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Ostwald ripening on a substrate: modeling local interparticle diffusion

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Abstract. — A model with local interparticle diffusion is considered, in contrast with the classical model of Ostwald ripening (the mean field model) and its multiparticle extensions which have long range interactions. Simulations of the evolution of the system show that the asymptotic behavior obeys a power law. It is also found that the scaled asymptotic distribution of particle radii is broader than in the previous models, even at low initial coverage where the multiparticle models have the same narrow scaled distribution as the mean field model. The scaling properties are independent of the initial particle size distribution.

1. Introduction.

The sintering of particles (grains consisting of atoms) on a substrate is of technological and fundamental interest. Among the technological applications, we recall the formation of solid thin films on a substrate [1] and the ageing of supported metal catalysts [2]. The challenging theoretical question of sintering is how to describe the evolution of the disperse droplet-like phase at late stages [3]. Ordinarily, whether sintering occurs in three dimensions or in two dimensions, it can be qualitatively explained by the curvature dependence of the chemical potential: small particles emit single atoms to the low density phase (called the vapor phase), the atoms then diffuse, and are finally captured by large particles. Thus the large particles grow at the expense of the small ones, reducing the total surface energy. The process is often called Ostwald ripening.

The models for Ostwald ripening have evolved from mean fields models (classical theory) to multiparticle models (modern theory) [4]. Early quantitative descriptions for Ostwald ripening in three dimensions were the models by Lifshitz and Slyozov [5] and by Wagner [6].

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Chakraverty extended the models to the coarsening of particles on a substrate [7]. The Chakraverty model, like its original three-dimensional versions, is based on the mean field assumption. In the mean field formalism, the vapor concentration reaches its uniform mean field value at a given distance (called screening distance) from the particles; each particle influences the vapor phase around it, but it is not influenced directly by the relative location and size of any other particle. These mean field models predict a temporal power law of the particle growth and a scaled form for the distribution of particle radii.

Despite the success of these models, there remains a major discrepancy between theory and experiment: the scaled particle size distributions obtained by experiments are broader and more symmetrical than the ones predicted by the classical theories. Recent studies have tried to explain this disagreement by taking into account the effect of interparticle diffusional interaction. As a result, multiparticle models have been proposed [4]. According to these models, the effect of interparticle diffusional interaction is related to the volume fraction (in three dimensions) or surface coverage (in two dimensions) of the coarsening particle phase.

The model developed by Dadyburjor et al. [8] is the two-dimensional example of this approach. According to the formulation of the multiparticle model, the emission or absorption of single atoms from growing or decaying particles are modeled by placing a point source or sink of the vapor phase at the center of each particle. The strengths of these point sources or sinks are determined by a general solution of the diffusion equation with appropriate boundary conditions. Since the diffusion field is of long-range nature, the diffusional interaction between particles is also of long-range nature. In other words, each particle interacts with all the other particles. The usefulness of this model is based on the postulate that the strength of each point source must converge when the number of particles in the system under consideration tends to infinity. This assumption is probably not fulfilled.

In the present work, we take the opposite point of view. We model coarsening on a substrate by a local model: a given particle interacts diffusively only with its nearest neighbors. As this model is short-ranged, it is called local interparticle diffusional interaction model. The interest in this model is not so much that it is more realistic than the mean field models, but that it represents the opposite limit to mean field theory: infinite range vs. short range. Its temporal asymptotic behavior and the scaled distribution of particle radii will be investigated by use of computer simulations. The results are compared with mean field and multiparticle models.

2. Model.

First, let us consider a system of two fixed hemispherical particles (labelled by \( i, \ i = 1, 2 \)) on a surface. They are far apart and coexist with a common two-dimensional vapor phase. At long times, the quasistationary approximation may be employed to describe the diffusional flux. Therefore, the concentration \( c_i \) of the vapor phase at the interface of the particles (i.e., the dissolution surface concentration) is given by the Gibbs-Thomson equation:

\[
\frac{c_i}{c_\infty} = \exp \left( \frac{L_c}{R_i} \right)
\]

where \( c_\infty \) is the surface equilibrium concentration of the vapor phase, \( R \), the radius of particle \( i \) and \( L_c \) the capillary length.

