Homogeneous nucleation near a second phase transition and Ostwald’s step rule

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Abstract
Homogeneous nucleation of the new phase of one transition near a second phase transition is considered. The system has two phase transitions, we study the nucleation of the new phase of one of these transitions under conditions such that we are near or at the second phase transition. The second transition is an Ising-like transition and lies within the coexistence region of the first transition. It affects the formation of the new phase in two ways. The first is by reducing the nucleation barrier to direct nucleation. The second is by the system undergoing the second transition and transforming to a state in which the barrier to nucleation is greatly reduced. The second way occurs when the barrier to undergoing the second phase transition is less than that of the first phase transition, and is in accordance with Ostwald’s rule.

1 Introduction
The formation of a new phase at a first-order phase transition is an activated process. A nucleus of the new phase must overcome a free energy barrier in order to form and then grow into the new phase. The rate at which such microscopic nuclei form is proportional to \( \exp(-\Delta F^*/kT) \), where \( \Delta F^* \) is the height of the free energy barrier which the nuclei must overcome. Here we consider nucleation of the new phase at a first-order phase transition and calculate \( \Delta F^* \) when the system is near a second phase transition. One of the examples of nucleation near a second transition is nucleation of a crystalline phase at a first-order fluid-crystal transition near a fluid-fluid phase transition. Such a process has been observed in globular proteins whose phase diagrams show a metastable fluid-fluid transition within a strongly first-order fluid-crystal transition. Crystallisation of globular proteins is the subject of interest as protein crystals are needed in order to study their structure by X-ray diffraction. It has been seen that globular proteins crystallize at temperatures near where we expect a metastable fluid-fluid critical point. Numerical work on nucleation near a critical point has been done by Talanquer and Oxtoby, where they obtained nuclei with very large numbers of molecules near the critical point. This followed pioneering computer simulations of ten Wolde and Frenkel, who found an anomalously low \( \Delta F^* \) for the nucleation of a crystalline phase near the critical point of a metastable fluid-fluid transition. Other recent theoretical work on nucleation near a metastable transition may be found in and references therein. Earlier theoretical work by one of us showed that as the critical point is approached, the derivatives of the free energy barrier to nucleation with respect to the chemical potential and temperature diverge. Therefore the presence of the critical point causes a rapid drop in the free energy barrier to nucleation and so facilitates nucleation.

The metastable transition we consider here is an Ising-like or a vapour-liquid-like transition. An Ising-like transition is a transition from a phase with a negative magnetisation to a phase with a positive magnetisation. A vapour-liquid-like transition is a transition between two fluid phases differing in density. The metastable transition lies within the coexistence region of the equilibrium transition. Thus when the system is in the coexistence region of the metastable phase transition, it also lies within the coexistence region of the equilibrium transition. Then one of two new phases can nucleate: the stable phase can nucleate, as can the liquid phase or the analogue of the liquid phase, from the vapour phase or the analogue of the vapour phase. Which of these occurs first depends on which free energy barrier is lower. Thus the stable phase can be formed via two processes. In one process the free energy barrier to nucleation of the stable phase becomes small enough to allow nucleation, but the barrier to formation of the liquid phase is still large, then the stable phase nucleates. When the sizes of the barriers are reversed, then the formation of the stable phase occurs via two steps: first the liquid phase nucleates, and second the stable phase nucleates in this liquid phase.

Our finding that nucleation of a metastable transition can occur before nucleation of the stable phase, is just that observed by Ostwald more than 100 years ago. Ostwald’s rule is that the phase that nucleates first is not necessarily the most thermodynamically stable phase, but is the one with closest free energy to the fluid phase. Later Stranski and Totomanow improved this rule and suggested that the nucleated phase is the one with the lowest free energy barrier to nucleation, and not the phase that is globally stable.

Nucleation can be heterogeneous or homogeneous. In most circumstances suspended and dissolved impurities, as well as the solid boundaries provide sites for the formation of the new phase. This process is known as heterogeneous nucleation. However, in the absence of impurities or solid surfaces, small nuclei of the new phase are formed within the

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We study nucleation of a new phase at a first-order transition near a second transition. The second transition is an Ising-like transition from the phase with a negative magnetisation to the phase with a positive magnetisation. In this work we use magnetic language, in fluid language the transition is from a low density phase to a high density phase. We present the results of numerical calculations for the temperatures below the critical point. The calculations are for the excess order parameter $\Delta m^*$ and the free energy barrier to nucleation of the new stable phase, $\Delta F^*$, in the critical nucleus. In the next section we study the theory of two types of homogeneous nucleation: nucleation of the new stable phase, and nucleation of the positive magnetisation phase from the negative magnetisation phase. We then discuss some of the numerical techniques we used in the calculations in section 3. In section 4 the results are presented and the last section is a conclusion.

