Fluctuations provide strong selection in Ostwald ripening

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A selection problem that appears in the Lifshitz-Slyozov (LS) theory of Ostwald ripening is reexamined. The problem concerns selection of a self-similar distribution function (DF) of the minority domains with respect to their sizes from a whole one-parameter family of solutions. A strong selection rule is found via an account of fluctuations. Fluctuations produce an infinite tail in the DF and drive the DF towards the ''limiting solution'' of LS or its analogs for other growth mechanisms. [S1063-651X(99)02709-9]

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Ostwald ripening (OR) [1] is a fascinating and generic process of self-organization in a physical system far from equilibrium. It develops in a late stage of a first-order phase transition, in two or three dimensions, when a two-phase mixture undergoes coarsening and the interfacial energy decreases subject to a global conservation law [2,3]. OR continues to attract considerable attention both in experiment [4] and in theory [5–9]. For a nonlinear physicist, the problem of OR is of great interest because of a long-standing selection problem [2,6–9] addressed below.

Lifshitz and Slyozov (LS) [2] and Wagner [3] developed a mean-field formulation of OR, valid in the limit of a negligibly small volume fraction of the minority domains. In this formulation, the dynamics of the distribution function (DF) $F(R,t)$ of the minority domain sizes are governed (in scaled variables) by a continuity equation,

$$\frac{\partial F}{\partial t}+\frac{\partial}{\partial R}(VF)=0, \quad V(R,t)=\frac{1}{R^n}\left(\frac{1}{R_c}-\frac{1}{R}\right), \tag{1}$$

where $R_c(t)$ is the critical radius for expansion/shrinkage of an individual domain, while n is determined by the growth mechanism. (For a review of different growth mechanisms see Refs. [10]. Most known are diffusion-controlled growth, $n=1$, and interface-controlled growth, $n=0$.) The dynamics are constrained by conservation of the total mass (or volume) of the minority domains:

$$\int_0^\infty R^3 F(R,t)\,dR=Q=\text{const}. \tag{2}$$

Scaling analysis of Eqs. (1) and (2) yields a similarity ansatz $F(R,t)=t^{-4/z}\Phi(Rt^{-1/z})$ and $R_c=(t/\sigma)^{1/z}$, where $z=n+2$ and $\sigma=$const. Upon substitution, one obtains a *family* of self-similar DFs (formally, for every $n\geqslant -1$). Each of the DFs is localized on a finite interval $[0,u_m]$ of the similarity variable $u=Rt^{-1/z}$. The self-similar DFs can be parametrized by σ, and there is a finite interval of allowed values of the scaled coefficient σ. For each solution, the average domain radius and the critical radius grow in time like $t^{1/z}$, while the concentration of domains decreases like $t^{-3/z}$. However, the *coefficients* in these scaling laws are σ-dependent. The scaling function $\Phi(\xi)$ has a markedly different shape depending on the value of σ. It should be stressed that the problem of OR, as described by Eqs. (1) and (2), is fully determined (of course, if one prescribes an initial condition). Therefore, the scaled coefficient σ is an observable quantity. It can be determined in a direct experiment or simulation by measuring, at large times, the *coefficient* in the power law for the critical radius R_c versus time. The reader is referred to Ref. [9] for a detailed description of the family of self-similar DFs for different values of n.

An important selection problem therefore arises. It has a long history [2,6–9], and its present status is as follows. There is only a ''weak'' selection within the framework of the ''classical'' model (1) and (2). The ''weak'' selection rule, obtained recently [8,9], is the following. If the initial DF $F(R,0)$ has a compact support $(0,R_m)$ and is describable by a power law $A(R_m-R)^\lambda$ in the close vicinity of $R=R_m$, then it is the exponent λ that selects the correct self-similar asymptotic DF. The selected value of parameter σ is

