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INTRODUCTION

When an external parameter such as the temperature T is changed, physical systems in a homogeneous state often become unstable and tend to an ordered phase with broken symmetry. The growth of new order takes place with coarsening of domains or defect structures on mesoscopic spatial scales much longer than the microscopic molecular scale. Such ordering processes are ubiquitously observed in many systems such as ferromagnetic (spin) systems, solid alloys, and fluids. Historically, structural ordering and phase separation in solid alloys has been one of central problems in metallurgy [1]. These are highly nonlinear and far-from-equilibrium processes and have been studied as challenging subjects in condensed matter physics, polymer science, and metallurgy [2–5]. Here a short review on phase ordering is given on the basis of prototype mathematical models.

PHASE ORDERING IN NONCONSERVED SYSTEMS

Let us consider phase ordering in a system with a scalar space-time dependent variable $\psi(\mathbf{r}, t)$. If its space integral is not conserved in time, it is called the nonconserved order parameter, representing magnetization, electric polarization, *etc.* After appropriate scaling of time t , space \mathbf{r} , and ψ , the simplest dynamic equation reads

$$\frac{\partial}{\partial t}\psi = \nabla^2\psi - \tau\psi - \psi^3 + h + \theta \quad (1)$$

The coefficient τ is related to the temperature by $\tau = A(T - T_c)$, where A is a constant and T_c is the critical temperature. The constant h is also an externally controllable parameter, proportional to the applied magnetic field for the ferromagnetic case. The last term is the Markovian Gaussian random noise needed when Eq.(1) is treated as a Langevin (stochastic differential) equation. In physics its stochastic property is usually expressed as

$$\langle \theta(\mathbf{r}, t)\theta(\mathbf{r}', t') \rangle = 2\varepsilon\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \quad (2)$$

where ε represents the strength of the noise (proportional to the temperature before the scaling). In the presence of θ , the variable ψ is a random variable, whose probability distribution $P(\{\psi\}, t)$ obeys the Fokker-Planck equation. The equilibrium (steady) distribution is given by

$$P_{\text{eq}}\{\psi\} = \text{const.} \exp(-F\{\psi\}/\varepsilon) \quad (3)$$

where F is the so-called Ginzburg-Landau free energy

$$F = \int d\mathbf{r} \left[\frac{\tau}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{1}{2}|\nabla\psi|^2 - h\psi \right] \quad (4)$$

Using F we rewrite Eq.(1) in a standard form of the Langevin equation,

$$\frac{\partial}{\partial t}\psi = -\frac{\delta F}{\delta\psi} + \theta \quad (5)$$

In equilibrium ψ consists of the average ψ_e and the deviation $\delta\psi$, where the latter is a Gaussian fluctuation in the limit of small ε . If $\tau > 0$ and $h = 0$, we obtain $\psi_e = 0$. If $\tau < 0$ and $h = 0$, there are two minima $\psi_e = \pm|\tau|^{1/2}$. These two states can coexist in equilibrium with a planar interface separating them at $h = 0$. If its normal is along the x axis, the interface solution is of the form,

$$\psi(x) = |\tau|^{1/2} \tanh(|\tau|^{1/2}x/\sqrt{2}) \quad (6)$$

which tends to $\pm|\tau|^{1/2}$ as $x \pm \infty$ and satisfies

$$\delta F/\delta\psi = (\tau + \psi^2)\psi - d^2\psi/dx^2 = 0 \quad (7)$$

It is well-known that the fluctuations of ψ are enhanced as the critical point is approached. The renormalization group theory shows how the equilibrium distribution $P_{\text{eq}}\{\psi\}$ in Eq.(3) depends on the upper cut-off wave number Λ of ψ , where we suppose that ψ consists of the Fourier components $\psi_{\mathbf{k}}$ with $k < \Lambda$ [5]. In our phase ordering problem the shortest relevant spatial scale is the interface width of the order of the thermal correlation length ξ at the final temperature. Therefore, near criticality, we may assume that the thermal fluctuations with wave numbers larger than ξ^{-1} have been eliminated in the model (or $\Lambda \sim \xi^{-1}$ at the starting point).

