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# THE AGING OF NUCLEI IN A BINARY MIXTURE

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A theory of nucleation for a metastable binary mixture is developed, based on the Cahn–Hilliard theory of phase separation. It is shown that at least in its intermediate stages the transition from a supersaturated state to an energetically favored separated state follows the typical mechanism of surface tension governed nucleation processes and long-time similarity solutions describing the distribution of nuclei are found, analagous to the results of Lifshitz et al. It is shown that spatially uniform nucleation is destabilized by diffusion and the modifications to the nucleation process due to spatial inhomogeneity are found.

## 1. Introduction

In the evolution of first order phase transitions, there is a stage called Ostwald Ripening, or aging [1]. At the onset, homogeneously distributed nuclei of one phase are surrounded by supersaturated medium consisting of the other phase. The larger nuclei grow and deplete the supersaturation of the surrounding phase, and this leads to the decay of the smaller nuclei. The demise of the smaller nuclei replenishes the supersaturation of the surrounding phase and supports the continued growth of the large nuclei. This phenomenology is described quantitatively in an analysis of I. Lifshitz and V. Slyozov [2]. They find that in a medium with a spatially uniform distribution of nuclei which occupy only a small fraction of the total volume, the supersaturation and density of nuclei decrease with time like $t^{-1/3}$ and $t^{-1}$ respectively, while the mean nuclear radius increases like $t^{1/3}$.

In practice, this description must be modified after sufficiently large times, due to processes such as coagulation or gravitational separation that might become important for large nuclei.

The subject of this analysis is an examination of Ostwald ripening in a binary mixture, where the transition from a homogeneous mixture to a spatially inhomogeneous, partially separated mixture is modeled by the Cahn–Hilliard theory [3]. We present new exact solutions of this theory which clearly correspond to the asymptotic results of [2].

Next, we consider the effects of spatial nonuniformity in the distribution of nuclei. This problem has been studied in the context of chemical precipitation [4] by use of linearized analysis. We present exact solutions of the full nonlinear theory which describe the development of localized spatial inhomogeneities. In the region of the inhomogeneity, the volume fraction occupied by nuclei grows like $t^{2/3}$, instead of asymptoting to a constant value as in the spatially homogeneous case.

## 2. Phase separation in binary mixture

We review the basics of Cahn–Hilliard theory [3] which describes phase separation in a binary

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mixture. The free energy $\varphi$ per unit volume is a functional of $c$, the fractional concentration of one component. For isotropic material with small variations and gradients in $c$,

$$\varphi[c] \approx f(c) + \frac{\kappa}{2}|\nabla c|^2, \quad \kappa > 0, \tag{2.1}$$

where $f(c)$ is the free energy per unit volume in a medium with uniform concentration $c$ and $(\kappa/2)|\nabla c|^2$ is the leading order effect of nonuniformities with small variations and gradients.

The dynamical evolution of small nonuniformities in $c$ may be described as follows: The chemical potential $\mu$ per unit volume is

$$\mu = \frac{\delta \varphi}{\delta c} = f'(c) - \kappa \Delta c. \tag{2.2}$$

The concentration $c$ is a locally conserved quantity whose flux is $-\Delta\mu$. Hence, $c$ satisfies the transport equation

$$c_t - \Delta\big(f'(c) - \kappa \Delta c\big) = 0. \tag{2.3}$$

We discuss the stability of uniform states $c \equiv c_0$. From a linearized analysis of (2.3) we find that a harmonic perturbation with wavenumber $k$ has growth rate

$$\sigma = -f''(c_0)k^2 - \kappa k^4. \tag{2.4}$$

If $f''(c_0) > 0$, then the medium is stable. If $f''(c_0) < 0$, then there is instability for $|k|^2 < k_c^2 \equiv -f''(c_0)/\kappa$ (fig. 1a).

