

Heterogeneous nucleation near a metastable vapour-liquid transition: the effect of wetting transitions

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 3693

(<http://iopscience.iop.org/0953-8984/14/14/302>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.104

The article was downloaded on 18/05/2010 at 06:25

Please note that [terms and conditions apply](#).

Heterogeneous nucleation near a metastable vapour–liquid transition: the effect of wetting transitions

Richard P Sear

Department of Physics, University of Surrey, Guildford, Surrey GU2 7XH, UK

E-mail: r.sear@surrey.ac.uk

Received 23 January 2002

Published 28 March 2002

Online at stacks.iop.org/JPhysCM/14/3693

Abstract

Phase transformations such as freezing typically start with heterogeneous nucleation. Heterogeneous nucleation near a wetting transition, of a crystalline phase, is studied. The wetting transition occurs at or near a vapour–liquid transition which occurs in a metastable fluid. The fluid is metastable with respect to crystallization, and it is the crystallization of this fluid phase that we are interested in. At a wetting transition a thick layer of a liquid phase forms at a surface in contact with the vapour phase. The crystalline nucleus is then immersed in this liquid layer, which reduces the free-energy barrier to nucleation and so dramatically increases the nucleation rate. The variation in the rate of heterogeneous nucleation close to wetting transitions is calculated for systems in which the longest-range forces are dispersion forces.

1. Introduction

When water is cooled below 0 °C at atmospheric pressure it freezes; it turns into ice. This conversion of one phase, water, into another, ice, starts with the nucleation of a microscopic nucleus of ice. This nucleus consists of only of order 10 molecules; its formation costs free energy and occurs not in the bulk of the water but at a surface in contact with the water. The free-energy cost provides a barrier to the nucleation of ice. If the free-energy cost or barrier is large, it will limit the rate of crystallization. When the barrier is very large the phase which is not the equilibrium one, for example water below 0 °C, will persist for very long times. The fluid phase is then called metastable. So to determine whether a phase which is not an equilibrium phase is metastable or whether the equilibrium phase nucleates rapidly we need to calculate the free-energy barrier to nucleation. We do this here near to and at *another* phase transition, a phase transition between two phases neither of which is the true equilibrium phase. The process of nucleation at a surface is called heterogeneous nucleation to distinguish it from homogeneous nucleation which occurs in the bulk; see [1] for an introduction to nucleation.

So, here we study the rate of heterogeneous nucleation of one phase transition, a fluid–crystal phase transition, near a second phase transition—a phase transition between phases

which are both metastable or unstable with respect to crystallization. This second phase transition is a vapour–liquid transition. At phase transitions the thermodynamic functions, including interfacial tensions, exhibit singular behaviour which is universal in the sense that many different systems show behaviour which is identical up to a few scale factors. Here we show that at the vapour–liquid transition the free-energy barrier to heterogeneous nucleation of a crystal shows behaviour which although not truly universal is the same near all vapour–liquid transitions, up to a few scale factors, assuming that the longest-range interactions are dispersion forces. This is due to wetting: the formation of a thick layer of the liquid phase on a surface in contact with the vapour phase [2–5]. The layer forms as coexistence is approached and causes a drop in the nucleation barrier to the nucleation of a dense phase such as a crystalline phase. The dependence on the nature of longest-range forces makes our findings not quite universal (unlike homogeneous nucleation near a bulk critical point [6] which is universal).

Motivation for our study is provided by the fact that some globular proteins have the correct set of phase transitions for exhibiting heterogeneous nucleation of a crystal near a vapour–liquid transition; see [7, 8] for the phase diagrams of a number of globular proteins. The crystallization of globular proteins is of great interest because protein crystals are required in order to determine the all-important three-dimensional structure of a protein [9]. Also, although we will always refer to the nucleus as being crystalline and the other transition as being a vapour–liquid transition, our findings are much more general. They refer to the nucleation of any non-critical phase near another, Ising-type, phase transition. We simply describe the phases as crystal, vapour, and liquid for simplicity and because having definite phases in mind is useful for pedagogical purposes.

Earlier work has found universal behaviour of the nucleation barrier for *homogeneous* nucleation near a bulk critical point; see [6, 10–13]. This earlier work, in particular that of ten Wolde and Frenkel [10], inspired this study of heterogeneous nucleation, and the results of [6, 10–14] are in a sense the homogeneous nucleation analogues of the results that we will obtain for heterogeneous nucleation. Also, Talanquer and Oxtoby [15] have studied heterogeneous nucleation of a liquid from a vapour phase. They studied the nucleation of the liquid phase at a surface when the liquid phase itself is close to wetting this surface. So, although they studied heterogeneous nucleation in the vicinity of a wetting transition, as we do below, they studied the nucleation of the liquid phase, the phase which is doing the wetting, whereas here we study the heterogeneous nucleation of another phase, the crystalline phase.

