Late stage droplet growth

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The phenomenon of Ostwald ripening, where large droplets in a supersaturated solution grow at the expense of small droplets, was theoretically explained by Lifshitz and Slyozov. Modern theories provide extensions of this classic work to the situation where the volume fraction of the phase appearing as droplets is appreciable. This has been done by perturbation expansions, mean-field theory, and numerical methods. Herein, those recent developments are reviewed.

1. Introduction

Nucleation and growth is the most commonplace of first-order phase transitions. It occurs when a binary mixture is cooled rapidly from a disordered phase into a two-phase coexistence region, if the volume fraction $\phi$ of the minority component is small. It is useful to think of this process in terms of early and late time regimes. Initially, the dynamics of the phase transition is controlled by the nucleation of droplets from a supercooled or supersaturated solution, and little growth of those droplets occurs as the supersaturation is relieved by nucleation. For late times, no significant nucleation takes place, instead the phase transition involves the competitive growth of many droplets, so as to minimize surface energy. There is no sharply defined time when these two regimes switch, instead for intermediate times nucleation takes place at the same time as droplet growth. Here we focus on droplet growth in the late stages of the phase transition. Hence we consider a two-phase system where one phase forms a background matrix, and the minority phase consists of many droplets, as shown in fig. 1. As time $t$ evolves, the total number of droplets decreases and the average droplet radius $\bar{R}(t)$ increases: Large droplets grow by the condensation of material diffused through the matrix from small evaporating droplets. This phenomenon is called Ostwald ripening [1].

The growth process is clearly shown in fig. 1, where configurations from a numerical simulation of Ostwald ripening are presented. Since the volume fraction is constant, surface area is decreased by the evaporation of droplets
smaller than an average size. The thermodynamic force conjugate to the surface area is the curvature $1/R$, which enters through the chemical potential [2]. This driving force leads particles to diffuse from regions of high curvature to those of low, thus reducing the total interfacial free energy of the two-phase system. These are the main features of Ostwald ripening.

The object of a theory of Ostwald ripening is to determine the dynamics and morphology of droplet growth. In what follows, we focus on the average droplet radius $\bar{R}(t)$ and the number density $n(R,t)$, although other quantities, such as the structure factor, are also of interest. For many years after Ostwald's original discovery in 1901 of the phenomenon [1], the understanding of growth was only qualitative, as described above. Early attempts [3,4] did not succeed because they did not properly address diffusion between droplets through the matrix. The major advance in the theory of Ostwald ripening was made by the

![Fig. 1. Sketch of Ostwald ripening in two dimensions. Shaded circles represent the droplets (the minority component) fixed in two-dimensional space. As time evolves (via the numerical method discussed in section 3) from (a) to (d), the total number of droplets decreases and the average droplet radius increases, but the volume fraction of droplets $\phi$ (the shaded area) is constant.](image-url)
Herein, we will review work done since that time, particularly our own recent work. It is an honor to have this paper included in a collection commemorating the research of Professor Kyozi Kawasaki. Professor Kawasaki’s contributions to all aspects of the modern theory of the kinetics of first-order phase transitions have been profound. In particular, with his collaborators Tokuyama and Enomoto, he has given a firm grounding to the modern theory of Ostwald ripening [7].

The physics of the problem is straightforward. After nucleation has ceased, one has many small droplets of various sizes, where all concentrations are at their local equilibrium values. That is, the droplets are at the concentration of the minority phase, while far from all droplets, the matrix has the concentration of the majority phase. Hence the only driving force for equilibration is the surface free energy of all the droplets; the bulk free energies are already equilibrated. The difficulty is that the total concentration of either phase is conserved, i.e., the total volume of all the droplets is the product of the minority phase’s volume fraction and the total volume of the system:

\[
\sum_i \frac{4}{3} \pi R_i^3 = \text{const.} = \phi L^3,
\]

where \(i\) is an index running over all \(N(t)\) droplets, \(R_i\) is the radius of the \(i\)th droplet, and \(L^3\) is the system volume. This means that, since all droplets are spherical and have locally equilibrated their surface energy, the total system of many droplets can only minimize surface energy further by some small droplets getting smaller, and large droplets getting larger. This requires the diffusion of material through the matrix between widely separated droplets. This long-range process makes the problem technically challenging. Indeed, as we will see, it becomes analogous to a time dependent, multi-charge Coulomb problem.