Typically, we find that a homogeneous binary mixture is stable at high temperatures, but unstable to phase separation at low temperatures. There is a critical temperature such that $T < T_c \to f''(c) < 0$ for some range of $c$. Fig. 1b shows the typical form of the free energy $f(c)$ in this case. The darkened segment on the $c$-axis represents the range of unstable $c$ values.

We review some basic results about steady equilibria. For an equilibrium state, the chemical potential $\mu$ assumes a steady, uniform value throughout the entire medium. From (2.2), we see

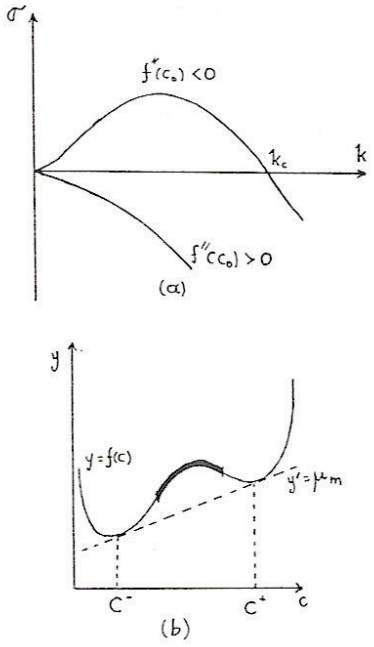


Fig. 1

that the steady equilibria satisfy

$$f'(c) - \kappa \Delta c = \mu. \tag{2.5}$$

States with uniform concentration $c$ satisfy $f'(c) = \mu$. To determine the concentrations corresponding to a given value of chemical potential $\mu$, we simply determine the points on the graph of $y = f(c)$ in fig. 1b where the slope is $\mu$. Given $\mu$ with $\min f'(c) < \mu < \max f'(c)$, we see from fig. 1b that there are in general two concentrations $c = c^{\pm}(\mu)$, $c^- < c^+$, which correspond to uniform stable equilibria satisfying $f'(c) = \mu$, $f''(c) > 0$.

## 3. The critical nucleus

A uniform state $c \equiv c_0$ with $c_0$ below the unstable band may be metastable in the sense that finite amplitude perturbation applied in a localized re-

gion of space for a limited time may be sufficient to create a growing nucleus whose interior has a uniform value $c = c_0'$ above the unstable band. If the initial perturbation is too small, the medium will relax back to the uniform value $c_0$.

There is a steady, nonuniform solution of the equilibrium equation (2.5) which represents the *critical nucleus*. Physically, the critical nucleus represents a perturbation which is just large enough to escape dissolution, but not large enough to grow. The size of the critical nucleus is a function of the chemical potential $\mu$ in the medium surrounding the nucleus.

We may think of the planar profile $C(x)$† corresponding to the chemical potential $\mu_m$ as a critical nucleus of infinite radius. Accordingly, we expect that the critical nucleus corresponding to a chemical potential $\mu$ with $0 < \mu - \mu_m \ll \mu_m$ will have a radius $r_0 \gg 1$. In this limit, we expect that there is a transition zone about the spherical surface of radius $r_0$ where the concentration $c$ adjusts from values close to $c^+(\mu)$ in the interior of the nucleus to the value $c = c^-(\mu)$ achieved at spatial infinity (fig. 2).

The radius $r_0$ is estimated in [3] in the limit $0 < \mu - \mu_m \ll \mu_m$ by a variational argument. The solutions of the equilibrium equation (2.5) which satisfy $c \to c^-(\mu)$ as $|x| \to \infty$ are stationary points of the free energy

$$G \equiv \int_{-\infty}^{\infty} \left( g(c) + \frac{\kappa}{2} |\nabla c|^2 \right) \mathrm{d}x^3. \tag{3.1}$$

