Coarsening Kinetics with Elastic Effects

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We discuss the coarsening process of melt inclusions inside a solid phase. Elastic effects lead to an oblate shape of the particles, resulting in a system with strong diffusional and elastic interactions between inclusions. The usual mean-field approximation breaks down and several independent length scales have to be taken into account. In a system of parallel oriented particles we find scaling laws for the coarsening of the different length scales involved. In particular, the lateral size of the particles obeys a nontrivial growth law, $R \sim t^{5/12}$.

The growth of crystals from the melt or from a solution is a typical example of first-order phase transition. Ostwald ripening is the late-stage process by which a new phase coarsens in order to lower the interfacial free energy. During this process the characteristic length scale of the precipitates increases in time, the supersaturation decreases, and the system moves towards phase equilibrium.

The classical coarsening theory was given by Lifshitz, Slyozov, and Wagner (LSW) [1] in the framework of a mean-field approach which is valid in the limit of small volume fractions of the new phase. In this approach all precipitated particles are assumed to be spherical and remote from each other. If the diffusional transport of mass or heat is the limiting kinetics of the process, the average size of the particles grows with a power law in time with an exponent of $1/3$. The particle distribution function shows a characteristic scaling behavior.

Novel aspects of kinetics of phase transitions appear if the initial metastable phase is a crystal. Generally, it is known that long-range elastic fields, which are inevitable in this situation, destroy the universal features of LSW growth, allowing other kinetics (see, for example, [2] and references therein). An oblate shape of the inclusions is often observed in experiments [3–5] and in computer simulations [2,6].

Because of a difference in the densities of the two cooperating phases, part of the crystal surrounding a particle of the new phase becomes deformed if the slow diffusion of the point defects is neglected. This modifies the system's behavior in comparison to an unstressed situation. If one assumes incoherence at the interface, as is definitely the case for the melting process or for gas inclusions, the precipitates have an oblate shape which is more favorable compared to a spherical shape because of its lower elastic energy. This effect leads to a substantial modification of the laws of nucleation and growth [7,8].

The main purpose of this Letter is to describe the last coarsening stage of this process which should also be very different from the one of classical LSW theory. The system inevitably arrives at a stage where the characteristic size of the particles is comparable to the distance between them. Indeed, if one assumes that these particles are very oblate lentils of radius R, height $h \ll R$, and distance L between them, the volume fraction $\Delta_0 \sim hR^2/L^3$ should remain almost constant during the coarsening stage. On the other hand, if particles are well separated ($L \gg R$), according to Ref. [7], $h \sim R\Delta$, where Δ is the dimensionless supersaturation parameter which decreases with time. Then the ratio $R/L \sim (\Delta_0/\Delta)^{1/3}$ becomes large in contradiction to the initial assumption $L \gg R$. This situation is very different from the case of spherical particles where, if the volume fraction Δ_0 is small, the ratio $R/L \sim \Delta_0^{1/3}$ remains small during the entire coarsening stage. Thus, for an oblate shape of inclusions the usual mean-field approximation has to be modified in order to account for several independent length scales and strong diffusional and elastic interactions between particles have to be taken into account. In the general case this problem is very difficult and we restrict our consideration to uniaxial crystals where the anisotropy orients the particles in parallel (see Fig. 1a).

We assume that the new phase is a homogeneous melt with a chemical potential μ and pressure P (the external pressure is zero). The melting process of crystals is usually initiated at heterogeneous sites such as grain boundaries or free surfaces [9]. However, crystals can be superheated above the equilibrium melting point, provided heterogeneous nucleation is avoided by means of experimental techniques [10,11]. Motion of a growing interface in this case is governed by the interplay between the irreversible diffusion of the latent heat (diffusional growth) and the reversible work done during elastic deformation and the formation of a new surface area.