Domain growth

Thermodynamic instability occurs when τ is changed from a positive value τ_i to a negative value τ_f at $t = 0$. We here assume $h = 0$. We set $\tau_f = -1$ using the scaling. At long wavelengths $k < 1$, small plane wave fluctuations with wave vector \mathbf{k} grow exponentially as

$$\psi_{\mathbf{k}}(t) \sim \exp[(1 - k^2)t] \quad (8)$$

with the growth rate largest at $k = 0$. This suggests that the nonlinear term in Eq.(1) becomes crucial after

a transient time. Numerically obtained snapshots of the subsequent $\psi(\mathbf{r}, t)$ are shown in Fig.1 in two dimensions (2D), where we can see the coarsening of the patterns. The characteristic domain size $\ell(t)$ grows algebraically as

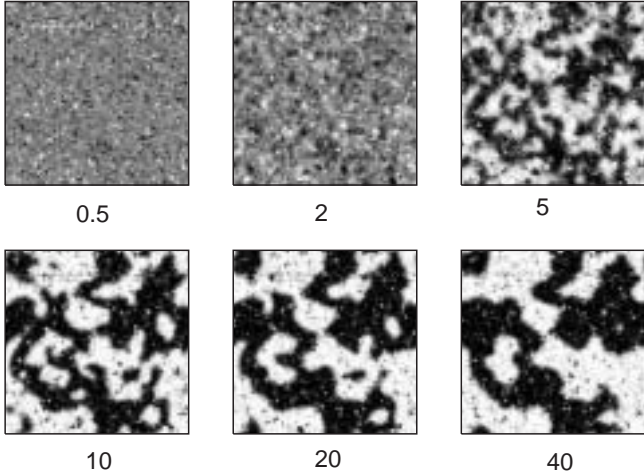


FIG. 1: Time evolution of ψ in model (1) in 2D with system length=128. The numbers are the times after quenching. Noise is added, but is not essential for large patterns or in the late stage.

$$\ell(t) \sim t^a \quad (9)$$

where $a = 1/2$ is known for the model (1). Scattering experiments detect the time-dependent correlation

$$g(\mathbf{r}, t) = \langle \delta\psi(\mathbf{r} + \mathbf{r}_0, t) \delta\psi(\mathbf{r}_0, t) \rangle, \quad (10)$$

$$S(k, t) = \int d\mathbf{r} g(\mathbf{r}, t) e^{i\mathbf{k} \cdot \mathbf{r}} \quad (11)$$

where $S(k, t)$ is called the structure factor. We assume the translational invariance and the spatial isotropy after the thermal average $\langle \dots \rangle$. If $\tau_1 \gg 1$, the quartic term in F is negligible, leading to the initial structure factor

$$S(k, 0) \cong \varepsilon / (\tau_i + k^2) \quad (12)$$

which is produced by the thermal fluctuations. However, when the domain size $\ell(t)$ much exceeds the microscopic length (lattice constant), the following scaling behavior emerges:

$$g(\mathbf{r}, t) = G(\mathbf{r}/\ell(t)), \quad (13)$$

$$S(k, t) = \ell(t)^d Q(\ell(t)k) \quad (14)$$

where d is the space dimensionality and $G(x)$ and $Q(x)$ are the scaling functions of order unity for $x \sim 1$. The correlation on the scale of $\ell(t)$ in Eq.(13) arises from large scale domain structures, while Eq.(14) is simply its Fourier transformation. The maximum of the structure factor grows as $\ell(t)^d$. When $\varepsilon \ll 1$, however, there

can be a well-defined initial stage in which $S(k, t)$ grows exponentially at long wavelengths.

We may explain the roles of the terms on the right hand side of Eq.(1) in phase ordering in a simple manner.