In the time interval \( \Delta t \), the mass change \( \Delta m_i \) of the particle \( i \) is expressed approximately by

\[
\Delta m_i = s_i \Delta t
\]

where \( s_i \) is the total diffusion flux across the particle perimeter on the substrate. In the following, we proceed to determine \( s_i \) for the two particle system.
When the two particles are treated as point sources or sinks, the quasistationary diffusion field \( c(r) \) satisfies the following equation:

\[
\nabla^2 c(r) = -2 \pi \sum_{i=1}^{2} B_i \delta(r - r_i)
\]

where \( r \) locates a field point, \( r_i \) signifies the position of the particle \( i \), and \( B_i \) is the strength of the source representing the particle. By use of Fick’s law and the divergence theorem, one obtains:

\[
s_i = 2 \pi DB_i.
\]

There is a general solution for equation (3) of the form

\[
c(r) = B_0 + B_1 \log |r - r_1| + B_2 \log |r - r_2|.
\]

Substituting the boundary conditions given by the Gibbs-Thomson relation into equation (5) yields:

\[
c_1 = B_0 + B_1 \log R_1 + B_2 \log d_{12}
\]

\[
c_2 = B_0 + B_1 \log d_{12} + B_2 \log R_2
\]

along with the constraint:

\[
B_1 + B_2 = 0.
\]

It follows from equation (6a), (6b), (7) and (4) that:

\[
s_1 = 2 \pi D \cdot \frac{c_2 - c_1}{\log \left( \frac{d_{12}^2}{R_1 R_2} \right)}
\]

\[
s_2 = 2 \pi D \cdot \frac{c_1 - c_2}{\log \left( \frac{d_{12}^2}{R_1 R_2} \right)} = -s_1.
\]

The above system of two particles can be extended to \( N \) hemispherical particle system at time \( t \) on a substrate. The position of the particle \( i \) on the substrate is denoted by its center, \( r_i \), and the spatial distribution of particles, \( f(r) \), is described by the summation of Dirac functions:

\[
f(r) = \sum_{i=1}^{N} \delta(r - r_i)
\]

where \( r \) locates the position on the planar surface of the substrate.

For any particle \( i \) we determine the closest particle \( j \) in the system. For each such pair \((i, j)\) we compute the flux \( s_{ij} = -s_{ji} \) according to the pair approximation, equation (8). The total flux away from or towards a particle \( i \) then is approximated by the sum over all the flux contributions \( s_{ij} \) of the particles which are paired with \( i \):

\[
s_i = \sum_{j, \text{paired with } i} s_{ij}.
\]
If \( i \) is paired with \( j \) and \( j \) is paired with \( i \), the contribution \( s_{ij} = - s_{ji} \) is only counted once.

In the simulations the flux defined above is calculated for each particle. The time step then is determined in the following way:

\[
1/\Delta t = \text{Max}_{i=1..N} [-s_i/m_i]
\]  

(11)

where \( m_i \) is the mass of the particle \( i \). If \( \Delta t \) is larger than a fixed cutoff \( \Delta T \), we set \( \Delta t \) equal to \( \Delta T \). Finally, the mass of every particle changes as indicated in equation (2), and the size of every particle is changed correspondingly. If the mass of a particle after the mass exchange is less than a given small value \( M \), the particle is supposed to disappear. Time then is increased from \( t \) to \( t + \Delta t \). The above process is repeated until only a single particle remains.

For convenience, length, time, concentration and mass are made dimensionless. The lengths will be scaled with the capillary length \( L_c \).

\[
L_c = \frac{2 \sigma V_m}{R_g T}
\]

(12)

where \( \sigma \) is the surface energy; \( V_m \) the molar volume, \( R_g \) the gas constant and \( T \) the temperature. Similarly, the concentrations \( c \) are scaled by \( c_\infty \) and the masses \( m \) by \( 2 \pi \rho L_c^3/3 \) (\( \rho \) is the volume density of particles). Finally time \( t \) is rescaled by \( \rho L_c^3/4 \) to make it dimensionless. Hereafter, all quantities are expressed in dimensionless form. The flux \( s_{ij} \) between the two particles \( i \) and \( j \) then is:

\[
s_{ij} = \exp(1/R_j) - \exp(1/R_i) \\
\log \left( \frac{d_{ij}^2}{R_i R_j} \right)
\]

(13)

The total flux around particle \( i \) (Eq. (10)), its mass change (Eq. (2)) and the time step (Eq. (11)) are unchanged in dimensionless units. The particle radius now varies with mass as \( m_i = R_i^3 \).

