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An anisotropic phase-field crystal model for heterogeneous nucleation of ellipsoidal colloids

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Abstract

We derive a generalized model for isotropic as well as anisotropic crystal lattice systems of arbitrary Poisson ratio within the framework of the continuum phase-field crystal (PFC) approach (Elder and Grant 2004 *Phys. Rev.* E **70** 051606). To this end we extend the simplest PFC model defined by a free energy functional, which is based upon the Swift–Hohenberg model of pattern formation (Swift and Hohenberg 1993 *Phys. Rev.* A **15** 851) to a conservative, anisotropic Langevin equation. By studying heterogeneous nucleation of ellipsoidal colloids at a wall, we demonstrate the capacity of our approach to contribute to the more precise understanding of condensed matter systems built up from non-spherical units at the atomic scale. In particular we address the question of how (a) the orientation of the ellipsoids as well as (b) the interaction potential with the wall determine the resulting contact angle.

1. Introduction

Over the past decades phase-field modeling has become an accepted model approach for studying the dynamics of systems out of equilibrium. In particular it has found numerous applications in materials science [1–4]. A classical example of such an application is solidification: consider a material that is disordered at high temperature and has two stable phases at low temperatures. Upon quenching the material from a high to a low temperature, grains of different stable phases will develop and evolve in competition with each other. Phase-field modeling is able to describe the time evolution of such a process. To do so, a continuous function of space and time $\phi(\mathbf{x}, t)$ is introduced—namely the phase-field—that assumes a different constant value for both stable phases. Close to an interface between two grains, the value of ϕ changes rapidly. The phase-field variable introduced in the context of this example can be interpreted as an order parameter to represent the relative mass fraction of both phases. It allows us to model and simulate the dynamics of interfaces, that change their topology during evolution in time—so-called Stefan problems [5]—elegantly, i.e. without the need to track that interface explicitly. Phase-field models are based the following Landau form of a free energy functional

$$F_1[\phi] = \int_V \left[\frac{\epsilon^2}{2}|\vec{\nabla}\phi|^2 + f(\phi)\right] \mathrm{d}V. \tag{1}$$

From (1) the dynamical evolution of the field equation can be derived via a variation of the form

$$\frac{\partial\phi}{\partial t} = \nabla^2 \frac{\delta F_i}{\delta\phi} \tag{2}$$

or

$$\frac{\partial\phi}{\partial t} = -\frac{\delta F_i}{\delta\phi}, \tag{3}$$

depending on whether ϕ can be assumed to be *locally conserved* (equation (2)) or locally *non-conserved* (equation (3)).

A functional of form (1) applies if the stable states of the system under investigation are locally uniform. If this assumption is not valid, an appropriate energy functional is given by

$$F = \int_V \left(\frac{1}{2}\phi[(q_0^2 + \nabla^2)^2 - \varepsilon]\phi + \frac{1}{4}\phi^4\right) \mathrm{d}r, \tag{4}$$

with now two phenomenological parameters q_0 and ε. Again an equation of motion can be derived based on the variational

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principle (2). This results in the simplistic formulation of the so-called phase-field crystal method, a recent extension of the phase-field method to the atomic scale originally derived in [6]. It is motivated by the Swift–Hohenberg equation [15] formulated to describe systems, where the stable states are periodic such as, for example, the case for Rayleigh–Bénard convection. Since its introduction, the phase-field crystal (PFC) method [6–8, 10, 11] has emerged as a computationally efficient alternative to molecular dynamics (MD) simulations for problems where the atomic and the continuum scale are tightly coupled. The reason is that it operates for atomic length scales and diffusive timescales. Thus for a simple application such as diffusion in gold or copper it runs 10^6–10^8 times faster than the corresponding MD calculation [12]. In that sense it provides, from the point of view of multiscale materials modeling, an interesting link between the phase-field method and MD. Moreover, a connection between classical density functional theory of freezing and phase-field crystal modeling could be identified in [8, 9]. Thereby a second theoretical foundation besides the Swift–Hohenberg amplitude equation approach could be established. Essentially it motivates the application of PFC models also for spatially non-uniform *non-periodic* states.