Here,

$$g(c) \equiv f(c) - f(c^-(\mu)) - \mu(c - c^-(\mu)). \tag{3.2}$$

In the interior of the nucleus, we expect that the concentration $c(x)$ is near the uniform value $c^-(\mu)$, so that $g(c) \approx g(c^+(\mu))$ in $r < r_0$. For $0 < \mu - \mu_m \ll \mu_m$, we have $g(c^+(\mu)) \approx (C^+ - C^-)(\mu - \mu_m)$. Hence the contribution to $G$ from the nucleus interior is approximately $(4\pi/3) r_0^3 (C^+ - C^-)(\mu - \mu_m)$. In (3.2), the term $(\kappa/2)|\nabla c|^2$ is significant only in the transition zone about $|x| = r_0$. Hence, we regard the integral $(\kappa/2)\int_{-\infty}^{\infty} |\nabla c|^2 \mathrm{d}x^3$ as a surface energy. Using the fact that the concentration profile is well approximated by the heteroclinic solution of the corresponding 1-D problem, $C(x)$, centered at $r - r_0$ [5], in the vicinity of the transition zone where $r - r_0 = \mathcal{O}(1)$, we find that the surface energy term is approximately $2\pi\kappa r_0^2 \int_{-\infty}^{\infty} C_x^2 \mathrm{d}x$. Summing the interior and surface contributions, we obtain for $G$ the approximate value

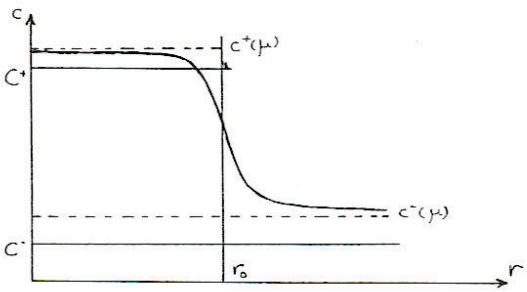


Fig. 2

$$G \approx -\tfrac{4}{3}\pi r_0^3 (C^+ - C^-)(\mu - \mu_m) + 2\pi\kappa r_0^2 \int_{-\infty}^{\infty} C_x^2 \mathrm{d}x. \tag{3.3}$$

$G$ is stationary with respect to variations in $r_0$ if

$$\mu - \mu_m = \frac{H}{r_0}, \quad H \equiv \frac{\kappa}{C^+ - C^-} \int_{-\infty}^{\infty} C_x^2 \mathrm{d}x. \tag{3.4}$$

(3.4) is the relation between the size $r_0$ of the critical nucleus and the chemical potential $\mu$ in the limit $\mu - \mu_m \to 0^+$. This result is analogous to the Gibbs–Thomson formula for the critical radius of a liquid nucleus in vapor. $H$ is analogous to surface tension, and $\mu - \mu_m$ is analogous to the supersaturation.

†$C(x)$ is the solution of $f'(C) - \kappa C_{xx} = \mu_m$, $C(\pm\infty) = C^{\pm}$, with $\max C_x$ occurring at $x = 0$, that is it is the phase-plane trajectory joining the two saddle points of the system. For usual $f(C)$ it can be found in terms of elliptic functions.

## 4. The time evolution of nuclei

We analyze the growth and decay of nuclei in a medium where the chemical potential $\mu$ is just above the critical value $\mu_m$. We view the physical process as follows: Outside the nucleus, where $c$ is close to $c^-(\mu)$ and the gradients of $c$ are much smaller than in the transition layer, the transport process of $c$, represented by the Cahn–Hilliard equation (2.3), may be approximated by simple diffusion,

$$c'_t = D\left(c'_{rr} + \frac{2}{r}c'_r\right), \quad \text{in} \quad r > r(t), \tag{4.1}$$

where $c' \equiv c - c^-(\mu)$, $D \equiv f''(C^-)$, and $r(t)$ is the radius of the nucleus at time $t$. If the nucleus is growing, it feeds on the surplus $c'$ in the exterior. If it is decaying, it augments the surplus. In other words, the surface of the nucleus acts as sink or source. The flux balance through the surface leads to the boundary condition

$$Dc'_r = \delta C \dot{r}(t), \quad \text{on} \quad r = r(t), \quad \delta C \equiv C^+ - C^-. \tag{4.2}$$

