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Return radius and volume of recrystallized material in Ostwald ripening

Frank Haußer[1,*] and Evgeny Lakshtanov[2,†]
[1]*Beuth Hochschule Berlin, University of Applied Sciences, Luxemburger Straße 10, 13353 Berlin, Germany*
[2]*Department of Mathematics, Aveiro University, Aveiro 3810, Portugal*

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Within the framework of the Lifshitz-Slyozov-Wagner theory of Ostwald ripening, the amount of volume of the second (solid) phase in a liquid solution that is newly formed by recrystallization is investigated. It is shown that in the late stage, the portion of the newly generated volume formed within an interval from time t_0 to t is a certain function of t/t_0 and an explicit expression of this volume is given. To achieve this, we introduce the notion of the *return radius* $r(t,t_0)$, which is the unique radius of a particle at time t_0 such that this particle has—after growing and shrinking—the same radius at time t. We derive a formula for the return radius, which later on is used to obtain the newly formed volume. Moreover, formulas for the growth rate of the return radius and the recrystallized material at time t_0 are derived.

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I. INTRODUCTION

Recrystallization of minerals is a combination of simultaneous processes of dissolution and precipitation that leads to the formation of larger mineral crystals. The driving force of this coarsening process, so-called Ostwald ripening, where larger particles are growing at the expense of smaller ones, is usually the dependence of the chemical potential at the interface on the grain size.

A prominent example is Ostwald ripening of calcite ($CaCO_3$) in an aqueous solution, which is the subject of a number of experimental investigations; see, e.g., [1–6]. In these experiments, one is interested in the amount of newly formed crystalline material, i.e., the volume of the solid phase present at time t, that has been precipitated from the solution after some time instant $t_0 < t$. Experimental methods tending to determine the newly formed material usually proceed as follows: An isotope of a crystal lattice constituent of the mineral—in the case of calcite ^{45}Ca or ^{14}C—is added as a radioactive tracer to the solution at time t_0. The isotope concentration in the solution is monitored during the experiment. If surface effects and diffusion into the bulk may be neglected, the isotope uptake does grow proportional to the newly formed material.

Surprisingly, there is, to the best of our knowledge, no theoretical investigation of the amount of newly formed material in the literature so far, which would be desirable to confirm the experimental results. This may also be interesting in the case of Ostwald ripening of crystalline particles initially being inhomogeneous in composition, since the newly formed material will be homogeneous.

In this Brief Report, we are going to calculate the newly formed volume theoretically in the late stage of the coarsening process in the setting of the mean field theory due to Lifshitz-Slyozov-Wagner (LSW); see [7,8]. Thus, it is assumed that the grains are spherical particles and the growth kinetics of a grain only depends on its size compared to the size distribution of all particles, and not on the local environment. Moreover, it is assumed that the total volume of the crystallized material is conserved, i.e., large particles grow exclusively at the expense of smaller ones.

For an ensemble of particles with radii $R_i(t_0)$, the newly formed volume $V^{\text{new}}(t,t_0)$ between time t_0 and time t is

$$V^{\text{new}}(t,t_0) = \frac{4}{3}\pi \sum_{i:R_i(t)\geqslant R_i(t_0)} [R_i(t)^3 - R_i(t_0)^3]. \qquad (1)$$

Note that due to the assumption of mass conservation of the solid phase, all of the newly formed crystalline material comes from the dissolution of smaller particles.

Let $R_c(t)$ denote the critical radius, such that at time t precisely, the particles with radius $R(t) > R_c(t)$ are growing. Since in the LSW theory $R_c(t)$ is growing faster than $R(t)$, particles that initially grow start to shrink at later times, and eventually vanish in finite time; see Fig. 1. Thus, there is a unique radius $r = r(t,t_0)$ such that $R_i(t_0) = R_i(t)$ if and only if $R_i(t_0) = r$. We will call this radius r the *return radius*, and $V^{\text{new}}(t,t_0)$ may be expressed as

$$V^{\text{new}}(t,t_0) = \frac{4}{3}\pi \sum_{i:R_i(t)\geqslant r(t,t_0)} [R_i(t)^3 - R_i(t_0)^3]. \qquad (2)$$