3. Simulations and results.

On a rectangle of size \( L_x \times L_y \) with periodic boundary, the centers \( r \) of hemispherical particles are placed at random. The initial distribution of particle sizes is uniform between \( R_{\text{min}} \) and \( R_{\text{max}} \), i.e. it is a box distribution. The ratio of the radius of a particle to the distance between the particle and its nearest neighbor is always less than 0.1.

The simulations of the present model use the following parameters: the total particle number is 20000, the size of the rectangle is \( L_x = L_y = 6000 \), the maximum time increment \( \Delta T = 100 \) and the minimal particle mass \( M = 0.001 \). The initial distribution has \( R_{\text{min}} = 0.1 \) and \( R_{\text{max}} = 2 \).

Let us call the monotonically decreasing number of particles \( N(t) \) and define the average radius \( \langle R \rangle \) by

\[
\langle R \rangle = \frac{1}{N} \sum_{i=1}^{N} R_i .
\]

(14)

The scaled distribution of particle radii, \( n(z) \), then can be defined by

\[
n(z) = N / N / \Delta z
\]

(15)
where \( z = R_i/\langle R \rangle \), \( \Delta z \) is a small interval around \( z \) and \( N \), the total number of the particles in the interval \((z - \Delta z/2, z + \Delta z/2)\). The interval \( \Delta z \) is chosen small enough such that the size distribution \( n(z) \) varies smoothly between \( z \) and \( z + \Delta z \) but large enough to avoid large statistical fluctuations.

We have measured the evolution of \( n(R_i/\langle R \rangle) \) at long times. In order to reduce the statistical fluctuation, ten samples with different initial conditions are averaged. The average \( n(R_i/\langle R \rangle) \) of the ten samples is presented in figure 1a. It is found that the system reaches an asymptotic regime where \( n(R_i/\langle R \rangle) \) is invariant. We have also measured the increase of the average \( \langle R \rangle \) and the decrease of the total particle number \( N \) with time \( t \). These curves are called sintering curves. It is found that these curves take the form of a power law:

\[
\langle R \rangle \propto t^a \\
N \propto t^{-b}
\]

where \( a \) and \( b \) are exponents. An example is given in figure 1c. The average of the exponents \( a \) and \( b \) obtained from each of the ten samples is \( a = 0.233 \pm 0.003 \) and \( b = 0.696 \pm 0.008 \), respectively.

Fig. 1. — Scaling behavior of the system at low initial coverage (20,000 particles on the 6,000 x 6,000 square): the scaled particle radius distribution for the box initial distribution (a) and the Gaussian initial distribution (b); the sintering curves of the average radius \( \langle R \rangle \) and the total particle number \( N \), respectively, for the box initial distribution (c) and the Gaussian initial distribution (d).
We also considered a Gaussian initial distribution with average 1 and variance 0.5 (cutoff at 0.1 and 2). Ten different samples are also used. The results show that the asymptotic power laws have nearly the same exponents as the simulations with a box initial distribution: $a = 0.228 \pm 0.002$ and $b = 0.680 \pm 0.006$, the sintering curves of one sample are demonstrated in figure 1d. Their scaled distributions are also given in figure 1b.

Furthermore we also simulated a system with a lower initial coverage. We increase the size of the square to $70000 \times 70000$, and keep all other quantities unchanged. Ten examples are tested respectively for both the box distribution and the Gaussian distribution. The average scaled particle size distributions are measured after transient processes have disappeared. The distributions are clearly invariant in time (Figs. 2a and b). In the asymptotic regime, the sintering curves of the average of the radius and the total particle number satisfy power laws, the curves for the two examples are given in figures 2c and 2d. The average of the exponents of the ten examples are $a = 0.234 \pm 0.002$ and $b = 0.701 \pm 0.005$ for the box initial distribution, and $a = 0.233 \pm 0.003$ and $b = 0.696 \pm 0.008$ for the Gaussian initial distribution, respectively.