In the next section, we introduce both our model of the process of heterogeneous nucleation and the phase behaviour of the systems that we are interested in. In section 3 we derive the variation in the rate of heterogeneous nucleation near wetting transitions. Then in section 4 we compare with homogeneous nucleation of a crystal near a bulk critical point. The last section is a conclusion.

2. Heterogeneous nucleation

Heterogeneous nucleation is an activated process [1]¹, and as such occurs at a rate which decreases exponentially with the height of the barrier ΔF , which must be overcome. If N_n is

¹ Formation of the crystalline phase at the surface does not have to be an activated process. If the crystal itself wets the fluid–surface interface (this is a phenomenon distinct from the wetting at vapour–liquid coexistence of the vapour–surface interface by the liquid), then as the fluid–crystal transition is approached, a layer of the crystal forms at the surface and this can grow into a macroscopic crystal. For example, if we move along the path of the arrow in figure 1, then as μ_x is approached from below, a layer of crystal forms at the surface and at $\mu = \mu_x$ there is a macroscopic crystal formed. Then the crystalline phase forms at $\mu = \mu_x$ and there is no barrier to its formation. Throughout this work we are assuming that the crystalline phase does not wet the fluid–surface interface.

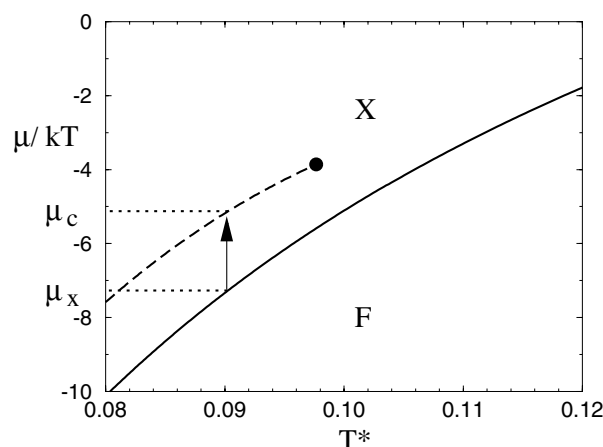


Figure 1. The bulk equilibrium phase diagram in the chemical-potential–temperature (μ – T) plane. The model is a simple model of a globular protein which has a metastable fluid–fluid transition, denoted by the dashed curve, which ends at a critical point, the black dot. The region in the chemical-potential–temperature plane where the equilibrium phase is the crystalline (fluid) phase is denoted by an X (F). For one particular temperature the chemical potential of the fluid–crystal transition, μ_x , and that at metastable fluid–fluid coexistence, μ_c are marked on the diagram. The reduced temperature $T^* = kT/\epsilon$ where ϵ is a bond energy.

the number of nuclei per unit area crossing the barrier per unit time, then N_n is given by an expression of the form [1]

$$N_n = \sigma \tau^{-1} \exp(-\Delta F/kT), \quad (1)$$

where σ is a surface density, i.e., it has the dimensions of inverse area, and τ is a characteristic time. We will refer to N_n as the nucleation rate or heterogeneous nucleation rate. The surface is smooth, perfectly planar, and chemically homogeneous. Equation (1) arises from the fact that the nucleus is a large, i.e., improbable, fluctuation. As a fluctuation, its probability of occurring in unit area is $\sigma \exp(-\Delta F/kT)$. The rate at which these fluctuations cross the barrier is then estimated as the number of fluctuations divided by τ , which is an estimate of how long it takes the nucleus to acquire one or a few extra molecules, enough for the nucleus to be big enough to grow irreversibly into a crystallite. Equation (1) is far from rigorous, but has been found for homogeneous nucleation to be a reasonable estimate. See the book of Debenedetti [1] for a discussion and [16] for a detailed comparison of an expression of the form of equation (1) with the results of computer simulation (for homogeneous nucleation). For the remainder of this work we will assume that τ and σ vary weakly with temperature and chemical potential and so the variation of the rate of heterogeneous nucleation is dominated by the variation in the free-energy barrier ΔF . Work on homogeneous nucleation has shown this assumption to be most often justified, except near a glass transition where τ increases sharply. However, verifying it requires a detailed calculation for a specific model system, which we do not do here.