The inclusions of the new phase are assumed to be very oblate lentils of characteristic lateral extent R and mean height $h \ll R$. Because of the density difference elastic deformations are necessarily present in the solid phase. The mass conservation law reads

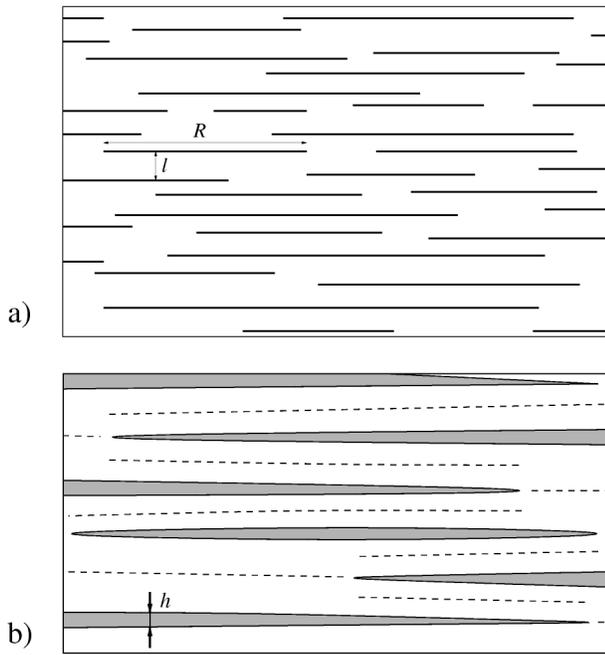$$(v_L - v_s)R^2h/v_s \sim W_d = \int u_n ds, \qquad (1)$$

FIG. 1.   Cross section of the arrangement of liquid inclusions in the solid phase. (b) is a magnified detail of (a); the dashed lines indicate the center lines of the bent plates.

where v_L and v_s are the atomic volumes of the liquid and solid phases, and W_d is the deformation volume (u_n is the normal component of the displacement vector at the interface).

Solving the elastic problem, we can, in first approximation, ignore the height of the lentil. In this case the pressure P, exerted on the crystal by the liquid, is given on a plane cut within the mean radius R. If the particles of the new phase are well separated, this problem is equivalent to the crack problem and the normal component of the displacement vector at the interface is given by solution of that problem (see, for example, [12]). The analogy to the crack problem has been used in our previous publications [7,8] concerning the analysis of the thermodynamics and growth of an isolated particle. However, in the present case the distance between particles is smaller than their size R and the elastic problem should be significantly modified compared to the usual crack problem.

We restrict our considerations to some simple order-of-magnitude estimates for the case of lentil shaped inclusions which are piled up to a layer structure as sketched in Fig. 1a.

Apart from radius and height of each lentil a new length scale, the distance between inclusions l in the vertical z direction, is introduced. Our goal is to calculate the coarsening with time of all three mentioned length scales during the last stage of phase separation. The strategy is as follows: By solving the elastic problem and using the mass conservation law and the local equilibrium condition at the interface, we estimate the pressure P and the characteristic temperature at the interface as functions of the introduced

length scales. Then estimating the existing gradients of temperature, we eventually find the growth law of a characteristic particle.

We confine our considerations to the case $R \gg l \gg h$ and will check the self-consistency of this assumption later. The pressure P_i inside the ith particle depends on its size and on the geometry of the neighborhood. Let us denote the average pressure over the system of particles as $\langle P \rangle$. To estimate the stresses in the crystal in the considered layered structure, using the linearity of the theory of elasticity, we write the displacement field as a sum of three fields: $\mathbf{u} = \mathbf{u}^{(1)} + \mathbf{u}^{(2)} + \mathbf{u}^{(3)}$. The first field $\mathbf{u}^{(1)}$ corresponds to the uniaxial stress of the crystal, $\sigma_{zz} = -\langle P \rangle$. The other components of the stress field are zero. The second field $\mathbf{u}^{(2)}$ satisfies the condition of zero normal and shear stresses at the solid-liquid interfaces and compensates the stresses due to the $\mathbf{u}^{(1)}$ field in order to fulfill the condition of vanishing external pressure. The field $\mathbf{u}^{(2)}$ corresponds to the field of a network of springs schematically depicted by the dashed lines in Fig. 1b. Finally, the field $\mathbf{u}^{(3)}$ satisfies the boundary conditions $\sigma_{zz}^{(i)} = -(P_i - \langle P \rangle)$ at the interfaces of the particles.