- (i) The linear term $-\tau\psi$ triggers instability for $\tau < 0$.
- (ii) The nonlinear term $-\psi^3$ gives rise to saturation of ψ into ± 1 . To see this, we neglect $\nabla^2\psi$ and θ to have $\partial\psi/\partial t = (1 - \psi^2)\psi$ for $\tau = -1$. This equation is solved to give

$$\psi(t) = \psi_0 / \sqrt{\psi_0^2 + (1 - \psi_0^2)e^{-2t}} \quad (15)$$

where $\psi_0 = \psi(0)$ is the initial value. Thus $\psi \rightarrow 1$ for $\psi_0 > 0$ and $\psi \rightarrow -1$ for $\psi_0 < 0$. (iii) The gradient term limits the instability only in the long wavelength region $k < 1$ in the initial stage (see Eq.(8)) and creates the interfaces in the late stage (see Eq.(7)). (iv) The noise term θ is relevant only in the early stage where ψ is still on the order of the initial thermal fluctuations. The range of the early stage is of order 1 for $\varepsilon \gtrsim 1$, but weakly grows as $\ln(1/\varepsilon)$ for $\varepsilon \ll 1$. The noise term can be neglected once the fluctuations much exceed the thermal level. (v) If h is a small positive number, it favors growth of regions with $\psi \cong 1$.

Interface dynamics

At long times $t \gg 1$ domains with typical size $\ell(t)$ are separated by sharp interfaces and the thermal noise is negligible. Allowing the presence of a small positive h , we may approximate the free energy F as

$$F = \sigma S(t) - 2hV_+(t) + \text{const.} \quad (16)$$

where σ is a constant (surface tension), $S(t)$ is the surface area, and $V_+(t)$ is the volume of the regions with $\psi \cong 1$. In this stage the interface velocity $v_{\text{int}} = \mathbf{v}_{\text{int}} \cdot \mathbf{n}$ is given by the Allen-Cahn formula [6]:

$$v_{\text{int}} = -\mathcal{K} + (2/\sigma)h \quad (17)$$

The normal unit vector \mathbf{n} is from a region with $\psi \cong 1$ to a region with $\psi \cong -1$. The \mathcal{K} is the sum of the principal curvatures $1/R_1 + 1/R_2$ in three dimensions (3D). This equation can be derived from Eq.(1). If the interface position \mathbf{r}_a moves to $\mathbf{r}_a + \delta\zeta\mathbf{n}$ infinitesimally, the surface area changes by $\delta S = \int da \mathcal{K} \delta\zeta$, where $\int da \dots$ denotes the surface integral. Therefore, F in Eq.(16) changes in time as

$$\frac{dF}{dt} = \int da (\sigma\mathcal{K} - 2h)v_{\text{int}} \leq 0 \quad (18)$$

which is non-negative-definite owing to Eq.(17). Furthermore, we may draw three results from Eq.(17). (i) If we set $v_{\text{int}} \sim \ell(t)/t$ and $\mathcal{K} \sim 1/\ell(t)$, we obtain $a = 1/2$ in the growth law (9). (ii) In phase ordering under very

small h , the balance $1/\ell(t) \sim h/\sigma$ yields the crossover time $t_h \sim h^{-2}$. For $t < t_h$ the effect of h is small, while for $t > t_h$ the regions with $\psi \cong 1$ becomes predominant. (iii) A spherical droplet with $\psi \cong 1$ evolves as

$$\frac{\partial R}{\partial t} = -\frac{2}{R} + \frac{2h}{\sigma} \quad (19)$$

from which the critical radius is determined as

$$R_c = \sigma/h \quad (20)$$

A droplet with $R > R_c$ ($R < R_c$) grows (shrinks).

