Ostwald Ripening in Two Dimensions: Treatment with Pairwise Interactions.

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We present a systematic extension of mean field models for Ostwald ripening in two dimensions. We derived, using a mean field type approximation, an analytic expression for pairwise interactions between the minority phase droplets. These interactions appear in dynamic equations for the droplets’ radii and positions, which are solved numerically for systems of tens of thousands of droplets, yielding very good agreement with recent experiments.

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Ostwald ripening is a coarsening process, observed during the late stage of the evolution of a two-phase system (say, solid in liquid), in the course of which the droplets of the minority phase exchange material by means of diffusion. This process leads towards a scaling state in which the characteristic length scale grows with time according to the Lifshitz-Slyozov law $R(t) \sim t^{1/3}$. When rescaled by $R(t)$, all statistical characteristics of the system (such as droplet size distribution, spatial correlations etc) are time-independent.

These characteristics were studied in a number of detailed numerical simulations. The Cahn-Hilliard equation solved in the entire system, provides the most basic model of Ostwald ripening. If the solid droplets are assumed to be uniform and only their boundaries are retained to describe the system, the problem becomes one of solving the diffusion equation for the concentration field $c(\vec{r})$ between droplets, with Gibbs-Thomson boundary conditions:

$$c_{\text{droplet}}(t) = c_{eq}(R(t)) = c_{\infty} + \frac{\alpha}{R(t)}.$$ (1)

The boundaries move in response to the incident flux;

$$\frac{dR}{dt} = -J_\perp \quad \vec{J} = -\nabla c|_R$$ (2)

At long times a quasi-static approximation can be used and the diffusion problem turns into Poisson’s equation in 2-d,

$$\nabla^2 c = 0.$$ (3)

This problem can be reduced to an implicit system of ordinary differential equations. Since these calculations take into account all the complicated interactions between the droplets, mediated by the diffusion field, they do not elucidate the relative importance of different aspects of these interactions. The number of droplets and the length of the simulations are also limited. On the other end of the complexity scale are analytical mean field treatments that neglect all spatial effects; these, however, are too simple to account for correlations in a system of non-vanishing volume fraction. Previous attempts to “interpolate” between these extremes, and provide an analytical treatment of the spatial effects contain uncontrolled approximations and lead to very complicated expressions.

Using a mean-field type approximation, we calculated analytically pairwise interactions between the droplets. These appear in closed-form dynamic equations for many interacting droplets which are integrated numerically. Our model gives rise to a very efficient numerical algorithm; the evolution of tens of thousands of droplets can be followed. Our work was motivated by and our results are compared with a recent experiment on a two-dimensional film of liquid and crystalline succinonitrile in coexistence. This experiment shows that even at $\varphi = 0.4$ the droplets are almost circular; therefore we characterize the system by the set of the droplets’ radii $R_i$ and the positions $\vec{r}_i$ of their centers.

We write the solution of Eq. (3) in terms of “charges” and “dipoles” placed at $\vec{r}_i$

$$c(\vec{r}) = \sum_i q_i \log(|\vec{r} - \vec{r}_i|/R_0) + \sum_i \left(\frac{q_i \cdot (\vec{r} - \vec{r}_i)}{|\vec{r} - \vec{r}_i|^2}\right)$$ (4)

($R_0$ is an arbitrary length). The boundary conditions on the surface of each droplet give rise to linear equations which determine the charges $q_i$ and the dipoles $\vec{p}_i$. When the resulting solution is used in (2) to derive the flux at droplet $i$, we find that it’s normal component has two terms. One is isotropic, due to the charges; it affects the droplet’s area and therefore determines the dynamics of the radii. The other is an anisotropic contribution, due to the dipoles which gives rise to a shift of the centers of the droplets. The charges and dipoles can be eliminated, yielding dynamic equations for the radii and positions of the droplets:

$$\dot{R}_i = \frac{q_i}{R_i} = \sum_j L_{i,j}^{-1} (1 + R_j/R_c) = \sum_j L_{i,j}^{-1},$$ (5)

$$\frac{d\vec{r}_i}{dt} = -2\vec{p}_i/R_i = 2\sum_j R_j \dot{R}_j \frac{\vec{X}_{i,j}}{|\vec{X}_{i,j}|^2},$$ (6)
where \( X_{i,j} = |\vec{r}_j - \vec{r}_i| \) and \( R_c = \alpha/c_\infty \) is a capillary length. The second equality in Eq. (1) is due to a sum rule. \( L_{i,j}^{-1} \) are the elements of the inverse of the matrix \( \hat{L} \), defined as:

\[
L_{i,j} = \begin{cases} 
\log(R_i/R_0) & \text{if } i = j \\
\log(X_{i,j}/R_0) & \text{otherwise}
\end{cases} \quad (7)
\]

