The role of discrete-particle noise in the Ostwald ripening

BARUCH MEERSON¹, LEONARD M. SANDER² and PETER SMEREKA³

¹ Racah Institute of Physics, Hebrew University of Jerusalem, Jerusalem 91904, Israel
² Michigan Center for Theoretical Physics, Department of Physics, University of Michigan, Ann Arbor, MI 48109-1120, USA
³ Department of Mathematics, University of Michigan, Ann Arbor, MI 48109-1120, USA

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Abstract. – We investigate the role of discrete-particle noise in interface-controlled Ostwald ripening. We introduce the noise within the framework of the Becker-Döring equations, and employ both Monte Carlo simulations and direct numerical solution of these equations. We find that the noise drives the system towards a unique scaling regime describable by a limiting solution of a classical continuum theory due to Lifshitz, Slyozov and Wagner. The convergence towards the scaling solution is extremely slow, and we report a systematic deviation between the observed small correction to scaling and a theoretical prediction of this quantity.

Introduction. – Ostwald ripening (OR) is a generic coarsening process which occurs in a late stage of phase separation, when the domains (or clusters) of the minority phase compete for monomers. As a result, the larger clusters grow at the expense of the smaller ones. Following the pioneering work of Lifshitz and Slyozov [1] and Wagner [2], experimental and theoretical investigations of OR have focused on the dynamic scaling properties of the probability distribution function (PDF) of cluster sizes, and of its moments. These properties are determined by the kinetics of the monomer transport. Simple limits of this kinetics are observed when the monomer transport is controlled either by diffusion of the monomers in the bulk, or by the processes of attachment and detachment of the monomers at cluster interfaces. The latter limit is called interface-controlled. In each of the two limits continuum mean-field theories have been formulated: for diffusion-controlled OR by Lifshitz and Slyozov (LS) [1], and for interface-controlled OR by Wagner [2]. The two models are often united under the name of the LSW model. The LSW model admits a family of self-similar solutions for the PDF of cluster sizes. However, the problem of selection of the correct self-similar solution is non-trivial. All of the LSW scaling functions have compact support and can be parameterized by the value, \( \lambda \), of the logarithmic derivative at the edge of the support; \(-1 < \lambda \leq \infty\). LS [1] argued that the selected PDF for the case of initial conditions with a long tail is the limiting PDF, corresponding to \( \lambda = \infty \). The scaled PDF should approach this function as \( t \to \infty \). On the other hand, if the initial data for the PDF has compact support the selected self-similar
PDF is determined by the behavior of the initial data near the edge of its support [3–5]. If the initial PDF has logarithmic derivative \( \lambda_0 \) at the edge of support, the selected self-similar solution is the one with the same value of the logarithmic derivative at the edge of its support: \( \lambda = \lambda_0 \) [3, 4]. If the logarithmic derivative of the PDF at the edge of support at \( t = 0 \) does not exist, the PDF does not approach any self-similar solution [5].

These results are in apparent contradiction to experimental results which appear to show strong selection, i.e. selection insensitive to initial conditions. To find strong selection we must consider dynamics beyond that of the classical LSW model. One possibility is to account for discreteness of atoms in any real system. This direction was explored by Velázquez [6] and Meerson [7], who employed the Becker-Döring (BD) equations [8], properly modified to account for conservation of the total number of atoms [9, 10]. In the limit of \( \bar{s} \gg 1 \), where \( \bar{s} \) is the average number of atoms in a cluster, the BD-equations reduce to the LSW model [9]. Taking into account the next order term in \( 1/\bar{s} \), one arrives at a Fokker-Planck (FP) equation for the cluster size PDF [6, 7], see below. The drift term of the FP-equation coincides with that of the LSW model, while the small diffusion term comes from discrete-particle noise. The diffusion term produces a tail in the PDF, even if the initial data has compact support at \( t = 0 \). According to Refs. [6, 7] (see also Ref. [11]), this tail drives the system towards the limiting self-similar solution corresponding to \( \lambda = \infty \).

These arguments assume, however, that the FP-equation is a faithful long-time description of the BD-equations. Though natural, this assumption is not obviously correct. There are many examples when the FP equation misses important aspects of discrete systems [12]. In this work we investigate the role of discrete-particle noise by dealing directly with the BD equations, without making the FP approximation. We focus on interface-controlled kinetics. This choice is motivated by experimental findings which showed the importance of this (sometimes overlooked) limit in a variety of environments, such as the coarsening of two-dimensional islands on Si(001) [13], coarsening of granular clusters in electrostatically driven granular powders [14], etc. There is an important additional motivation. Both the LSW model and the BD-equations neglect spatial correlations. As a result, the quantitative validity of the LSW model is limited, in the case of the diffusion-controlled OR, to extremely small area fractions [15]. By contrast, spatial correlations in interface-controlled OR are much weaker [16]. Therefore, for the same value of area fraction, the BD-equations are more accurate in describing interface-controlled OR, than diffusion-controlled OR [17].