We mention a statistical theory of interface dynamics at $h = 0$ by Ohta, Jasnow, and Kawasaki [7]. There, a smooth subsidiary field $u(\mathbf{r}, t)$ is introduced to represent surfaces by $u = \text{const}$. The differential geometry is much simplified in terms of such a field. The two-phase boundaries are represented by $u = 0$. If all the surfaces follow $v_{\text{int}} = -\mathcal{K}$ in Eq.(17) in the whole space, u obeys

$$\frac{\partial}{\partial t} u = [\nabla^2 - \sum_{ij} n_i n_j \nabla_i \nabla_j] u \quad (21)$$

where $\nabla_i = \partial/\partial x_i$ and $n_i = \nabla_i u / |\nabla u|$. This equation becomes a linear diffusion equation if $n_i n_j \nabla_i \nabla_j$ is replaced by $d^{-1} \delta_{ij} \nabla^2$. Then u can be expressed in terms of its initial value and the correlation function of $\psi(\mathbf{r}, t) (\cong u(\mathbf{r}, t)/|u(\mathbf{r}, t)|$ in the late stage) is calculated in the form of Eq.(13) with

$$G(x) = \frac{2}{\pi} \sin^{-1} \left[\exp \left(-\frac{1}{8(1-1/d)} x^2 \right) \right] \quad (22)$$

which excellently agrees with simulations.

SPINODAL DECOMPOSITION IN CONSERVED SYSTEMS

The order parameter ψ can be a conserved variable such as the density or composition in fluids or alloys. With the same F in Eq.(4), a simple dynamic model in such cases reads

$$\frac{\partial}{\partial t} \psi = \nabla^2 \frac{\delta F}{\delta \psi} - \nabla \cdot \mathbf{j}^R. \quad (23)$$

Here \mathbf{j}^R is the random current characterized by

$$\langle j_\alpha^R(\mathbf{r}, t) j_\beta^R(\mathbf{r}', t') \rangle = 2\varepsilon \delta_{\alpha\beta} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (24)$$

which ensures the equilibrium distribution (3) of ψ . However, the noise \mathbf{j}^R is negligible in late-stage phase separation as in the nonconserved case. Note that h in the conserved case is the chemical potential conjugate to ψ and, if it is homogeneous, it vanishes in the dynamic equation (23). In experiments the average order parameter

$$M = \langle \psi \rangle = \int d\mathbf{r} \psi(\mathbf{r}) / V \quad (25)$$

is used as a control parameter instead of h , where the integral is within the system with volume V . If there is no flux from outside, M is constant in time. Here the instability occurs below the so-called spinodal $M^2 < 1/3$ ($M^2 < |\tau|/3$ for general $\tau < 0$). In fact small fluctuations with wave vector \mathbf{k} grow exponentially as

$$\psi_{\mathbf{k}}(t) \sim \exp[k^2(1 - 3M^2 - k^2)t] \quad (26)$$

right after the quenching as in Eq.(8). The growth rate is largest at an intermediate wave number $k = k_m$ with

$$k_m = [(1 - 3M^2)/2]^{1/2} \quad (27)$$

This behavior and the exponential growth of the structure factor have been observed in polymer mixtures where the parameter ε in Eq.(3) or (12) is expected to be small [5]. In late stage coarsening the peak position of $S(k, t)$ decreases in time as

$$k_m(t) \sim 2\pi/\ell(t) \quad (28)$$

in terms of the domain size $\ell(t)$. The growth exponent in Eq.(9) is given by 1/3 for the simple model (23) (see Eq.(33) below).

In Fig.2 we show the patterns after quenching in 2D. For $M = 0$ the two phases are symmetric and the patterns are bicontinuous, while for $M \neq 0$ the minority phase eventually appears as droplets in the percolating region of the majority phase.