It will be shown in Sec. III that the return radius $r(t,t_0)$ is a function of t/t_0 and can be easily computed by inverting an explicitly given function. Moreover, we obtain an analytic expression for the growth rate of $r(t,t_0)$ at $t = t_0$. This will lead, in Sec. IV, to our main result: The volume $V^{\text{new}}(t,t_0)$ or, equivalently, the volume fraction $\Phi^{\text{new}}(t,t_0)$ of the newly formed solid phase within the interval from t_0 to t also depends on t/t_0 and may be calculated by function inversion of the explicitly given expressions. We also give an explicit expression for the initial rate of the formation of new solid material.

II. LSW THEORY

We will shortly review some results of the LSW analysis given in [7,8]; for a more detailed description, see, e.g., [9]. The representation and the notation follow [10], where the two-dimensional case is discussed. The kinetics of Ostwald ripening is governed by two different processes: the mass

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[*] hausser@beuth-hochschule.de

[†] lakshtanov@rambler.ru

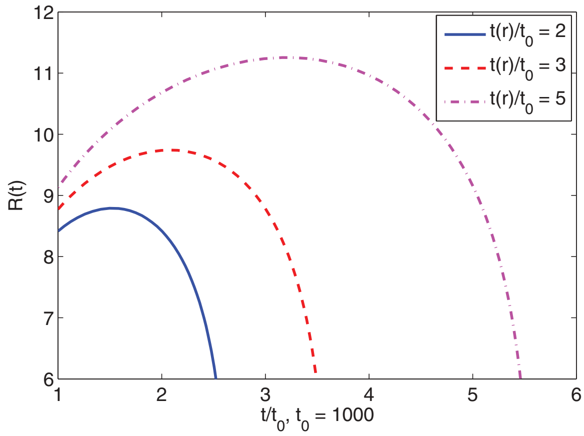

FIG. 1. (Color online) Examples of the time evolution of the radius $R(t)$ of a spherical particle in the LSW theory. For example, the solid blue line indicates that $R(2t_0) = R(t_0)$, i.e., the return time is $t = 2t_0$ and the return radius for $t = 2t_0$ is given by $R(t_0) \approx 8.42$.

transport between the mineral grains via diffusion in the solution and the attachment or detachment process at the grain boundaries. The two limiting kinetic regimes are termed *attachment limited* (AL) growth and *diffusion limited* (DL) growth.

In LSW theory, the ensemble of spherical particles is characterized in terms of a particle radius distribution function, $F(R,t)$, which obeys the continuity equation

$$\partial_t F + \partial_R(\dot{R}F) = 0, \tag{3}$$

since it is assumed that no nucleation and coalescence of particles takes place. Note that the number of particles per unit volume, $n(t) = \int_0^\infty F(R,t)dR$, may only change due to radii decreasing to zero in finite time.

The growth rate $\dot{R}(t)$ of a single particle with radius R is derived from the quasistationary diffusion equation for the solute concentration $c(x,t)$ and the Gibbs-Thomson law for the equilibrium concentration $c_{\mathrm{eq}}(R)$ at the particle surface, $c_{\mathrm{eq}}(R) = c_\infty(1 + l_c/R)$, where c_∞ is the equilibrium concentration at a flat surface and $l_c = 2\gamma V_m/R_gT$ is the capillary length, γ is the interfacial free energy, V_m is the molar volume, T is the temperature, and R_g is the gas constant. Measuring length in units of l_c and time in units of $l_c^2/(Dc_\infty V_m)$ (DL) or $l_c/kc_\infty V_m$ (AL), with diffusion constant D, molar volume V_m, and attachment rate k, one does obtain

$$\dot{R}(t) = \frac{1}{R^\lambda}\left(\frac{R}{R_c} - 1\right), \quad \lambda = \begin{cases} 2 : (\mathrm{DL}) \\ 1 : (\mathrm{AL}) \end{cases}. \tag{4}$$

The critical radius $R_c(t)$ is given in terms of the solute concentration $\bar{c}(t)$ far away from the particle as $R_c(t) = c_\infty/[\bar{c}(t) - c_\infty]$. Introducing the new variables

$$z = \frac{R}{R_c}, \quad \tau = \ln\left[\frac{R_c(t)}{R_c(0)}\right], \tag{5}$$

