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Philosophical Magazine Letters
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tphl20

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Published online: 09 Jan 2009.

To cite this article: R. Backofen, A. Rätz & A. Voigt (2007) Nucleation and growth by a phase field crystal (PFC) model, Philosophical Magazine Letters, 87:11, 813-820

To link to this article: http://dx.doi.org/10.1080/09500830701481737

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Philosophical Magazine Letters,
Vol. 87, No. 11, November 2007, 813–820

Nucleation and growth by a phase field crystal (PFC) model

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(*Received 8 March 2007; in final form 31 May 2007*)

We review the derivation of a phase field crystal (PFC) model from classical density functional theory (DFT). Through a gradient flow of the Helmholtz free energy functional and appropriate approximations of the correlation functions, higher order nonlinear equations are derived for the evolution of a time averaged density. The equation is solved by finite elements using a semi-implicit time discretization.

1. Introduction

Classical density functional theory (DFT) is a very successful theory to describe thermodynamics and equilibrium structures of fluids. It is based upon a minimization principle for a free energy density functional and determines the equilibrium ensemble average one body density profile of a classical fluid. In practice, DFT is only an approximation because the free energy functional is generally unknown. However, for many systems rather accurate approximations of the Helmholtz free energy functional exist. Given the success of DFT, it is very appealing to construct a dynamical theory from it. To obtain an equation of motion for the one-body density profile $\rho(\mathbf{x}, t)$ an ensemble average over the possible configurations of the system at time t, given an ensemble at $t = 0$ is needed. On this basis Marconi and Tarazana construct a deterministic dynamical density functional theory (DDFT) [1]. It is assumed that the gradient of the chemical potential $\nabla\mu(\mathbf{x}, t)$ is the thermodynamic driving force for the particle current $\mathbf{j}(\mathbf{x}, t) = -\Gamma\nabla\mu(\mathbf{x}, t)$, where Γ is a mobility function. Thereby the chemical potential μ is given by the functional derivative of the Helmholtz free energy functional with respect to the density profile. Altogether they give the continuity equation

$$\partial_t\rho(\mathbf{x}, t) = -\nabla \cdot \mathbf{j}(\mathbf{x}, t), \tag{1}$$

and provide the basis for DDFT. Equations of this form have been used in various fields and their agreement with results from Brownian dynamics simulations have

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Philosophical Magazine Letters
ISSN 0950-0839 print/ISSN 1362-3036 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/09500830701481737

generally been very good. We are interested here in the dynamics of freezing, in the theoretical understanding of nucleation and the subsequent growth of crystals. In this context the emergence of an ordered phase can be viewed as a transition to a phase in which $\rho(\mathbf{x}, t)$ is highly non-homogenous and possesses the spatial symmetries of the crystal, see e.g. [2, 3]. Following [4], we expand the free energy functional about a density ρ_l, corresponding to a liquid state lying on the liquidus line of the solid–liquid coexistence phase diagram. The free energy functional then reads

$$\begin{aligned}\frac{\mathcal{F}}{k_B T} &= \int \rho(\mathbf{x}, t) \ln\left(\frac{\rho(\mathbf{x}, t)}{\rho_l}\right) - \delta\rho(\mathbf{x}, t)\, \mathrm{d}\mathbf{x} \\ &\quad - \frac{1}{2}\int\int \delta\rho(\mathbf{x}_1, t) C_2(\mathbf{x}_1, \mathbf{x}_2) \delta\rho(\mathbf{x}_2, t)\, \mathrm{d}\mathbf{x}_1\, \mathrm{d}\mathbf{x}_2 + \cdots \end{aligned} \tag{2}$$

with $\delta\rho(\mathbf{x}, t) = \rho(\mathbf{x}, t) - \rho_l$, the two point direct correlation function

$$C_2(\mathbf{x}_1, \mathbf{x}_2) = \frac{\delta^2 \Phi}{\delta\rho(\mathbf{x}_1)\delta\rho(\mathbf{x}_2)}, \tag{3}$$

and additional higher order terms, where Φ is the total potential energy of interaction between the particles in the material. As the exact form of these higher order terms is only known for very few systems, various approximations have been derived which usually truncate the free energy functional after the term with the two point correlation function. In [1] the two point correlation function is approximated with the help of equilibrium DFT. A different approach is used by Elder *et al.* [4], where the two point correlation function is expanded in a Fourier series, i.e. $\hat{C} = \hat{C}_0 + k^2 \hat{C}_2 + k^4 \hat{C}_4 + \cdots$, which is truncated after the fourth order term. Thus the material is characterized only through the three parameters $\hat{C}_0$, $\hat{C}_2$ and $\hat{C}_4$, which correspond to the liquid phase thermal compressibility, the bulk modulus of the crystal and the lattice constant, respectively. Rewriting the free energy functional in dimensionless units leads to

