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Early stages of Ostwald ripening

Vitaly A. Shneidman
Department of Physics, New Jersey Institute of Technology, Newark, New Jersey 07102, USA
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The Becker-Döring (BD) nucleation equation is known to predict a narrow double-exponential front (DEF) in the distribution of growing particles over sizes, which is due to early transient effects. When mass conservation is included, nucleation is eventually exhausted while independent growth is replaced by ripening. Despite the enormous difference in the associated time scales, and the resulting demand on numerics, within the generalized BD model the early DEF is shown to be crucial for the selection of the unique self-similar Lifshitz-Slyozov-Wagner asymptotic regime. Being preserved till the latest stages of growth, the DEF provides a universal part of the initial conditions for the ripening problem, regardless of the mass exchange mechanism between the nucleus and the matrix.

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In 1958 Lifshitz and Slyozov (LS) wrote one of the most influential papers on phase transformation kinetics [1]. When considering diffusion-limited growth of grains in supersaturated solid solutions, they showed that asymptotically the distribution over sizes tends to a self-similar universal shape, while the critical, average, and maximum sizes all change as a cubic root of time (the $t^{1/3}$ law). In sequel Refs. [2,3] it was further demonstrated that these results were extremely robust, and remained valid even if elastic stress, anisotropy, and other effects were taken into consideration. Shortly after, Wagner [4] described a similar scenario for the ballistic (interface-limited) growth, with characteristic sizes changing as $t^{1/2}$. Since then, the LSW theory of "ripening" (i.e., growth of large particles at the expense of small ones) was applied to an enormous variety of problems in condensed matter physics and materials science [5,6].

The nonlinear integro-differential equations describing ripening also received much attention in mathematical literature [7–11]. In particular, it was shown [8] that at large times these equations follow as a deterministic limit of the Becker-Döring nucleation equation (BDE) combined with a mass conservation law. Other self-similar solutions have been constructed for the ripening equations (e.g., Ref. [8]), and the formal extreme sensitivity to initial conditions (IC), labeled as "mathematical chaos" [9], was demonstrated both analytically and numerically [12]. Despite the resulting "selection dilemma" (e.g., [9,13–15]), the current consensus is that there is no realistic alternative to the classical LSW limit. One needs, however, to identify adequate *physical* IC for the ripening equations. Such IC are supplied by the generalized BDE, yet so far a transition to the LSW asymptotic regime starting from proper nucleation distributions has not been observed.

From an experimental point, the unknown sensitivity to IC can be especially detrimental. While ripening particles are typically large and can be detected by conventional optical methods, it remains unclear how the elusive information about earlier stages can be reliably extracted from such observations. For example, in many applied papers the $t^{1/3}$ law is modified as $a_*(t)^3 \approx a_*(0)^3 + \text{const.} \times t$ and used to assess the nucleation critical radius $a_*(0)$, which is incorrect. Numerical description (e.g., [12,16], and references therein) can be only of limited assistance here since while direct solutions of the BDE on the nucleation stage are straightforward [17,18], the ripening equations require much larger, often unknown time scales and need additional analytical insight. Still less is known about the deviation from the LSW limiting values of the key ripening parameters, such as γ, the dimensionless time derivative of the critical size (see the definition below). The original suggestion [3,19] that for noncompact IC the limit is approached from *above* has not been tested, and is in contradiction with observations of the present Rapid Communication, albeit for rather different IC.