Eq. (4) becomes

$$\frac{dz}{d\tau} = \nu\,\frac{z-1}{z^\lambda} - z, \tag{6}$$

where ν is a function of the critical radius R_c. Note that $z = 1$ corresponds to the critical radius $R_c(t)$ of a particle, which is neither growing nor shrinking. In the LSW analysis, it is argued that ν becomes constant at late times approaching the unique values [7,8] $\nu = 27/4$ (DL) and $\nu = 4$ (AL). This in turn implies the scaling law

$$R_c(t) = \begin{cases} \left[R_c(0)^3 + \frac{4}{9}t\right]^{1/3} & (\mathrm{DL}) \\ \left[R_c(0)^2 + \frac{1}{2}t\right]^{1/2} & (\mathrm{AL}). \end{cases} \tag{7}$$

Moreover, $z(\tau)$ may be obtained from (6) by inverting the explicit solution of $\tau(z)$ given by

$$\begin{aligned}\tau(z) &= \int \left(\nu\frac{z-1}{z^\lambda} - z\right)^{-1} dz \\ &= \begin{cases} \frac{1}{2z-3} - \frac{4}{9}\ln(z+3) - \frac{5}{9}\ln(3-z) & (\mathrm{DL}) \\ \frac{2}{z-2} - \ln(2-z) & (\mathrm{AL}), \end{cases}\end{aligned} \tag{8}$$

where we have omitted a constant of integration, since later on only differences $\tau(z) - \tau(z_0)$ will be used. Note that the right-hand side of (6) is negative for all $z < z_{\max}$, where

$$z_{\max} = 3/2\,(\mathrm{DL}), \quad z_{\max} = 2\,(\mathrm{AL}), \tag{9}$$

and therefore $z(\tau)$ is decreasing also for particles with $z > 1$, i.e., $R(t) > R_c(t)$.

The continuity equation (3) for $f(z,\tau) = F(R_cz,t(\tau))R_c$ can now be solved by a separation ansatz, $f(z,\tau) = g(\tau)h(z)$, yielding the scaled normalized island size distribution function (see [7,8])

$$h(z) = \begin{cases} 81e2^{-\frac{5}{3}}z^2(z+3)^{-\frac{7}{3}}\left(\frac{3}{2} - z\right)^{-\frac{11}{3}}\exp\left(\frac{-3}{3-2z}\right) : (\mathrm{DL}) \\ 24z(2-z)^{-5}\exp\left(\frac{-3z}{2-z}\right) : \qquad (\mathrm{AL}), \end{cases} \tag{10}$$

with a cutoff of the particle size, $z \leqslant z_{\max}$, and the scaling

$$g(\tau) = g_0\exp(-3\tau) = g_0\frac{R_c(0)^3}{R_c(t)^3}. \tag{11}$$

Using a change of variables, the volume fraction Φ of the solid phase may be written in terms of $g(\tau)$ and $h(z)$ as

$$\begin{aligned}\Phi(0) = \Phi(t) &= \frac{4}{3}\pi\int_0^\infty F(R,t)R^3dR \\ &= \frac{4}{3}\pi g_0 R_c(0)^3\overline{z^3}, \quad \overline{z^3} := \int_0^{z_{\max}} h(x)x^3dx.\end{aligned} \tag{12}$$

Finally, we remark that the critical radius R_c may be expressed in terms of the mean radius $\bar{R}$ as $R_c = \bar{R}$ and $R_c = \frac{9}{8}\bar{R}$ for the DL and the AL ripening, respectively [8].

III. RETURN RADIUS

As has been sketched in Sec. I, to calculate the newly formed volume between time t_0 and time t, we need to calculate what we have called the *return radius* $r = r(t,t_0)$, i.e., the unique radius r such that a particle with radius $R(t_0) = r$ will have the same radius at later time t, $R(t) = r$. In fact, this amounts to solving a boundary value problem for the differential equations (4). We will see, however, that the return radius may be calculated quite easily in the asymptotic regime of LSW, i.e., for t_0 large enough, without explicitly solving the boundary value problem.