Consider the phase diagram in the chemical-potential–temperature plane shown in figure 1. It is the phase diagram of a simple model of a globular protein, calculated using an approximate theory. See [17] for the precise definition of the model; the model parameters have the same values as they do for figure 4 of that reference. Also, see this reference for the same phase diagram in the density–temperature plane which can be seen to be qualitatively like that of a number of globular proteins [7, 8]. At true equilibrium there is only one phase transition,

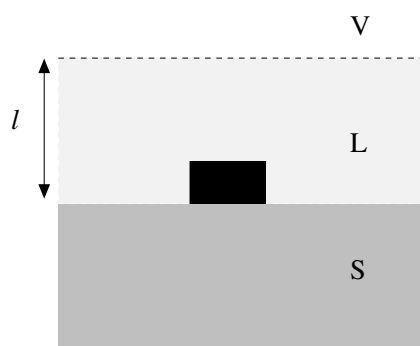


Figure 2. A schematic diagram of a wetting layer atop a surface, with a nucleus of the crystalline phase in contact with the surface and so within the wetting layer. The material of the surface (S) is shaded dark grey, the liquid (L) is lightly shaded, and the nucleus is black. The vapour (V) is left unshaded. The thickness l of the layer of liquid is indicated.

from a fluid phase, the equilibrium phase below the solid curve, to a crystal, the equilibrium phase above the curve. However, if the barrier to formation of the crystal phase is high, then the chemical potential can be increased at constant temperature along a path such as that indicated by the arrow in figure 1, until the metastable fluid undergoes another phase transition: a transition from a vapour phase to a liquid phase. The vapour is below the dashed curve, the liquid above. We have used the phase diagram of a model protein because it has the correct form: it has a vapour–liquid transition near where we expect the nucleation of the crystalline phase to occur. However, the behaviour that we find will apply whenever heterogeneous nucleation occurs at a surface which passes through a wetting transition.

Figure 2 is a schematic diagram of a crystalline nucleus in contact with a surface and immersed in a liquid layer of thickness l , with a vapour phase on top. This is the situation of interest; there is a bulk vapour phase against a smooth surface which attracts the molecules causing a layer of liquid to form near and at vapour–liquid coexistence. At coexistence and if we are above the wetting temperature—see [3, 5] and section 3—there is a very thick layer of liquid covering the surface and separating the vapour phase from the surface. The thickness l is then limited only by gravity. This wetting layer will reduce the nucleation barrier greatly if the interfacial tension between the liquid and the nucleus, γ_{xl} , is lower than that between the vapour and the nucleus, γ_{xv} . If the surface area of the nucleus not in contact with the surface is S , then the free-energy reduction will be $S(\gamma_{xl} - \gamma_{xv})$ when the wetting layer forms. For S of order 10 times the area per molecule of the surface of a crystal, and the difference $\gamma_{xl} - \gamma_{xv}$ of order kT divided by the area of one molecule, the reduction in the surface contribution to the free-energy barrier is of order $10kT$. This reduction will occur on moving in the vapour phase from conditions of chemical potential and temperature far from vapour–liquid coexistence, where there is no wetting layer, to at or very near coexistence—a large reduction which will lead, equation (1), to a very large increase in the nucleation rate N_n , which should be easily large enough to observe in an experiment.

3. Variation in the rate of heterogeneous nucleation as a wetting transition is approached

In this section we start with the assumption that the variation of the rate is dominated by that in the free-energy barrier ΔF and then calculate how ΔF varies near wetting transitions of

different types. Near a wetting transition the qualitative behaviour, in particular the form of the singularities, can be determined without knowing any specific details of the interactions or of the phase which is nucleating; we only require that the longest-range interactions be dispersion forces [18]. This is true, as the singularities come from long-length-scale phenomena for which the small-length-scale chemical details are irrelevant.

There are a number of different wetting phase transitions; see for example the excellent review of Schick [3]. We will deal with the three most common, starting with complete wetting. In each case we will work very close to the wetting transition, at temperatures or chemical potentials very close to their values at the transition. We will determine the leading-order singular terms in the temperature or chemical-potential variation of the nucleation rate near the transition.

