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Density functional approaches to the dynamics of phase transitions

David W Oxtoby and Yu Chen Shen

James Franck Institute, University of Chicago, 5640 South Ellis Avenue, Chicago, IL 60637, USA

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Abstract. Density functional approaches have become well known in applications of equilibrium statistical mechanics to phase diagrams, interfacial structures, and free energies. This paper describes how these methods can be extended to the dynamics of phase transitions. Two aspects are emphasized: the calculation of free-energy barriers in nucleation and of growth velocities for crystallization from the melt. Significant deviations from classical nucleation theory and from diffusion-based theories of crystal growth are found. The continuum density functional approach is effective in describing the dynamics of collective-mode fluctuations, which dominate single-particle dynamics in these cases. The role of body-centred ordering at the interface between a face-centred crystal and the melt is described.

Density functional methods in statistical mechanics start from the mathematically rigorous statement [1, 2] that the exact free-energy functional of a system determines all its equilibrium properties: phase diagram, interfacial profiles and free energies, and response to time-independent external potentials. Such methods have become useful over the last fifteen years as calculations have demonstrated that approximate free-energy functionals give rise to accurate predictions of equilibrium properties. Among the problems most successfully addressed with density functional methods are the density profiles of fluids near free surfaces and at walls, and the gas–liquid–solid phase transitions of simple materials.

Time-dependent extensions of density functional methods are more problematical. Results from equilibrium statistical mechanics nearly always lose their mathematical rigour when extended into the non-equilibrium domain, and that is certainly true of density functional theory. The importance of problems in dynamics, and the satisfactory equilibrium results from density functionals, make this effort worthwhile. In this paper we discuss how density functional approaches can be extended to two important stages in the dynamics of first-order phase transitions: nucleation and growth. Applications to crystallization from the melt are emphasized here, although the approaches described have also been successful in predicting rates for the gas–liquid transition [3].

The density in a periodic solid can be expanded in Fourier components:

$$\rho(\mathbf{r}) = \rho_0 + \rho_s \sum_i m_i \exp(i\mathbf{k}_i \cdot \mathbf{r}). \quad (1)$$

The coefficients m_i are order parameters for the liquid-to-crystal transition, zero in the liquid but finite in the crystal; the average density ρ_0 also differs between the two phases ($\rho_0 = \rho_s$ in the solid). In a non-uniform crystal–liquid system these order parameters vary through space. It has been found that a Gaussian (quasi-harmonic) description applies reasonably

well to crystalline solids, even close to the melting point. This implies that the Fourier components in equation (1) are not independent; each can be related to the first through

$$m_i = (m_1)^{(k_i/k_1)^2}. \quad (2)$$

This two-order-parameter model (average density ρ_0 and first structural order parameter m_1 , henceforth called m) is used throughout this paper.

Several approaches have been developed to calculate free-energy functionals $F[\rho(\mathbf{r})]$ for crystallization. The free energy is written as

$$F[\rho(\mathbf{r})] = F_{id}[\rho(\mathbf{r})] + F_{ex}[\rho(\mathbf{r})] \quad (3)$$

where F_{id} is the exact free energy of an ideal (non-interacting) system of particles and F_{ex} is the excess free energy. The second functional derivative of F_{ex} , evaluated for a uniform fluid, is related to the pair correlation function of the liquid [2]. This constraint on the free-energy functional is employed in approximate theories. One approach [4] is simply to functionally expand F about the liquid density and truncate it at second order, but this is of limited value in more strongly inhomogeneous fluids. A second approach is the weighted-density approximation [5], in which the excess free energy is written as a function not of the local density but of a smoothed (or weighted) density. This is a powerful approach, but is lengthy to implement for inhomogeneous systems. We have therefore adopted a compromise, first applied by Ohnesorge *et al* [6] to surface melting. The Lennard-Jones potential we study is separated into a hard-sphere part and an attractive tail. The hard-sphere free energy is treated in the modified weighted-density approximation [7], and the attractive tail via perturbation theory. Ordinarily, the MWDA could not be used for inhomogeneous systems; here it is extended via a square-gradient approximation applied throughout order parameter space. Further details of the functional are given in references [6] and [8]. The resulting equilibrium phase diagram [6] and surface free energy [8] are in good agreement with simulation results.