We will use the rescaled coordinates z,τ as introduced in (5). First note that in the rescaled coordinate z, the return radius r does take two different values at time t_0 and at time t, namely, $z(t_0,r)$ and $z(t,r)$. We will use the notation $\tau_0 = \tau(t_0)$, $\tau = \tau(t)$, $z_0 = z(\tau_0) = z(t_0,r)$, and $z = z(\tau) = z(t,r)$. From (5) follows that r being the return radius is equivalent to

$$\ln z - \ln z_0 = \tau_0 - \tau. \tag{13}$$

Moreover, the scaling law (7) implies

$$\frac{z}{z_0} = \frac{z(t,r)}{z(t_0,r)} = \frac{R_c(t_0)}{R_c(t)} = \left(\frac{t_0}{t}\right)^{1/\gamma}, \tag{14}$$

for $t,t_0 \gg R_c(0)^\gamma$, where $\gamma = 3$ (DL) and $\gamma = 2$ (AL). Note that this condition is valid in good approximation, as soon as the average radius $\overline{R}$ at time t, t_0 is at least twice or triple the size of the average radius at time $t = 0$ for DL or AL ripening, respectively. This can be realized in ripening experiments; see, e.g., [11].

The two identities (13) and (14) uniquely fix the return radius $r = r(t,t_0)$, which may be calculated as follows. Since the time dependence of the rescaled radius $z = z(\tau)$ is given by Eq. (6), we use the explicit solution of $\tau(z)$ given in (8) to express (13) as

$$\alpha(z) = \alpha(z_0), \quad \text{with } \alpha(x) = \ln x + \tau(x). \tag{15}$$

Since the return radius has to be larger than the rescaled radius, $r \geqslant R_c(t_0)$, we may assume $z_0 = z(t_0,r) \geqslant 1$. One easily checks that

$$\alpha'(z) \begin{cases} > 0 : z \in (0,1) \\ = 0 : z = 1 \\ < 0 : z \in (1,z_{\max}), \end{cases}$$

and

$$\lim_{z\to 0} \alpha(z) = \lim_{z\to z_{\max}} \alpha(z) = -\infty.$$

Thus, Eq. (15) allows for a unique solution for $z_0 \in [1,z_{\max})$. Denoting this inverse of α on $(-\infty,\alpha(1)]$ by ψ, we may express $z = z(t,r)$ as a function $z = \rho(z_0)$,

$$\begin{aligned} \rho : [1,z_{\max}] \to [0,1], \quad & \rho(z_0) := \psi[\alpha(z_0)], \\ z_0 \in (1,z_{\max}), \quad & \rho(1) = 1, \quad \rho(z_{\max}) = 0. \end{aligned} \tag{16}$$

This function is easily evaluated numerically, e.g., using bisection, and depicted in Fig. 2(b).

Now we may calculate the return time $t(r)$ for any initial radius r, i.e., the time t, such that $R(t) = R(t_0) = r$. By Eq. (14), we have

$$t(r) = t_0 \left[\frac{z_0}{\rho(z_0)}\right]^\gamma, \quad z_0 = r/R_c(t_0). \tag{17}$$

Inverting $t = t(r)$ in (17) numerically yields the return radius $r(t)$. We point out that according to (17), the return radius $r(t,t_0)$ is a function of t/t_0. As it will turn out in the next section, we only need the pair z_0, $\rho(z_0)$ in order to calculate the amount of material which has been produced by recrystallization. Let us finally calculate the growth rate $\dot{r}(t)$ of the return radius at time $t = t_0$. Using (17), we get

$$\dot{r}(t) = \left[\frac{d}{dr}t(r)\right]^{-1} = \left(\frac{dt}{dz_0}\right)^{-1} R_c(t_0),$$