2 Theory

2.1 Nucleation of a stable phase

We study nucleation of a new phase at a first-order transition near a second transition. The second transition is an Ising-like transition with an order parameter $m$. We work below the critical or Curie temperature and so we have a transition from negative $m$ to positive $m$ on increasing the field $h$. $h$ is as usual the field which couples to $m$. Following earlier work by one of us we split the nucleus of the new phase into two parts: the core and the fringe. That part of nucleus less than $r_c$ from the origin is the core and the part farther than $r_c$ is the fringe of the nucleus. We assume that the fringe of the nucleus is spherically symmetric. Therefore the order parameter $m(r)$ is a function only of $r$, the distance from the centre of the nucleus. As the universal behaviour of the nucleus is derived from the fringe, we therefore substitute the core by a boundary condition on $m(r)$ of the fringe. Thus for simplicity we fix $m(r \leq r_c) = m_c$, where the subscript $c$ stands for the core of the nucleus. $m_c$ is a positive constant independent of temperature and of $h$, and is essentially the value of the order parameter $m$ in the nucleating phase. We require the excess free energy of the nucleus, $\Delta F$, which is the free energy with a nucleus present minus that without a nucleus. Here we use a standard square-gradient functional for the fringe of the nucleus as a functional of the order parameter profile of the nucleus, $m(r)$.

$$\Delta F = \Delta F_c + \int_{r > r_c} \left[ \Delta \omega(m) + \kappa (\nabla m)^2 \right] dr,$$

where the first term is the contribution from the core of the nucleus, $\Delta F_c = \frac{1}{4} \pi r_c^3 \Delta \omega_{core}$, and the integral term is the contribution from the fringe of the nucleus. In Eq. (1) and all other equations, our free energies are in units of $kT$; $k$ and $T$, Boltzmann’s constant and the temperature, respectively. $\Delta \omega_{core}$ is a constant and is the excess free energy per unit volume of the core. As the core is close to the bulk equilibrium phase, $\Delta \omega_{core} < 0$ because the free energy is lower in the equilibrium phase. The gradient term in the integrand of Eq. (1) is due to the variations in space of $m(r)$. This is the lowest order term in a gradient expansion and is adequate when $m$ is slowly varying. The coefficient $\kappa$ is assumed to be a constant. In Eq. (1), $\Delta \omega$ in the integrand is given by

$$\Delta \omega = f(m) - f(m_b) - h(m - m_b),$$

where $m_b$ is the order parameter in the bulk. $\Delta \omega$ is the work required per unit volume to change the order parameter from its bulk value $m_b$ to $m$ in the presence of an external field $h$. $f(m)$ is the bulk Helmholtz free energy per unit volume as a function of the order parameter $m(r)$. The critical nucleus is at the top of the free energy barrier and therefore at the maximum of $\Delta F$. So we set the functional derivative of $\Delta F$ with respect to the order parameter profile $m(r)$, to zero,

$$\frac{\partial \Delta \omega(m)}{\partial m(r)} - 2\kappa \nabla^2 m(r) = 0, \quad r \geq r_c,$$

where $r$ is the distance from the centre of the nucleus. As the universal behaviour of the nucleus is derived from the fringe, we therefore substitute the core by a boundary condition on $m(r)$ of the fringe. Thus for simplicity we fix $m(r \leq r_c) = m_c$, where the subscript $c$ stands for the core of the nucleus. $m_c$ is a positive constant independent of temperature and of $h$, and is essentially the value of the order parameter $m$ in the nucleating phase. We require the excess free energy of the nucleus, $\Delta F$, which is the free energy with a nucleus present minus that without a nucleus. Here we use a standard square-gradient functional for the fringe of the nucleus as a functional of the order parameter profile of the nucleus, $m(r)$.
The total excess of the order parameter due to the presence of the nucleus, which is the total order parameter with the nucleus present minus that without the nucleus, is obtained as
\[
\Delta m = \int (m(r) - m_b) dr.
\] (4)