The value of the parameter \( R_0 \) is arbitrary; it does not affect the dynamics of the system. Once \( \hat{L} \) has been inverted, we can evaluate the radii at the next time step. One must invert the \( N \times N \) matrix \( L_{i,j} \) at each time step (which takes \( O(N^3) \) operations); since we need \( O(N) \) time steps, each run would cost \( O(N^4) \) computations.

Beenakker solved an analogous problem in 3-d by truncating the matrix \( L_{i,j} \). Motivated by the effect of screening, he took into account only interactions between those droplets whose separation does not exceed a threshold. Akaiwa and Meiron used the analogous truncation procedure in 2-d. However, formal truncation of the matrix seems problematic. Since the matrix elements grow with \( X_{i,j} \), the elements of the inverse matrix \( \hat{L}^{-1} \) as functions of the cutoff should contain large fast oscillating components. Apparently, the success of Akaiwa and Meiron is due to the fact that these oscillations are effectively averaged out during the run.

Rather than discarding large matrix elements and proceeding to invert the truncated matrix numerically, we calculate analytically the elements of \( \hat{L}^{-1} \), using a mean field approximation. First, represent \( \hat{L} \) as the sum of its diagonal and off-diagonal parts, \( \hat{L} = L_0 - L_1 \), where \((L_0)_{i,j} = \delta_{i,j} R_c^2 \log(R_i/R_0)\) and \((L_1)_{i,j} = -(1 - \delta_{i,j}) R_i R_j \log(X_{i,j}/R_0)\) and introduce a new matrix \( \hat{T} \) defined by

\[
\hat{T}^{-1} = L_0^{-1} + L_0^{-1} \hat{T} L_0^{-1}
\]

This is indeed the inverse of \( \hat{L} \) if \( \hat{T} \) satisfies the equation

\[
\hat{T} = L_1 + L_1 \hat{T} L_1^{-1}
\]

For convenience we represent \( T_{i,j} = R_i R_j \phi_{i,j} \); Eq. (2) now becomes a condition on the matrix \( \phi \), which we write separately for the diagonal and off-diagonal elements:

\[
\phi_{k,k} = -\sum_{j\neq k} \frac{\log(X_{j,k}/R_0)}{\log(R_j/R_0)} \phi_{j,k}
\]

\[
\sum_{j\neq k} \frac{\log(X_{i,j}/R_0)}{\log(R_j/R_0)} \phi_{j,k} + \phi_{i,k} = -\gamma_k \log(X_{i,k}/R_0)
\]

with

\[
\gamma_k = 1 + \frac{\phi_{k,k}}{\log(R_k/R_0)}
\]

The set of equations (2-5) is exact but solving it is as difficult as inverting \( \hat{L} \). The advantage of this formalism is that it serves as a convenient starting point to generate approximate expressions for \( \phi_{i,j} \) - in particular, a manageable mean-field approximation.

We give now an outline of the main ideas and formal steps of the derivation of our approximation to \( \phi_{i,j} \); details will be presented elsewhere. First of all we assume that the \( i,j \) matrix element depends only on the corresponding distance, \( \phi_{i,j} = \phi(X_{i,j}) \), and that \( \phi(X) \) varies only on scales \( \zeta \) such that the number of droplets within an area \( \zeta^2 \) is large. If this holds we can replace in Eqs. (10) and (2) the factor \( 1/\log(R_i/R_0) \) by its mean value and the sums by integrals. Within this mean-field approximation Eq. (11) implies \( \phi_{k,k}^{(mf)} \) - const. = 0; this leads to a self-consistent expression for \( \phi(X_{i,j}) \) only if we set \( \gamma_k \) = const. = \( \gamma_0 \) which, in turn, means (see Eq. (1) that \( \phi_0 = 0 \) and \( \gamma_0 = 1 \). Thus within our mean-field treatment of \( \phi \), Eq. (11) becomes

\[
\frac{1}{2\pi \zeta^2} \int \log\left(\frac{X_{i,j}}{R_0}\right) \phi(X_{j,k}) d^2 r_j - \phi(X_{i,k}) = \log\left(\frac{X_{i,k}}{R_0}\right)
\]

where we introduced a constant length, defined by

\[
\zeta^{-2} = 2\pi n \left( \frac{1}{\log(R_0/R)} \right) \approx 2\pi n \frac{1}{\log(R_0/\langle R \rangle)}
\]