Nevertheless one can still anticipate the main results, and hence focus on issues which theory and experiment can usefully address. First, it is clear that the interface of a droplet moves so as to minimize its surface area. The thermodynamic force conjugate to the area is interface curvature 1/\(R\), so we expect that the velocity \(v = dR/dt \approx 1/R\). But the relief of this thermodynamic force, by redistributing matter through the matrix to other droplets, requires diffusion through that matrix, which is limited by 1/\(R\). Hence we anticipate \(v \sim 1/R^2\). Indeed, this gives the correct growth law from dimensional analysis,

\[
\tilde{R}(t) = (Kt)^{1/3},
\]
for the average droplet size, where the constant $K$ is called the coarsening rate. Now since $R \to \infty$ as $t \to \infty$, all quantities that depend on length should scale with this diverging length. For instance, let the number density of droplets be

$$n(R, t) = \sum_i \delta(R - R_i(t)),$$

(3)

so that

$$\int dR n(R, t) = N(t),$$

(4)

the total number of droplets, which evidently decreases in time. Clearly the total number $N(t) \sim [L/R(t)]^3$ in three dimensions, so that the scaling form for the number density is

$$n(R, t) = R^{-d} g(R/R(t)),$$

(5)

where $R(t)$ is given above, and $g(z)$ is the scaling function.

The arguments giving these results are rather simple, and therefore turn out to be general. It is expected that thermal fluctuations are irrelevant in first-order transitions (they affect small length scales such as the thermal correlation length, which do not diverge), so that one finds the same scaling and form for algebraic growth for a large class of systems where a conservation law limits phase separation. In that sense, these results are superuniversal, since they are valid for different dimensions of space, and bridge the nominal universality classes of critical dynamics [8]. Of course, by this it is only meant that scaling and growth involve power laws determined by dimensional analysis, without anomalous dimensions.

Hence, the task of theory—besides the fundamental justification of algebraic growth of the average radius, and the scaling of the number density—is to calculate the numerical value of the coarsening rate $K$, the form of the scaling function $g(z)$, and other observable quantities. We shall be concerned with the dependence of these quantities on the dimension of space, and in particular, their dependence on volume fraction $\phi$. It is straightforward to anticipate the effect of an appreciable volume fraction: since there is more minority-phase material present, droplets will grow faster, and droplets of increasingly different relative sizes will be present. That is, $K$ should increase while $g(z)$ broadens with $\phi$. To obtain quantitative results, we must begin with the fundamental equations of motion.
2. Theoretical approaches

The starting point of the dynamic theory is to describe the diffusion of material between droplets. The diffusion equation for the (dimensionless) excess concentration field $c$ is

$$\frac{\partial c}{\partial t} = \nabla^2 c - \text{source} \approx 0,$$

where the source is due to all the droplets, and we shall consider the steady-state limit where the concentration is everywhere relaxed to its local equilibrium value. Each droplet serves as a source or sink of diffusion current, so we may rewrite this equation as

$$\nabla^2 c = 4\pi \sum_i Q_i(t) \delta(r - r_i),$$

where $r_i$ points to the center of each droplet, and the currents $Q_i$ at the surface of each droplet will be determined below. We have chosen this notation to promote the analogy between this problem and a Coulomb problem, which is striking when one notes that the conserved concentration obeys

$$\frac{d}{dt} \int d\mathbf{r} c(\mathbf{r}) = 0,$$

so that one must have

$$\sum_i Q_i = 0.$$

Henceforth we will sometimes call the currents $Q_i$ charges.

The boundary condition at the surface of each droplet is

$$c(\mathbf{r}) = \frac{1}{R_i}$$

for $|\mathbf{r} - \mathbf{r}_i| = R_i$, which is called the Gibbs–Thomson condition, while far from all droplets the concentration field is its value in the majority phase.

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*1 Units of length and time are given in terms of a characteristic length $l = (D - 1)\gamma V_m/R_g T$ (where $D$ is the dimension of space, $\gamma$ is the surface tension, $V_m$ is the molar volume, $R_g$ is the gas constant, and $T$ is temperature) and a characteristic time $t^2/\mathcal{D} C_m V_m$ (where $\mathcal{D}$ is the diffusion constant and $C_m$ is the concentration above a flat interface). The dimensionless excess concentration field is $c(\mathbf{r}) = [C(\mathbf{r}) - C_*]/C_*$, where $C$ is the concentration.
Using these boundary conditions, it is worthwhile to write down the formal solution of the diffusion equation in the steady-state limit as

\[ c(r) = Q_0 - \sum_{i=1}^{N} \frac{Q_i}{|r - r_i|}, \]  