To estimate the displacement fields $\mathbf{u}^{(2)}$ and $\mathbf{u}^{(3)}$ we can use the theory of elasticity of thin plates, since the ratio l/R is small (see, for example, [13]). For the field $\mathbf{u}^{(2)}$ the problem reduces to one for the u_z component of the centerline displacement (dashed lines in Fig. 1b) for each plate:

$$\frac{El^3}{12(1 - \nu^2)} \Delta^2 u_z(x, y) = 0. \tag{2}$$

Here $\Delta = \partial_x^2 + \partial_y^2$ is the two-dimensional Laplacian; ν and E are the Poisson and Young coefficients. The problem for the field $\mathbf{u}^{(3)}$ reduces to the local problem of a plate bent due to the pressure difference $\delta P = P_i - P_j$ at opposite sides of the plate:

$$\frac{El^3}{12(1 - \nu^2)} \Delta^2 u_z(x, y) = \delta P. \tag{3}$$

Equations (2) and (3) are subject to the natural boundary conditions at the lines connecting three plates of different thickness (at the edges of the inclusions): continuous displacements and orientations of all three plates and vanishing total force and torque acting on the triple junction from all three plates [13]. If we assume that the characteristic pressure difference δP is of the same order as the average pressure, then both fields are of the same order

$$u_z \sim P \frac{1 - \nu^2}{El^3} R^4 \tag{4}$$

and the corresponding deformation volume is

$$W_d \sim P \frac{1 - \nu^2}{El^3} R^6. \tag{5}$$

Basically Eqs. (4) and (5) can be understood as a scaling analysis of the elastic situation. Indeed, in the framework of linear theory of elasticity the displacement must be

linear in P and, since Young's modulus appears only in the combination El^3 in bending problems, u_z must have the structure (4) in order to have the right units.

We assume local equilibrium conditions at the interface which relate the interface temperature and the pressure P inside the particle:

$$\Delta_{\text{int}} = \frac{(T_{\text{int}} - T_M)c_p}{L_p} = \frac{P(v_L - v_s)T_M c_p}{L_p^2 v_s}, \quad (6)$$

where we have neglected elastic and capillary corrections [7,8]; Δ_{int} is the dimensionless interface superheating; T_M is the melting temperature at zero pressure P; c_p and L_p are the specific and the latent heat, respectively.

The edge of the cracklike inclusion is singular. The condition of local equilibrium also requires an additional variation of the free energy

$$\Delta F = -\frac{1}{2} P W_d + \alpha S \quad (7)$$

with respect to R [7,8], where α is the surface energy and $S \sim R^2$ is the area of the inclusion. This results in

$$P \frac{dW_d}{dR} \sim R\alpha. \quad (8)$$

The last expression is just a generalization of the Griffith condition for cracks to our case. It is a very important ingredient of our theory which allows us to relate the pressure P to the characteristic length scales of the problem. Now, using this condition (8) together with the solution of the elastic problem, Eq. (5), and with the mass conservation law, Eq. (1), we can find a relation between the different length scales of the problem:

$$h \sim \frac{\rho^{1/2}R^2}{l^{3/2}}, \quad (9)$$

where the microscopic length scale

$$\rho = \alpha(1 - \nu^2)v_s^2/[E(v_L - v_s)^2]$$

depends only on material parameters. On the other hand, using the local equilibrium condition, Eq. (6), together with Eq. (1) and Griffith condition, Eq. (8), we can present the interfacial superheating in the following form:

$$\Delta_{\text{int}} \sim \frac{d_0}{h} \frac{W_d}{W_d' R}, \quad (10)$$

where $d_0 = \alpha T_M c_p/L_p^2$ is the capillary length. This is quite a remarkable result: Since the ratio $W_d/(W_d'R)$ is just a number, the interface superheating is basically of capillary origin and depends only on the height h of the inclusion. In other words, the result formally looks like the Gibbs-Thomson correction for the curved interface with curvature of the order $1/h$. However, the real curvature at the smooth part of the interface is of order h/R^2 and has been neglected. Therefore, the result is basically due to the Griffith condition and not a consequence of the Gibbs-Thomson correction in its usual meaning.