Recently the phase-field crystal method has been applied to a variety of different growth phenomena. One of its interesting features is that other than the phase-field method, in which elasticity explicitly needs to be integrated in the functional to be taken into account [13], it includes elastic effects inherently. Thus it allows us to simulate, for example, features of crack propagation [8] and plasticity [7, 14] from the atomic to the microscale. To model the elastic behavior of different kinds of materials, the parameters of the phase-field crystal model equation can be adjusted to match the elastic moduli of a given experimental system. However, in its most simplistic form, in which it is a reformulation of the Swift–Hohenberg equation [15] with a conserved dynamics as introduced by Elder *et al* [6, 7] the Poisson ratios that can be modeled are restricted to 1/3 (in the one mode approximation). Moreover, since in the simplistic PFC model the material is defined by only three parameters, it is restricted with respect to the crystal lattice structures which it can describe as well. These are triangular symmetries in two dimensions and BCC symmetry in three dimensions [16]. Another crystal symmetry applying to protein crystals in a membrane could be obtained by including higher order correlation functions [17]. Moreover, liquid crystals have been simulated by combining the original phase-field crystal equation with an orientational field [18].

Here we follow the above direction to extend the phase-field to apply to a larger class of condensed matter systems following a different route: we derive a generalized PFC model for isotropic as well as anisotropic crystal lattice systems of arbitrary Poisson ratios as well as condensed matter systems built up from non-spherical units such as, for example, colloids and liquid crystals. To this end we extend the simplest PFC model (SPFC in the following) as, for example, given in [6], to a conservative, anisotropic Langevin equation. We demonstrate the capacity of our approach to contribute to the more precise understanding of condensed matter systems built up from non-spherical units at the atomic scale by studying heterogeneous nucleation of ellipsoidal colloids at a wall. In particular we address the question how (a) the orientation of the ellipsoids, as well as (b) the interaction potential with the wall determine the resulting contact angle.

To do so we proceed as follows. First, in section 2 of this paper, we describe our anisotropic phase-field crystal model, which we present here for the first time. In section 3 a brief review of model approaches to heterogeneous nucleation as well as to ellipsoidal colloids and the understanding gained in this context are presented. In section 4 we then report our own studies and the understanding we can thereby obtain for the contact angle formation of this system. Finally, in section 5, we put our results in a broader context and discuss the further perspectives as well as the limitations of our approach for nucleation studies.

2. The anisotropic phase-field crystal model

The SPFC model as derived originally in [6] is based on the free energy functional (4) and a stochastic extension of the equation of motion (2) for the local mass density ϕ given by

$$\frac{\partial \phi}{\partial t} = \nabla^2 \left(\frac{\delta F}{\delta \phi} \right) + \eta \tag{5}$$

with a stochastic noise η of zero mean value and correlations $\langle \eta(\vec{r}, t)\eta(\vec{r}', t') \rangle = -G\nabla^2 \delta(\vec{r} - \vec{r}')\delta(t - t')$ [6]. Moreover, q_0 and ε are constant and $G = 0$ in the SPFC case. Thus the equation of motion can be cast in the following form:

$$\varrho \dot{\phi} = \Delta([(q_0^2 + \Delta)^2 - \varepsilon]\phi + \phi^3). \tag{6}$$

As pointed out above, the crystal lattice structures minimizing the free energy functional (4) are restricted to constant, striped and hexagonal symmetries in two dimensions (2D) and an additional BCC symmetry in three dimensions (3D), as well as to a Poisson ratio 1/3 (in the one mode approximation)—as is reasonable to simulate, for example, copper and aluminum. However, anisotropic materials systems might have completely different Poisson numbers, and steel and iron, for example, have Poisson numbers in the range (0.21–0.3). To be able to model the behavior of such materials from the atomic to microscale within the phase-field crystal formalism as well, an extension overcoming the above limitations is required.