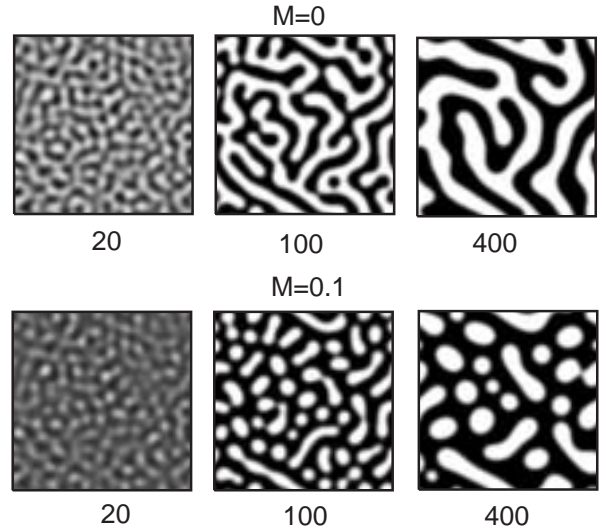


FIG. 2: Time evolution of ψ in model (23) in 2D with system length=128 without thermal noise. $M = 0$ in the upper figures and $M = 0.1$ in the lower figures. The numbers are the times after quenching.

Interface dynamics

Interface dynamics in the conserved case is much more complicated than in the nonconserved case, because the

coarsening can proceed only through diffusion. Long-distance correlations arise among the domains and the interface velocity cannot be written in terms of the local quantities like the curvature. As a simple example, we give the counterpart of Eq.(19). In 3D a spherical droplet with $\psi \cong 1$ appears in a nearly homogeneous matrix with $\psi = M$ far from the droplet. The droplet radius R is then governed by [8]

$$\frac{\partial}{\partial t}R = D \left(\frac{\Delta}{R} - \frac{2d_0}{R^2} \right) \quad (29)$$

where $\Delta = (M + 1)/2$ is called the supersaturation, while D and d_0 are constants (equal to 2 and $\sigma/8$, respectively, after the scaling). The critical radius is written as

$$R_c = 2d_0/\Delta \quad (30)$$

The general definition of the supersaturation is

$$\Delta = (M - \psi_{\text{cx}}^{(2)})/(\psi_{\text{cx}}^{(1)} - \psi_{\text{cx}}^{(2)}) \quad (31)$$

Here the equilibrium values of ψ are written as $\psi_{\text{cx}}^{(1)}$ and $\psi_{\text{cx}}^{(2)}$ and M is supposed to be slightly different from $\psi_{\text{cx}}^{(2)}$.

Lifshitz and Slyozov analyzed domain coarsening in binary AB alloys when the volume fraction q of the A-rich domains is small [8]. They noticed that the supersaturation Δ around each domain decreases in time with coarsening. That is, the A component atoms in the B-rich matrix are slowly absorbed onto the growing A-rich domains, while a certain fraction of the A-rich domains disappear. Thus $q(t)$ and $\Delta(t)$ both depend on time, but satisfy the conservation law:

$$q(t) + \Delta(t) = \Delta(0) = (M + 1)/2 \quad (32)$$

With this overall constraint, they found the asymptotic late stage behavior

$$\ell(t) \sim \Delta(t)^{-1} \sim t^{1/3} \quad (33)$$

where $\ell(t)$ is the average droplet radius. Notice that this behavior is consistent with the droplet equation (29), where each term is of order $R/t \sim t^{-2/3}$.

NUCLEATION

In metastable states the free energy is at a local minimum but not at the true minimum. Such states are stable for infinitesimal fluctuations, but rare spatially localized fluctuations, called critical nuclei, can continue to grow, leading to macroscopic phase ordering [5, 9]. The birth of a critical droplet is governed by the Boltzmann factor $\exp(-F_c/k_B T)$ at finite temperatures, where F_c is the free energy needed to create a critical droplet and $k_B T$ is the thermal energy with k_B being the Boltzmann constant. In this section we explicitly write $k_B T$, but we may scale ψ and space such that $\tau = -1$ at the final temperature.