We employ Landau theory \[25, 26\] for the bulk free energy,
\[
f(m, T) = \frac{1}{2} atm^2 + bm^4,
\] (5)
where \(a\) and \(b\) are constants, and \(t = T - T_c\) with \(T_c\) the critical temperature \[26\]. The bulk order parameter \(m_b(h, T)\) is obtained by solving
\[
\frac{\partial \omega}{\partial m} \bigg|_{m=m_b} = 0,
\] (6)
where \(\omega(m) = f(m) - hm\). Then using Eqs. (5,6) gives
\[
 atm + 4bm^3 - h = 0.
\] (7)
When \(h = 0\) the bulk order parameter is that at coexistence and we call it \(m_{co}\). For \(h = 0\), Eq. (7) has just one real solution \(m_{co} = 0\) for \(T > T_c\). For \(h = 0\) and \(T < T_c\), Eq. (7) has three solutions, and consequently the free energy has two minima with the same free energy at \(m_{co} = \pm \frac{1}{2} (-at/b)^{1/2}\), and a maximum at \(m = 0\). In the presence of an external field \(h\), Eq. (7) has one real solution for \(T > T_c\), which corresponds to a single minimum for \(\omega(m)\). When \(T < T_c\) and \(h \neq 0\) with \(|h|\) not too large, there are two inequivalent minima in \(\omega(m)\). For a fixed \(h\), the absolute minimum corresponds to the equilibrium state and the higher minimum is a metastable state.

To get the order parameter profile we substitute Eq. (5) in Eq. (3), which gives
\[
\frac{d^2m}{dr^2} + \frac{2}{r} \frac{dm}{dr} - \frac{1}{2\kappa} (4bm^3 + atm - h) = 0,
\] (8)
for \(r > r_c\), subject to boundary conditions
\[
m(r = r_c) = m_c
\] (9)
and
\[
m(r \to \infty) = m_b.
\] (10)
The former is the order parameter at the boundary between the fringe and the core, and the latter is the obvious condition that \(m\) tends towards its bulk value far from the nucleus. Eq. (8) is a nonlinear second-order differential equation which can not be solved analytically. We therefore use numerical methods to solve Eq. (8) for the order parameter profile, and then substitute it in Eq. (1) to obtain the excess free energy of the nucleus. The barrier to nucleation is at the maximum of the excess free energy and so will occur at a radius \(r^*_c\) given by \(\partial \Delta F/\partial r_c = 0\). Thus we need to use a maximization method numerically to find \(r^*_c\) and hence \(\Delta F^*\), which is the free energy barrier to nucleation for a critical nucleus. This also gives \(m^*(r)\) which is the order parameter profile of the critical nucleus. Substituting this profile in Eq. (1) we then find the excess order parameter of the critical nucleus \(\Delta m^*\).

### 2.2 Nucleation of \(+m\) phase from \(-m\) phase, Classical Nucleation Theory

Starting in the \(-m\) phase and increasing \(m\) (or equivalently \(h\)), we cross the phase transition from the \(-m\) to the \(+m\) phase. Then our system can not only nucleate the equilibrium phase but also the \(+m\) phase. Then we are within both the \(-m\) to \(+m\) coexistence region and the coexistence region between the equilibrium phases. The nucleus of the \(+m\) phase must overcome a free energy barrier in order to form, and then it grows to the new phase. The free energy barrier to form such critical nucleus is given by
\[ \Delta F^* = \frac{16\pi\sigma^3}{3h^2}, \]  

which is the standard classical nucleation theory expression \([1, 26, 27]\). This expression is valid for nucleation not too close to the spinodal \([28]\). The subscript \(I\) indicates that the transition is an Ising-like phase transition. In Eq. (11) \(\sigma\) is the surface free energy of the equilibrium interface between \(+m\) and \(−m\) phases, and is given by

\[ \sigma = 2 \int_{-m_c}^{m_c} \sqrt{\kappa \Delta f(m)} \, dm, \]  

where \(\Delta f(m) = f(m) - f(m_b)\) is the excess bulk free energy, Eq. (5).