An extension of the SPFC equation meeting the above challenge and allowing us to model materials of a wider class of condensed matter systems and Poisson ratios, as we will report in [20], can be obtained by replacing the Laplacian in (4) by more general differential operators allowing spatial anisotropy. Doing so and setting $\tau = -(q_0^2 - \varepsilon)$ we arrive at the free energy functional of an anisotropic PFC model (APFC model in the following), which we suggest here for the first time:

$$F = \int_V \left(\frac{1}{2}\phi \left[-\tau + a_{ij}\frac{\partial^2}{\partial x_i \partial x_j} + b_{ijkl}\frac{\partial^4}{\partial x_i \partial x_j \partial x_k \partial x_l} \right] \phi + \frac{1}{4}c\phi^4 \right) \mathrm{d}r \tag{7}$$

where a_{ij} is a symmetric matrix and b_{ijkl} is a tensor of rank 4 with the symmetry of an elastic tensor: $i \leftrightarrow j, k \leftrightarrow l, (i, j) \leftrightarrow (k, l)$.

The corresponding Langevin differential equation of motion is given by

$$\varrho\dot{\phi} = \Delta\left(\left[-\tau + a_{ij}\frac{\partial^2}{\partial x_i \partial x_j} + b_{ijkl}\frac{\partial^4}{\partial x_i \partial x_j \partial x_k \partial x_l}\right]\phi + c\phi^3\right). \tag{8}$$

Solutions to the SPFC model are inherently solutions of the APFC model as well.

Finding the general steady state solutions for the SPFC respectively the APFC model involves finding solutions to:

$$\dot{\phi} = 0 \leftrightarrow \Delta([(q_0^2 + \nabla^2)^2 - \varepsilon]\phi + \phi^3) = 0, \tag{9}$$

in the SPFC case, respectively

$$0 = \Delta\left(\left[-\tau + a_{ij}\frac{\partial^2}{\partial x_i \partial x_j} + b_{ijkl}\frac{\partial^4}{\partial x_i \partial x_j \partial x_k \partial x_l}\right]\phi + c\phi^3\right) \tag{10}$$

in the APFC case.

Note that the resulting model equations of our APFC model are not rotationally invariant—just like the ones of the famous Warren–Boettinger–McFadden model [19]. This might cause problems when studying, for example, several grains and issues of their orientation with respect to each other might play an important role. We will show in a forthcoming paper how to overcome this problem [20]. Here, however, we will restrict our focus to the study of an individual grain.

3. Heterogeneous nucleation of ellipsoidal colloids at a wall

Nucleation is the key event necessary to occur, so that a liquid, which is quenched below its melting temperature, will undergo a phase transition and freeze eventually. Thus nucleation plays an important role in almost all aspects of materials science [21–25], which is fully accepted across many areas of modern surface and materials science and technology. One reason is that a large range of material properties from mechanical ones such as ductility and hardness to electrical and magnetic ones such as electrical conductivity and magnetic hardness depend largely on the specific crystalline structure that forms in nucleation and subsequent initial microstructure growth. In the study of nucleation, one distinguishes between homogeneous and heterogeneous nucleation. The first occurs in an idealized pure material, the second in ‘impure’ materials, where walls or seed particles usually substantially larger than the atomic scale facilitate nucleation by reducing the energetic barrier for the phase transition to occur. Despite its technological importance, in particular heterogeneous nucleation is poorly understood due to difficulties in describing the interaction between the foreign matter and the solidifying melt.