As a result of the diffusion process represented by (4.1)–(4.2), the chemical potential that the nucleus sees at its surface is not $\mu$, but rather the value consistent with the local value of $c'$ at the surface, which is approximately $\mu' \equiv Dc' + \mu^- - \mu_m$. If we assume that the nucleus is in a quasi-static equilibrium with this value, then (3.4) applies with $\mu = \mu'$, and we obtain a second boundary condition

$$Dc' = \frac{H}{r(t)} - \delta\mu, \quad \text{on} \quad r = r(t), \quad \delta\mu \equiv \mu^- - \mu_m. \tag{4.3}$$

Eqs. (4.1)–(4.3), together with the boundary condition $c' \to 0$ as $r \to \infty$, constitute a Stefan problem for determining $r(t)$ and $c'(r,t)$ in $r > r(t)$. The solution of (4.1) that goes to 0 as $|x| \to \infty$ is

$$c' = \frac{A}{r}. \tag{4.4}$$

Substituting into the boundary conditions (4.2)–(4.3) and eliminating $A$, we obtain an equation for the size of the nucleus, $r = r(t)$:

$$\dot{r} = \frac{1}{\delta C}\frac{1}{r}\left(\delta\mu - \frac{H}{r}\right). \tag{4.5}$$

This result for the time evolution of the nuclear radius in a binary medium has appeared in other contexts, most notably in describing the precipitation of crystals from ionic solutions [2, 4]. From (4.5), we read off the following results: If $r(t)$ is initially less than the critical size $r_0 = H/\delta\mu$, then $r(t)$ collapses to zero in finite time. If $r(t)$ is initially greater than $r_0$, then $r(t)$ grows like $t^{1/2}$ as $t \to \infty$.

## 5. Evolving distributions of nuclei

We consider a medium with a distribution of nuclei in which the volume fraction of nuclei is assumed to be small. The consequence of this assumption is that the diffusion zones around each nucleus have small radius compared with the internuclear distance. Any given nucleus sees a uniform value of supersaturation $\delta\mu$ around itself and grows in size according to the rate (4.5). The background supersaturation, on the other hand, feels the growth and decay of nuclei as sinks and sources. The macroscopic physics of this process may be described quantitatively as follows: Let $f(r,x,t)\,dr\,dx^3$ be the number of nuclei in volume $dx^3$ whose radii are between $r$ and $r+dr$. $f(r,x,t)$ and the background concentration surplus $C(x,t) \equiv c(x,t) - C^-$ satisfy equations

$$f_t + \frac{D}{\delta C}\left(\frac{1}{r}\left(C - \frac{H}{Dr}\right)f\right)_r = 0, \tag{5.1}$$

$$C_t - D\Delta C = -\frac{4\pi}{3}\delta C \int_0^\infty r^3 f_t\,dr. \tag{5.2}$$

(5.1) expresses the transport of nuclei in $r$ space due to this growth or decay. (5.2) is a mass balance equation: Whatever material is gained by the nuclei must be taken from the concentration surplus field $C$. This is the meaning of the sink term on the

r.h.s. The constants $\delta C, D, H$ in eqs. (5.1)–(5.2) may be absorbed by a rescaling of the variables. The units of the variables we adopt are given in the table below:

| Variable | $r$ | $x$ | $t$ | $c$ | $t$ |
|---|---|---|---|---|---|
| Unit | $R$ | $\left(\frac{DH}{\delta CR^3}\right)^{1/2}$ | $\frac{\delta CR^3}{H}$ | $\frac{H}{DR}$ | $\frac{H}{D\delta CR^5}$ |

(5.3)