3.1. Complete wetting

As heterogeneous nucleation occurs at a surface in contact with the fluid, it is rather obviously controlled by what happens at the surface. Now, if the surface attracts the molecules of the fluid, then not too far from the critical point [2, 4, 5], we will have wetting. Wetting is where at vapour–liquid coexistence a thick layer of the liquid phase interposes itself between the surface and the vapour phase, replacing the surface–vapour interface by a surface–liquid interface plus a liquid–vapour interface. It is also called complete wetting [3]. At coexistence the thickness of the layer is generally limited only by gravity. Thus, our first result is the, rather obvious, fact that if the surface is wetted by a thick layer of liquid, the rate of heterogeneous nucleation will be the *same* at surfaces in contact with the two coexisting phases, the vapour and the liquid. This result is universal; it is true whenever the surface is wet. The free-energy cost of forming a nucleus at the surface in contact with the bulk vapour is the same as the cost of forming a nucleus at the surface in contact with the bulk liquid, as both surfaces are covered by liquid.

This is at coexistence: the chemical potential $\mu = \mu_c$, where μ_c is the chemical potential at vapour–liquid coexistence at this temperature. In the vapour phase away from coexistence, $\mu < \mu_c$, there is still a layer of liquid at the surface provided that $h = \mu - \mu_c$ is not too negative. But this layer thins as h becomes more negative as we move further from coexistence. How it thins depends on the nature of the longest-range forces present in the system [3]. Here we assume that the longest-range forces are dispersion forces, which is most often the case. Then the free energy per unit area, f , of a film of liquid between the surface and the vapour of thickness l is [3, 18]

$$f = \frac{a}{l^2} - h \delta\rho l, \quad (2)$$

where we have included only those parts which depend on the thickness of the layer. The first term is the contribution of the dispersion forces, a is a positive constant, and the l^{-2} -dependence comes from starting with the usual l^{-6} -dependence, integrating over a volume, for the solid substrate, and then over the thickness of the layer of liquid. This fourfold integration changes the l^{-6} -dependence to an l^{-2} -dependence [18]. The second term is the increase in free energy due to the formation of a layer of liquid of thickness l when the chemical potential of the liquid, μ_c , is higher than the chemical potential. In this term, $\delta\rho$ is the difference in number density between the liquid and vapour phases. Minimizing the free-energy equation (2), we obtain the thickness

$$l = (2a/(-h \delta\rho))^{1/3}, \quad (3)$$

which diverges at coexistence: this divergence is in practice cut off at some large thickness by gravity. The divergence at coexistence is a genuine phase transition: l^{-1} is analogous to an order parameter and the exponent $1/3$ in equation (3) is a critical exponent [3].

So, what is the free-energy barrier to heterogeneous nucleation away from coexistence: $h < 0$ but small? We know that at coexistence the liquid layer is very thick and so the free energy of a nucleus in the vapour phase is the same as that in the liquid, call it $\Delta F_L(\mu, T)$. As we move away from coexistence, the liquid layer thins and the nucleus will ‘notice’ this because it will interact with the vapour phase once l is not too large. See figure 2 for a schematic diagram of a nucleus at a substrate in a liquid layer. For l larger than the radius of the nucleus, the nucleus will interact with the vapour as a point object. The interaction of a small object with the vapour across the liquid layer varies as l^{-3} and is proportional to the volume of the nucleus, v_n [18]. So the nucleus–vapour interaction increases the nucleation barrier to ΔF , where ΔF is given by

$$\Delta F(\mu, T) = \Delta F_L(\mu, T) + \frac{A v_n}{l^3} \quad l \text{ large}, \quad (4)$$

where A is a coefficient for the interaction of the nucleus with the vapour across a slab of liquid. A dense nucleus will generally repel a dilute vapour and so A will then be positive [4, 18]. Here, we focus on nucleation of a crystal phase, and crystalline phases are rather dense. Also, note that $\Delta F_L(\mu, T)$ is a function of μ and we will use it for $\mu < \mu_c$ where the vapour phase is more stable than the liquid. We assume that we can continue $\Delta F_L(\mu, T)$ into the region where the liquid is metastable with respect to the vapour, h negative but small, and that $\Delta F_L(\mu, T)$ is analytic at $h = 0$, at coexistence. Using equation (3) for the thickness we obtain

$$\Delta F(\mu, T) = \Delta F_L(\mu, T) - h \frac{A \delta \rho v_n}{2a} \quad h < 0, |h| \text{ small}, \quad (5)$$

which implies that $\Delta F \geq \Delta F_L$ as h is negative in the vapour. For small h the variation in ΔF is linear—the exponent is 1. This result holds for any system at fluid–fluid coexistence with dispersion forces near a complete-wetting transition.