**BD-equations and the LSW model.** – Let \( s \) be the number of atoms in a cluster, and \( N_s(t) \) be the number of clusters of size \( s \). The BD-equations [8–10] are master equations for the populations of clusters, \( s \geq 2 \):

\[
\dot{N}_s = N_1 (K_{s-1} N_{s-1} - K_s N_s) - \frac{N_s}{\tau_s} + \frac{N_{s+1}}{\tau_{s+1}},
\]

and monomers:

\[
\dot{N}_1 = -2K_1 N_1^2 - N_1 \sum_{s \geq 2} K_s N_s + \frac{2N_2}{\tau_2} + \sum_{s \geq 3} \frac{N_s}{\tau_s}.
\]

Here \( K_s = K_1 s^p \) is the rate of attachment of monomers to the cluster of size \( s \), and \( \tau_s = a s^q \) is the inverse rate of detachment of monomers from the cluster of size \( s \). One can always choose \( a = 1 \): this corresponds to a rescaled time \( \tilde{t} = t/a \) (the tilde will be omitted in the following), and a rescaled attachment rate coefficient \( \alpha = K_1 a \). Equations 1 and 2 preserve the total number of atoms \( N \):

\[
N_1 + \sum_{s=2}^{s_{\text{max}}} s N_s = N.
\]
To set the stage for our analysis, let us briefly review the predictions of the underlying continuum theories. When the dynamics (1) and (2) reach the stage of OR, one can proceed to the limit of \( s \gg 1 \) and treat \( s \) as a continuum variable (except for the monomers, \( s = 1 \), which should be taken care of separately). Then, by a truncated Taylor expansion, one obtains the FP-equation \([6, 7]\)

\[
\frac{\partial n_s}{\partial t} + \frac{\partial}{\partial s} \left( V_s n_s \right) = \frac{1}{2} \frac{\partial^2}{\partial s^2} \left( D_s n_s \right),
\]

(4)

where

\[
V_s(t) = An_1 s^p - s^{-q} \quad \text{and} \quad D_s(t) = An_1 s^p + s^{-q}
\]

(5)

are the drift velocity and the diffusion coefficient in \( s \)-space, \( n_s(t) = N_s(t)/N \) and \( A = K_1 aN \).

The LSW model neglects the diffusion term in Eq. (4) and deals with the continuity equation

\[
\frac{\partial n_s}{\partial t} + \frac{\partial}{\partial s} \left[ (An_1 s^p - s^{-q}) n_s \right] = 0,
\]

(6)

combined with the conservation law

\[
n_1 + \int_0^\infty s n_s(t) \, ds = 1,
\]

(7)

see Ref. [7] for details. For interface–controlled OR one obtains \( p = 1/2 \) and \( q = 0 \) in two dimensions, and \( p = 2/3 \) and \( q = -1/3 \) in three dimensions [7]. In the following we will focus on the two-dimensional case. At late times the contribution of the monomers to the total number of atoms in the system becomes negligible, and Eq. (7) becomes

\[
\int_0^\infty s n_s(t) \, ds \simeq 1.
\]

(8)

It follows from Eqs. (6) and (8) that

\[
s_c^{1/2}(t) = \langle s^{1/2} \rangle = \frac{\int_0^\infty s^{1/2} n_s \, ds}{\int_0^\infty n_s \, ds},
\]

(9)

where \( s_c = (An_1)^{-2} \) is the time-dependent critical size of the clusters; that is clusters with \( s > s_c \) grow, while clusters with \( s < s_c \) shrink. Equations (6) and (8) admit a family of self-similar solutions:

\[
n_s = \frac{1}{s_c^\beta} \phi \left( \frac{s}{s_c} \right), \quad n_1 = \frac{\beta}{A t^{1/2}},
\]

(10)

parameterized by \( \beta = \text{const.} \) According to Ref. [6, 7], the discrete-particle noise selects the \textit{limiting} solution with \( \beta = 2 \). The corresponding scaling function [2,18]

\[
\phi(x) = \left\{ \begin{array}{ll}
\frac{C}{(2-\sqrt{2})} \exp \left( -\frac{4}{2-\sqrt{2}} x \right) & \text{if } 0 < x < 4, \\
0 & \text{if } x \geq 4,
\end{array} \right.
\]