Furthermore, the number of inclusions per unit volume behaves like $n \sim R^{-2}l^{-1}$ and thus, by global heat conservation, $nR^2h \sim \Delta_0$, which results in the simple expression

$$h/l \sim \Delta_0, \quad (11)$$

where Δ_0 is the initial superheating of the crystal.

The growth kinetics is controlled by thermodiffusion. The temperature field in the solid phase obeys the diffusion equation and the following boundary conditions:

$$D\nabla^2 w = \partial w/\partial t, \quad (12)$$

$$v_n = D\vec{n} \cdot \nabla w|_{\text{int}}, \quad (13)$$

$$w|_{\text{int}} = \Delta_{\text{int}} \sim d_0/h. \quad (14)$$

Here $w = (T - T_M)c_p/L_p$ is the rescaled temperature field, measured from the melting temperature T_M; D is the thermal diffusion constant. A melting front absorbs latent heat that diffuses as expressed by (12); the requirement of heat conservation at the interface gives (13) ($\vec{n}$ is the normal to the interface and v_n is the normal velocity). Equation (14) is the local equilibrium condition (10). The bigger particles are less overheated and grow to the expense of the smaller ones. We note that the kinetics of the growth of cracklike inclusions during the melting process is very different from fast crack propagation. In the latter case, the absorption of latent heat and thermodiffusion are not present and the velocity of crack propagation is restricted by the Rayleigh speed.

The characteristic gradients of temperature are of the order Δ_{int}/l (see Fig. 1), and the continuity equation (13) together with the relation (11) gives the evolution law for the characteristic height h of the particle:

$$\dot{h} \sim Dd_0\Delta_0/h^2. \quad (15)$$

This evolution equation is qualitatively close to the corresponding one in the classical LSW theory and leads to the coarsening law

$$h(t) \sim (\Delta_0 d_0 D t)^{1/3} \quad (16)$$

with the same scaling exponent $1/3$. However, there is an important difference between these two cases. First of all, our evolution equation is nothing but an order-of-magnitude estimate. In fact we deal with a many particle problem where the local gradients depend on the structure of the close neighborhood and not on the mean-field temperature. On the other hand, the mean-field approach for spherical particles is exact for small volume fractions Δ_0. Second, this small volume fraction enters into the final scaling, Eq. (16), which makes the coarsening process in our case slower than for the spherical particles.

Using Eq. (10), we find that the superheating of the system decreases as

$$\Delta(t) \sim d_0^{2/3}/(\Delta_0 D t)^{1/3}. \quad (17)$$

Of course, the coarsening stage corresponds to the time range when $\Delta(t) \ll \Delta_0$. Finally, the coarsening laws for

the other length scales of the problem, l and R, can be found from Eq. (11) and Eq. (9), respectively:

$$l(t) \sim (d_0 D t)^{1/3} \Delta_0^{-2/3}, \tag{18}$$

$$R(t) \sim l(t)(d_0/\rho)^{1/4}[\Delta_0/\Delta(t)]^{1/4} \sim t^{5/12}. \tag{19}$$

We note that the elastic properties and the density difference enter only into the scaling for the radius R through the microscopic length scale ρ. Equations (16)–(19) are the main results of this Letter.

Let us discuss the consistency of the used approximations. First of all, the basic assumption about the hierarchy of the length scales involved, $R \gg l \gg h$, is clearly valid for small initial superheating $\Delta_0 \ll 1$. Second, we have used the hydrostatic approximation and have neglected the viscous flow necessarily present inside the inclusions due to mass redistribution. The characteristic difference in pressure, arising from the viscous flow with the velocity of the order of $\dot{R}$, is $\delta P \sim \eta \dot{R} R / h^2$, where η is the viscosity. In the coarsening stage this pressure is small compared to the hydrostatic pressure,

$$\frac{\delta P}{P} \sim \frac{\eta D(v_L - v_s)}{\alpha v_s} \frac{1}{h(t)} \left(\frac{d_0}{\rho}\right)^{1/2} \left(\frac{\Delta(t)}{\Delta_0}\right)^{1/2} \ll 1,$$

since $h(t)$ grows and $\Delta(t)$ decays in time. Thus, the used hydrostatic approximation is legitimate.