In the nonconserved case we prepare a spin-down state with $\psi \cong -1$ in the time region $t < 0$ and then apply a small positive field h at $t = 0$. For $t > 0$ a spin-up droplet with radius R requires a free energy change

$$F(R) = 4\pi\sigma R^2 - \frac{8\pi}{3}hR^3. \quad (34)$$

The first term is the surface free energy and the second term is the bulk decrease due to h . The critical radius R_c in Eq.(20) gives the maximum of $F(R)$ given by

$$F_c = \frac{4\pi}{3}\sigma R_c^2 \quad (35)$$

In fact $F'(R) = \partial F(R)/\partial R$ is written as

$$F'(R) = 8\pi\sigma(R - R^2/R_c). \quad (36)$$

In conserved systems such as fluids or alloys, we lower the temperature slightly below the coexistence curve with the average order parameter M held fixed. We again obtain the droplet free energy (34), but

$$h = (\sigma/2d_0)\Delta \quad (37)$$

in terms of the (initial) supersaturation $\Delta = \Delta(0)$. Let the equilibrium values $\psi_{\text{cx}}^{(1)}$ and $\psi_{\text{cx}}^{(2)}$ in the two phases be written as $\pm A(T_c - T)^\beta$ with A and β being constants ($\beta \cong 1/3$ as $T \rightarrow T_c$). For each given M we define the coexistence temperature T_{cx} by $M = \psi_{\text{cx}}^{(2)} = -A(T_c - T_{\text{cx}})^\beta$. In nucleation experiments the final temperature T is slightly below T_{cx} and $\delta T \equiv T_{\text{cx}} - T$ is a positive temperature increment. For small δT we find

$$\Delta \cong \frac{\beta}{2}\Delta T/(T_c - T_{\text{cx}}) \quad (38)$$

Droplet size distribution and nucleation rate

In a homogeneous metastable matrix, droplets of the new phase appear as rare thermal fluctuations. We describe this process by adding a thermal noise term to the droplet equation (19) or (29). The droplet size distribution $n(R, t)$ then obeys the Fokker-Planck equation

$$\frac{\partial}{\partial t}n = \frac{\partial}{\partial R}\mathcal{L}(R) \left[\frac{\partial}{\partial R} + \frac{F'(R)}{k_B T} \right] n \quad (39)$$

Here $n(R, t)dR$ denotes the droplet number density in the range $[R, R + dR]$. We determine the kinetic coefficient $\mathcal{L}(R)$ such that

$$v(R) \equiv -\mathcal{L}(R)F'(R)/k_B T \quad (40)$$

is the right hand side of Eq.(19) or (29). It is equal to $\partial R/\partial t$ when the thermal noise is neglected. Thus $\mathcal{L}(R) \propto$

R^{-2} or R^{-3} for the nonconserved or conserved case. The second derivative $(\partial/\partial R)\mathcal{L}(R)(\partial/\partial R)$ in Eq.(39) stems from the thermal noise and is negligible for $R - R_c \gtrsim 1$ in 3D [5]. Hence, for $R - R_c \gtrsim 1$, the droplets follow the deterministic equation (19) or (29) and n obeys

$$\frac{\partial}{\partial t}n = -\frac{\partial}{\partial R}[v(R)n] \quad (41)$$

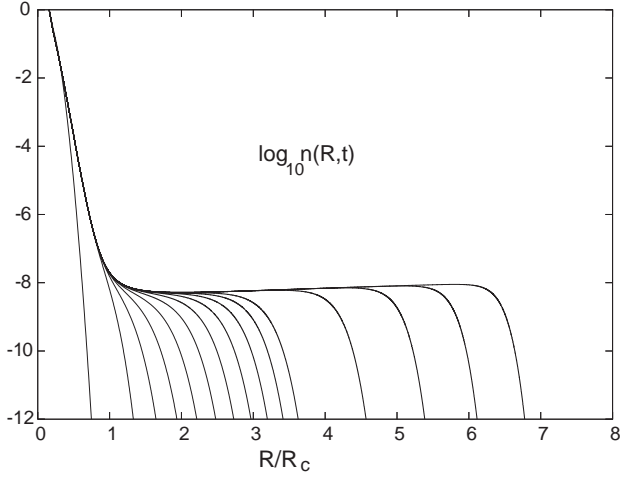


FIG. 3: Time evolution of the droplet size distribution $n(R, t)$ on a semi-logarithmic scale as a solution of Eq.(39) in the 3D conserved case. The first 11 curves correspond to the times at $\Gamma_c t = 0, 1, \dots, \text{and } 10$. The last 4 curves are those at $\Gamma_c t = 15, 20, 25, \text{and } 30$.