The development of physically relevant models for this scenario depends on key parameters in the interaction region, which are experimentally difficult to access in the classical structure material systems such as metals due to experimental limitations arising, for example, from non-transmittance of optical light. This is one reason why lately colloids, which have fewer experimental restrictions, could establish themselves more and more as important model systems for phase transition scenarios in crystalline as well as other kinds of granular matter. Another reason is that from the point of view of theory they allow us to reduce the problem of evaluating a many-body partition function arising in their MD treatment to a slightly simpler, geometrical problem, namely the evaluation of entropic contributions only. Thus phase transition scenarios in hard ellipsoidal colloids have already been addressed by Monte Carlo simulations before, first by Frenkel and Mulder [26]. Since then the focus has been on the nematic to isotropic-nematic transition [27–29], and biaxial hard ellipsoids [30, 31]. The high density phase of these ellipsoidal systems, a crucial basis for addressing nucleation, has only been studied more recently in [32]. Here we continue along that line and introduce the phase-field crystal method as a new method to study this class of systems, with the advantage outlined above, i.e. an increased computational capacity to carry out computer simulations of longer time intervals and larger system sizes due to operating on atomic length scales but diffusive timescales. This allows us to access the question of how (a) the orientation of the ellipsoids, as well as (b) the interaction potential with the wall determine the resulting contact angle, and thereby contribute to a more detailed understanding of heterogeneous nucleation in atomistically anisotropic condensed matter material systems in general. Due to the direct experimental accessibility of such systematics as well as the contact angles as such in colloids [36], this bears the potential to gain new insight into the interaction potential between the nucleus and wall and its appropriate formulation in a continuum model formalism via comparison with experiments.

4. Numerical studies and interpretation

The initial conditions for the studies which we report in the following are a rectangular domain on one side of which we place the wall and initialize the nucleus as a half sphere on top of it. As boundary conditions, we set periodic to the left and right and no boundary condition at the top. As, dimensionless, constants for τ, a, b, c according to equation (8) we chose: $\varrho = 1$, $\tau = -3/4$, $a_{11} = a_{22} = 2$, $a_{12} = -0.4$, $b_{1111} = b_{2222} = b_{1122} = 1$, $b_{1212} = 0$, $b_{1112} = -0.2$ and $c = 1$.

From an atomistic point this does not describe the situation fully, since inside the sphere the ellipsoids can take different orientations with respect to the wall. We vary their initial orientation in different simulation runs. We then let the sphere evolve according to equation (8) and measure the contact angle once it becomes stationary. Additionally we study different boundary conditions at the wall to contribute to the open issue of finding consistent descriptions for the substrate–nucleus interaction. An investigation of this kind has also been carried out in [33], however with a phase-field rather than a phase-field crystal model, which resolves the nucleus solely as one phase, i.e. a single nano-structural particle without inner structure at the atomic scale.

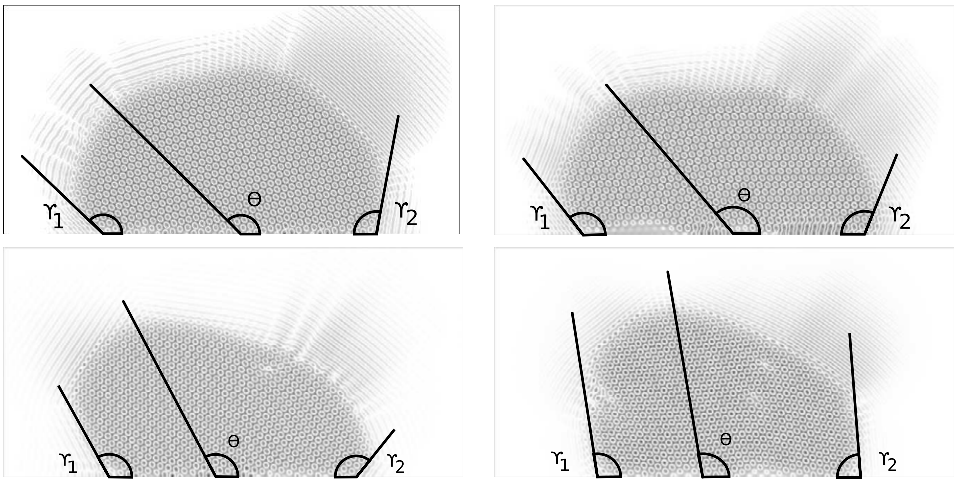

Figure 1. Resulting morphologies using the 'hard wall' boundary condition for different orientations of the nucleus.