Assuming equation (1) holds for the rate and using equation (5) for ΔF , we see that if $\Delta F_L(\mu, T)$ and $\sigma \tau^{-1}$ vary smoothly with μ around μ_c , then near coexistence ΔF has the following form:

$$N_n = \begin{cases} N_{nL} + \left[N'_{nL} + N_{nL} \frac{A \delta \rho v_n}{2a} \right] (\mu - \mu_c) & \mu < \mu_c \\ N_{nL} + N'_{nL} (\mu - \mu_c) & \mu > \mu_c, \end{cases} \quad (6)$$

where N_{nL} is the nucleation rate in the liquid at coexistence, $\mu = \mu_c$, and N'_{nL} is the derivative of the nucleation rate, with respect to the chemical potential in the liquid, at $\mu = \mu_c$. Equation (6) states that the first derivative of the nucleation rate is discontinuous at the vapour–liquid transition because this derivative contains a contribution from the thickening wetting layer on the vapour side of the coexistence curve but not on the liquid side. Figure 3 is a schematic diagram of the variation of the rate of heterogeneous nucleation near the vapour–liquid transition (the solid curve).

3.2. Critical wetting

For complete wetting, the thickness l of the layer of liquid diverges as coexistence is approached, as in equation (3). Now, on moving away from the critical point of the vapour–liquid transition, if the attraction of the surface for the molecules is not too strong, then the surface–vapour interface may cease to be wetted by the liquid phase. Then as coexistence is approached, the thickness of the layer of liquid between the surface and the vapour does not diverge; it remains finite. This is called partial wetting [3]. The transition from complete

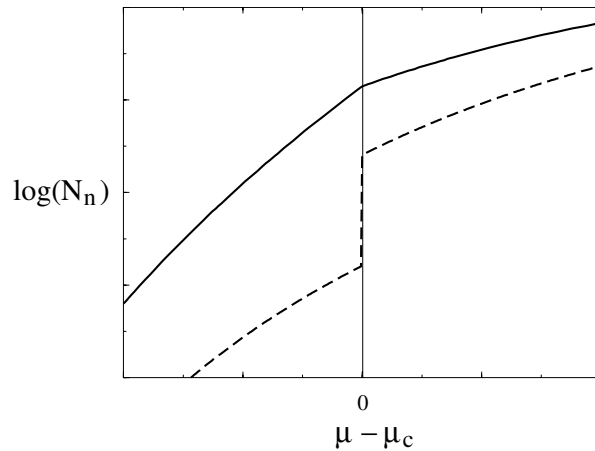


Figure 3. A schematic diagram of the variation in nucleation rate with chemical potential μ near vapour–liquid coexistence at μ_c . For $\mu - \mu_c < 0$ the nucleation is occurring at a surface in contact with the vapour and for $\mu - \mu_c > 0$ the nucleation is occurring at a surface in contact with the liquid phase. The solid curve is where there is complete wetting of the surface by the liquid, the dashed curve for where there is partial wetting.

wetting to partial wetting is a phase transition. It can be continuous, called a critical wetting transition, or it can be first order. We will deal with each in turn.

First, critical wetting. This occurs when the coefficient of the l^{-2} -term in the free energy per unit area, f , changes sign. To deal with this we need the next-order term in an expansion in l^{-1} . This is the l^{-3} -term, and adding such a term to the free energy of equation (2), we have

$$f = \frac{t}{l^2} + \frac{b}{l^3} - hl, \quad (7)$$

where t is a measure of the distance from the critical wetting transition which occurs at $t = 0$, and b is a positive constant. Above the transition, where there is complete wetting, as the two terms are of the same sign, we can neglect the l^{-3} -term as being small for thick layers; then with t fixed we recover equation (2). The transition occurs at coexistence, so $h = 0$. Then minimizing f , we have

$$l = \begin{cases} \infty & t \geq 0 \\ 3b/(-2t) & t < 0; \end{cases} \quad (8)$$

l varies as $(-t)^{-1}$ near and below the transition. The leading-order interaction of the nucleus with the vapour phase is still given by the second term in equation (4) when the layer is thick, i.e., near the transition. Thus, using equation (8) for l we have

$$\Delta F(T) = \begin{cases} \Delta F_L(T) & t \geq 0 \\ \Delta F_L(T) - [8Av_n/(27b^3)]t^3 & t < 0; \end{cases} \quad (9)$$

the difference between the nucleation barrier in the vapour phase and that in the liquid varies as t^3 (t small) below the transition, while they are the same above it. Again this holds for any system at fluid–fluid coexistence with dispersion forces near a critical wetting transition. The exponent 3 is rather large; this means that ΔF and its first, second, and third derivatives are all continuous at the transition. The singularity in ΔF is very weak and so detecting its effect on the variation in the nucleation rate N_n near the wetting transition in an experiment may be very difficult.