It is worth mentioning that in this paper we have used a magnetic rather than a fluid language to describe the phase transitions. To switch from the magnetic language with a transition from \(−m\) to \(+m\) phase, to the fluid language with a vapour-liquid-like transition, the external field \(h\) becomes the chemical potential \(\mu\) minus that at the coexistence \(\mu_{co}\), the order parameter \(m\) becomes density \(\rho\), the bulk order parameters \(−m_b\) and \(+m_b\) become the vapour and liquid densities, \(\rho_v\) and \(\rho_l\), respectively, and the axis \(m = 0\) becomes the critical density \(\rho_{cp} = (\rho_v + \rho_l)/2\) in the coexistence curve. Also in the fluid language the total order parameter \(\Delta m^*\) is equivalent to the total number of molecules in the critical nucleus.

3 Numerical Techniques

In the fringe far from the core, \(m(r)\) is near the bulk order parameter \(m_b\), we therefore use a Taylor expansion of \(\Delta \omega(m)\) about \(m = m_b\),

\[ \Delta \omega(m) = \frac{1}{2} \chi^{-1}(m - m_b)^2 + \cdots \]  

\[ \frac{\partial \Delta \omega(m)}{\partial m} = \chi^{-1}(m - m_b) + \cdots, \]  

where \(\Delta \omega\) and its first derivative are zero at \(m = m_b\). Here \(\chi\) is the response function of \(m\), defined by

\[ \chi^{-1} = \frac{\partial^2 f}{\partial m^2} \bigg|_{m=m_b}, \]  

where \(f(m)\) is the bulk free energy Eq. (3). Substituting Eq. (14) in Eq. (3) gives

\[ \chi^{-1}(m - m_b) - 2\kappa \nabla^2 (m - m_b) = 0, \]  

which has a solution of Yukawa form

\[ m(r) = m_b + B \frac{\exp(-r/\xi)}{r}, \]  

for large values of \(r\). To obtain Eq. (17) we used the boundary condition Eq. (10). In Eq. (17) \(B\) is a constant value which we will fix later, and \(\xi\) is the correlation length for \(m(r)\) which is given by

\[ \xi = (2\kappa \chi)^{1/2}. \]  

The solution of \(m(r)\) for large values of \(r\) has the form of Eq. (17). In numerical calculations we therefore use a large distance from the center of the core, \(R\), to be the outer boundary of our numerical integration of Eq. (8), and use Eq. (17) beyond \(R\).

For our numerical calculations we employ the Runge-Kutta method to solve the second-order differential Eq. (8) for the order parameter profile, subject to boundary conditions at \(r_c\) and \(R\), Eq. (8) and Eq. (17), respectively. The
constant value $B$ in Eq. (17) is then obtained by finding the root of the nonlinear equation $m(r_c) - m_c = 0$, for which we used Ridders’ method [3]. Substituting the order parameter profile $m(r)$ in Eq. (1) gives the excess free energy of the nucleus. The barrier to nucleation is at a maximum of $\Delta F$ and so will occur at a radius $r^*_c$ given by $\partial \Delta F/\partial r_c = 0$. We then use a maximization method to obtain $r^*_c$ and consequently $m^*(r)$ and the barrier to nucleation $\Delta F^*$. In the numerical calculations we used a large radius $R$ for the boundary condition of the fringe of the nucleus. We need such a value to enable us to carry out the numerical calculations. We calculate the contribution of distances larger than $R$ analytically and add it to the corresponding numerical quantity for the range $r_c$ to $R$, as a correction term. The correction term for the excess order parameter of the critical nucleus, $\Delta m^*$, can be calculated using Eq. (1) with the limits for the integral from $R$ to $\infty$. Then by substituting Eq. (17) for $m(r)$ for all values of $r \geq R$, the correction term is

$$\Delta m^*_c = 4\pi KB\xi(R + \xi)e^{-R/\xi},$$

where $ct$ stands for the correction term. The correction term for the free energy barrier to nucleation $\Delta F^*$, is calculated using the integral term in Eq. (1) for all values of $r$ from $R$ to $\infty$. Then by substituting Eq. (13) in $\Delta \omega(m)$ and using the normal gradient of Eq. (17) for $\nabla m(r)$, the correction term is given by

$$\Delta F^*_c = 4\pi KB^2 \left(\frac{1}{R} + \frac{1}{\xi}\right) e^{-2R/\xi},$$

which we have used the definition of $\xi$, Eq. (18).