$$\sigma=\frac{v_0^{n+2}}{(n+2)(v_0-1)}, \tag{3}$$

where

$$v_0=\frac{(n+2)\lambda+n+5}{(n+1)\lambda+n+4} \tag{4}$$

(see Ref. [9] for details). The celebrated ''limiting'' DFs obtained by LS [2] for $n=1$, and by Wagner [3] for $n=0$, correspond to *extended* initial DFs or, formally, to $\lambda\to+\infty$. In this case Eqs. (3) and (4) yield the well-known ''universal'' value $\sigma=9/4$ for the diffusion-controlled OR, $n=1$, found by LS [2]. On the contrary, as it is clear from Eqs. (3) and (4), for initial DFs with compact support and finite λ, different values of the scaled coefficient σ are obtained. Finally, for those initial DFs with compact support that cannot be described by a power-law asymptotics near $R=R_m$, convergence to *any* self-similar solution is impossible [11]. A rigorous mathematical proof of these results is presently available [11].

It has become clear after the analyses of Refs. [8,9,11] that in order to get strong selection, one must go beyond the ''classical'' model. In the present paper I report on progress

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in this direction. Here is an outline. I will employ a mean-field cluster formulation of the problem and proceed to the long-time limit, when only large clusters and single atoms dominate. Using the characteristic inverse number of atoms in a cluster as a small parameter, I will arrive at a Fokker-Planck (FP) equation for the cluster size distribution function. The drift term of the FP equation describes growth/shrinkage of clusters due to an interplay between attachments and detachments of single atoms, and it corresponds to the ''classical'' LS theory. The diffusion term of the FP equation accounts for fluctuations, and it is not present in the LS theory. This term becomes irrelevant at long times, however it can play a very important role. Indeed, even if the initial DF has compact support, the diffusion term produces an infinite tail in the DF. As a result, the DF will finally approach the limiting solution of LS [2] (or its analogs for other growth mechanisms).

The mean-field rate equations of the cluster model (see, e.g., [12–14]) represent a natural extension of the mean-field continuum models, as these equations account for the discrete nature of atoms:

$$\dot{N}_1 = -2K_1N_1^2 - N_1\sum_{s\geqslant 2} K_sN_s + 2\frac{N_2}{\tau_2} + \sum_{s\geqslant 3}\frac{N_s}{\tau_s}, \qquad (5)$$

$$\dot{N}_s = N_1(K_{s-1}N_{s-1} - K_sN_s) - \frac{N_s}{\tau_s} + \frac{N_{s+1}}{\tau_{s+1}}. \qquad (6)$$

Here $N_s(t)$ is the cluster size distribution function (s is the number of atoms in a cluster), K_s are the rates of attachment of single atoms to a cluster of size s, and τ_s are the inverse rates of detachment of single atoms from a cluster of size s. Rare events of direct intercluster coalescence (coagulation) are neglected in Eq. (6); this requires a small volume fraction of the ''cluster phase.'' As no external source of atoms is present in Eqs. (5) and (6), these equations preserve the total concentration of atoms:

$$\frac{d}{dt}\sum_{s=1}^{\infty} sN_s(t) = 0, \qquad (7)$$

a discrete equivalent of Eq. (2).

For most growth mechanisms (including the growth processes, controlled by diffusion and by interface), the attachment-detachment kinetics, combined with mass conservation, promotes growth of larger clusters at the expense of smaller ones, and this process is nothing but OR. Therefore, if the total concentration of atoms is large enough, the system undergoes coarsening: the average cluster size grows in time and the total number of clusters decreases. The late time asymptotics of this process should reproduce OR quantitatively [12,13]. At the coarsening stage the number of clusters with small s becomes very small, except for the concentration of single atoms N_1 that remains relatively large because of the ongoing detachment processes. Therefore, one should consider the population of single atoms separately. As far as a description of clusters is concerned, one can proceed to the limit of $s \gg 1$, treat s as a continuous variable, and use the Taylor expansion in $1/s$ in Eqs. (5) and (6). Essentially, this derivation follows the paper of Binder [12]. However, in order to account for fluctuations, we should keep the second-order terms in $1/s$ (in contrast to the approach of Binder, who kept such terms in his description of the nucleation stage, but neglected them in the coarsening stage). As a result, Eq. (6) takes the form of a FP equation:

$$\frac{\partial N_s}{\partial t} + \frac{\partial}{\partial s}(V_sN_s) = \frac{1}{2}\frac{\partial^2}{\partial s^2}(D_sN_s), \qquad (8)$$

where

$$V_s(t) = K_sN_1 - 1/\tau_s \quad \text{and} \quad D_s(t) = K_sN_1 + 1/\tau_s \qquad (9)$$

are the drift velocity and diffusion coefficient in the s space.