In the initial, fluctuational stage of a phase transformation one can single out the "fast" and "slow" stages. During the fast stage transient nucleation takes place and the quasi-steady-state (QSS) or the "Zeldovich" [20] nucleation rate J is established. During the slow stage the metastable phase gets depleted by growing particles of the new one, and J gradually vanishes, indicating the end of nucleation. The fast stage can be described from the matched asymptotic solution of the BDE [21,22], which leads to a characteristic double-exponential "front" (DEF) in the distribution of the largest particles. In principle, those particles should eventually determine the peculiarities of the transition to the LSW asymptotic regime [21], although the actual path to the latter was not elucidated. Also, it remained unclear what happens if the transient stage is neglected. In a recent Ref. [23] it was demonstrated that the LSW regime will *never* be established starting from the slow stage alone due to discontinuity of the QSS distribution. General nucleation distributions, which combine both the fast and slow stages and which have no discontinuity, were constructed in Ref. [24]. In the present communication these distributions are used as the IC for growth and ripening, and they are sufficient for subsequent convergence to the LSW limit. Numerics is similar to the growth part of the earlier scheme [24], with an additional "ripening" feature: Particles with subzero sizes are removed. The initial number of representative sizes is chosen around $N \sim 5 \times 10^3$, with about half of this value assigned to the DEF, which replaces the QSS discontinuity. Typically, a simulation is stopped for $N \lesssim 100$.

Main notations will be close to standard [19], with γ being the inverse of the one used in the textbook. Consider deterministic growth of particles of radius a: $\dot{a} = \lambda a_* u^{-\theta}(1 - 1/u)$,

with $u \equiv a/a_*$, $\lambda \propto a_*^{-\theta-2}$, and $\theta = 0, 1$ corresponding to interface- and diffusion-limited growth, respectively. (The case $\theta = -1$ with *linear* growth is special [25] and will not be discussed here.) Furthermore, let us redefine the "time" to have the growth law as

$$a_*\dot{u} = u^{-\theta}(1 - 1/u) - \gamma u\,, \quad \gamma \equiv \dot{a}_*\,. \tag{1}$$

With the new definition $a_*(t)$ becomes *linear* in the LSW limit, and a uniform time step can be used in numerical integration. The distribution $f(a,t)$ follows the continuity equation $\partial f/\partial t + \partial/\partial a\,(\dot{a} f) = 0$, and will be represented as $\Omega_0(t)P(u,t)$ with a normalized P and with $\Omega_k \equiv \int_0^\infty a^k f(a,t)\,da$. The conservation law is written as $1/a_* \propto \text{const.} - \Omega_3$ with $\text{const.} = (S_0 - 1)/S_0$, the initial supersaturation, to comply with notations of Ref. [24].

For a self-similar distribution $P(u,t) = P(u)$ the continuity equation requires $\gamma = \text{const.}$, while the conservation law leads to a time-independent product $\Omega_0 a_*^3$. One thus has $a_* = \gamma t$, $\Omega_0 \propto 1/t^3$, and

$$P_\gamma(u) = \frac{3\gamma}{-a_*\dot{u}} \exp[3\gamma\tau(u)]\,\Theta(u_1 - u)\,,$$
$$\tau(u) = \int_0^u \frac{du'}{a_*\dot{u}'}, \tag{2}$$

where u_1 is the smaller positive root of $\dot{u}$, with $\tau(u_1) = -\infty$. This is in general agreement with previous studies mentioned in the Introduction. The explicit Θ function is useful for further construction of a non-self-similar approximation. The LSW case corresponds to $\gamma = \gamma_{\max}$ when the two roots coalesce, with $\gamma_{\max} = 1/4$ or $4/27$ for $\theta = 0$ or 1, and the distributions given by $P^0_{1/4}(u) = 24u\exp[3 - 6/(2-u)]\,(2-u)^{-5}$ and $P^1_{4/27} = 324u^2\exp[1 - 3/(3-2u)]\,(3-2u)^{-11/3}(3+u)^{-7/3}$.