$$\mathcal{F} = \int \frac{1}{2}\psi\left(-\epsilon + (\Delta + 1)^2\right)\psi + \frac{1}{4}\psi^4\, \mathrm{d}\mathbf{x} \tag{4}$$

with a dimensionless parameter ϵ and a dimensionless density field ψ. The resulting evolution equation is the one-mode phase field crystal (PFC) model introduced by Elder *et al.* [5]. It should be noted, that at this level of simplification, the model always predicts a BCC symmetry of the crystal. Other symmetries can be obtained by higher order approximations of the two point correlation function. In dimensionless form the free energy functional corresponding to FCC symmetry reads

$$\mathcal{F} = \int \frac{1}{2}\psi\left\{-\epsilon + (\Delta + 1)^2\left(\left(\Delta + \frac{4}{3}\right)^2 + R\right)\right\}\psi + \frac{1}{4}\psi^4\, \mathrm{d}\mathbf{x}, \tag{5}$$

see Wu [6], which gives a two-mode PFC model and the dynamic law

$$\partial_t \psi = \Delta\left\{-\epsilon + (\Delta + 1)^2\left(\left(\Delta + \frac{4}{3}\right)^2 + R\right) + \psi^3\right\}, \tag{6}$$

which is of 10th order. In the limit that $R \gg 1$ this model reduces to the one-mode PFC model. We will here concentrate on the one-mode PFC model, for which the sixth order evolution equation with mobility function $\Gamma = 1$ reads

$$\partial_t \psi = \Delta\left\{(-\epsilon + (1+\Delta)^2)\psi + \psi^3\right\}. \tag{7}$$

Since the introduction of the PFC model, there have been several extensions and applications, e.g. [7, 8] to study strain induced phase transformations and [9] to derive surface energy coefficients.

2. Numerical approach

Discretizations of higher order nonlinear equations, as (7), require some care, as standard explicit schemes lead to severe time step restrictions which will make long time simulations extremely demanding. Fully implicit schemes on the other hand lead to nonlinear equations, which have to be solved in each time step and are therefore not efficient. Here we use a semi-implicit discretization in time, which allows for large time steps and only requires the solution of a linear system in each time step. Thereby we linearize the derivative of the potential $(\psi^{n+1})^3 \approx 3(\psi^n)^2\psi^{n+1} - 2(\psi^n)^3$. The discretization in space is done by linear finite elements. The discrete form for (7) written as a system of second order equations with periodic boundary conditions thus read:

$$\begin{aligned}
\int \nu^{n+1}\eta \, d\mathbf{x} &= -\int \nabla\psi^{n+1}\cdot\nabla\eta \, d\mathbf{x}\\
\int \frac{\psi^{n+1}-\psi^n}{\tau^n}\eta \, d\mathbf{x} &= -\int \nabla u^{n+1}\cdot\nabla\eta \, d\mathbf{x}\\
\int u^{n+1}\eta \, d\mathbf{x} &= \int \left(-\epsilon\psi^{n+1} + \psi^{n+1} + 3(\psi^n)^2\psi^{n+1} - 2(\psi^n)^3\right)\eta \, d\mathbf{x}\\
&\quad - \int \nabla\nu^{n+1}\cdot\nabla\eta \, d\mathbf{x} - 2\int \nabla\psi^{n+1}\cdot\nabla\eta \, d\mathbf{x},
\end{aligned}$$

for all test functions η and time steps τ^n. The linear system to be solved reads with mass and stiffness matrices $\mathbf{M} = (M_{ij})$, $M_{ij} = (\eta_i, \eta_j)$ and $\mathbf{A} = (A_{ij})$, $A_{ij} = (\nabla\eta_i, \nabla\eta_j)$, respectively, and with $\mathbf{F}^{\mathrm{i}} = (F^{\mathrm{i}}_{ij})$, $F^{\mathrm{i}}_{ij} = (3(\psi^n)^2\eta_i, \eta_j)$ as well as $\mathbf{F}^{\mathrm{e}} = (F^{\mathrm{e}}_i)$, $F^{\mathrm{e}}_i = (2(\psi^n)^3, \eta_i)$, where $(\cdot,\cdot)$ denotes the usual L^2-scalar product and η_i the standard piecewise linear nodal basis functions:

$$\begin{pmatrix} \mathbf{A} & \mathbf{0} & \mathbf{M} \\ \frac{1}{\tau^n}\mathbf{M} & \mathbf{A} & \mathbf{0} \\ 2\mathbf{A} + (\epsilon - 1)\mathbf{M} - \mathbf{F}^{\mathrm{i}} & \mathbf{M} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \Psi^{n+1} \\ U^{n+1} \\ V^{n+1} \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{1}{\tau^n}\mathbf{M}\Psi^n \\ -\mathbf{F}^{\mathrm{e}} \end{pmatrix}. \tag{8}$$

The resulting equation is nonsymmetric and solved by a GMRES-solver. The problem is implemented in the adaptive finite element toolbox AMDiS [10], but solved on a uniform grid.

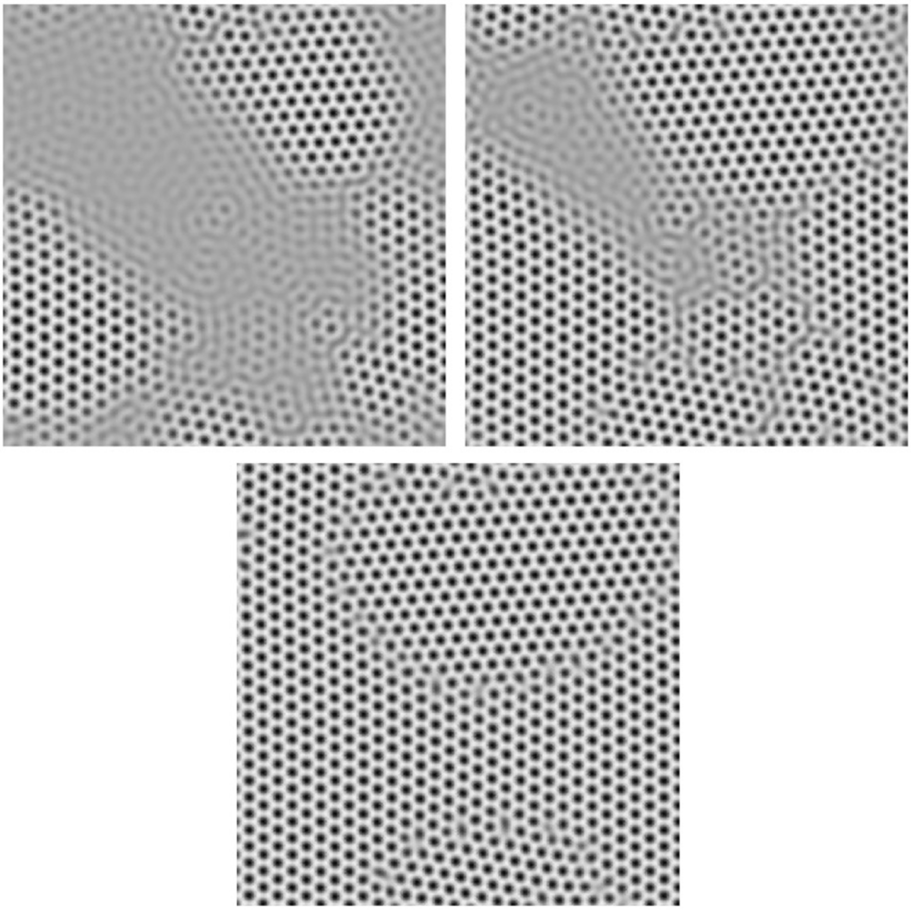
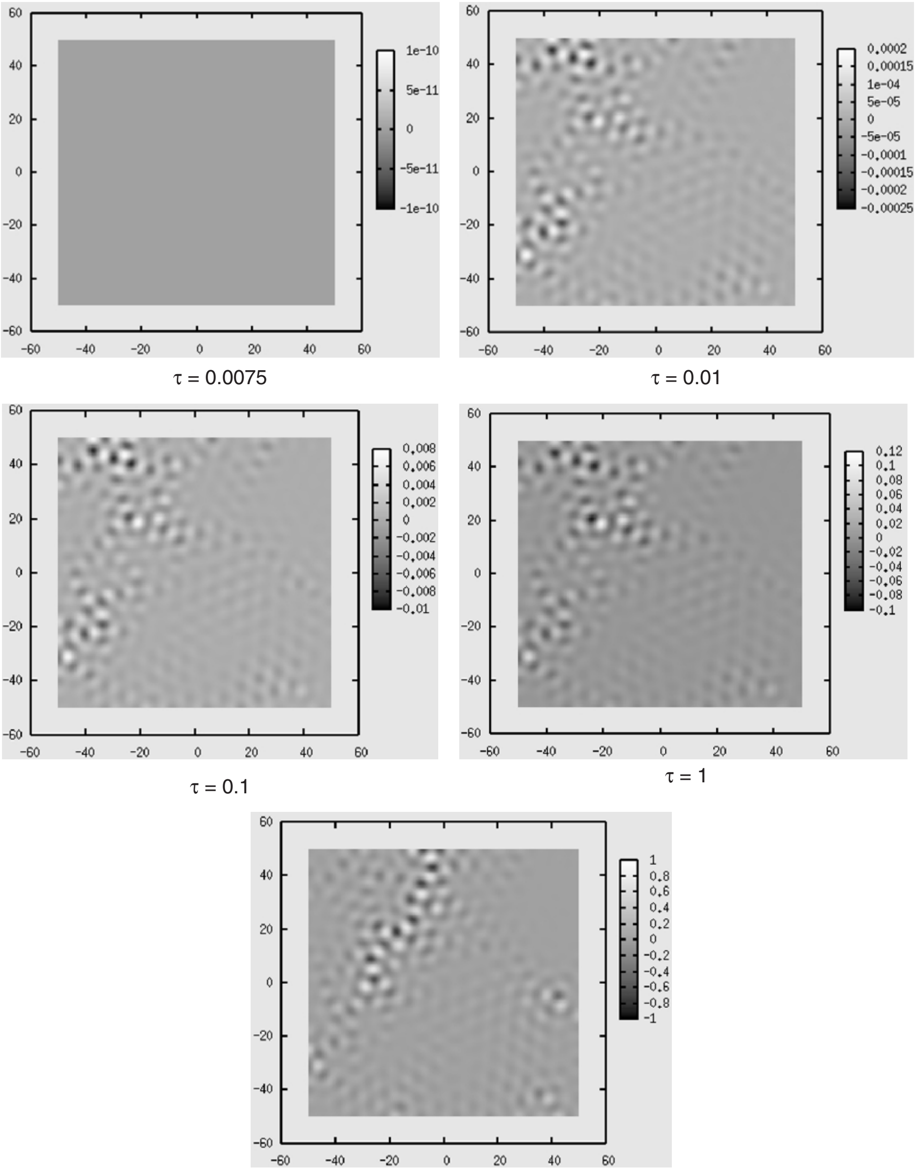