A continuous version of the equation for $\dot{N}_1$ follows from the discrete equation (5). We can assume (and check *a posteriori*) that in the late coarsening stage there is a (quasi-steady-state) balance between the processes of attachment and detachment of single atoms by large clusters:

$$-N_1\sum_{s\geqslant 2} K_sN_s + \sum_{s\geqslant 3}\frac{N_s}{\tau_s} \simeq 0, \qquad (10)$$

while the rest of the terms of Eq. (5) become irrelevant. Treating s as a continuous variable, we obtain

$$N_1(t) = \frac{\int_0^\infty \tau_s^{-1}N_s\,ds}{\int_0^\infty K_sN_s\,ds}. \qquad (11)$$

(Again, we can assume that the number of clusters with small s is very small and formally shifts to zero the lower limit of integration over the continuous variable s.)

The same Eq. (11) can be formally obtained if we multiply both sides of Eq. (8) by s, integrate over s, and use the conservation law Eq. (7). Then, performing integration by parts in the two remaining terms, we again arrive at Eq. (11). In this derivation one should disregard the boundary terms produced by integration by parts. As will be checked later, the ''upper'' boundary terms sV_sN_s and $s(\partial/\partial s)(D_sN_s)$ at $s\to\infty$ vanish. In this case the third term vanishes there automatically. The boundary terms corresponding to the lower limit of integration are assumed to be negligible compared to the terms that we take into account. Formally, one should require that N_s vanishes sufficiently fast at $s\to 0$. (Remember, that the number of single atoms N_1 is described separately.)

Equations (8)–(11) (supplemented by appropriate initial and boundary conditions) represent a complete set of equations for the late coarsening stage. If one neglects the diffusion term, he recovers the Lifshitz-Slyozov-Wagner description and corresponding self-similar asymptotics and scalings for large times [12,13]. To make this recovery explicit, one should specify the dependences of K_s and τ_s on s. Looking for scale invariance, we should assume power laws: $K_s = K_1s^p$ and $\tau_s = as^q$. Now, assuming a compact cluster morphology (d-dimensional spherical ''drop,'' where d is equal to 2 or 3), I require that Eqs. (8) and (11) (without the diffusion term) coincide (after scaling down the coefficients) with Eqs. (1). This gives a direct correspondence between

the drift velocities $V_s(t)$, entering Eq. (9), and $V(R,t)$, entering Eq. (1). Using this ''correspondence principle'' I find that the concentration of single atoms $N_1(t)$ scales like the inverse critical radius $R_c(t)$, while the exponents p and q must be the following: $p=(d-n-1)/d$ and $q=(n-d+2)/d$. In particular, for the diffusion-controlled growth ($n=1$) one obtains $p=1/3$ and $q=0$ in three dimensions and $p=0$ and $q=1/2$ in two dimensions. For the interface-controlled growth ($n=0$) one gets $p=2/3$ and $q=-1/3$ in three dimensions and $p=1/2$ and $q=0$ in two dimensions [15]. Note that, returning to the original, dimensional version of Eq. (1) (see, e.g. Ref. [10]) and demanding an exact coincidence with the zero-diffusion limit of Eqs. (8) and (9), we can find the coefficients K_1 and a as well, for every growth mechanism.

Let us return to the case of nonzero diffusion in Eq. (8). As it is seen from the second formula of Eq. (9), the mapping procedure, described above, completely determines the diffusion coefficient D. Simple scaling arguments show that the diffusion term becomes irrelevant at long times [16]. However, even without going into much detail in Eq. (8), one can see that this term produces (already at $t>0$) an exponentially small tail in the DF, even if the DF had a compact support at $t=0$. In essence, small fluctuations transform a strictly bounded DF into an extended one. It was shown already by LS that an extended DF approaches, for long times, the *limiting* self-similar solution [2]. In the language of Eqs. (3) and (4), one can say, therefore, that fluctuations select

$$v_0=\frac{n+2}{n+1} \quad \text{and} \quad \sigma=\left(\frac{n+2}{n+1}\right)^{n+1}. \tag{12}$$

Therefore, fluctuations provide a strong selection rule in favor of the limiting solutions of LS (for $n=1$), of Wagner (for $n=0$), and of its counterparts for other growth mechanisms.