(11)

where \( Q_0(t) \) is an integration constant determined by the conservation of charge (it is of course the concentration in the majority phase). At the surface of each droplet, the Gibbs–Thomson condition gives

\[ \frac{1}{R_i} = Q_0 - \frac{Q_i}{R_i} - \sum_{i=1,i\neq j}^{N} \frac{Q_j}{|r_j - r_i|}. \]  

(12)

Therefore, once one knows the sizes and positions of all the droplets, it is straightforward to calculate the charges \( Q_i \) of each droplet. Note also that, coincidentally, the excess concentration at the surface of the droplet, and the contribution from diffusion from other droplets, both vary as \( 1/R \), when the droplets are widely separated, i.e., in the limit as the volume fraction vanishes.

The rate of change of the volume of each droplet is simply determined by those charges, which give the diffusion current \( J_D \) over that droplet, i.e.,

\[ \frac{d}{dt} \left( \frac{4\pi}{3} R_i^3 \right) = \oint J_D \cdot dS_i = \int \nabla^2 c \, dr, \]  

(13)

where the first equality over the surface \( S_i \) of droplet \( i \) has been changed to a volume integral in the second equality. On using the form for the source above, we obtain

\[ \frac{dR_i}{dt} = \frac{Q_i}{R_i^2}. \]  

(14)

Formally, the problem is now complete; after determining the charges of each droplet from a set of initial conditions, one can use the equation of motion to find how each droplet evolves with time. Indeed, as shown originally by Voorhees and Glicksman [9], whose convenient notation we are following here, one can simply solve the equations numerically, as we will discuss below. However, most approaches consider a mean-field theory. Indeed, it is from this starting point that the theory of Lifshitz and Slyozov begins, although many approximations have already been made. For example, note that we have neglected all fluctuations. The important fluctuation not included is nucleation, since we have assumed that rate is now negligible. While this is a good description of many experimental systems with small volume fractions, as the
volume fraction becomes large, it should be noted that nucleation can conceivably compete with droplet growth. It should also be noted that we have neglected the possibilities of fluid convection in a liquid matrix or stress relaxation if the droplets are solid crystallites. Nevertheless, the formulation of Ostwald ripening is clear and nontrivial in this form; generalizations can be made to incorporate other effects if they are found to be important experimentally.

We will now briefly review the mean-field theory of Lifshitz and Slyozov. Consider a droplet separated an arbitrary distance from all other droplets, i.e., consider the limit in which the volume fraction \( \phi \to 0 \). Then in eq. (12) above \( |r_i - r_j| \to \infty \), and

\[
\frac{1}{R_i} = Q_0 - \frac{Q_i}{R_i} .
\]  

(15)

Rewriting this as \( Q_i = Q_0 R_i - 1 \), and summing over all droplets gives \( 0 = Q_0 \Sigma_i R_i - \Sigma_i \), or

\[
Q_0 = \frac{1}{\bar{R}(t)} ,
\]

(16)

where the bar denotes an average. Then the equation of motion for \( R_i \) is

\[
\frac{\partial R_i}{\partial t} = \frac{1}{R_i} \left( \frac{1}{\bar{R}(t)} - \frac{1}{R_i} \right) .
\]

(17)

Note that a droplet smaller than the average size shrinks and disappears, while one larger than that size will continue to grow.

To make further progress, we consider the number density \( n(R, t) \), where continuity in \( R \)-space implies

\[
\frac{\partial n(R, t)}{\partial t} + \frac{\partial}{\partial R} \left( n(R, t) \frac{\partial R}{\partial t} \right) = 0 .
\]

(18)

It is straightforward to solve for the growth law \( \bar{R}(t) \) and the number density \( n(R, t) \) if one makes the scaling ansatz as above of

\[
n(R, t) = \bar{R}^{-4} g(R/\bar{R}) ,
\]

(19)

where \( g(z) \) is the scaling function, and all the time dependence of \( n \) enters through \( \bar{R}(t) \). Using the equation of motion above, the continuity equation for
the number density becomes separable in the two independent variables $t$ and $z = R/R(t)$:

$$\bar{R}^2(t) \frac{d\bar{R}}{dt} = \frac{(2 - z)g(z) + (z^2 - z)(dg/dz)}{4z^2g(z) + z^4dg/dz}.$$  \hspace{1cm} (20)