Below the wetting transition, $t < 0$, the surface is partially wet: either covered by a thin film of molecules or with only a few molecules on the surface. Then as the coexistence curve is crossed at constant $t < 0$, we go from a nucleus on a surface which is essentially in direct contact with the vapour (with at most a thin film between them) to a nucleus on a surface in contact with the liquid phase. The rate of heterogeneous nucleation then has a discontinuity at coexistence, $\mu = \mu_c$. It will jump upwards, as shown schematically in figure 3 (the dashed curve).

3.3. First-order wetting

Now for a first-order partial-wetting-to-complete-wetting transition. This occurs when the l^{-3} -term is negative, $b < 0$. Then for stability we require a l^{-4} -term. This is just as in a Landau expansion for the free energy near a phase transition. Adding a l^{-4} -term with a positive coefficient c to the f of equation (7), we have

$$f = \left(\frac{b^2}{4c} + t \right) \frac{1}{l^2} + \frac{b}{l^3} + \frac{c}{l^4} - hl, \quad (10)$$

where in order to keep the transition at $t = 0$ we have added a constant, $b^2/(4c)$ to the coefficient of l^{-2} . At coexistence $h = 0$, and we minimize to obtain l :

$$l = \begin{cases} \infty & t \geq 0 \\ 8c/[(b^2 - 32ct)^{1/2} - 3b] & t \leq 0, \end{cases} \quad (11)$$

giving a jump from $l = -2c/b$ to ∞ at the transition. Putting this jump in equation (4) for the free energy of the nucleus, we have a jump in the free-energy barrier of $Av_n/(-2c/b)^3$. Near the transition the barrier varies as

$$\Delta F(T) = \begin{cases} \Delta F_L(T) & t \geq 0 \\ \Delta F_L(T) + [Av_n/(-2c/b)^3][1 - 12ct/b^2 + O(t^2)] & t < 0. \end{cases} \quad (12)$$

Above the transition, $t > 0$, the free-energy barriers are the same in the vapour and liquid phases, while just below the transition, the difference between the two is $Av_n/(-2c/b)^3$. The jump in the free-energy barrier to heterogeneous nucleation will cause a jump in the nucleation rate N_n , from equation (1). As coexisting vapour and liquid phases are cooled, the rate of heterogeneous nucleation at surfaces in contact with the vapour phase will jump downwards when the first-order wetting transition is crossed. Assuming σ and τ vary smoothly through the transition, the ratio of the nucleation rate N_n just above the wetting transition to that just below it is $\exp[Av_n/(-2c/b)^3]$.

In general we expect that the deeper we are into the region where the crystal is in the equilibrium phase, the larger the nucleation rate. Thus we expect that if we cool coexisting vapour and liquid phases, then the rate of heterogeneous nucleation will increase in both; see figure 1. However, we have just shown that if there is a first-order wetting transition, then the rate of heterogeneous nucleation will jump *downwards* as we cross this transition. Potentially at least, the nucleation rate may not be a monotonic function of temperature: in the vapour phase it may increase and then jump downwards as the transition is crossed. A non-monotonic variation in ΔF is very rare, we are aware of only one example [20]. The non-monotonic variation in ΔF found by Auer and Frenkel [20] is (presumably) not due the presence of another phase transition.

When the wetting transition at coexistence is first order, a prewetting transition branches off from the coexistence curve into the vapour away from coexistence [3, 5]. This prewetting transition does not go far into the vapour phase; it ends at a critical point which is at a value of h which depends on b and c but is always small. At the prewetting transition there is a jump in

the value of l ; this jump decreases as h decreases until the jump reaches zero at the prewetting critical point. At the prewetting transition, as l jumps, so does the barrier to nucleation, from equation (4). This transition including the critical point may be calculated from the free-energy equation (10). As this free energy is analytic it yields mean-field exponents for the critical point [19]. Thus at the temperature of the prewetting critical point, t_{cp} , and near the critical point, the thickness difference $l - l_{cp} \sim \text{sgn}(h - h_{cp})|h - h_{cp}|^{1/3}$, where l_{cp} and h_{cp} are the liquid layer thickness and value of h at the critical point. This corresponds to the critical exponent $\delta = 3$ —its mean-field value. Putting this variation of l into our expression for the interaction of the nucleus with the vapour phase across the liquid layer, we obtain

$$\Delta F - \Delta F_{cp} \sim -\text{sgn}(h - h_{cp})|h - h_{cp}|^{1/3} \quad \text{mean field}; \quad (13)$$

the nucleation barrier varies with the chemical potential minus that at the critical point to the one-third power. ΔF_{cp} is the free energy of the nucleus at the prewetting critical point, and equation (13) holds for $t = t_{cp}$ and $|h - h_{cp}|$ small.