Now we can go back and justify the disregard of the upper boundary terms arising from the integration by parts in the derivation of Eq. (11). For a DF with an exponentially small tail at large s, the boundary terms obviously vanish in the scaling regime, as a power-law increase of V_s with s is too slow to change anything. This case is relevant for an initially compact DF, as fluctuations produce an exponentially small tail. For an extended initial DF with a *power-law* tail, $N_s(t=0)\propto s^{-\mu}$, finiteness of the cluster concentration,

$$\int_0^\infty N_s(t)ds<\infty,$$

requires $\mu>2$. Then, using the assumed power laws for K_s and τ_s and evaluating the boundary terms sV_sN_s and $s(\partial/\partial s)(D_sN_s)$, we must require the following inequalities $p<1$ and $q>-1$. Using the values of the exponents p and q determined from the ''correspondence principle,'' we see that these two inequalities are satisfied for any $n>-1$, that is, for all cases of physical interest.

One can suggest the following physical argument supporting the strong selection rule. In the absence of fluctuations, a bounded DF always remains bounded [8,9,11]. In other words, there is exactly *zero* probability to have clusters with a size larger than some finite time-dependent size. On the contrary, the presence of fluctuations leads to a small but *nonzero* probability of the appearance of clusters with *any* number of atoms. As the dynamics of OR is very sensitive to small changes in the region of the largest available clusters, the presence of the infinite tail in the DF will ultimately affect the whole dynamics, driving the DF towards the limiting DF. Of course, as fluctuations in macroscopic systems are extremely small, the time necessary for the DF to actually converge to the selected limiting solution can be extremely long (if one starts from a bounded DF). In this case I expect that, on a (quite long) intermediate time scale, a self-similar DF selected by λ will develop, and only at much later times will crossover to the limiting DF be observed. This crossover can happen much earlier if coarsening in *mesoscopic* systems is considered, where the role of the discrete nature of atoms increases dramatically. For example, I expect this effect to be observable in the processes of submonolayer relaxation of atomic clusters on surfaces, after epitaxial deposition is stopped.

Let us compare the cluster approach used in this work with the approach of Mullins [17]. Mullins accounted for the fact that droplets with the same radius do not necessarily have the same expansion/shrinkage rates (because of correlations). He generalized the classical LS model by replacing the deterministic growth law for a droplet, $\dot{R}=V(R,t)$ [where V is given by the second equation in Eq. (1)], by the equation $\langle\dot{R}|R\rangle=V(R,t)$, where $\langle\dot{R}|R\rangle$ is the *average* value of $\dot{R}$ for droplets with a given R. Then he inserted this relationship in the continuity equation (1). In contrast to the cluster approach, the approach of Mullins does not produce a diffusion term (as it does not account for fluctuations related to the discrete character of particles), therefore it does not provide a strong selection mechanism for OR.

Finally, I briefly speculate on possible additional mechanisms of strong selection. An account of fluctuations represents only one possible way of going beyond the ''classical'' LS formulation. Various finite volume fraction effects can provide alternative ways. One such alternative is rare coagulation events that can be accounted for already in the mean-field formulation. This alternative was briefly discussed by LS already in 1961 [2]. As the result of the rare coagulation events, a DF that had a compact support at $t=0$ is also expected to develop a tail which will drive it towards the limiting solution. No quantitative analysis of this scenario is presently available. Another possibility involves correlation effects, completely ignored by any mean-field description. Here I should mention the work of Marder [18], who studied screening effects in OR and arrived at a *different* FP equation for the DF. In his analysis, the diffusion term results from the screening effects rather than from fluctuations, and it is proportional to the square root of the volume fraction. Of course, the presence of any linear diffusion term in the FP equation will produce a tail in the DF and drive the DF towards the limiting solution (if the diffusion term is small enough and does not interfere in the scaling regime). The comparative role of these possible selecting mechanisms is obviously volume-fraction-dependent. Of course, nonuniversal transients and convergence rates towards the selected DF are expected to differ significantly in the different scenarios.