Figure 1. Time averaged density profile at different time steps. The initial condition is a randomly perturbed uniform configuration for an undercooled melt. Periodic boundary conditions are used.

3. Results

Figure 1 shows on an atomistic resolution the solidification of a BCC crystal from an undercooled melt. Nucleation and subsequent growth of multiple grains with different orientations are shown. As the grains come together dislocations form.

We would now like to demonstrate the advantages of our numerical approach compared to standard explicit schemes. We therefore chose a benchmark simulation in which we compare our results with [11]. We use the same model parameters and their time step as a reference solution. Figure 2 shows the deviation of solutions obtained with larger time steps from the reference solution. The plotted deviation is a hard measure. It increases with increasing time steps but remains localized, even for time steps which are four orders of magnitude larger then in the reference solution. If we compute the relative L^{∞} error we obtain for $\tau = 0.01$ an error of 0.04%, for



τ = 0.0075

τ = 0.01

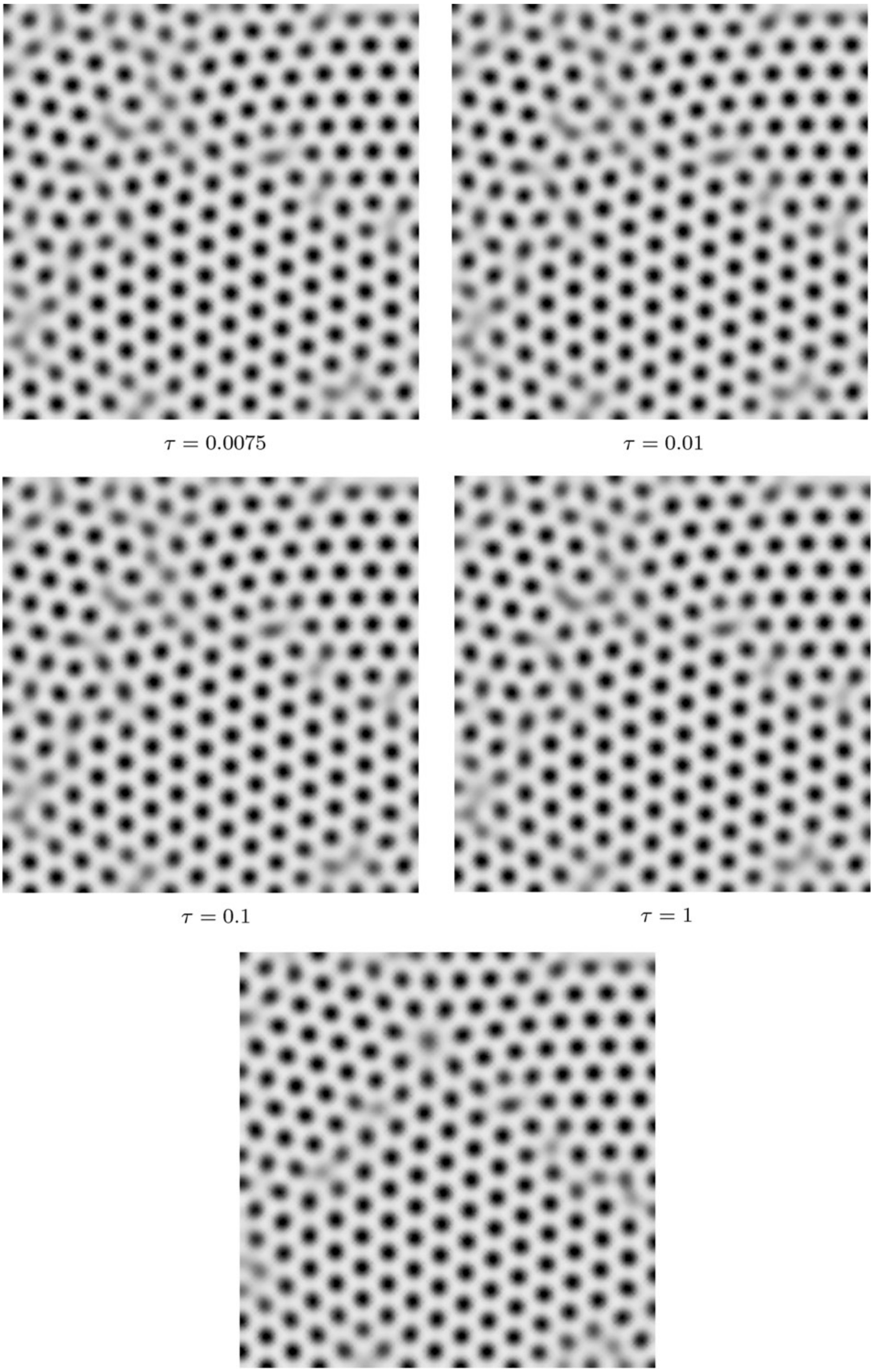
τ = 0.1

τ = 1

τ = 10

Figure 2. Difference between solution of (8) for $\tau = 0.0075$ and $\tau = 0.0075$, $\tau = 0.01$, $\tau = 0.1$, $\tau = 1$, $\tau = 10$, for $t = 600$. No-flux boundary conditions are used.

$\tau = 0.1$ an error of 1.4% and for $\tau = 1$ an error of 17%. For $\tau = 10$ the error is of the same order as the solution, thus such time steps are too large. An error of 17% also might seem to be too high, but looking at the solution and not the deviation shows that qualitatively all main features of the solution are still resolved, see figure 3, which shows the solution at $t = 600$ for different τ. For $\tau = 10$ also the qualitative