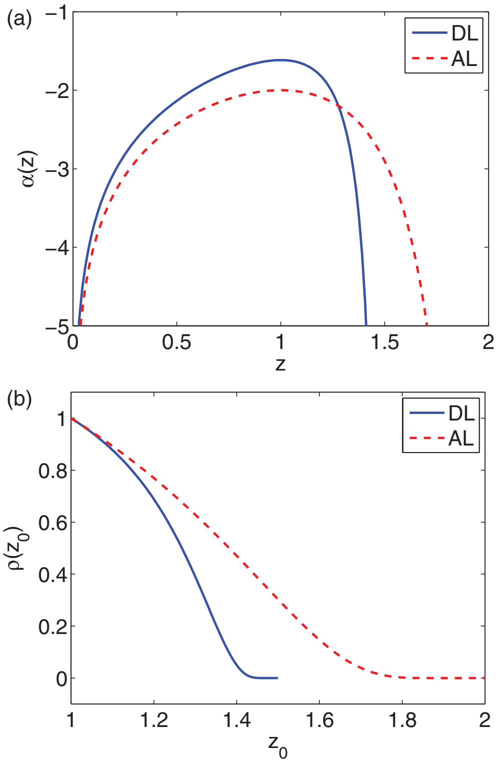

FIG. 2. (Color online) (a) The function $\alpha(z) = \ln z + \tau(z)$ in (15) has a unique maximum at $z = 1$. Choosing $z_0 > 1$, there is a unique $z := \rho(z_0) < 1$ with $\alpha(z) = \alpha(z_0)$. (b) The function ρ has been evaluated numerically using bisection.

and Eq. (17) gives

$$\frac{dt}{dz_0} = t_0\gamma \left[\frac{z_0}{\rho(z_0)}\right]^{\gamma-1} \frac{\rho(z_0) - z_0\rho'(z_0)}{\rho(z_0)^2}. \tag{18}$$

To proceed further, the derivative of $\rho(z_0)$ defined in (16) is needed at $z_0 = 1$. Since $\alpha'(1) = 0$, $\alpha''(1) \neq 0$, we have

$$\rho(1+h) = 1 - h + O(h^2), \quad \text{i.e., } \rho'(1) = -1. \tag{19}$$

Evaluating (18) at $z_0 = 1$ and using $\rho(1) = 1$ yields

$$\left.\frac{dt}{dz_0}\right|_{z_0=1} = 2\gamma t_0 \quad \text{and} \quad \dot{r}(t_0) = \frac{R_c(t_0)}{2\gamma t_0}. \tag{20}$$

IV. VOLUME FRACTION OF RECRYSTALLIZED MATERIAL

Now let $\Phi^{\text{new}}(t,t_0)$ denote the newly formed volume $V_{\text{new}}(t,t_0)$ per unit volume, i.e., the volume fraction of that part of the solid phase at time t that was produced between time t_0

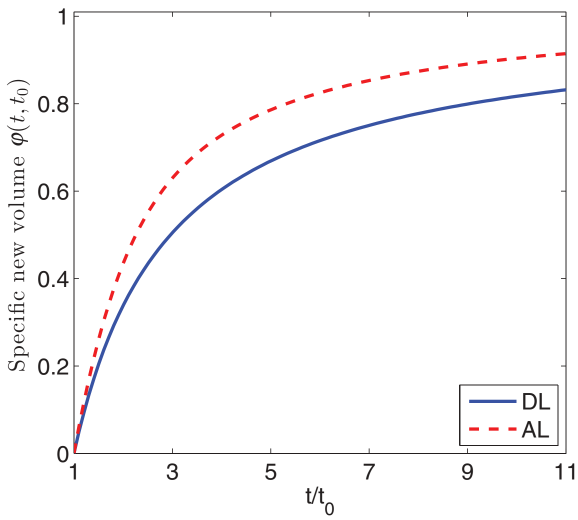

FIG. 3. (Color online) Specific volume $\varphi(t,t_0)$ of recrystallized material from time t_0 to time t over normalized time t/t_0, as defined in (23).

and time t through recrystallization. Only those particles that have grown between t_0 and t, i.e., $R(t) \geqslant R(t_0)$, contribute, which are precisely the ones for which $R(t)$ is larger than the return radius $r = r(t,t_0)$, or, equivalently, $R(t_0) > r$. In terms of $F(R,t)$, we get, as in Eq. (2),

$$\Phi^{\text{new}}(t,t_0) = \frac{4}{3}\pi\left[\int_r^\infty F(R,t)R^3 dR - \int_r^\infty F(R,t_0)R^3 dR\right]. \tag{21}$$