Finally, we note that unlike complete and critical wetting, a first-order wetting transition proceeds via nucleation and growth; see [5,21]. So for example on cooling below the transition, a metastable thick wetting layer may persist, where by metastable we mean that the thickness of the layer is not the thickness which occurs at the absolute minimum of the free-energy equation (10). Note that this layer is then doubly metastable; its free energy is higher than that of a thinner film and the system with either of these two layer thicknesses has of course a higher free energy than at true equilibrium where there is dilute-fluid–crystal coexistence. Above we have, for simplicity, neglected the time taken to reach equilibrium thickness and assumed that the thickness of the layer is always that at the minimum in the free-energy equation (10). In reality, the transition from a thick to thin layer will follow some set of dynamics which will complicate the analysis. See [5, 21] and references therein for the dynamics at first-order wetting transitions. See [14] for an explicit study of the analogous problem of homogeneous nucleation near another transition where nucleation of the equilibrium and a metastable phase compete.

4. Comparison with homogeneous nucleation near a bulk critical point

Essentially by definition, phase transitions are where the thermodynamic functions of an equilibrium system have singularities. In earlier work [6, 12–14] we showed that the rate of *homogeneous* nucleation has a singularity at an Ising-type phase transition in the *bulk* and here we have shown that the rate of *heterogeneous* nucleation has a singularity at *surface* phase transitions associated with an Ising-type phase transition in the bulk. The presence of a singularity at a phase transition is common to both homogeneous and heterogeneous nucleation.

Our findings here for heterogeneous nucleation near a prewetting critical point and our earlier findings for homogeneous nucleation are particularly closely related. In both cases we have a nucleus which is a small (point-like) perturbation which couples to the order parameter of the transition [6, 12]. The order parameter is the density for the bulk transition and the thickness in the prewetting surface transition. In earlier work [6] we used scaling arguments to obtain the correct exponents for homogeneous nucleation near the critical point of an Ising-type transition. In heterogeneous nucleation the nucleus will couple to the order parameter of the prewetting transition, which is an Ising-type transition in two dimensions. In [6] we showed that near an Ising-type critical point the behaviour is fixed and universal providing only that the nucleus couples to the order parameter. Thus heterogeneous nucleation near a prewetting critical point is completely analogous to homogeneous nucleation in a two-dimensional system

near a bulk critical point. We can apply the scaling approach of [6] to heterogeneous nucleation near a prewetting critical point. We then obtain the correct and universal exponents for the variation of the free-energy barrier near the critical point. For example, along the prewetting critical isotherm the free-energy barrier scales with distance to the critical point as

$$\Delta F - \Delta F_{cp} \sim -\text{sgn}(h - h_{cp})|h - h_{cp}|^{1/15} \quad \text{universal}, \quad (14)$$

where the exponent, which is $1/\delta$, is obtained from the exact value $\delta = 15$ for the Ising model in two dimensions. In two dimensions the mean-field predictions for the critical exponents like δ are very poor: the mean-field prediction, equation (13), has an exponent which is five times too large²; see [19] for definitions of the critical exponents. Equation (14) is just (14) of [6] in two dimensions; see that reference for a derivation.

5. Conclusions

Almost invariably, a first-order phase transformation starts with heterogeneous nucleation. The nucleus of the new phase forms at a surface; see figure 2. Thus, the free-energy barrier to the formation of the nucleus and therefore the rate of nucleation in a phase depend sensitively on anything which happens at the interface between the surface and the phase. If the phase in contact with the surface is a vapour phase close to a second, vapour–liquid, phase transition, then if the surface attracts the molecules a wetting layer may form at the surface. This is a layer of liquid at the surface, separating the surface from the vapour. The wetting layer will reduce the nucleation barrier greatly if the interfacial tension between the liquid and the nucleus, γ_{xl} , is lower than that between the vapour and the nucleus, γ_{xv} . We estimated in section 2 that the reduction in the surface contribution to the free-energy barrier is of order $10kT$ —a large reduction which should be easily large enough to observe in an experiment. The formation of a wetting layer, either as coexistence is approached (complete wetting), or along the coexistence curve (critical wetting or a first-order wetting transition), is a phase transition. We found that at complete wetting the derivative of the barrier as a function of chemical potential was discontinuous, while the barrier itself has a discontinuity as the temperature is varied through a first-order wetting transition. Thus the rate of heterogeneous nucleation has a discontinuity in its slope as the coexistence curve is crossed at constant temperature, when there is complete wetting. The rate of change of the nucleation rate in the vapour phase just below coexistence is not the same as its rate of change in the liquid phase just above coexistence. ‘Above’ and ‘below’ mean at values of the chemical potential above and below that at coexistence. The rate of heterogeneous nucleation has a discontinuity as a first-order wetting transition is crossed.