Hence

$$\bar{R}^2(t) \frac{d\bar{R}}{dt} = K ,$$  \hspace{1cm} (21)

where $K$ is a constant independent of $t$ or $z$, which is determined by positivity and normalization of $g$. The classic results of Lifshitz and Slyozov for $\phi \to 0$ in dimension $D = 3$ are then recovered:

$$R(t) = (Kt)^{1/3} ,$$  \hspace{1cm} (22)

for late times, where $K = 4/9$, and

$$g(z) = \left\{ \begin{array}{ll} 
(3^4e/2^{5/3})z^2 \exp[-1/(1 - \frac{2}{3}z)]/[(z + 3)^{7/3}(\frac{3}{2} - z)^{11/3}] & \text{if } 0 < z < \frac{3}{2} , \\
0 & \text{otherwise} . \end{array} \right.$$  \hspace{1cm} (23)

These features, power-law growth and scaling, are now considered universal characteristics of the kinetics of a first-order phase transition [8], and have been observed experimentally [10–12].

Nevertheless, it has proved difficult to rigorously test the Lifshitz–Slyozov theory by experiment or by numerical simulation. Experiments typically study volume fractions which are appreciably larger than zero, while numerical work has the additional problem of being practically difficult in three dimensions. Furthermore, large scale numerical work has been limited by previous computer facilities. Hence modern theories give the form of the coarsening rate $K = K(\phi)$, and the scaling function $g = g(z, \phi)$. For the most part, analytic extensions have been based either on ad hoc assumptions [13–15], or on perturbative expansions in $\phi$, typically taken to order $\sqrt{\phi}$ [7,16]. Numerical work of good accuracy has become feasible only recently.

The phenomenological theory of Ardell [13] provides a physical though ad hoc method to extend the Lifshitz–Slyozov result to nonzero volume fractions. When the volume fraction is appreciable, Ardell noted that the droplets of different “charges”, that is with currents acting as sources and sinks, will screen each other, just as electric charges do. Say the average distance between droplets, which is determined by the volume fraction, is $\xi$. Ardell suggested
that the diffusion current from other droplets was screened effectively at a
distance $\xi/2$ from the surface of a droplet. This then replaces one of the boundary conditions on the concentration field.

Indeed, this idea of screening appears in all modern approaches, and Ardell's ensuing theory is physically appealing. However, it is not rigorous; for example, as noted by him, the choice of $\xi/2$, rather than some other fraction of $\xi$, is arbitrary. Nevertheless, the major features of Ostwald ripening with nonzero volume fraction, the increase in $K$ and broadening of $g(z)$ with $\phi$, are captured, although the dependence is not quantitatively correct, as we shall see.

A rigorous treatment by perturbation in the volume fraction has been done mainly by two groups, Marqusee and Ross (MR) [16], and Tokuyama, Kawasaki and Enomoto (TKE) [7]. In the MR approach, one perturbs in the bare Coulomb propagator from the Laplace equation using a formal scattering expansion, while TKE make use of a modified growth law and separately perturb the so-called drift and soft-collision terms, respectively. Both theories are technically demanding, and give results to leading order in $\sqrt{\phi}$, and so apply to exceedingly small volume fractions. There are small but we suspect unobservable differences between the predictions of these theories in the extremely small volume fraction limit to which they apply. These are due to the difference between the way the two groups treat direct correlations between droplets (called soft collisions by TKE).

In somewhat the same spirit, the possible effect of two-particle correlations was studied by Mardar in an ambitious theory [17]. While his starting point may prove to be useful to future work, many of his approximations are difficult to justify, and his results are not consistent with the rigorous perturbation theories of MR and TKE.

Recently, there has been interest in two-dimensional systems, where experimental work can be done, for example, on droplets absorbed on a surface or films. The issues in $D = 2$ are similar to those above, but there are additional difficulties. Theoretically, the technical problem is the logarithmic divergence encountered in the propagator of the Laplace equation. Indeed, the original LSW approach cannot be applied to two-dimensional systems, since the general solution for two-dimensional steady-state diffusion in eq. (6), $c(r) \sim \ln r$, cannot simultaneously satisfy the boundary conditions at the surface of a droplet and far from all droplets. One must identify the appropriate length to cut off the range of diffusion far from all droplets. Various theories have been proposed.

In the zero-volume fraction limit, Rogers and Desai (RD) [18] proposed a non-steady-state approach, where that extra length is essentially the evolving droplet size. (We shall continue to call $\phi$ a volume fraction although it is an
area fraction in $D = 2$.) Solving the time-dependent diffusion equation they obtained the modified growth law for the average droplet size, $\tilde{R} \sim (t/\ln t)^{1/3}$ for $\phi = 0$.