In case of $\gamma < \gamma_{\max}$ in Eq. (2), the singularity in the pre-exponential at $u \to u_1$ can be compensated by the divergence of $\tau(u)$ only for $\gamma \geqslant \gamma_{\min}$ with $\gamma_{\min} = 4/25$ and $25/216$ for $\theta = 0, 1$ (and outside of the interval $[\gamma_{\min}, \gamma_{\max}]$ a physically reasonable self-similar solution does not exist). For $\gamma = \gamma_{\min}$ the distributions are discontinuous:

$$P^0_{4/25}(u) = 1500u(5-u)^{-5}\Theta(5/4 - u) \tag{3}$$

and

$$P^1_{25/216}(u) = \frac{16200u^2}{(36 - 6u - 5u^2)^3}\left(\frac{12 + (\sqrt{21} - 1)u}{12 - (\sqrt{21} + 1)u}\right)^{\sqrt{3/7}}$$
$$\times\,\Theta\left(\frac{6}{5} - u\right). \tag{4}$$

Except for normalization constant and the theta function, the second equation ($\theta = 1$) is equivalent to a combination of exponential and inverse hyperbolic functions of Ref. [23].

We are now interested in whether and how fast the distributions discussed above are established. The dimensionless input parameters are the nucleation barrier $B \gg 1$, which determines the exponential part of the initial QSS rate $J \propto \lambda\exp(-B)$, and the initial "critical radius" (cubic root of the number of monomers in a nucleus) $a_*^0 \gg B^{1/3}$, with supersaturation $S \simeq 1 + 2B/a_*^3$. The characteristic nucleation physical time is $\tilde{t} \propto (J_0)^{-1/\alpha} \gg 1/\lambda$ with $\alpha = (\theta+4)/(\theta+1)$ and with

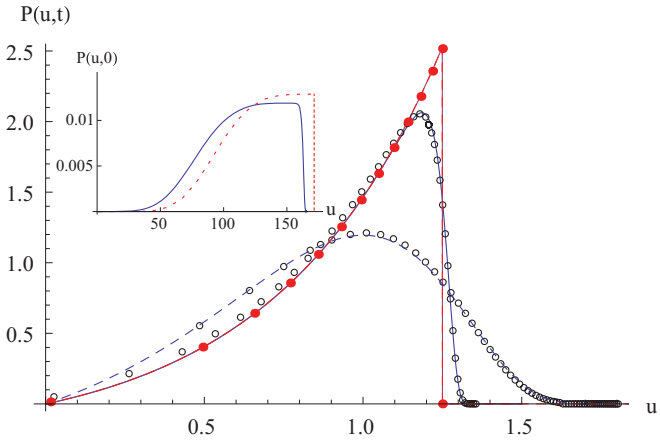

FIG. 1. (Color online) Selection between the LSW distribution (lower bell-shaped dashed curve) and the discontinuous distribution, Eq. (3) (sharply peaked solid line). Initial conditions (IC) for growth and ripening (inset) are either QSS (dotted) or with transient nucleation (line). The distribution with QSS IC is shown at $t = 200\,000$ by solid symbols, closely approaching the discontinuous curve. With transient IC (open symbols), the smoothed distribution given by Eqs. (3), (6) is initially approached (middle line at $t = 80\,000$); later the distribution broadens (shown at $t = 800\,000$) and practically blends in with the LSW curve.

$\Omega_0 \sim J_0\tilde{t}$. The post-nucleation distributions [24] depend on the time $t_n \gtrsim \tilde{t}$ during which the system is allowed to nucleate, and with selected $a_*^0 = 6$, $t_n = 2\tilde{t}$ are shown in the insets in Figs. 1 and 2 for $\theta = 0$ ($B = 32.5$) and $\theta = 1$ ($B = 30$), respectively. These distributions are confined between some $a^0_{\min} \gtrsim a_*^0$ and $a^0_{\max} \gg a_*^0$. The value of t_n which affects both $a^0_{\min}$ and $a^0_{\max}$ should be selected before a_* changes significantly, but otherwise t_n only shifts the "ripening time" t (which, in the current definition, starts from zero once the nucleation is over). Similarly, the structure of the initial distribution of small