Nucleation is an activated process, so the nucleation rate has the form

$$J = J_0 \exp(-\Delta\Omega^*/kT) \quad (4)$$

where J_0 is a dynamic prefactor and $\Delta\Omega^*$ the free-energy barrier. Nucleation rates are only weakly sensitive to the prefactor, which can be estimated by relating dynamical equations for the two order parameters to the width of the dynamic structure factor of the liquid [8]. (This is the dynamical analogue of constraining the second derivative of the free energy to the equilibrium liquid correlation function.) The role of density functional theory is to calculate the nucleation barrier. It might appear that a critical nucleus, being thermodynamically unstable to growth or decay, could not be calculated using an equilibrium theory. This is not true, however, because the instability occurs only in the grand canonical ensemble [9]. A system constrained to have a density just above the liquid density (and well below the solid density) will consist at equilibrium of a small crystalline cluster surrounded by liquid. By varying the amount of matter in the container, the size of the nucleus will change and the saddle point that corresponds to the critical nucleus can be calculated and its free energy determined.

The resulting predictions of nucleation rates for crystallization in Lennard-Jones fluids [10] differ strikingly between crystal formation in an undercooled liquid and liquid drop formation in a bulk superheated crystal. In the undercooled liquid, there is no evidence for a spinodal instability, and the crystal–melt interface sharpens as the temperature is lowered. In the superheated crystal, an instability appears above the equilibrium freezing point, and the barrier to nucleation vanishes as the spinodal instability is approached. Near the spinodal,

the centre of the critical nucleus no longer resembles bulk liquid. Classical nucleation theory significantly overestimates the barrier to nucleation (and thus underestimates the nucleation rate) in both cases. (Note that this is opposite to the behaviour found earlier [11] for a less accurate free-energy functional.)

Once a crystal has nucleated, a liquid–solid interface is created that can move via crystal or melt growth in an undercooled or superheated system. The dependence of growth velocity on temperature is an important variable in rapid-solidification processing of materials, and our goal is to calculate it using non-equilibrium density functional theory. Of the two order parameters in our theory, the average density ρ_0 is a conserved variable and the structural order parameter m is non-conserved. These satisfy different time-dependent equations, because in the case of ρ_0 matter must be transported from a distance, while m can fluctuate purely locally. At first sight, it might appear that the presence of a conserved order parameter would prevent steady-state growth, but we have shown [12] that including convective motion (as well as diffusive) leads to a pair of dynamical equations that resemble those for two coupled non-conserved order parameters. In highly viscous liquids, crystal growth is governed by the rate of mass transport to the interface and is viscosity dependent; in low-viscosity liquids (such as liquid metals) it is controlled by the structural order parameter dynamics with the latter mobility obtained from the dynamic structure factor of the liquid, as described above and in reference [8].

For a Lennard-Jones fluid [8], we find a strong asymmetry between crystal and melt growth, just as we found an asymmetry between undercooled and superheated nucleation. First, near the freezing point T_f there is a rather sudden change in slope of growth velocity against temperature. Second, the velocity and order parameter profiles approach large undercooling and superheating differently. In the undercooled liquid, there is no evidence for a spinodal instability, but a density deficit appears in front of the interface that eventually leads to viscosity-limited growth. In the superheated crystal, on the other hand, the interface between the two phases gradually disappears. Growth rates are higher for superheated crystals than for undercooled liquids, at a given temperature difference from the freezing point.

The two-order-parameter description we have employed has many of the physical features of the real liquid-to-crystal phase transition. It is not flexible enough, however, to include the very interesting behaviour recently found for the equilibrium planar interface and nucleation crystallites. Ten Wolde *et al* [13] simulated the interface between a face-centred-cubic crystal and the melt in a Lennard-Jones system. By carefully analysing local bond ordering, they found that at the centre of the interface, a characteristic body-centred-cubic ordering appeared. In other words, in passing from liquid to fcc crystal, an intermediate bcc phase intervenes over a distance scale of the order of a few lattice spacings. The same observation affects the nucleation behaviour strongly: the critical nucleus (which is mostly interface) has considerable bcc character. Only during the later growth stage does its centre transform into the stable fcc crystal.

