξ being a random factor. Periodic boundary conditions are applied at the top and bottom borders.

Several merits result from employing the above Monte Carlo algorithm for the evolution of the orientational order parameter. Most significantly, this method would be suitable to handle discontinuities in the orientation profiles. In this way, and due to the fact that the number of allowed orientations is finite, formation of non-physically diffuse orientational boundaries is prevented. Moreover, due to the probabilistic nature of the method, not only curvature-driven grain coarsening, but also stochastic coarsening, can be modelled. The latter is especially relevant for coarsening of grains in the nanometre range [109].

In general one can state that the coupling of the Potts and phase-field approach eliminates the common limitations of both methods, i.e. problems with non-zero bulk driving forces in the Potts [111], and with curvature-driven coarsening in the frame-invariant phase-field approach [101]. Moreover, it allows for an implicit modelling of nucleation behaviour at high undercoolings—an important feature not offered by Potts.

5. Phase-field modelling in soft matter physics

In the field of soft matter physics phase-field modelling is certainly still less established than in the field of metal physics. Nonetheless figure 9, which captures the basic concept underlying the priority programme [40], demonstrates the perspective of approaching soft matter systems with phase-field models for the example of nucleation in alloys: in this context the deliberate collaborative advance jointly with molecular modelling methods, DFT and respective experimental studies appears as a promising scientific route to develop phase-field models as truly scale-bridging models, overlapping the simulation scales of the methods at the molecular scale to some extent and extending it further to the dynamics at considerable larger time and length scales— all with the aim of obtaining a powerful tool to identify how mechanisms of different scales act together for the precise kinetics and energetics of such a fundamental problem of condensed matter physics as nucleation. Since this is a big challenge for any kind of complex condensed matter system, it

seems challenging to have a closer look at still other fields of soft matter physics, where in the past molecular models were the main computational tools, with an analogous aim. The basic potential of phase-field modelling in soft matter physics is demonstrated for three prominent examples of that field in the following—namely for polymer solutions, liquid crystals and vesicles and thereby mainly for phenomena occurring at the microscale. The chosen examples reveal that there is an analogy in the step-by-step development of phase-field models for soft matter systems compared to the one in metal physics: starting from a phase-field model formulation for a paradigmatic problem (spinodal decomposition) the further development runs over multi-phase extension—as relevant for liquid crystals—to multi-physics extension, which is obviously essential to model vesicle dynamics. Any kind of soft matter system displaying phenomena that involve an evolving, phase-separating interface, could be a further example along this line, such as, for example, a swelling polymer membrane [113] and void–fluid interaction in ascorbic acids [114].

Exploiting the chance to develop scale- and system-bridging approaches based on phase-field modelling also in the context of the above three examples would basically have to follow the same collaborative route as described and illustrated for nucleation in figure 9. In the sense of that figure it would strongly be tied to the identification of accompanying condensed matter systems, where similar dynamical processes occur at a different scale. However, a first step in this direction might be to intensify efforts to tackle the relevant issue of multi-scale model development solely in the context of an individual soft matter system. In the field of soft matter physics, even the latter is still much more of an open issue than in the field of metal physics. A very recent step showing the potential of scale-bridging modelling in the soft matter field was taken by Shi and Voth [115]. They investigated phase separation in mixed lipid bilayers based on a combined phase-field/molecular dynamics approach.

5.1. The paradigmatic problems of spinodal decomposition and crystallization of polymer solutions

Two widespread and well-studied phenomena in polymer solutions, for which phase-field theory could already successfully be applied, are spinodal decomposition and polymer crystallization. With respect to the first one of the most generic extensions of the Landau–Khalatnikov ansatz to describe non-equilibrium phenomena is the Cahn–Hilliard equation [18]. It can be understood as the classical theory for the early stages of spinodal decomposition in polymer blends, based on non-equilibrium thermodynamics [9]. In this context the Cahn–Hilliard equation was obtained by postulating that the local interdiffusion currents are proportional to the gradients of the local chemical potential. Moreover, it has to be assumed that this chemical potential can be derived from a free energy functional of Ginzburg–Landau type. The proportionality constant arising in proceeding like this is the atomic mobility, which remains a phenomenological parameter in this approach. To study homogeneous initial states, the Cahn–Hilliard equation has been linearized around the average

composition and analysed in terms of Fourier modes. These studies reveal an exponential growth of long wavelength perturbations with time, whereas short wavelength fluctuations are damped by the gradient terms related to the surface tension. A typical length scale of the resulting domain pattern is then given by the wavelength of the fastest growing mode.