Here \( n = \phi/\pi \langle R \rangle^2 \) is the number of droplets per unit area; the angular brackets denote averaging over the droplet size distribution. Operating with \( \nabla^2 \) on Eq. (12) yields the differential equation

\[
-\zeta^{-2} \phi + \nabla^2 \phi = -2\pi \delta(\vec{r}),
\]

which is solved by the zeroth order modified Bessel function of the second kind (also called MacDonald function), \( \phi(X) = K_0(X/\zeta) \). This determines the off-diagonal elements of \( \phi_{i,j} \) up to the length \( \zeta \) which depends on the arbitrary parameter \( R_0 \). Since the value of this parameter does not affect the exact solution of the problem, we can tune it to improve our approximation. Note that when our \( \phi(X) \) is used in the integral form of Eq. (1), we get

\[
\frac{1}{2\pi \zeta^2} \int \log(X_{j,k}/R_0) K_0(X_{j,k}/\zeta) d^2 r_j = \phi_{k,k} = \phi_0 = 0
\]

After some lengthy algebra, presented elsewhere, we can show that this condition is satisfied when \( R_0 \) satisfies the following approximate expression:

\[
\frac{1}{\log(R_0/R)} \approx \frac{1}{K_0(R/\zeta)}
\]

By substituting Eq. (16) in Eq. (13) we eliminate \( R_0 \) from the problem and obtain an equation for \( \zeta \):

\[
\zeta^{-2} = 2\pi n \left( \frac{1}{K_0(R/\zeta)} \right) ,
\]

is that it serves as a convenient starting point to generate approximate expressions for \( \phi_{i,j} \) - in particular, a manageable mean-field approximation.
which is almost identical to Marqusee’s expression for the screening length. The solution for \( \phi(X) \) determines the matrix \( T \) and we get an expression for the matrix elements \( L^{-1} \) which, when used in Eq. (15) together with the relation

\[
- \sum_{j \neq i} \frac{1}{\log(R_j/R_0)} K_0 \left( \frac{X_{i,j}}{\zeta} \right) \approx \frac{1}{2\pi\zeta^2} \int K_0 \left( \frac{r}{\zeta} \right) d^2r = 1,
\]

finally yields our central result:

\[
R_i \frac{dR_i}{dt} = R_i \sum_j L_{i,j}^{-1} = \frac{1}{K_0(R_i/\zeta)} \times \sum_{j \neq i} \frac{K_0(X_{i,j}/\zeta)}{K_0(R_j/\zeta)} \left( \frac{1}{R_j} - \frac{1}{R_i} \right). (18)
\]

Since \( K_0(x) \sim \exp(-x) \) for large \( x \), \( \zeta \) indeed has the meaning of a screening length. Note that the total area of the droplets is conserved by Eq. (18).

The approximations made, of replacing the sums by integrals and \( 1/\log(R_j/R_0) \) by its average value \( 1/(2\pi\zeta^2) \), are valid if the function \( \phi(X) \) is smooth and the number of droplets in the screening zone is large: \( N_{\zeta} = n\zeta^2 \gg 1 \). For \( \varphi = 0.13 \) (as used in the experiment) the approach outlined above gave a much too small value for \( \zeta \). A somewhat larger value was obtained by taking into account the fact that each of the droplets is surrounded by a depletion zone, from which all neighbors are excluded. Including depletion zones retains an equation of the same form as Eq. (18) for the evolution of the radii, but with the mean-field \( \zeta \) replaced by \( \zeta_{\text{sc}} > \zeta \). For \( \varphi = 0.13 \) it becomes \( \zeta_{\text{sc}} = 2.73 \bar{R} \approx 0.56X \) where \( X \) is the typical distance between neighbors. Although \( \zeta_{\text{sc}} \) is still too small to provide a formal support to our approach, we tested it by integrating (numerically) Eqs. (15) and (16).