In Fig.3 we plot the solution of Eq.(39) for the conserved case with $F_c = 17.4/k_B T$ [5]. The time is measured in units of $1/\Gamma_c$, which is the time scale of a critical droplet defined by

$$\Gamma_c = (\partial v(R)/\partial R)_{R=R_c} \quad (42)$$

We notice $\Gamma_c \propto R_c^{-3}$ from Eq.(29) so Γ_c is small. The initial distribution is given by

$$n(R, 0) = n_0 \exp(-4\pi\sigma R^2/k_B T) \quad (43)$$

with n_0 being a constant number density. This form has been observed in computer simulations as the droplet size distribution on the coexistence curve. Fig.3 indicates that $n(R, t)$ tends to a steady solution $n_s(R)$ which satisfies

$$\mathcal{L}(R) \left[\frac{\partial}{\partial R} + \frac{F'(R)}{k_B T} \right] n_s = -I \quad (44)$$

where I is a constant. Imposing the condition $n_s(R) \rightarrow 0$ as $R \rightarrow \infty$, we integrate the above equation as

$$n_s(R) = I \int_R^\infty dR_1 \frac{1}{\mathcal{L}(R_1)} \exp \left[\frac{F(R_1) - F(R)}{k_B T} \right] \quad (45)$$

For $R - R_c \gg 1$ we may replace $F(R_1) - F(R)$ by $F'(R)(R_1 - R)$ in the integrand of Eq.(45) to obtain

$$n_s(R) \cong I/v(R) \quad (46)$$

which also follows from Eq.(41). Thus

$$n_s(R)dR = I dt \quad (dR = v(R)dt) \quad (47)$$

This means that I is the nucleation rate of droplets with radii larger than R_c emerging per unit volume and per unit time. Furthermore, as $R \rightarrow 0$, we require $n_s(R) \rightarrow n_0 = \text{const.}$ in Eq.(43) so that

$$n_0 = I \int_0^\infty dR_1 \frac{1}{\mathcal{L}(R_1)} \exp \left[\frac{F(R_1)}{k_B T} \right] \quad (48)$$

where the integrand becomes maximum around R_c . Using the expansion $F(R) = F_c + F''(R_c)(R - R_c)^2/2 + \dots$ we obtain the famous formula for the nucleation rate

$$I = I_0 \exp(-F_c/k_B T) \quad (49)$$

$$= I_0 \exp(-C_0/\Delta^2) \quad (50)$$

where the coefficient I_0 is of order $n_0 \Gamma_c$. The second line holds in the 3D conserved case. Here $C_0 \sim 10^{-3}$ typically and I_0 is a very large number in units of $\text{cm}^{-3}\text{sec}^{-1}$, say, 10^{30} . Then the exponential factor in I changes abruptly from a very small to a very large number with only a slight increase of Δ at small $\Delta \ll 1$. For example, if $C_0/\Delta^2 = 50$, I is increased by $\exp(100\delta\Delta/\Delta)$ with a small increase of Δ to $\Delta + \delta\Delta$. This factor can be of order 10^3 even for $\delta\Delta/\Delta = 0.05$. Unless close to criticality, simple metastable fluids become opaque suddenly with increasing Δ or δT at a rather definite cloud point. In near-critical fluids, however, I_0 becomes small ($\propto \xi^{-6}$) such that the cloud point considerably depends on the experimental time scale (observation time).

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