In summary, small fluctuations provide a strong selection rule in the problem of Ostwald ripening, as they drive the system, at long times, towards the limiting Lifshitz-Slyozov solution.

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[1] W. Ostwald, Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **34**, 495 (1900).
[2] I. M. Lifshitz and V. V. Slyozov, Zh. Éksp. Teor. Fiz. **35**, 479 (1959) [Sov. Phys. JETP **8**, 331 (1959)]; J. Phys. Chem. Solids **19**, 35 (1961).
[3] C. Wagner, Z. Elektrochem. **65**, 581 (1961).
[4] O. Krichevsky and J. Stavans, Phys. Rev. E **52**, 1818 (1995); W. Theis, N. C. Bartelt, and R. M. Tromp, Phys. Rev. Lett. **75**, 3328 (1995); J.-M. Wen *et al.*, *ibid.* **76**, 652 (1996); K. Morgenstern, G. Rosenfeld, and G. Comsa, *ibid.* **76**, 2113 (1996); G. R. Carlow and M. Zinke-Allmang, *ibid.* **78**, 4601 (1997); J. B. Hannon, *et al.*, *ibid.* **79**, 2506 (1997).
[5] J. H. Yao *et al.*, Phys. Rev. B **47**, 14 110 (1993); A. J. Bray, Adv. Phys. **43**, 357 (1994); N. Akaiwa and P. W. Voorhees, Phys. Rev. E **49**, 3860 (1994); V. G. Karpov, Phys. Rev. Lett. **74**, 3185 (1995). **75**, 2702 (1995); N. Akaiwa and D. I. Meiron, Phys. Rev. E **54**, R13 (1996); C. Sagui, D. S. O'Gorman, and M. Grant, *ibid.* **56**, R21 (1997).
[6] L. C. Brown, Acta Metall. **37**, 71 (1989); Scr. Metall. Mater. **24**, 963 (1990); **24**, 2231 (1990).
[7] M. K. Chen and P. W. Voorhees, Modell. Simul. Mater. Sci. Eng. **1**, 591 (1993).
[8] B. Meerson and P. V. Sasorov, Phys. Rev. E **53**, 3491 (1996).
[9] B. Giron, B. Meerson, and P. V. Sasorov, Phys. Rev. E **58**, 4213 (1998).
[10] V. V. Slyozov and V. V. Sagalovich, Usp. Fiz. Nauk **151**, 67 (1987) [Sov. Phys. Usp. **30**, 23 (1987)]; M. Zinke-Allmang, L. C. Feldman, and M. H. Grabow, Surf. Sci. Rep. **16**, 377 (1992).
[11] B. Niethammer and R. L. Pego, e-print cond-mat/9808036.
[12] K. Binder, Phys. Rev. B **15**, 4425 (1977).
[13] J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic Press, London, 1983).
[14] D. D. Vvedensky *et al.*, in *Fluctuations and Order. The New Synthesis*, edited by M. Milonas (Springer, New York, 1996).
[15] As a side remark, we note that a reasonable choice of the exponents p and q is very important in mean-field models of many nonequilibrium growth processes, such as submonolayer epitaxial growth. In these models an additional *driving* term (deposition rate) appears in Eq. (5) [14]. As we have shown, the problem of ''arrested deposition'' (that is, relaxation to equilibrium) that we consider in this work enables one to calculate these exponents for large clusters (and for a low coverage) by mapping the problem into a well-studied macroscopic problem of OR.
[16] Indeed, the second derivative with respect to s includes an additional small factor of order $1/\bar{s}$ that decreases with time. Here $\bar{s}$ is the characteristic value of s (for example, the average number of particles in a cluster).
[17] W. W. Mullins, Acta Metall. Mater. **39**, 2081 (1991).
[18] M. Marder, Phys. Rev. A **36**, 858 (1987).