For nonzero volume fractions, evidently the appropriate length to make the propagator well defined is due to the nonzero volume fraction. Theories have been proposed by Ardell [13], Marqusee [19], and Zheng and Gunton [20]. None of these approaches are rigorous, in the sense of the perturbation theories mentioned above. They all obtain a scaling form for the number density with the conventional $\tilde{R} \sim t^{1/3}$ result. Ardell has generalized his three-dimensional phenomenological theory to $D = 2$. The approach taken by Marqusee in two dimensions [19] is significantly different from his three-dimensional work. The idea used in this work is similar to that of Ardell in that a screening length is introduced in the diffusion equation, whose value is then self-consistently determined. Finally, to study two-droplet correlations in two dimensions, Zheng and Gunton [20] combined Marqusee’s two-dimensional theory with a generalization of Mardar’s theory.

We now review our work, which applies to $D = 2$ or $D = 3$ [21–24]. The results of that theory cannot be distinguished from the perturbation theories in the very small volume fraction limit, and since our approach is by mean field, we have results to all orders in the volume fraction. Our main approximation is the complete neglect of direct correlations between droplets. Following the next section, we will compare our work to the results of other theories and numerical work, finding that it fares rather well. One other advantage of our approach is that it is simple analytically, and hence straightforward to generalize. In fact, we have generalized it in other works to consider excitonic systems [23] and systems where phase separation is limited by surfactants [24].

For nonzero volume fractions, we approximate the spatial correlations contained in eq. (12) above by mean-field theory. We make use of the fact that, for non-zero $\phi$, the steady-state problem resembles a homogeneous electron gas, since droplets interact via the Laplace equation in the steady-state limit and charge neutrality is invoked. We introduce screening effects among the droplets and approximate the many-droplet correlation effects in the same manner as the Thomas–Fermi mechanism for Coulomb systems. We replace the sum over multiple droplets with an effective potential $\psi$, which is determined self-consistently. That is, we find the excess concentration at the surface of a droplet to be

$$\frac{1}{\tilde{R}_i} = Q_0 - Q_1 \psi(R_i/\xi, \xi), \quad (24)$$

where $\xi$ is a screening length due to the other droplets, related to the volume
fraction of the minority phase, where $\psi(\xi \to \infty) \to 1/R_i$. It only remains to establish the form of $\psi$, and the conditions determining $\xi$ by the volume fraction. As one would expect, the effective potential turns out to have the Yukawa form $\psi = (1/R)[\exp(-R/\xi)]$ in three dimensions.

To obtain an effective potential, we reconsider the growth law. First we replace the spatial coupling between droplets with an effective current $J(R, R')$ which only depends on the size of all droplets. Then

$$\frac{d}{dt} \frac{4\pi}{3} R_i^3 = \sum_j J(R_i, R_j) \Delta c(R_j),$$

where $\Delta c(R_j)$ is the individual driving force due to each droplet given by the concentrations deviation from its value in the majority phase (i.e., $\Delta c(R) = Q_n - c(R)$). Within our mean-field approximation, all droplets are equivalent, so $J(R, R') = J(R) \delta_{R,R'}$, and

$$\frac{d}{dt} \frac{4\pi}{3} R_i^3 = J(R_i) \Delta c(R_i),$$

where it remains to determine $J(R_i)$. The mean-field approximation results from the assumption that the flux determining the growth rate for each droplet is only proportional to the difference between the boundary concentration and the average bulk concentration.

We now postulate an equation of motion for the local concentration field $c(r, t)$ in the vicinity of the $i$th droplet. The most simple form it can satisfy is

$$\frac{\partial c}{\partial t} = \nabla^2 c - \xi^{-2} c + S - 4\pi Q_i \delta(r - r_i).$$

Herein, local diffusion is modified by the effective diffusion field from the other droplets, giving rise to the screening length $\xi$ and the background field $S\xi^{-2}$. These quantities can be related to $J(R)$ by integrating the equation above and comparing it with eq. (26), i.e.,

$$\xi^{-2} = \frac{1}{L^3} \int_0^\infty J(R) n(R, t) \, dR,$$

$$S = \frac{1}{L^3} \int_0^\infty J(R) c(R) n(R, t) \, dR.$$
Consistency between these two equations is enforced by

$$S = \frac{Q_0}{\xi^2}$$

for the effective field. Now it is straightforward to obtain an effective field $\psi$ which gives the effect of the other charges $Q_j$ away from the droplet. Furthermore, from the growth law, this will determine the coupling current $J$, which turns out to be proportional to the inverse of $\psi$.