Here, $R$ may be thought of as a typical nuclear size in the initial distribution. In the units adopted above, (5.1)–(5.2) read

$$f_t + \left(\frac{1}{r}\left(c - \frac{1}{r}\right)f\right)_r = 0, \tag{5.4}$$

$$\left(c + \frac{4\pi}{3}\int_0^\infty r^3 f\,\mathrm{d}r\right)_t = \Delta c. \tag{5.5}$$

The systems (5.4)–(5.5) has been studied in various contexts. I. Lifshitz and V. Slyozov [2] considered the spatially uniform case. They show that a distribution $f$ evolving according to (5.4)–(5.5) takes on a limiting form as $t \to \infty$, in which the mean radius of the nuclei grows like $t^{1/3}$ and the number of particles decays like $t^{-1}$. The concentration surplus $C$ decays like $t^{-1/3}$. Later work has shown that spatially uniform solutions are unstable to spatial fluctuations. The instability appears to be the origin of the spatial inhomogeneities observed in precipitate patterns, because the initial distribution of nuclei is experimentally observed to be uniform [4].

We begin our analysis of (5.4)–(5.5) with a re-examination of spatially homogeneous distributions. We obtain exact solutions of the spatially homogeneous problem which clearly correspond to asymptotic solutions obtained by I. Lifshitz and V. Slyozov for large time.

In the spatially homogeneous case, $\Delta c = 0$ and (5.4) can be integrated once with respect to time, and we obtain an integral form of mass balance equation,

$$c + \frac{4\pi}{3}\int_0^\infty r^3 f\,\mathrm{d}r = C. \tag{5.6}$$

Here, $c_0$ is a constant independent of time. We may regard $c_0$ as the total amount of material per unit volume in excess of $C^-$ contained either in the nuclei or the surrounding medium. (5.4) and (5.6) are the governing equations of $f(r,t)$ and $c(t)$.

We seek solutions of (5.4) and (5.6) as follows: (5.4) has similarity solutions of the form

$$f = t^{-n/3} f_n(s,\gamma), \quad s = rt^{-1/3}, \tag{5.7}$$

$$c = \gamma t^{-1/3}, \tag{5.8}$$

where $\gamma$ and $n$ are constants. Substitution of (5.7) and (5.8) into (5.4) gives

$$sPF_n' = Q_n F_n, \tag{5.9}$$

where

$$P \equiv 1 - \gamma s + \frac{s^3}{3}, \quad Q_n = 2 - \gamma s - \frac{n}{3}s^3. \tag{5.10}$$

It is necessary to determine which of the similarity solutions (5.7) are relevant to construction of physical distribution functions. Certain required properties may be anticipated from the characteristics of the transport equation (5.4). With $c$ given by (5.8), the ODE of the characteristics reads

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{1}{r}\left(\gamma t^{-1/3} - \frac{1}{r}\right)$$

or

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{3}(r^3)\right) = \gamma r t^{-1/3} - 1. \tag{5.11}$$

Introducing $s = rt^{-1/3}$ as the dependent variable, (5.11) becomes

$$t\frac{\mathrm{d}s}{\mathrm{d}t} = -\frac{1}{5}\left(1 - \gamma s + \frac{s^3}{3}\right) = -\frac{1}{s^2}P, \tag{5.12}$$

where $P$ is the cubic in $s$ given by (5.10). If

$$\gamma > \left(\tfrac{3}{2}\right)^{2/3}, \tag{5.13}$$

then $P \equiv 1 - \gamma s + s^3/3$ has two positive zeros $s^-, s^+$ with $s^- < \gamma_{1/2} < s^+$. In this case, the characteristics in $(s,t)$ space have the aspect depicted in fig. 3a. The corresponding structure of the char-