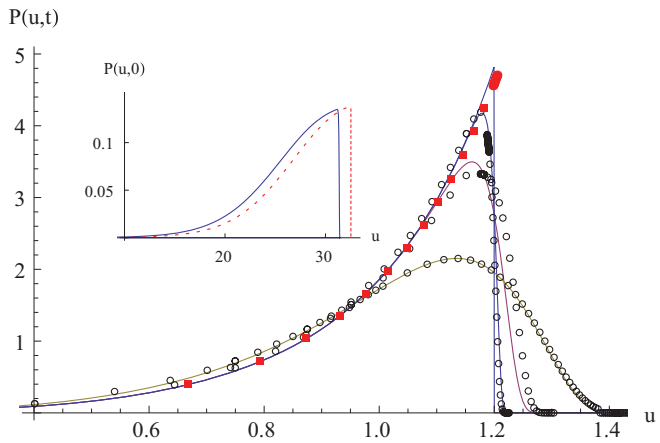

FIG. 2. (Color online) Same as in Fig. 1 but for diffusion-limited growth. The discontinuous distribution is Eq. (4) (solid line); it is approached starting from QSS initial conditions (solid symbols, at $t = 1\,500\,000$). The distributions from non-QSS IC are shown by open symbols. At early ripening times they are approximated by Eqs. (4), (6) (smooth tall and intermediate solid lines, at $t = 1\,500\,000$ and $t = 1\,550\,000$, respectively). At $t = 3\,000\,000$ the LSW shape (lower line) is approached.

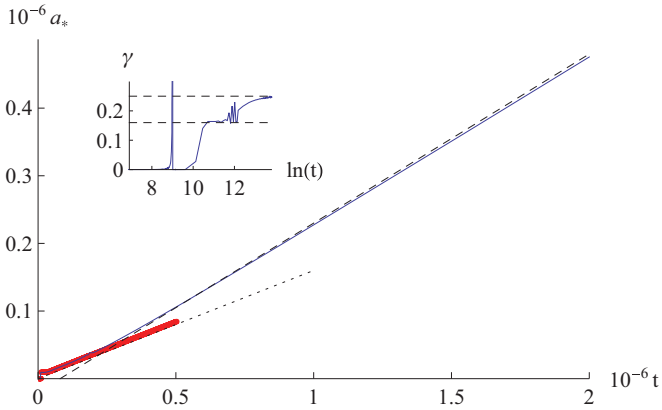

FIG. 3. (Color online) Time dependence of the critical size (main panel) and its derivative γ (inset) in the ballistic case. Main panel: Symbols (thick line), with QSS IC; thin solid line, with transient nucleation IC. Dashed straight line has the LSW slope $\gamma = 1/4$; dotted straight line has $\gamma = 4/25$, as for the discontinuous distribution. Inset: Horizontal dashed lines, $\gamma_{\min} = 4/25$ and $\gamma_{\max} = 1/4$; solid line, numerical γ, averaged over a number of steps (with transient nucleation IC). A sharp peak at $t \sim 10^4$ indicates the end of growth and the onset of pre-ripening.

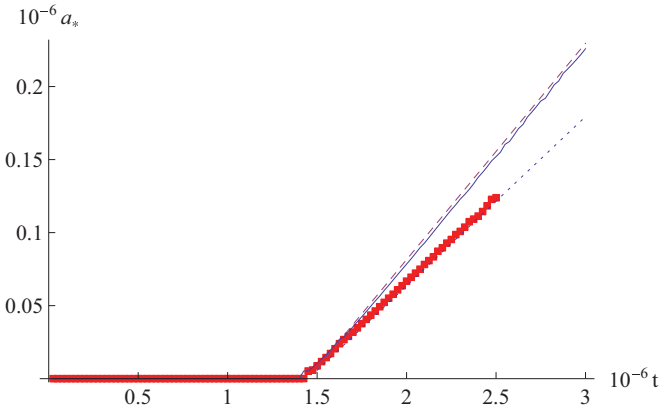

FIG. 4. (Color online) The diffusion case; lines and symbols as in Fig. 3. The dashed and the dotted straight lines have slopes $\gamma = 4/27$ and $\gamma = 25/216$, respectively.