The solution of Eq. (17) for the order parameter for $r \geq R$ is derived using the Taylor expansion of $\Delta \omega(m)$ about $m = m_b$, Eq. (13). In this expansion we have used up to the second-order term of $(m - m_b)$ and have ignored the higher orders. We therefore need to obtain the conditions under which we are allowed to use this approximation. To do so we see that in Eq. (13) by ignoring terms of orders greater than 2, we have assumed that these values are less than the second-order term. The biggest of all ignored terms is the third order one, we have therefore assumed that

$$\frac{\partial^3 \Delta \omega(m)}{\partial m^3} \bigg|_{m=m_b} \frac{(m - m_b)^3}{3!} \ll \frac{1}{2} \lambda^{-1} (m - m_b)^2.$$  

Using Eqs. (18) in Eq. (21) gives

$$\frac{4b}{\kappa} m_b \xi^2 (m(R) - m_b) \ll 1,$$

as the requirement that must be satisfied. Here $m(R)$ is given by Eq. (17) at $r = R$.

4 Results

The free energy barriers to nucleation of the stable phase and of the $+m$ phase are $\Delta F^*$ and $\Delta F^*_+$, respectively. In each nucleation the formation of the new phase occurs when the free energy barrier is of roughly $30kT$. The figure $30kT$ is rather arbitrary [9] but the nucleation rate is of order, number of molecules times $\exp(-\Delta F^*/kT)$ divided by the characteristic time scale of the solution. The characteristic time scale of protein solutions is of order $1 \mu s$ [10]. Thus a volume of the solution containing $10^9$ protein molecules has a nucleation rate of order $10^9 \times e^{-30} \times 10^6 \approx 10^8 \mu s^{-1}$. Thus in a volume of the solution containing a billion molecules, nuclei will appear in a fraction of a second. When the barrier reaches $30kT$ the $-m$ phase is unstable and the stable $+m$ phase nucleates immediately. A barrier of about twice this, $60kT$, is required for the $-m$ phase to be stable over long times, i.e., for it to be metastable. Homogeneous nucleation of a new stable phase near a second phase transition has been studied before [9–16]. Here we carried out numerical calculations for $\Delta m^*$ and $\Delta F^*$. Near the critical point the scaling of the size of the critical nucleus is [13-14],

$$\Delta m^* \sim |t|^{\gamma} g_\pm (h/|t|)^{\beta \delta},$$

and that of the free energy is

$$\Delta F^*_c \sim |t|^{\beta \delta} f_\pm (h/|t|)^{\beta \delta},$$

\[5\]
Figure 1: $\Delta m^*$ versus $h$ at two temperatures below the critical temperature, when $\kappa = 1$ and $\Delta\omega_{\text{core}} = -0.5$. Solid and long-dashed curves correspond to $t = -0.5$ and $t = -0.25$, respectively.

for both temperatures above and below the critical temperature. Here $\pm$ are related to $t > 0$ and $t < 0$, $\gamma$, $\beta$ and $\delta$ are the usual critical exponents, and take values of $1$, $1/2$ and $3$ within mean-field theory. In Eq. (24) subscript $s$ stands for singular part of the fringe. These results were predicted in earlier work [14–16] and we confirmed them by numerical calculations. As the critical point is approached, the magnetisation of the critical nucleus $\Delta m^*$ diverges, and so does the derivative of the free energy barrier to nucleation $\Delta F^*$, with respect to the temperature and to $h$. We are also interested in the behaviour of $\Delta m^*$ and $\Delta F^*$ far from the critical point.

4.1 Far from the critical point

Here we study the total magnetisation and the free energy of the critical nucleus, $\Delta m^*$ and $\Delta F^*$, respectively, far from the critical point — $|t|$ not small. In all the calculations we have fixed $a = b = m_c = 1$. In Figs. 1 and 2 there are graphs of $\Delta m^*$ and $\Delta F^*$, respectively, for two different temperatures below and far from the critical temperature, $t = -0.25$ and $t = -0.5$ with $\kappa = 1$ and $\Delta\omega_{\text{core}} = -0.5$. For each temperature, when $h < 0$ the system is in a state with a negative order parameter $m < 0$ less than that at the coexistence. When $h > 0$ the system can be found in a state with a positive order parameter $m > 0$ greater than that at the coexistence. For $h > 0$ there are also states with $m < 0$ between the $-m$ branch of the coexistence curve and the spinodal. These states are within two coexistence regions: the coexistence region between $-m$ and $+m$ phases, and that between the equilibrium phases. Therefore in both Figs. 1 and 2 for each temperature there are values of $h > 0$ for which $\Delta m^*$ and $\Delta F^*$ are double valued. These values correspond to the $-m$ phase between the coexistence and spinodal curves, and the $+m$ phase with a lower $\Delta m^*$ and $\Delta F^*$.