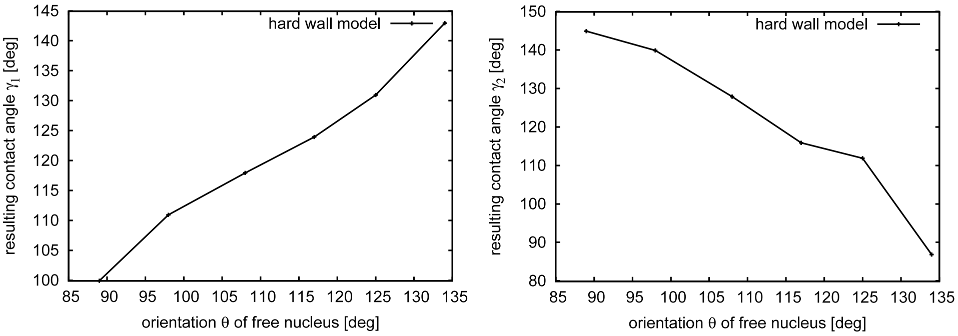

Figure 2. Resulting contact angles using the 'hard wall' boundary condition for different orientations of the nucleus.

The first boundary condition we tested in our studies corresponds formally to model B of [33], i.e. we set ϕ = const, with the constant corresponding to $\phi_{\max}$, i.e. a state of highest atomic density. Figure 1 gives an impression of the stationary nucleus morphologies we obtain with this boundary condition describing a 'hard wall' interaction potential for different initial orientations of the ellipsoids with respect to the wall. The orientation of the ellipsoids to the wall is denoted by θ, the contact angles at the left-hand and the right-hand side by γ_1 and γ_2 respectively. The result of our simulations implying this boundary condition, investigating systematically the effect of different initial orientations of the ellipsoids with respect to the wall, are given in figure 2. Here the left diagram depicts the resulting contact angles to the left and the right diagram the ones to the right of the nuclei in figure 1. We can see that the contact angle depends piecewise linear on the orientation. The slope of the curve changes whenever a new facet occurs. This corresponds to the morphologies which arise: as shown in figure 1 the nucleus becomes facetted, i.e. due to the 'hard wall' interaction with the wall no further modification from the shape it would take in the volume away from the wall arises. Interestingly this is observed for model A rather than model B in the phase-field studies of [33] (except that there the nucleus is spherical not facetted). This difference can be understood from the different kinds of conservation assumptions underlying the phase-field and the phase-field crystal approach [20].

The 'hard wall' interaction with the above morphological results is not a realistic description for a lot of nucleation scenarios known for condensed matter systems, such as wetting transitions at a foreign wall. In the phase-field model of [33] it is possible to formulate an interaction of the nucleus with an external wall able to recover features of those scenarios based on ideas following Cahn [34] by imposing an 'interface function' (see equations (9), (10), (11) and (13) of [33]). These ideas cannot directly be transferred to the APFC model, since the APFC model does not inherently include an interfacial function. This shortcoming can be overcome in two ways, which we will present in [20]. Here we will focus on a more *ad hoc* formulation guided by an idea of main physical mechanisms to recover in more realistic systems. These are surface tension effects having their origin in (a) adhesive and (b) capillary forces as important driving forces for the nucleus' morphological evolution at the wall.

To realize (a) we carried out additional sets of simulations, in which we chose the following form for the boundary condition at the wall:

$$\phi = (\phi_{\min} + \phi_{\text{liq}}/w)/(1 + 1/w), \tag{11}$$

where $\phi_{\min}$ represents the state of smallest atomic density, and ϕ_{liq} denotes the atomic density in the unordered, i.e. liquid, system. w is a parameter, which can be understood as an interaction strength.