To extend these investigations to far-from-equilibrium conditions, several authors have developed nonlinear kinetic equations based on Ising and lattice gas models [123–127], which can be cast in the form of generalized Cahn–Hilliard equations. The characteristic new feature of these approaches is an atomic mobility, which depends explicitly on the details of the microscopic dynamics. Such equations have successfully been applied to the study of phase-separation dynamics in binary and ternary systems [128–130] just as to dendritic growth [131]. A further extension resulting in a phase-field model taking into account also asymmetrical interaction energies, respectively compositions, was developed in [132]. Based on the resulting model equations it became possible to study also morphological features of decomposing polymer blends far from equilibrium and to relate them to the interaction parameters of the underlying microscopic model, such as, for example, the decomposition of a metastable lamellar phase to a stable cylindrical phase.

Focusing on the crystallization behaviour of polymers one realizes a distinct difference to that of metallic systems: unlike crystallization in the latter, polymer crystallization rarely reaches thermodynamic equilibrium. Rather, most polymer crystals are kinetically stabilized in some metastable states. Xu *et al* [133] proved that the phase-field approach is capable of describing this kind of phase transition phenomenon as well. To capture the various possible metastable configurations of a polymer crystal, Xu *et al* assumed the phase-field order parameter in the solidification potential to be supercooling-dependent, i.e. it can take intermediate values between 0 (labelling the molten phase) and 1 (labelling the perfect crystal) even in the volume phases to mimic the imperfect polycrystalline nature of polymer crystals. Qualitatively this model approach allows us to identify various single-crystal morphologies of isotactic polystyrene crystals such as faceted hexagonal patterns transforming to non-facetted snowflake-like morphologies with increasing undercooling.

Further phase-field studies of polymer blends concern polycrystalline growth after the introduction of foreign (clay) particles. The result is disordered dendritic structures termed *dizzy* dendrites. These structures are formed by the engulfment of the clay particles into the crystal, inducing the formation of new grains. This phenomenon is driven by the impetus to reduce the crystallographic misfit along the perimeter of clay particles by creating grain boundaries within the polymer crystal. This process changes the crystal orientation at the dendrite tip, changing thus the tip trajectory (*tip deflection*). To describe this phenomenon, Granasy *et al* [116] incorporated a simple model of foreign crystalline particles into the phase-field theory: in that framework the latter are represented by orientation pinning centres—small areas of random but fixed orientation—which are assumed to be of a foreign material, which is *not* the solid reference phase. Phenomenologically

this picture describes morphological changes originating from clay particles in an efficient manner.

The development of a more quantitative phase-field approach to polymer systems, which models the imperfect polycrystalline nature in the volume phases rigorously taking into account its physical origin, is still an open issue.

5.2. Phase and structure dynamics in liquid crystals

In the nematic phase of a liquid crystal its molecules are locally oriented, giving rise to anisotropy in the viscosity and surface tension. The degree of orientation depends on the proximity of the other phases, namely the isotropic and for some liquid crystals also the smectic phase. In that sense it still depends on temperature, and so does the anisotropy, mainly in the viscosity [117].

This appearance of different kinds of anisotropy and also their clear dependence on temperature is a complication which is beyond that of microstructure selection in dendritic solidification in metallic alloys. Nevertheless the question of how the pattern selection process in such a system is influenced by anisotropy effects has been motivated by the great influence it could be shown to have in dendritic systems (see, e.g., [42]). Just as for dendritic growth respective studies for liquid crystals were accompanied by phase-field simulations [118–120]. These investigations helped to establish a connection between the different kinds of anisotropies described above and their influence on pattern selection [120]. Moreover, their sensitivity to external perturbations could be identified [121]. In that sense phase-field models proved to be a valuable simulation alternative to study the nonlinear dynamics at the micro- and nanoscale also in such liquid crystal systems, which are otherwise predominantly investigated via molecular simulations. (For a recent review of molecular computer simulations for liquid crystal systems, see [122].).

5.3. Vesicle dynamics driven by hydrodynamical and mechanical forces

At the microscale vesicles can be viewed as closed membranes which are suspended in an aqueous solution [134]. They constitute a model system of biological membranes, which separate an interior domain of usually larger viscosity from an external domain of smaller viscosity. A prominent example are red blood cells, where the ratio of the viscosity of their interior fluid to the viscosity of the surrounding fluid *in vivo* ranges between 5 and 10. The hydrostatics, hydrodynamics and elastomechanics of such liquid capsules enclosed by thin elastic shells or chemical and biological membranes consisting of molecular networks have recently received considerable attention in cellular biology, bioengineering and micro-encapsulation technology (see, e.g., [135] and references therein). Theoretical models at this scale have to be able to describe the deformation dynamics of the cells taking into account the effect of membrane bending stiffness [135], effects of in-plane elastic tension [136, 137], membrane viscosity [136, 138] and membrane incompressibility [139] in a consistent manner.