The detailed description of our numerical algorithm is presented elsewhere. An advantage of our method is that it conserves the total area of the droplets at each time step. Computational efficiency is very high: an entire run, starting with \( N \) droplets initially and running till most disappear (i.e. reach \( R_i \approx 0 \)) takes only \( O(N \log N) \) operations. This is due to the fact that we are able to keep the time step reasonably large, eliminating a large number of droplets at each step. At the same time, unlike previous studies, we ensure exact conservation of the total area of the droplets at each time step. This makes our approach useful for an extensive study of the Ostwald problem.

We used initial systems of 50000 droplets with toroidal boundary conditions. First evaluate \( R_i \) using Eq. (15) with \( \zeta = 2.73 \bar{R} \); next use Eq. (16) to calculate the motion of the droplets’ centers.

Regarding this motion, one can use Eq. (15) to estimate its importance by comparing the characteristic times for significant shift versus a shrinking droplet’s lifetime: \( \tau_{\text{shift}}/\tau_{\text{life}} \sim \frac{1}{X^2} \approx \pi/\varphi \). Hence for small fractions (and even for \( \varphi = 0.13 \)) the shift of the droplets is adiabatically slower than the droplets’ growth and one is tempted to neglect the motion of the centers. Indeed we tried this, but the resulting solution of the dynamics of the radii alone led to severe inconsistencies (manifest in significant overlap of neighboring droplets, i.e. \( R_i + R_j > X_{i,j} \)). This convinced us that the correlations induced by the proper movement of the droplets are essential for a physically sensible solution.

The sum on the r.h.s. of Eq. (16) appears to have convergence problems; assuming that the charges are uncorrelated random variables, with zero mean (as required by the total area conservation) one can easily get

\[
\left\langle \left( \frac{dR_i}{dt} \right)^2 \right\rangle \sim \left\langle \frac{1}{|X_{i,j}|^2} \right\rangle \sim \left\langle q_i^2 \right\rangle \log L_s, \quad (19)
\]

where \( L_s \) is the size of the system. The charges, however, are correlated (the effect of screening) and this causes fast convergence. We performed in some cases the entire sum and then repeated the simulations, summing only over droplets \( j \) with \( |X_{i,j}| < b \), using \( b = 2.3X \) and \( b = 3.25X \) (the latter value corresponds to about 10 terms in the sum); no significant difference between these three simulations was found.

For 50,000 initial droplets at \( \varphi = 0.13 \) the system approached the scaling state at \( N \approx 3000 \); this is when we started our measurements. In order to reduce fluctuations we averaged all the data over 8 runs. Such a run took about 105 minutes on a single processor of an HP-9000 (series K200) workstation. First we present the distribution of the droplets’ radii in the scaling state (see Fig. 1). The agreement with the experimental points is reasonable.
A much more demanding comparison is that of various correlation functions. Fig. 2 presents the correlation function \( G(r) \) - the probability to find a droplet's center at a distance \( r \) from a given droplet's center, as obtained by our numerical solution and experiment. We recover the positions of the initial rise of \( G(r) \) as well as the existence and position of its maximum. The value of our curve at the maximum is smaller than the experimental one; our \( G(r) \) is rather close to the result of Masbaum, obtained by solving the Cahn-Hilliard equation (see Fig. 1a in ref. 4), that also exhibits a small peak.

We measured also the correlation functions of the charges defined first in ref. 13, which contain more detailed information about the system. For a charge \( q_i \), calculate \( Q_+(r) \), the total amount of similar charge as \( q_i \) within an annulus \([r, r + dr]\) around \( r_i \), and define the function

\[
g_+(r) = \langle q_i Q_+(r) \rangle.
\]

Similarly we define \( g_-(r) \) in terms of the opposite charges. These two functions, as obtained by our simulations, are presented in Fig. 3 together with the corresponding experimental data of Krichevsky and Stavans. The agreement between theory and experiment is quite impressive.

In summary, we introduced and tested a model for the Ostwald ripening process in two dimensions. Our model approximates the exchange of material between the droplets, as determined by the complicated diffusive interaction, by simple pairwise couplings. An approximate mean field type approach is used to evaluate these pairwise interactions. The resulting dynamic equations are then solved numerically. Our model gives good agreement with experiment for a fairly large value of area fraction. We found that the shift of the droplets plays an important role at \( \varphi = 0.13 \). Our method leads to a very efficient numerical algorithm that can be useful for future studies of this problem. This research was supported by grants from the Germany-Israel Science Foundation (GIF). B. L. thanks the Clore Foundation for financial support. We thank O. Krichevsky, J. Stavans and D. Kandel for discussions.

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