Our model system is highly idealized; the surface is assumed perfectly smooth and homogeneous, and the dynamics of the formation of wetting layers have been neglected: the thickness was always taken to be at equilibrium. Future work should address how the dynamics of formation of wetting layers can affect nucleation; near a first-order wetting transition this will presumably be analogous to homogeneous nucleation near a metastable first-order bulk transition [14]. Also, an understanding of the effects of chemical heterogeneity and of curvature would be useful, as in practice surfaces will not be perfectly homogeneous or smooth, and

² A mean-field theory [12, 13] for the variation of the barrier to homogeneous nucleation along the critical isotherm of a bulk critical point yields the same exponent as equation (13). The exponent for the variation in the nucleation barrier along the critical isotherm was not calculated explicitly in either of [12, 13] but the exponent is implicit in equation (14) of [13]. This equation contains a factor of $(m_c - m)^2$ which dominates the variation along the critical isotherm near the critical point. m is the order parameter of the transition (0 at the critical point) and m_c is the value of the order parameter in the core of the nucleus, $m_c = O(1)$. Near the critical point, m is small and we may expand to obtain $m_c^2 - 2m_c m + O(m^2)$. Near the critical point the second term scales as the order parameter which scales as $\text{sgn}(h - h_{cp})|h - h_{cp}|^{1/3}$ within a mean-field theory. The first term is just a constant.

heterogeneous nucleation can occur on particles whose surfaces are inherently curved. But the most urgent requirement is for experiments on heterogeneous nucleation on simple, well characterized surfaces.

Acknowledgments

It is a pleasure to acknowledge helpful discussions with A Parry. This work was supported by the EPSRC (GR/N36981).

References

- [1] Debenedetti P G 1996 *Metastable Liquids* (Princeton, NJ: Princeton University Press)
- [2] Cahn J W 1977 *J. Chem. Phys.* **66** 3667
- [3] Schick M 1990 *Liquids at Interfaces (Les Houches XLVIII)* ed J Charvolin, J F Joanny and J Zinn-Justin (Amsterdam: Elsevier)
- [4] Indekeu J O 1995 *Acta Phys. Pol. B* **26** 1065
- [5] Bonn D and Ross D 2001 *Rep. Prog. Phys.* **64** 1085
- [6] Sear R P 2002 *J. Chem. Phys.* **116** 2922
- [7] Broide M L, Berland C R, Pande J, Ogun O O and Benedek G B 1991 *Proc. Natl Acad. Sci. USA* **88** 5660
- [8] Muschol M and Rosenberger F 1997 *J. Chem. Phys.* **107** 1953
- [9] Rosenberger F, Vekilov P G, Muschol M and Thomas B R 1996 *J. Cryst. Growth* **167** 1
- [10] ten Wolde P R and Frenkel D 1997 *Science* **277** 1975
- [11] Talanquer V and Oxtoby D W 1998 *J. Chem. Phys.* **109** 223
- [12] Sear R P 2001 *J. Chem. Phys.* **114** 3170
- [13] Sear R P 2001 *Phys. Rev. E* **63** 066105
- [14] Tavassoli Z and Sear R P 2002 *J. Chem. Phys.* at press (cond-mat/0111362)
- [15] Talanquer V and Oxtoby D W 1996 *J. Chem. Phys.* **104** 1483
- [16] ten Wolde P R, Ruiz-Montero M J and Frenkel D 1996 *J. Chem. Phys.* **104** 9932
- [17] Sear R P 1999 *J. Chem. Phys.* **111** 4800
- [18] Israelachvili J 1992 *Intermolecular and Surface Forces* (London: Academic)
- [19] Chaikin P M and Lubensky T C 1995 *Principles of Condensed Matter Physics* (Cambridge: Cambridge University Press)
- [20] Auer S and Frenkel D 2001 *Nature* **413** 711
- [21] Bonn D, Bertrand E, Meunier J and Blossey R 2000 *Phys. Rev. Lett.* **84** 4661