In this field the classical numerical approach to study the moving interfaces of the cells modelled accordingly is to employ a computational mesh that has grid points directly on the interfaces and thus constitutes a sharp interface approach. Then the mesh has to deform due to the motion of the boundary. Numerically this can, for example, be achieved based on the boundary integral and boundary element methods (see [140–142] and references therein). Keeping track of the moving mesh may entail computational difficulties, and large displacement in internal domains may cause mesh entanglement. Typically, sophisticated remeshing schemes have to be used in these cases. As an alternative, fixed-grid methods that regularize the interface have been highly successful in treating deforming interfaces. These include the volume-of-fluid (VOF) method [143, 144], the front-tracking method [145, 146] and the level-set method [147–149]. Instead of formulating the flow of two domains separated by an interface, these methods represent the interfacial tension as a body-force or bulk-stress spreading over a narrow region covering the interface. Then a single set of governing equations can be written over the entire domain and solved on a fixed grid in a purely Eulerian framework.

In this context the phase-field model approach can be viewed as a physically motivated level-set method, which allows for a rigorous derivation of dynamic model equations based on the variation of an underlying energy functional[4]. Thus instead of choosing an artificial smoothing function for the interface, the phase-field model describes the interface by a mixing energy. Again the idea can be traced back to van der Waals [15, 16]. However, there are several peculiarities to take into account compared to phase-field modelling in the context of metallic material systems: first, vesicles have no surface tension. Therefore the interfacial term has to be constructed in a manner that it cancels the wall free energy of the vesicle [154]. This is analogous to the situation encountered in phase-field modelling of liquid crystals [118] (see also section 5.2). Second, the phase-field approach raises a complication due to the local membrane incompressibility, which imposes a non-trivial constraint on the membrane. This second problem can, for example, be cured by introducing the dynamics of an additional tension field [155].

Lately such phase-field model constructions have successfully been applied to some phenomena of microscopic vesicle dynamics: Du *et al* [150] were able to compute the equilibrium configurations of a vesicle membrane under elastic bending energy, with prescribed volume and surface area based on the phase-field method. Successively Biben *et al* [154, 155] extended this phase-field model for vesicle membranes to hydrodynamic flow. This allowed them to study the kinetic evolution toward equilibrium shapes under the influence of shear flow, as well as tank treading and tumbling. The latter is a large step towards a more detailed understanding of circulation physiology and rheology [156, 157], since red blood cells are known to undergo such a tumbling process if diluted enough with plasma [158].

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[4] Appropriate functionals involving the distribution of mean and Gaussian curvature have been proposed by Canham [151] and Helfrich [152] and reviewed by Seifert [153].

6. Summary and outlook

The main concern of this review is to provide a brief overview of the conceptual backgrounds of the phase-field method and the recent issues the phase-field community is focusing on as a basis for its application regarding the topic of this volume and thus the following individual papers. Afterwards, the two most prominent fields to which phase-field modelling has been applied so far, namely metal physics and soft matter physics, were reviewed for the contributions to these fields based on the phase-field method, with special focus on nucleation in the case of the metallic systems. Doing so, a particular focus was put on demonstrating analogous steps in advancing in these two different fields. Moreover, special emphasis was put on pointing out that with respect to one of the large challenges of modelling in condensed matter physics, namely scale-bridging modelling, phase-field modelling—in particular when applied in a system-bridging manner to similar phenomena occurring at different scales in different condensed matter systems (see figure 9)—seems to be a very promising approach for three reasons:

(i) First, because phase-field models can easily be extended starting from paradigmatic model formulations to increasingly more dynamics driving physical mechanisms due to the variational nature of the approach starting from a free energy density formulation of the system [38, 3].

(ii) Second, because phase-field modelling is an approach at one of the intermediate scales relevant in condensed matter physics, naturally overlapping the simulation scales of the methods at the molecular scale to some exteny and extending it further to the dynamics at considerable larger time and length scales.

(iii) Third, because it is quite easy to tune to different material systems as long as it can be described in terms of well-established phase diagrams and energy densities applying to its different phases. Thus it seems feasible to exploit a 'smearing' of scales for similar phenomena in different condensed matter systems to identify intermediate length scales, where a full overlap of different modelling approaches as depicted in figure 9 arises and can give input to the development of rigorous methodological concepts applying over the scales.

To my knowledge the most advanced phase-field-based theory taking this idea further is the *phase-field crystal* method [159]. Yet it applies only to periodic systems, leaving ample room for further development to support the investigation of interfacial dynamics in condensed matter systems along the lines of this review.

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