We have extended our parametrization of the density to account for this possibility. An fcc crystal can be continuously deformed into a bcc crystal (via intermediate tetragonal states) through a Bain distortion [14]. The parameter χ which characterizes the stage of the transformation varies from 1 (bcc crystal) to 1.414 (fcc crystal) and serves as an additional order parameter that distinguishes the two solid phases. In our first calculations we have simplified the problem by fixing ρ_0 at a value intermediate between the density of the liquid and of the fcc crystal. The two order parameters χ and m then are treated in a square-gradient approximation as before, and the bulk and surface free energies calculated. A metastable bcc bulk phase appears at $\chi = 1$ and $m = 0.750$, in addition to the stable

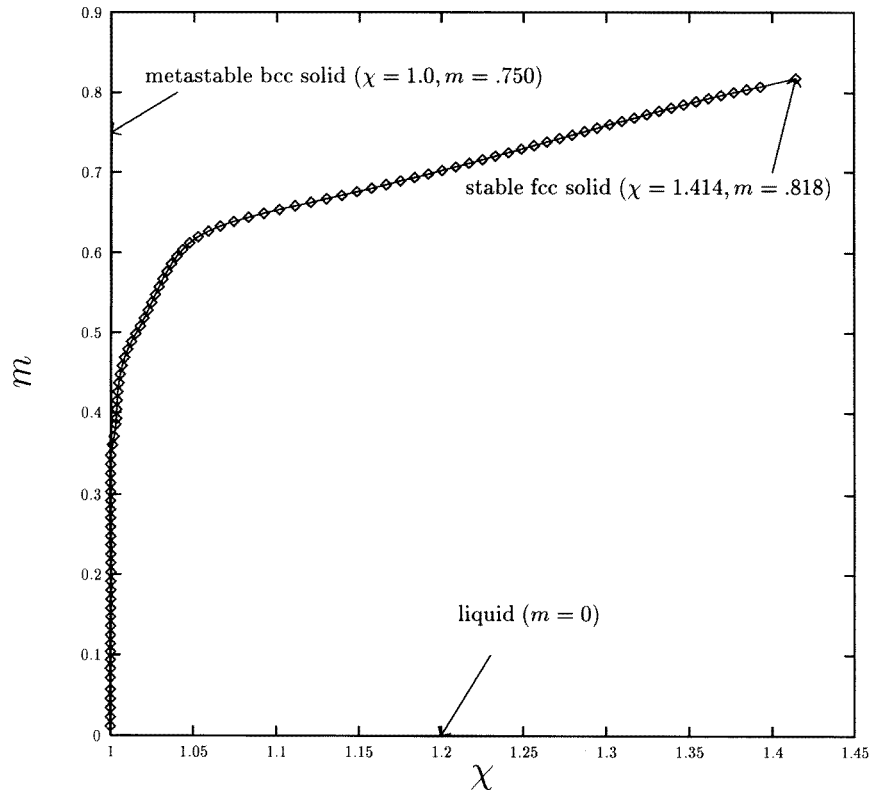


Figure 1. A plot of the two order parameters m and χ as they depend parametrically on the position z through a planar equilibrium crystal–melt interface. In the equilibrium path shown, the structure has changed from fcc to bcc by the middle of the interface (near $m = 0.4$), as shown by the fact that χ has decreased from 1.414 to near 1 by that point. The simpler path in which m changes at constant χ is of higher free energy and is not followed.

fcc phase at $\chi = 1.414$ and $m = 0.818$, and the stable liquid at $m = 0$ (the value of χ is irrelevant for the liquid).

It is striking that the equilibrium interface again shows strong evidence of bcc ordering: the value of χ changes from 1.414 to close to 1 as the crystal gradually becomes less ordered and approaches the liquid (see figure 1). The simpler path in which only m changes is of higher free energy. This in turn results from the geometry of the free-energy surface. The lowest barrier between liquid and crystal appears near the bcc crystal, and the equilibrium interfacial profile passes almost through this saddle point. The results of computer simulations are thus confirmed by our calculations. Further work will include the effect of changes in the average density and will look at the nucleation behaviour.

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