In Fig. 1 for each temperature as $h$ increases the curves on the right-hand side decrease. Those on the left-hand side decrease first and then increase rapidly. Decreasing $\Delta m^*$ is due to the fact that for a higher $h$, the bulk order parameter $m_b$ is higher and thus it leads to a lower excess order parameter $\Delta m^*$ in Eq. (1). However the large and rapidly increasing values of $\Delta m^*$ are due to the proximity to the spinodal. As we approach the spinodal the response function of the order parameter, $\chi$ defined as in Eq. (13) diverges. Therefore the total excess order parameter $\Delta m^*$ which scales as $\chi$ will diverge as well. As the temperature approaches $T_c$ ($|t|$ decreases), $\Delta m^*$ diverges at a lower value of $h$. This is because, as $T$ approaches $T_c$, the gap between the coexistence and the spinodal curves decreases. In Fig. 2, for each temperature as $h$ increases $\Delta F^*$ decreases, due to the increase in the bulk order parameter $m_b$. The phase with the higher order parameter must overcome a lower free energy barrier $\Delta F^*$ to form a nucleus of the equilibrium phase, whose order parameter we have set equal to $1$. Also in Fig. 2, $\Delta F^*$ varies rapidly as it approaches the spinodal.
This is due to what is called the nucleation theorem \[30–32\] and states that the derivative of the free energy barrier with respect to \(h\) is equal to minus the excess \(m\), \(\partial \Delta F^* / \partial h = -\Delta m^*\) \[14–16\]. It shows that the larger \(\Delta m^*\) is, the more rapidly the free energy barrier varies with \(h\). As the spinodal is approached \(\Delta m^*\) diverges and thus \(\Delta F^*\) drops rapidly with \(h\). When a transition from \(-m\) to \(+m\) phase occurs both \(\Delta m^*\) and \(\Delta F^*\) in Figs. 1 and 2 jump to lower values, because of the increase in \(m_0\). The height of this reduction is temperature-dependent because the bulk order parameters \(m_{co} = \pm \sqrt{(-t/4)}\) are functions of \(t = T - T_c\). As the temperature decreases, the difference between these two order parameters increases, and therefore the height of the drop in both \(\Delta m^*\) and \(\Delta F^*\) increases.

For each temperature as \(h\) increases \(\Delta F^*_f\) decreases, Eq. (3), and for energy barriers of about \(30kT\) a transition of \(-m\) phase to \(+m\) phase with lower values of \(\Delta m^*\) and \(\Delta F^*\) occurs. The cross marks on the graphs in Figs. 1 and 2 are the points where \(\Delta F^*_f = 30kT\). Also in the region with \(h > 0\) and \(m < 0\) the solutions to \(\Delta m^*\) and \(\Delta F^*\) disappear at a value of \(h\) before the spinodal. The circle marks on the graphs are the points for which the solutions disappear. For this value of \(h\) in our numerical calculations the solution to the order parameter profile of the critical nucleus, \(m^*(r)\), disappears. The solution to \(m^*(r)\) is obtained by solving Eq. (3) subject to the boundary condition \(m^*(r = r^*_c) = m_{co}\). In the region between the \(-m\) branch of the coexistence and the spinodal with \(h > 0\), Eq. (3) gives two solutions for \(m^*(r)\), out of which we choose the one with lower free energy barrier, \(\Delta F^*\). As \(h\) increases, these two solutions approach each other until they become equal at a specific value of \(h > 0\). For any value of \(h\) greater than this, there is no solution. This means that the critical nucleus does not exist anymore and there is no well defined free energy barrier to nucleation. As we see in Figs. 1 and 2 for each temperature the points with \(\Delta F^*_f = 30kT\) (cross marks) are at the left side of those for which the solutions disappear (circle marks). As for energy barriers of \(\Delta F^*_f = 30kT\) a transition of \(-m\) to \(+m\) phase occurs, therefore for these parameter values as the system approaches the cross marks, the \(-m\) phase will transform to \(+m\) phase. Thus in the experiments the states after the cross marks are not accessible. As we see in Figs. 1 and 2 as the temperature approaches \(T_c\) (\(|t|\) decreases), the solution disappears at a lower value of \(h > 0\). This is because as \(T\) approaches \(T_c\), the coexistence and the spinodal curves approach each other.