$\tau = 0.0075$

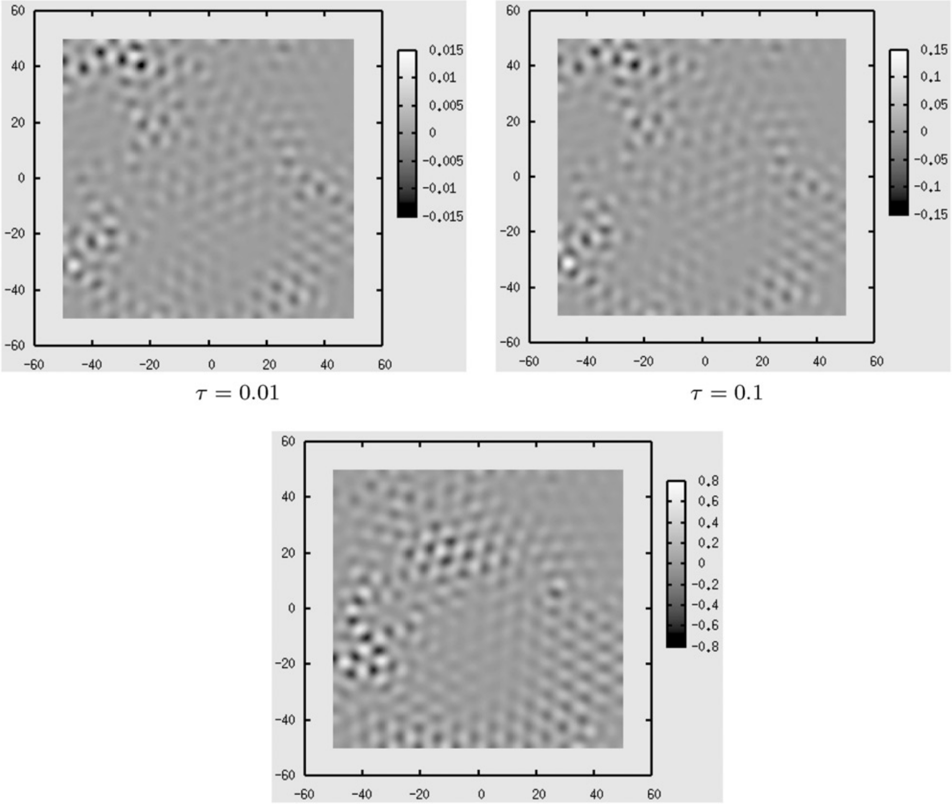
$\tau = 0.01$

$\tau = 0.1$

$\tau = 1$

$\tau = 10$

Figure 3. Solution of (8) for $\tau = 0.0075$, $\tau = 0.01$, $\tau = 0.1$, $\tau = 1$, $\tau = 10$, for $t = 600$. No-flux boundary conditions are used.



$\tau = 0.01$ $\tau = 0.1$

$\tau = 1$

Figure 4. Difference between solution of (8) for $\tau = 0.0075$ and $\tau = 0.01$, $\tau = 0.1$, $\tau = 1$ with derivative of potential explicitly treated, for $t = 600$. No-flux boundary conditions are used.

agreement is lost. Thus the results suggest that time step sizes up to $\tau = 1$ will lead to reasonable results. We would further like to mention that the chosen benchmark is a hard test, as the structure evolves from an undercooled melt, with randomly perturbed initial data. We expect even better results if the initial data is already a crystalline structure.

The next test shows the effect of the implicit treatment of the derivative of the potential in the algorithm. In analogy to figure 2 we now compare the solution using an explicit discretization of the derivative of the potential, see figure 4. The results clearly indicate the advantage of the implicit treatment of the derivative of the potential, which leads to a gain in at least one order of magnitude larger time steps.

To conclude, the results indicate that the semi-implicit treatment of the equations allows us to use at least one order of magnitude larger time steps than an explicit scheme would require; and, the linearization of the derivative of the potential yields a further improvement of at least one order of magnitude.

4. Conclusions

To model nucleation and growth several important features must be included: multiple crystal orientations, interfacial energies, elastic and plastic deformations. Perhaps the most straightforward method of modelling these is to solve Newton's equation of motion for a collection of particles, i.e. molecular dynamics (MD). Unfortunately the time scale in these simulations is limited by lattice vibrations (∼ps) and the spatial scale by lattice constant (∼Å), which makes it unfeasible even on high performance computers to reach appropriate time and length scales of practical interest. Another approach is to use classical phase field models (PF). While this approach can access much larger time and length scales it is very challenging to incorporate all the required features.

The described phase field crystal (PFC) approach might be viewed as an intermediate model between MD and PF. It includes, by construction, the most relevant features which are involved in MD, it solves the problem as MD on an atomic scale, but the time scale is larger and comparable to PF. Thus the PFC model offers the possibility to reach time scales of practical interest. The computational cost however is very demanding, as the spatial resolution has to be even higher than in MD. Each atom requires approximately 10^2 grid points in 2D. This requires efficient numerical algorithms. Besides the described approach by finite elements, investigations towards multigrid methods and parallelization are under way, which will allow us also to perform simulations in 3D.

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