(11)

has an infinite number of vanishing derivatives at the edge of its support \( x_{\text{max}} = 4 \) and \( \lambda = \infty \). In Eq. (11) \( C = e^{-2} + 2 \text{Ei}(-2) = 26.6423 \ldots \), where \text{Ei} is the exponential integral function [19].
Fig. 1 – The number density of monomers \( n_1 \) (a) and the average cluster size \( s_a \) (b) versus time. The circles are averages over \( 10^3 \) realizations, obtained in Monte Carlo simulations with \( N = 3,001 \times 10^6 \) atoms. The parameter \( \alpha = 10^{-4} \). The initial conditions are: \( N_1 = 10^3 \), \( N_{50} = 6 \times 10^4 \), the rest of \( N_s \) is zero. The red lines show the theoretical prediction from Eq. (10) with \( \beta = 2 \) (a) and a linear fit of the data (b).

Monte-Carlo simulations. – Direct Monte-Carlo simulations of interface-controlled OR are inefficient, because most of the computation time is spent to resolve the fast monomer diffusion in the bulk, while the kinetic bottleneck here is the slow attachment and detachment of monomers at the clusters interface [20]. To accelerate the simulations we assume that the monomer transport in the bulk is instantaneous. Therefore, we deal with a collection of clusters, \( s \geq 2 \), and a pool of monomers, without taking care of the spatial distribution of any of them. Essentially, this corresponds to a stochastic simulation of the BD equations.

We start with a collection of clusters in some initial condition, and some initial number of monomers, \( N_1 \). We repeatedly choose a cluster at random and let it either grow, by absorbing monomers with rate \( \alpha N_1 s_1^{1/2} \), or shrink by emitting monomers with unit rate. This is achieved by rejection Monte Carlo: we calculate the rate for the largest cluster, \( s = s_{\text{max}} \), to either grow or shrink, \( f_{\text{max}} = \alpha N_1 s_{\text{max}}^{1/2} + 1 \), and the corresponding quantity for the cluster at hand, \( f = \alpha N_1 s^{1/2} + 1 \). Then we choose a random number \( u \) between 0 and \( f_{\text{max}} \). If \( u > f \) we do nothing. If \( 1 < u \leq f \) we make the cluster grow by increasing \( s \) by 1, and decreasing \( N_1 \) by 1. If \( u \leq 1 \) we shrink the cluster, that is decrease \( s \) by 1 and increase \( N_1 \) by 1. We need to adjoin a special rule for clusters of size 2. If they shrink we add two monomers to \( N_1 \) and remove the cluster in question from the list. The time was advanced, at each step, by \( \delta t = 1/(N_{\text{cl}} f_{\text{max}}) \), where \( N_{\text{cl}} \) is the current total number of clusters (excluding monomers).

Typical results of these Monte Carlo simulations are shown in Figs. 1 and 2. Figure 1a depicts the number density of monomers \( n_1 \) versus time, and the theoretical prediction for \( n_1 \) from Eq. (10) with \( \beta = 2 \). Good agreement is observed. The average cluster size, which we define as \( s_a = (s^{1/2})^2 \) is plotted versus time in Fig. 1b. Linear growth is observed as expected. The observed slope 0.268, however, is slightly higher than the theoretical value 0.25. The scaled PDFs of the cluster sizes, \( s_c^2(t) n_c(t) \), are plotted versus \( x = s/s_c(t) \) at three different times in Fig. 2. Only times up to \( t = 3,200 \) are used, because at later times the measured PDFs become too noisy. The three scaled PDFs in Fig. 2 show a good collapse, but the scaling function is slightly different from the theoretical prediction (11). Where does the deviation come from? The LSW-problem notoriously has very slow convergence to the limiting self-similar solution [1, 21]. Therefore, one can attempt to attribute the observed deviation to very slow convergence, masked by fluctuations.
Fig. 2 – The scaled PDFs of the cluster sizes at times 400 (black), 800 (blue) and 3200 (green) as obtained in Monte Carlo simulations. Because of the relatively large noise at late times the black and blue lines are masked by the green line. The parameters are the same as in Fig. 1. The red dashed line is the theoretical scaling function \[ (11) \].

**Numerical solution of the BD-equations.** – To test this interpretation and reach later times, we solved the BD-equations numerically. Equations (1) and (2) for \( 1 \leq s \leq 10^5 \) were solved using a fourth order Runge-Kutta algorithm. The conservation law (3) was used for accuracy control. The time step chosen was \( \Delta t = \min \left[ 0.007 / (\alpha N_1), 0.125 \right] \). This choice resulted in excellent mass conservation and enabled us to probe very long times. For the results reported below only \( 10^{-7} \) of a single particle was lost by \( t = 10^5 \).