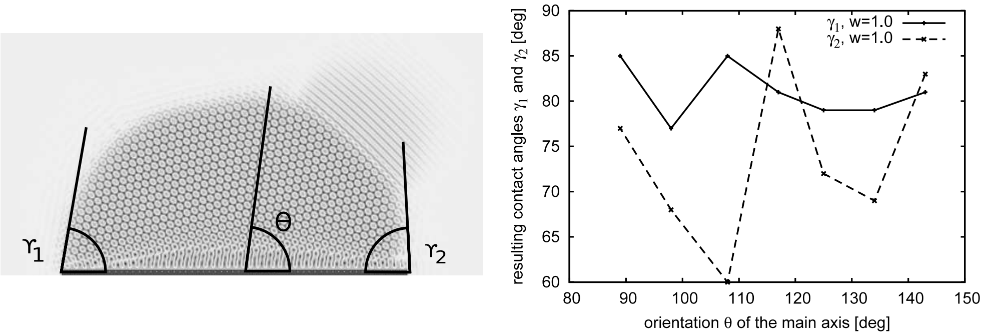

Figure 3. Typical structure of the nucleus using the boundary condition of equation (11) (left), as well as the resulting contact angles γ_1 and γ_2 for $w = 1$ and different orientations θ of the nucleus (right).

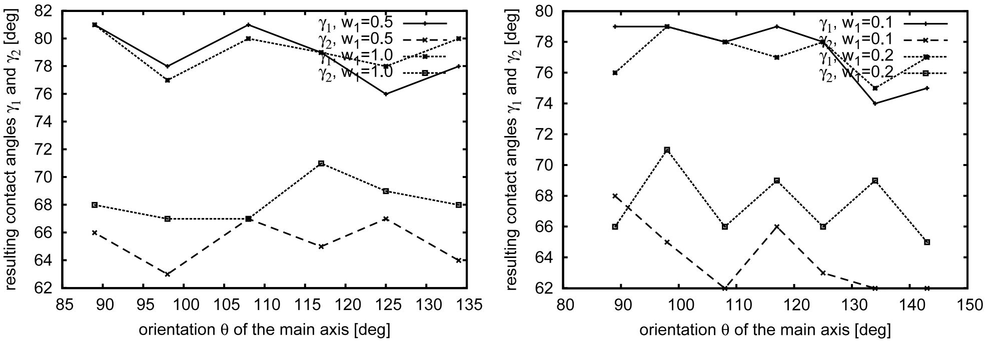

Figure 4. Resulting contact angles γ_1 and γ_2 for different orientations θ of the nucleus and different ratios w_1:w_2. On the left, the upper two curves present simulations for $w_1 = 0.5$ and $w_2 = 3$, the two lower curves for $w_1 = 1$ and $w_2 = 6$. For each set the contact angles to the left of the nucleus (given be the lines for γ_1) and to the right of the nucleus (γ_2) are plotted. The diagram to the right shows an analogous plot for a ratio w_1:$w_2 = 1 : 20$ and $w_1 = 0.1$ and $w_2 = 2$ (upper curves), as well as $w_1 = 0.2$ and $w_2 = 40$ (lower curves).

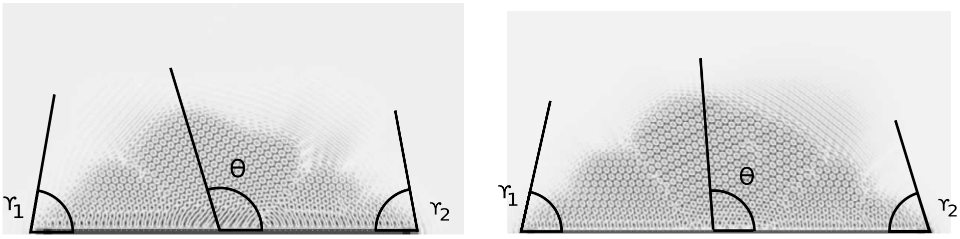

Figure 5. Typical resulting morphologies for different ratios of w_1:w_2:w_1:$w_2 = 1$:6 (left) and w_1:$w_2 = 1$:20 (right).