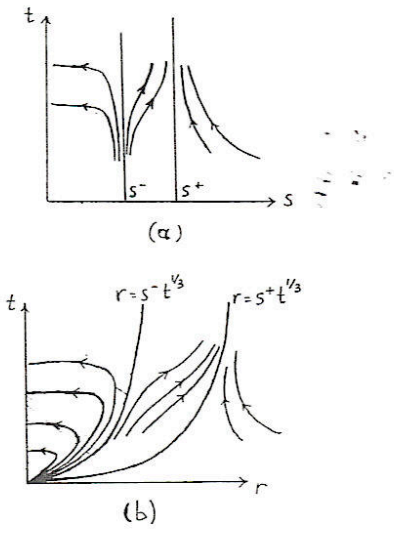


Fig. 3

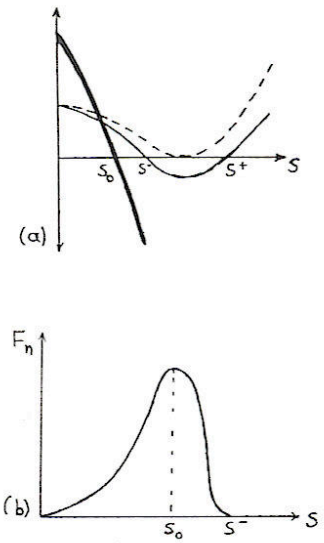


Fig. 4

acteristics in $(r, t)$ space is depicted in fig. 3b. The characteristics in the shaded region of fig. 3b where $0 < \dot{r} < s^- t^{1/3}$ correspond well with the known phenomenology of aging nuclei. Each characteristic in the shaded region eventually collides with the $r = 0$ axis. On the other hand, to the right of the curve $r = s^- t^{1/3}$ in fig. 3b, no characteristic terminates on the axis $r = 0$, so nuclei corresponding to these characteristics are never destroyed. Along these characteristics, $r \approx t^{1/3}$ as $t \to \infty$. Hence, the total amount of material in nuclei to the right of $r = s^- t^{1/3}$ would be proportional to $t$ if such nuclei existed. Mass conservation would eventually be violated, hence there can't be nuclei in $r > s^- t^{1/3}$, and we must therefore seek solutions of (5.9) for $F_n$ with $F_n \equiv 0$ in $s > s^-$.

We turn to the solution of $F_n$ in $0 < s < s^-$. The cubic $Q_n \equiv 2 - \gamma s - (n/3)s^3$ in (5.10) is positive at $s = 0$ and has only one positive root $s_0$. In order for the solution for $F_n$ to be free of a nonintegrable singularity at $s = s^-$, we must have $s_0 < s^-$. We show that there is a range of $\gamma$ with $\gamma > (3/2)^{2/3}$ for which $s_0 < s^-$ if $n > 1$. If $\gamma = (3/2)^{2/3}$, then $s^- = (3/2)^{1/3}$ is a double root of $P(s)$. The dashed curve in fig. 4a depicts $P(s)$ for $\gamma = (3/2)^{2/3}$. The value of $Q_n$ at $s = (3/2)^{1/3}$ is $2 - (3/2)(1 + n/3)$, which is negative if $n > 1$. In this case $s_0 < (3/2)^{1/3}$ and $Q_n$ has the aspect depicted by the blackened curve. Hence, we have shown that $s^- - s_0 > 0$ will remain true for $\gamma$ in some range of values above $(3/2)^{2/3}$. The solid curve just below the dashed curve depicts $P(s)$ for a $\gamma$ in this range. In the case $s^- > s_0$, eq. (5.9) may be integrated to produce a solution for $F_n(s)$ which has the qualitative behavior shown in fig. 4b.