particles is expected to have only a quantitative effect on the delay of ripening, which, however, will crucially depend on the distribution in the vicinity of the front. The latter can be defined as a size a_f^0, close to $a_{\max}^0$, where the distribution abruptly drops to $1/e$ of its "smooth" value. Here the distribution has a near-universal shape

$$f(\rho,0) \simeq A(\rho)\exp(-e^{\rho}),\ \rho \simeq \frac{a-a_f^0}{a_*^0}\left(\frac{a}{a_*^0}\right)^{\theta}, \qquad (5)$$

where $A(\rho)$ [24] is a slowly changing function (otherwise, the explicit analytical form of $A(\rho)$ is unimportant for the present study and can be treated just as a time-saving alternative to direct numerical solution of the BDE [24]). In the u variables the front is exceptionally narrow (see the insets in Figs. 1 and 2), but it is this double-exponential transient front (DEF) which eventually selects the true LSW ripening regime, as shown in the main panels.

The importance of early transient nucleation is also clear from the late time dependence of the critical size, as in Figs. 3 and 4. Ignoring the DEF leads to non-LSW slopes of $\gamma \simeq \gamma_{\min}$ (dotted lines in both figures), instead of the proper values of $\gamma = \gamma_{\max}$.

In intermediate evolution of the distribution one can single out several stages. At first, the depletion effects are minor, and the characteristic median size $\bar{a}$ is much larger than $a_*(t) \simeq a_*^0$. The growth law can be approximated as $\dot{\bar{a}} \approx (a_*^0/\bar{a})^{\theta}$, valid during $t_{gr} \sim a_*^0[1/a_*^0((S_0-1)/(S_0\Omega_0^0))^{1/3}]^{\theta+1}/(\theta+1)$. The values of γ are extremely small here. Next, due to depletion $a_*(t)$ catches up with $\bar{a}$ with a value $a_*^+ \sim t_{gr} \simeq 8.9\times 10^3$ for $\theta = 0$, which can be examined in somewhat more detail. The change in a_* happens fast, leading to a sharp peak in $\gamma(t)$, as in the inset of Fig. 3. An estimation gives $(4/9)a_*^+/a_*^0 \sim 10^3$ for the height of the peak.

The subsequent interval with a_* remaining close to a_*^+ can be called *pre-ripening*, which continues as long as the smallest particles remain in the system. Here both moments Ω_0 and Ω_3 are conserved. From the condition $a_{\min}(t) = 0$ one has the duration of pre-ripening: $\Delta t = a_*^+ B_x(2+\theta,0)$ with $x = a_{\min}(t_{gr})/a_*^+$ and $B_x(a,b)$ being the incomplete beta function with a logarithmic asymptote for $x \to 1$. The value of x can be estimated from $\bar{a}(t) - a_{\min}(t) \approx [(\theta+1)t/a_*^0]^{-\theta/\theta+1}(\bar{a}^0/a_*^0)^{\theta}(\bar{a}^0 - a_{\min}^0)$ with $\bar{a}(t_{gr}) \simeq a_*^+$. Transition from growth to pre-ripening resembles the one in a nucleation pulse [26] where the critical size undergoes a similar abrupt increase between two near-constant values. In the case $\theta = 0$ this allows one to approximate the distribution analytically in terms of a Lambert W function. With current parameters, such an approximation can be shown to be reasonably accurate for $t_{gr} < t \lesssim 25000$, and at this stage there yet is no visible difference between distributions due to either the QSS or the transient nucleation IC.