The stable phase can be attained via two processes \[33\]. In one process \(\Delta F^*\) drops below \(30kT\) when \(\Delta F^*_f\) is still large, then the stable phase is reached in one step through nucleating in \(-m\) phase. In the second process \(\Delta F^*_f\) drops below \(30kT\) when \(\Delta F^*\) is still large, then the stable phase will be reached in two steps: first the \(+m\) phase nucleates in the \(-m\) phase and grows and then second, the stable phase nucleates in this \(+m\) phase. The fact that the nucleated phase is the one which has lower free energy barrier and not necessarily the stable phase, is in accordance with Ostwald’s step rule. In Fig. 2 with \(\Delta \omega_{core} = -0.5\) the barrier \(\Delta F^*\) is always greater than \(30kT\) when \(\Delta F^*_f\) drops below \(30kT\).
Thus on increasing $h$ the $+m$ phase nucleates before the equilibrium phase. The equilibrium phase then nucleates in the $+m$ phase. But as $\Delta \omega_{\text{core}} < 0$, when $\Delta \omega_{\text{core}}$ becomes more negative then $\Delta F^*_{\text{core}}$ becomes more negative and therefore $\Delta F^*$ in Eq. (1) drops. So for sufficiently negative values of $\Delta \omega_{\text{core}}$, $\Delta F^*$ drops below $30kT$ before $\Delta F_{\text{m}}^*$ does and the stable phase nucleates before the $+m$ phase. To show this, in Fig. 3 graphs of $\Delta F^*$ are plotted for two values of $\Delta \omega_{\text{core}} = -0.75$ and $\Delta \omega_{\text{core}} = -1.25$, when $t = -0.25$. Just as in the previous figures, the cross marks on each graph correspond to where $\Delta F_{\text{m}}^* = 30kT$ and the circle marks are where the solutions disappear. For $\Delta \omega_{\text{core}} = -0.75$, $\Delta F^*$ is greater than $30kT$ when $\Delta F_{\text{m}}^*$ drops below $30kT$. Thus the $+m$ phase nucleates first and then the equilibrium phase nucleates in the $+m$ phase. For $\Delta \omega_{\text{core}} = -1.25$ however $\Delta F^*$ drops below $30kT$ before $\Delta F_{\text{m}}^*$ does. Thus the equilibrium phase nucleates before the $+m$ phase. The values of $h$ for which $\Delta F_{\text{m}}^* = 30kT$ (the cross marks) are independent of $\Delta \omega_{\text{core}}$ and are the same on both graphs. This is because $\Delta F_{\text{m}}^*$ in Eqs. (11,12) depends only on the temperature and on $h$, and is independent of $\Delta \omega_{\text{core}}$.

The two step route to the equilibrium phase that we find is not dissimilar to that proposed for the crystallisation of some polymer melts by Olmsted et. al. [34]. They study a system with the same phase diagram as considered here, but their equivalent of the $-m$ to $+m$ phase transition proceeds via spinodal decomposition and not nucleation as here. Thus the results here apply to liquids and colloidal suspensions, whereas Olmsted et. al.’s approach is more applicable to polymers.