Since the transport equation (5.4) for $f(r, t)$ is linear, we may construct solutions for $f$ by superposition of the similarity solutions (5.7) whose $F_n$ functions meet the criteria discussed above. The superposition must satisfy the mass balance equation (5.6). In the similarity variables, (5.6) reads

$$\gamma t^{-1/3} + \frac{4\pi}{3} t^{4/3} \int_0^{s^-} s^3 f \, ds = C. \tag{5.14}$$

Assuming that the $F_n$ are normalized according to

$$\frac{4\pi}{3} \int_0^{s^-} s^3 F_n(s, \gamma) \, ds = 1, \tag{5.15}$$

we see immediately from (5.14) that the superposition must be

$$f = c_0\left(t^{-4/3}F_4(s,\gamma) - \gamma t^{-5/3}F_5(s,\gamma)\right). \tag{5.16}$$

Since $4.5 > 1$, we know from the previous discussion that there is a range of $\gamma$ values with $\gamma > (3/2)^{2/3}$ for which acceptable $F_4$, $F_5$ functions are defined.

We note a basic limitation of this solution (5.16): Since $F_4$, $F_5 > 0$, we see that (5.16) gives negative $f$ values for sufficiently small times. Hence, we expect that (5.16) really represents a limiting form of physically realizable solutions in the limit $t \to \infty$. For $t \to \infty$, (5.6) reduces to

$$f \approx c_0 t^{-4/3}F_4(rt^{-1/3}).$$

From this form of the asymptotic solution, the results of I. Lifshitz and V. Slyozov for the density of nuclei and mean nucleus radius follow immediately.

## 6. Spatially inhomogeneous aging processes

The method employed in section 5 to construct spatially independent solutions for $f$ and $c$ can be extended to the spatially dependent case. In equations (5.4), (5.5) we introduce the variable

$$s = rt^{-1/3} \tag{6.1}$$

and write $f$ and $c$ in the forms

$$f = f(s,x,t), \quad c = t^{-1/3}\gamma(x,t). \tag{6.2}$$

The equations for $f$ and $\gamma$ as functions of $s, x, t$ are

$$\left(\partial_t - \frac{1}{3t}s\partial_s\right)f + \frac{1}{t}\left(\frac{1}{\delta}\left(\gamma - \frac{1}{\delta}\right)f\right)_s = 0, \tag{6.3}$$

$$\partial_t\left(t^{-1/3}\gamma + \frac{4\pi}{3}\int_0^\infty s^3 f\,\mathrm{d}s\right) = t^{-1/3}\Delta\gamma. \tag{6.4}$$

We obtain solutions of (6.3), (6.4) in the special case when $\gamma$ is independent of $t$. That is,

$$\gamma = \gamma(x). \tag{6.5}$$

In this case, for any $n > 1$, there is a range of $\gamma$ values with $\gamma > (3/2)^{2/3}$ for which

$$f_n \equiv t^{-n/3}F_n(s,\gamma) \tag{6.6}$$

is a solution of (6.3), where the $F_n$ functions are identical to those employed in the spatially homogeneous analysis of section 5. More general solutions for $f$ may be formed by superpositions of the $f_n$. These superpositions must satisfy the mass balance equation (6.4). From the form of (6.4), we see that it is sufficient to take a superposition of $f_2$, $f_4$ and $f_5$. The most general superposition of $f_2, f_4, f_5$ which satisfies the mass balance equation (6.4) is

$$f = \tfrac{3}{2}\Delta\gamma t^{-2/3}F_2(s,\gamma) + v(x)t^{-4/3}F_4(s,\gamma) - \gamma t^{-5/3}F_5(s,\gamma). \tag{6.7}$$

Here, $v(x)$ is an arbitrary function of $x$. As in the case of the spatially independent solution (5.16), (6.7) yields solutions of the physical problem only during intervals of time for which $f$ is positive.