The smooth shape of a growing nucleus should undergo a Mullins-Sekerka instability. In the usual case of the spherical nucleus this happens when the radius of the nucleus becomes a few times larger than the critical radius [14]. However, this instability is irrelevant in the coarsening regime since all important radii in the distribution function are still stable. In our case of oblate inclusions the Mullins-Sekerka length is $\lambda_{MS} \sim (d_0 D/\dot{h})^{1/2} \sim (lh)^{1/2}$ and one may naively expect the development of an instability. However, the perturbation grows in time as $\exp(\gamma t)$, where γ itself decays in time as $\gamma \sim \dot{h}/\lambda_{MS} \sim \Delta_0^{1/2}/t$. Thus, $\gamma t \sim \Delta_0^{1/2}$ never becomes large and the instability is not important.

Our results should be relevant to other types of phase transitions inside a solid phase. The coarsening of gaseous cracklike pores (see, for example, [15] and references therein) requires diffusion of the impurities towards the crack, while elastic deformations arise due to the nonva-nishing gas volume and pressure. We also mention the transition of a metastable metallic crystal phase into an insulating amorphous state. Based on resistance measurements [5] the authors draw the conclusion that the growing amorphous phase has a very oblate shape.

In summary, we have investigated the coarsening process dominated by elastic effects which lead to a system with strong diffusional and elastic interaction between inclusions. The scaling laws for the coarsening of the different length scales involved are very different from the classical LSW theory.

[1] I. M. Lifshitz and V. V. Slyozov, J. Chem. Solids **19**, 35 (1961); C. Wagner, Z. Elektrochem. **65**, 581 (1961).

[2] C. Sagui, D. Orlikowski, A. Somoza, and C. Roland, Phys. Rev. E **58**, 4092 (1998).

[3] H. Schroeder, W. Kesternich, and H. Ullmaier, Nucl. Eng. Des./Fusion **2**, 65 (1985).

[4] J. H. Neethling, H. C. Snyman, and C. A. B. Ball, J. Appl. Phys. **63**, 704 (1988).

[5] V. F. Gantmakher, S. E. Esipov, and V. M. Teplinskii, Zh. Eksp. Teor. Fiz. **97**, 373 (1990) [Sov. Phys. JETP **70**, 211 (1990)].

[6] Y. Wang *et al.,* J. Am. Ceram. Soc. **78**, 657 (1995); **87**, 377 (1952).

[7] E. A. Brener and V. I. Marchenko, Pis'ma Zh. Eksp. Teor. Fiz. **56**, 381 (1992) [Sov. JETP Lett. **56**, 368 (1992)].

[8] E. A. Brener, S. V. Iordanskii, and V. I. Marchenko, Phys. Rev. Lett. **82**, 1506 (1999).

[9] R. W. Cahn, Nature (London) **323**, 668 (1986).

[10] J. Daeges, H. Gleiter, and J. H. Perepezko, Phys. Lett. A **119**, 79 (1986).

[11] D. L. Zhang and B. Cantor, Acta Metall. Mater. **39**, 1595 (1991).

[12] I. N. Sneddon, Proc. R. Soc. London A **187**, 229 (1946); J. R. Rice, in *Fracture: An Advanced Treatise,* edited by H. Liebowitz (Academic, New York, 1968), Vol. 2, Chap. 3.

[13] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon Press, Oxford, 1987).

[14] W. W. Mullins and R. F. Sekerka, J. Appl. Phys. **35**, 444 (1964).

[15] H. Trinkaus and H. Ullmaier, J. Nucl. Mater. **212–215**, 303 (1994).