We are also interested to study where the free energy barrier $\Delta F_{\text{m}}^* = 30kT$, and a nucleation from the $-m$ phase to the $+m$ phase occurs. Up to now we considered systems with $\kappa = 1$. We also like to know the effect of increasing $\kappa$ on the calculations. In Figs. 4 and 5 there are diagrams of $t$ versus $m$, and $t$ versus $h$, respectively for three different values of $\kappa$ when $\Delta \omega_{\text{core}} = -0.5$. In Fig. 4 the solid (outermost) and long-dashed (innermost) curves represent the coexistence and the spinodal, respectively. The other curves in Fig. 4 between the coexistence and spinodal curves correspond to the points with energy barriers of $\Delta F_{\text{m}}^* = 30kT$ for different $\kappa$. From left to right, dotted, dashed and dot-dashed curves are for $\kappa = 1, 1.5$ and $2$, respectively. In Fig. 5 the solid line $h = 0$ along axis $t$ corresponds to coexistence, and the long-dashed curve (the outermost) represents spinodal. The other curves in Fig. 5 between the coexistence and the spinodal correspond to the points with $\Delta F_{\text{m}}^* = 30kT$ for different $\kappa$. From left to right, dotted, dashed and dot-dashed curves represents $\kappa = 1, 1.5$ and $2$, respectively. As $\kappa$ increases there is a shift towards larger values of both $m$ and $h$ for $\Delta F_{\text{m}}^* = 30kT$. This shift can be explained as follows. For a fixed temperature and external field $h$, a higher $\kappa$ yields a higher free energy barrier to nucleation of the $+m$ phase $\Delta F_{\text{m}}^*$. Now for each fixed temperature and $\kappa$, as $h$ increases the energy barrier $\Delta F_{\text{m}}^*$, Eq. (11), decreases until it reaches energies of about $30kT$. Therefore at each

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Figure 3: $\Delta F^*$ versus $h$ for two $\Delta \omega_{\text{core}}$, when $\kappa = 1$ and $t = -0.25$. Solid and long-dashed curves correspond to $\Delta \omega_{\text{core}} = -0.75$ and $\Delta \omega_{\text{core}} = -1.25$, respectively.
fixed temperature, for a higher $\kappa$ the nucleation occurs at a higher external field $h$ and consequently at a higher order parameter $m$. Increasing $\kappa$ also increases $\Delta F^*$ Eq. [1], thus increasing $\kappa$ pushes nucleation to both the $+m$ and the stable phase to larger values of $h$.

5 Conclusions

Homogeneous nucleation of a new phase at a first-order transition near a second transition is considered. The second transition is an Ising-like or a vapour-liquid-like transition, and lies within the coexistence region of the equilibrium transition. Numerical calculations were performed to calculate the excess order parameter $\Delta m^*$ and the free energy barrier to nucleation $\Delta F^*$, of the critical nucleus. For the states in the negative magnetisation phase with $h > 0$ the system is within the coexistence regions of both transitions. Then in these states either the positive magnetisation phase or the equilibrium phase can nucleate. The free energy barriers to nucleation are equal to $\Delta F^I$ and $\Delta F^*$, for the former and the latter, respectively. The phase which nucleates is the one with the lower free energy barrier. This is in accordance with Ostwald’s step rule, which states that the nucleated phase is not necessarily the stable phase, but is the one with the lowest free energy barrier to nucleation. The stable phase can be attained via two processes. In the first process $\Delta F^*$ becomes small enough to allow nucleation when $\Delta F^I$ is still large, then the stable phase nucleates. In the second process $\Delta F^I$ becomes small enough to allow nucleation when $\Delta F^*$ is still large, then the stable phase will be reached in two steps: first the positive magnetisation phase nucleates and grows and then second, the stable phase nucleates in this positive magnetisation phase.

When the Ising-like phase transition occurs, both $\Delta m^*$ and $\Delta F^*$ jump to lower values, due to the increase in the bulk order parameter. As the bulk order parameter at coexistence is a function of the temperature, then the height of the jump is temperature-dependent. For a lower temperature, the jump in the order parameter increases and therefore the jumps in $\Delta m^*$ and the barrier to nucleation $\Delta F^*$ increase. This may mean a jump from a nucleation barrier too high to permit significant nucleation, to a very small barrier that results in rapid nucleation with many nuclei forming. This effect may cause problems for crystallographers wanting to achieve a small but non-zero rate of nucleation in order to obtain a few large crystals. We also observed that as the spinodal is approached, $\Delta m^*$ diverges and the free energy barrier $\Delta F^*$ varies rapidly with $h$. 

Figure 4: Phase diagram for $t$ versus $m$. Solid and long-dashed lines are coexistence and spinodal, respectively. The others correspond to $\Delta F^I = 30kT$, dotted, dashed and dot-dashed lines are for $\kappa = 1, 1.5$ and 2, respectively.
Figure 5: Phase diagram for $t$ versus $h$. Coexistence lies along the $t$ axis. Long-dashed curve is the spinodal. The others correspond to $\Delta F^*_I = 30kT$, dotted, dashed and dot-dashed lines are for $\kappa = 1, 1.5$ and 2, respectively.

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