The volume fraction occupied by nuclei is

$$V = \frac{4\pi}{3}\int_0^1 r^3 f\,\mathrm{d}r = \frac{4\pi}{3}t^{4/3}\int_0^\infty s^3 f\,\mathrm{d}s. \tag{6.8}$$

Substituting into (6.8) the solution (6.7) for $f$ and recalling the normalization condition $(4\pi/3)\int_0^\infty s^3 F_n\,\mathrm{d}s = 1$, we obtain for $V$ the result

$$V = \tfrac{3}{2}t^{2/3}\Delta\gamma + v(x) - \gamma t^{-1/3}. \tag{6.9}$$

We consider the instructive special case of an isolated inhomogeneity. We take

$$v(x) = v_0 > 0, \tag{6.10}$$

$$\Delta\gamma = h(r), \quad r \equiv |x|, \tag{6.11}$$

where $h(r)$ is nonnegative and $\int_0^\infty r^2 h(r)\,\mathrm{d}r < \infty$.

The solution of (6.11) is

$$\gamma = \gamma_0 + \int_0^r \frac{1}{r'} \int_0^{r'} r''^2 h(r'')\, dr'' dr', \tag{6.12}$$

where $\gamma_0 = \gamma(0)$. For $\gamma$ given by (6.12), we deduce that $\gamma_r > 0$ and $\lim_{r\to\infty}\gamma = \gamma_\infty$ is finite and greater than $\gamma_0$. If we assume that $\gamma_0, \gamma_\infty$ are both in the range of $\gamma$ values for which the functions $F_2(s,\gamma), F_4(s,\gamma), F_5(s,\gamma)$ exist, then (6.7) provide a positive solution for $f$ when $t$ is sufficiently large. The values of $c$ and $V$ corresponding to this solution are given by

$$c = t^{-1/3}\gamma(r), \tag{6.13}$$

$$V = \tfrac{3}{2}t^{2/3}h(r) + v_0 - \gamma(r)t^{-1/3}, \tag{6.14}$$

where $\gamma(r)$ is given by (6.12). Fig. 5 depicts snapshots of $c$ and $V$ at successive instants in time in a typical case.

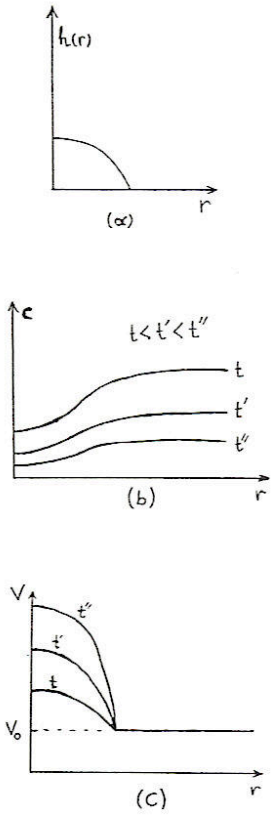


Fig. 5

We briefly discuss the physics contained in the results (6.13), (6.14). In the case of no spatial inhomogeneity with $h \equiv 0$, the volume fraction $V$ occupied by nuclei tends to the constant $v_0$. If there is spatial inhomogeneity and $h \not\equiv 0$, then the volume fraction occupied by nuclei grows like $t^{2/3}$ in those regions where $h(r) \neq 0$. The reason for this growth in the spatially inhomogeneous case is the following: The voracious nuclei in the region of the inhomogeneity can feed upon the more abundant supersaturation in the distant surroundings, which are populated by smaller and less voracious nuclei.

## References

[1] W. Dunning, Particle Growth in Suspensions, L. Smith, ed. (Academic Press, New York, 1973).

[2] I. Lifshitz and V. Slyozov, The kinetics of precipitation from supersaturated solid solutions, JPCS, V. 19, no. 1 (1961).

[3] J. Cahn and H. Hilliard, Free energy of a non-uniform system, I. Interfacial free energy, JCP, V. 28, no. 2 (1958); III. Nucleation, JCP, V. 31, no. 3 (1959).

[4] R. Lovett, P. Ortoleva and J. Ross, Kinetic instabilities in first order phase transitions, JCP, V. 69, no. 3 (1978); G. Venzl and J. Ross, Pattern formations in precipitation, JCP, V. 77, no. 3 (1982).