Moreover, to realize (b) we set w to a higher value w_2 in the contact angle region compared to a lower value of w_1 in the remaining 'interior' part of the wall. Several ratios of w_1 and w_2 were investigated. For each ratio we varied the basic interaction strength as well. An impression of the nuclei morphologies resulting from this approach can be obtained from figure 5. The results of these studies are summarized in figure 4. They allow the following conclusions.

(i) Comparing the diagram at the right-hand side of figure 3 with the ones in figure 4 we can see that the realization of capillary forces as described above results in smaller contact angles. Moreover, the contact angle values for different orientations have smaller fluctuations from a mean value than without realization of capillary forces.

(ii) The larger the interaction strength, the smaller the contact angle. However, there appears to be a saturation of that effect: values of $w_2 = 40$ result in similar contact angles to values of $w_2 = 6$.

(iii) It appears that moderate ratios of w_1 to w_2 result in contact angle values which for different orientations fluctuate least around a mean value. However, this needs to be checked by the study of still different ratios. What is obvious, though, from figure 4 is that an interaction potential realizing adhesive as well as capillary forces results in contact angles that lose their obvious dependence on the orientation of the ellipsoids with respect to the wall, which is obvious for the 'hard wall' interaction (see figure 3, right-hand side).

The final conclusion can be checked quite easily experimentally. A more quantitative comparison to experimental contact angles would even allow us to evaluate the description of the interaction potential between substrate and nucleus which we formulate in equation (11). This would contribute to this still difficult issue in heterogeneous nucleation theory. Further insight can also be expected from the further development of this approach such that it will also include surface energies, as we will show in more detail in [20] and discuss from the point of view of its perspectives in section 5.

5. Summary and outlook

In this paper we have introduced for the first time an anisotropic version of the simplest phase-field crystal model (see e.g. [6]), which we termed the APFC model. The model allows us to simulate isotropic as well as anisotropic crystal lattice systems of arbitrary Poisson ratios as well as condensed matter systems built up from non-spherical units such as, for example, colloids and liquid crystals. In this paper we applied this to the heterogeneous nucleation of ellipsoids at a wall. The particular focus of our study was concerned with the question of how (a) the orientation of the ellipsoids as well as (b) the interaction potential with the wall determine the resulting contact angle. Our studies reveal that:

(i) the realization of capillary forces as described above results in smaller contact angles and, moreover, the contact angle values for different orientations have smaller fluctuations from a mean value than without the realization of capillary forces;
(ii) the larger the interaction strength, the smaller the contact angle;
(iii) an interaction potential realizing adhesive as well as capillary forces results in contact angles that lose their obvious dependence on the orientation of the ellipsoids with respect to the wall, which is obvious for the 'hard wall' interaction (see figure 3, right-hand side).

At this point our model still does not include a notion of surface energies, thus it neither allows for a comparison with or a validation of important experimentally accessible mesoscopic parameters, nor does it allow us to make use of important continuum model concepts already developed in the field (see e.g. [33, 34] and references therein). This shortcoming can be overcome in two ways, as we will demonstrate in [20]. One of these two ways is based on a renormalization group approach as already used previously in the context of phase-field crystal modeling [35]. With these upcoming extensions the phase-field crystal model presented here appears to be a very promising approach to address problems of heterogeneous nucleation in general condensed matter systems as we did here, since it provides a comprehensive scale-bridging view: taking into account that it can be parametrized with density functional theory calculations [8, 9], which themselves can obtain input with respect to specific potential formulations from MD simulations, it provides a very quantitative description of the atomic processes underlying, for example, nucleation, at the same time providing a link to continuum theoretical concepts as well as to the possibilities of experimental validation at the mesoscopic scale. In particular, with the anisotropic extension of the phase-field crystal approach, which we propose here, and the resulting capacity to simulate any kind of colloidal system, it bears the potential to gain—via comparison to experiments—new insight into the interaction potential between the nucleus and wall and its appropriate formulation in continuum models due to the direct experimental accessibility of the contact angles in such colloidal systems [36].

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