Assuming the LSW theory to be valid, we may express $F(R,t)$ and $F(R,t_0)$ in terms of $f(z,\tau) = g(\tau)h(z)$ and $f(z,\tau_0) = g(\tau_0)h(z)$, respectively, as given in (10) and (11). Since $F(R,t) = f(z,\tau)/R_c(t)$, a change of variables in (21) leads to

$$\Phi^{\text{new}}(t,t_0) = \frac{4}{3}\pi g_0 R_c(0)^3 \int_{z(t,r)}^{z(t_0,r)} h(x)x^3 dx, \tag{22}$$

where the return radius $r = r(t,t_0)$ may be calculated from Eq. (17), as described in the last section. In fact, it is sufficient to solve for $z_0 = z(t_0,r)$ in order to evaluate (22), i.e., to invert the function $t = t(z_0)$ in (17), and to calculate $z(t,r) = \rho(z_0)$; see Eq. (16).

Thus, with Eq. (12), the percentage of the volume of the solid phase at time t that has been produced by recrystallization between time t_0 and time t is given by

$$\varphi(t,t_0) := \Phi^{\text{new}}(t,t_0)/\Phi = \frac{1}{\overline{z^3}} \int_{\rho(z_0)}^{z_0} h(x)x^3 dx, \tag{23}$$

and may be easily computed by determining $z_0 = z(t_0,r)$ and $\rho(z_0) = z(t,r)$ as described in Sec. III and using numerical quadrature. Again, we point out that $\varphi(t,t_0)$ may be expressed as a function of t/t_0, since $r(t,t_0)$ depends on t/t_0 only.

In Fig. 3, the specific produced volume $\varphi(t,t_0)$ is depicted over the normalized time $s := t/t_0$. As expected from (23), we observe that $\varphi(s)$ approaches the value $\varphi = 1$ for $s \to \infty$. Moreover, the growth of the recrystallized volume is nearly linear up to the value $\varphi(s) \approx 1/4$. The growth rate of $\varphi(t,t_0)$ at time $t = t_0$ may be calculated using Eqs. (19) and (20) as follows:

$$\begin{aligned}
&\overline{z^3}\,\frac{d}{dt}\varphi(t,t_0)\bigg|_{t=t_0}\\
&\quad= \frac{d}{dz_0}\int_{\rho(z_0)}^{z_0} h(x)x^3\,dx\bigg|_{z_0=1}\frac{d}{dt}z_0(t)\bigg|_{t=t_0}\\
&\quad= \left\{(h(z_0) - h[\rho(z_0)]\frac{d}{dz_0}\rho(z_0)\right\}\bigg|_{z_0=1}\frac{1}{2\gamma t_0} = \frac{h(1)}{\gamma t_0}.
\end{aligned} \tag{24}$$

Here, in the last equality, we have again used that $\rho(1) = 1$ and $\rho'(1) = -1$; see Sec. III. Using (24) and (10), we obtain the numerical values

$$\frac{d}{dt}\varphi(t,t_0)\bigg|_{t=t_0} = \frac{h(1)}{\gamma t_0\,\overline{z^3}} \approx \begin{cases} 0.51/t_0 : \text{(DL)} \\ 0.62/t_0 : \text{(AL)} \end{cases}. \tag{25}$$

V. CONCLUSIONS AND OUTLOOK

Besides being able to quantitatively calculate the newly formed volume by turning back to dimensional units, we may draw some further qualitative conclusions. By (14) and the last remark in Sec. II, the quotient t/t_0 may be expressed in terms of the length scale of the coarsening system given by the average particle radius $\bar{R}$ as $t/t_0 = [\bar{R}(t)/\bar{R}(t_0)]^\gamma$. Thus, we can see from Fig. 3 that more than two-thirds of the solid material is newly formed, if the average radius has doubled from t_0 to t.

In a forthcoming paper, we plan to apply our findings to the isotope uptake during Ostwald ripening. Here one also has to account for the adsorption of the tracer material at the surface of the solid phase and therefore the change of surface area during ripening may play a role. Moreover, a generalization to the case of large volume fractions, where the LSW theory is not valid, needs further investigation.

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