Fig. 2.— Scaling behavior of the system at very low initial coverage (20 000 particles on the $70000 \times 70000$ square): the scaled particle radius distribution for the box initial distribution (a) and the Gaussian initial distribution (b); the sintering curves of the average radius $\langle R \rangle$ and the total particle number $N$, respectively, for the box initial distribution (c) and the Gaussian initial distribution (d).
4. Discussion.

Theoretically, the Ostwald ripening process is usually studied in two extreme cases: reaction controlled or diffusion controlled [7]. In the reaction controlled case, single atoms diffuse very fast on the substrate, such that the growth (or decay) of particles is dominated by reactions at the surface of the particles. In the diffusion controlled case, the surface process happens so fast that it can be neglected, hence the Ostwald ripening is controlled by the diffusion of single atoms on the substrate. Evidently, the model proposed above describes the diffusion controlled process. In the mean field model by Chakraverty [7], the sintering curve of the average particle radius has a power law with the exponent $1/4$ when the coarsening is controlled by diffusion. The simulations of the present model show that the sintering curves also follow a power law but with a slightly different exponents: about 0.23 for our model. Scaling arguments would suggest that the two models have the same asymptotic exponents. The discrepancy may be related to logarithmic corrections (see Eq. (13)) or to the changing effective particle density: the average shortest distance between neighboring particles, $\langle d \rangle$ (defined as the average distance between the center of a given particle and the center of the particle closest to it) scales with the average particle radius like

$$\langle d \rangle \propto \langle R \rangle^{3/2}$$

for three-dimensional particles on a two-dimensional substrate. The most important result of the local model is that it has a broader scaled distribution of particle radii than the mean field model (Fig. 3). This is not surprising as in the present model, the growth or decay of a particle is only determined by its surroundings. The diffusional interaction between particles is forced

![Fig. 3. Comparison between the scaled particle radius distributions of the Chakraverty model (a) and of the present model: the box initial distribution on the $6000 \times 6000$ square (b), the box initial distribution on the $70000 \times 70000$ square (c), the Gaussian initial distribution on the $6000 \times 6000$ square (d), and the Gaussian initial distribution on the $70000 \times 70000$ square (e).]
to be short range. In contrast, in the mean field model, the effect of a given particle on the growth or decay of another particle is independent of the distance between them; the diffusional interaction is of infinite range.

In the multiparticle model by Dadyburjor et al. [8], it is supposed that the system of particles consists of a basis set and its infinite periodic translations in two dimensions. Thus it can be resolved numerically by use of the Ewald construction. Their results indicate that the curves of the average radius as a function of time vary from concave to convex as the initial coverage increases. They probably do not reach a universal asymptotic power law because of the limited simulation time. Their results also show that for low initial coverage the particle size distribution is narrower than for high initial coverage. In particular, at very low coverage, the distribution is only marginally different from the mean field distribution. As the particles are 3-dimensional and the support is 2-dimensional, the density decreases with time. The distribution of a system with a heigh initial coverage gradually changes to a system with low coverage.

In our simulation, very different initial distributions of particle radii (such as box and Gaussian) finally reach the same scaled distribution. The initial coverage in our simulation is always very low. Nevertheless, the scaled distribution of particle radii at late stages is broader than both the mean field model and the multiparticle model by Dadyburjor et al. [8] at low initial coverage. We conclude that the local coarsening mechanism is the reason for the broadening of the scaled distribution.

According to the prediction of the mean field model, the sintering curve of total particle number \( N(t) \) is a power law with an exponent 3/4. In the multiparticle model by Dadyburjor et al., the evolution of the average particle number has not been calculated. In the local model studied here, \( N \) is found to have a power law form with a slightly different exponent from 3/4. The exponent ratio \( b/a \) is close to 3, a consequence of the exact mass conservation.

References