The results are shown in Figs. 3 and 4. The number density of monomers \( n_1 \) versus time (Fig. 3a) agrees very well with the theoretical prediction. The average cluster size \( s_a = \langle s^{1/2} \rangle^2 \) shows linear growth with time, see Fig. 3b. The slope 0.262, obtained on the interval \( 10^3 < t < 10^5 \), is still slightly higher than the theoretical value 0.25. The scaled PDF (Fig. 4a), though still different from the theoretical scaling function \[ (11) \], apparently slowly approaches it.

**Logarithmic corrections to scaling.** – LS [1] investigated, in the context of diffusion-controlled OR in three dimensions, the convergence towards the limiting self-similar solution.

Fig. 3 – The number density of monomers \( n_1 \) (a) and the average cluster size \( s_a \) (b) versus time, obtained by solving Eqs. (1) and (2) numerically for \( N = 3 \times 10^6 \). The parameter \( \alpha = 10^{-4} \). The initial conditions are: \( N_1 = 1.5 \times 10^3, N_{50} = 59970 \), the rest of \( N_s \) is zero. The thin red lines show a linear fit of the data (a) and the theoretical prediction from Eq. (10) with \( \beta = 2 \) (b).
Fig. 4 – The solid lines in (a) show the scaled PDFs at times 1350 (black), 10350 (blue) and 85350 (green), obtained by solving Eqs. 1 and 2 numerically. The parameters are the same as in Fig. 3. The red dashed line is the theoretical scaling function (11). The black dashed line in (b) shows \( \Delta(t) \) (see text), while the red solid line shows \( \ln^{-2} t \), see Eq. (15).

Here we will employ their argument (see also Ref. [6]) in the problem of interface-controlled OR in two dimensions, and compare it with our simulations.

The characteristics of Eq. (12) are described by the equation

\[
\dot{s} = \left( s/s_c \right)^{1/2} - 1.
\]

In the rescaled variable \( x = s/s_c \) Eq. (12) becomes

\[
s_c \dot{x} = -s_c x + x^{1/2} - 1.
\]

The limiting self-similar solution requires that \( s_c(t) \to t/4 \) as \( t \to \infty \), so that the right hand side of Eq. (13) becomes a perfect square: \( t \dot{x} = -(\sqrt{x} - 2)^2 \). As shown by LS, this is the only possibility to have a non-diverging normalization integral \( \mathcal{S} \), when the full PDF has a tail. Following LS, we are looking for the leading correction in the following form:

\[
s_c(t) = (t/4) \left[ 1 + \varepsilon(t) \right], \]

where \( \varepsilon(t) \ll 1 \). Consider a small region of \( x \) around the “blocking point” \( x = 4 \) (the edge of support of the similarity solution). Let \( y(t) = [x(t) - 4]/\varepsilon(t) \). Equations (13) becomes, in the leading order,

\[
\frac{1}{4\varepsilon} \frac{dy}{d\tau} = -1 + \frac{y}{4} \frac{d}{d\tau} \left( \frac{1}{\varepsilon} \right) - \frac{y^2}{64},
\]

where \( \tau = \ln t \). By the same normalization argument, the right hand side should become a perfect square as \( t \to \infty \), which yields \( \varepsilon = 1/\tau = 1/\ln t \). Therefore, we obtain

\[
s_a = (s^{1/2})^2 = s_c(t) = \frac{t}{4} \left( 1 + \frac{1}{\ln^2 t} + \ldots \right).
\]

The logarithmic correction \( \ln^{-2} t \) implies that the apparent dynamic exponent would be slightly larger than 0.25 and decreasing in time, as indeed observed in our simulations. However, a more detailed comparison of Eq. (15) with our simulation data is disappointing. Figure 4b shows the quantity \( \delta = 4s_a(t)/t - 1 \) versus \( t \). Though \( \delta \) does go down with time (apparently, logarithmically slowly), it clearly disagrees, at these times, with the prediction of Eq. (15).
Summary. – We have investigated interface-controlled OR in the framework of conserved BD-equations. We performed Monte-Carlo simulations of the system, and also solved the BD equations numerically. We observed that discrete-particle noise drives the system towards a limiting self-similarity solution described by the LSW theory. However, the convergence towards the scaling regime is extremely slow. Furthermore, there is a clear disagreement between the observed small correction to scaling and a theoretical prediction of this quantity, obtained in the spirit of the LS theory. At present we cannot pinpoint the reason for the disagreement in the subleading order of the theory. Clarifying this important issue should be the next step of theory.

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