The first self-similar solution is approached when γ increases close to $\gamma_{\min}$, although precise identification of γ was hard to achieve due to observed oscillations. Those distributions, however, still contain a non-self-similar part due to the front which cannot be treated as infinitely thin anymore, and which keeps spreading with a rate determined by $\lambda^f = \frac{\partial}{\partial u}\dot{u}$ at $u \simeq u_1(\gamma_{\min})$. As long as the spread remains small, the shape of the front is close to double exponential. This suggests using the discontinuous self-similar solution with the Θ function smoothed in accord with

$$\Theta(u_1-u) \to \exp\left[-\exp\left(\frac{u-u_1}{\delta(t)} - C\right)\right],$$
$$C = 0.5772\ldots \qquad (6)$$

[the Euler constant C preserves normalization of $P_\gamma(u)$ in the leading order in δ]. As seen from Figs. 1 and 2 accuracy of such an approximation can be quite reasonable; the value of $\delta(t)$ was evaluated numerically by tracking the difference between a^f and $a^f + a_*\delta(t)$ with $\delta(0) = [a_*^0/a^f(0)]^{\theta}$ to comply with the initial front width in Eq. (5). Since λ^f is inversely proportional to a_*, at the initial stages of ripening δ should approach a power law. Numerics seems to confirm this, especially in the ballistic case with a power index slightly less than 2.

Once the double-exponential front (DEF) spreads enough to violate the condition $\delta(t) \ll 1$, the distribution gradually evolves towards the LSW limit; γ also increases towards $\gamma_{\max}$, although not quite monotonically, as mentioned above. However, since typical t are large and the "physical time" is proportional to t^2 or t^3 for $\theta = 0$ or 1, in practice the LSW limit can be nonrealizable for sufficiently high nucleation barriers. This increases the potential role of other self-similar solutions $P_\gamma(u)$ in Eq. (2) evaluated for current (numerical) values of γ. For a distribution approximated by a histogram at N representative sizes u_i, one can define an "error" of a given analytical approximation: $E = \frac{1}{N}\sum_{i=1}^{N}[P^{an}(u_i) - P^{num}(u_i)]^2$. Once fluctuations in γ are over (see the inset of Fig. 3) this error is typically almost one order of magnitude smaller for P_γ than for the LSW distribution with $\gamma = \gamma_{\max} = 1/4$ (in the diffusion-limited case fluctuations in γ are much larger, which prevented a similar comparison).

Finally, one should mention that the DEF can be not the only reason for selection of the LSW regime, which can emerge from a variety of smooth IC. Nevertheless, the DEF appears to remain crucial for such selection if one remains within the generalized Becker-Döring scheme, starting from a "pure" metastable system and avoiding any external intervention such as injection of particles or control of parameters. In principle, fluctuations which are an inherent part of the BDE can provide additional spreading by adding a diffusion-like term $-D\partial f/\partial a$ to the flux in the size space, with $D(a) \propto (a/a_*)^{-\theta-2}$. At the early stage fluctuations are crucial for nucleation and are responsible for the formation of DEF [21], but generally they should be of minor effect during growth (small D) and ripening (small $\partial f/\partial a$). In a numerical study [27], which started from rather broad IC, no accelerated transition to LSW regime due to fluctuations was observed. However, in view of the exceptionally narrow initial DEF and the large time scales before the LSW regime is approached, additional studies are required here, especially for $\theta = 1$. Other types of fluctuations, which are beyond the BDE, also can drive the system towards the LSW regime [11,13,14] but the effect of those fluctuations on nucleation still needs to be investigated.

In summary, during a brief initial period at the start of a phase transformation the distribution of largest particles acquires a double-exponential front (DEF) which is due to transient nucleation. When used as initial conditions (IC) for subsequent growth and ripening in an isolated system, as in the present study, the distribution undergoes a series of distinct transformations with the last stage—the LSW asymptotic regime—being selected exclusively due to the initial DEF.

At the very beginning of ripening the distribution is close to a discontinuous non-LSW solution, analogous to the one established in neglect of transient effects [23], but with the discontinuity smoothed out by a double-exponential in a non-self-similar manner, as in Eq. (6). Such a distribution, with the width δ determined by preceding stages, can serve as semi-universal IC for the late-stage ripening problem regardless of the type of mass exchange (the value of θ) between the nucleus and the matrix. Due to rapid decay with size this IC appears to defy the standard mathematical classification of "compact" or "noncompact."

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