Eqs. (26) and (27) completely specify our mean-field approximation; indeed, they are the only approximations needed to solve the equations in the steady-state limit. Their form implies that we consider a one-body problem without correlations. A systematic derivation of these equations from first principles would be valuable, since corrections to our equations, involving correlations, could be calculated. However, we have not been able to obtain such a derivation, although, of course, a coarse graining of the microscopic equations, with the requirement that only a one-body distribution function is involved, will lead to our self-consistent starting point.

The analysis follows the same route as the above for Lifshitz and Slyozov, with the potential derived from the solution of eq. (27) for $c$ at the surface of the droplet being of the Yukawa form in three dimensions, as noted above. One finds that the equations are again separable, and the growth law and number density are straightforwardly determined. The complete details, including analysis for two-dimensional systems, are given in our original papers [21–24].

As in other theories, we find that $K$ increases and $g(z)$ is broader as the volume fraction increases. For example, in two dimensions, as $\phi \to 0$, we find $\bar{R}(t) \sim [t/\ln(\phi^{-1/2})]^{1/3}$. Hence the $(\ln t)$ singularity found in the non-steady-state calculation of Rogers and Desai for $\phi = 0$ is replaced by a $(\ln \phi)$ piece in our steady-state approach. Presumably one could derive a crossover form for very small $\phi$ where the Rogers and Desai result is obeyed for early times, crossing over to this result for later times. Finally, we note that solutions can only be found for our mean-field equations for restricted values of volume fraction: Our approach is self-consistently correct for $\phi \leq 0.06$ in three dimensions and $\phi \leq 0.085$ in two dimensions.

To conclude this section, we note that all theories agree on the qualitative behavior for nonzero-volume fractions, but there are large quantitative differences. After briefly reviewing numerical approaches in the next section, we will compare theories to numerical work and experiment.
3. Numerical simulations

For small volume fractions, a beautiful numerical scheme based on a potential method was introduced in 1984 by Voorhees and Glicksman [9]. They carried out numerical simulations by an Ewald-sum technique. Unfortunately that work, and subsequent numerical work [25], was hampered by the computing facilities available at that time, so that statistics were unreliable. However, recently we [21,22] have been able to carry out larger scale simulations in both two and three dimensions, in which 1000 droplets were considered. Some of these results will be reported below. We should note that other methods are possible, for example Chakrabarti et al. have integrated the nonlinear Langevin equation corresponding to the universality class of Ostwald ripening, and obtained interesting results [26]. Nevertheless, at present the potential method is the most accurate to our knowledge.

The basic equations for the three-dimensional simulation are given above. Given an initial configuration of droplets, one inverts the matrix of eq. (12), which formally solves the diffusion problem, to obtain the charges \( \{Q_i\} \) from the droplet radii \( \{R_i\} \) at positions \( \{r_i\} \). (The extra current \( Q_0 \) is determined by conservation of charge.) Then the sizes of droplets are updated by the equation of motion eq. (14).

However, simply integrating the equations in this form is awkward numerically because of long-range interactions. For example, in two dimensions, one has

\[
\frac{1}{R_j} = Q_0 + Q_j \ln R_j + \sum_{i=1, i \neq j}^{N} Q_i \ln |r_j - r_i|.
\]

A tractable form of this equation can be obtained by means of Ewald-sum techniques [10,21,22], which give

\[
\frac{1}{R_j} = \frac{Q_0}{L^2} + \frac{Q_j}{r_j} \ln \left( \frac{R_j}{L} \right) - \int_{0}^{L^2} \frac{e^{-r^2}}{r} \, dr - \int_{1}^{\infty} e^{-r^2} \, dr
\]

\[
- \sum_{i=1, i \neq j}^{N} Q_i \int_{|r_j - r_i|/L}^{\infty} \frac{e^{-r^2}}{r} \, dr - \frac{2\pi}{L^2} \sum_{i=1}^{N} Q_i \sum_{k \neq 0} \frac{e^{-k^2/4L^2}}{k^2} e^{ik(r_j - r_i)},
\]

where \( L^2 \) is the system size. The remainder of the numerical analysis is straightforward though tedious. For example, in order to keep the volume
fraction constant during the iterations, the time increment must be determined self-consistently by shrinking, at most, one droplet in each single time step.

4. Comparison of different theories

Fig. 2 gives the time evolution of the average droplet radius obtained from our simulations, showing that the numerical data is consistent with $R(t) = [K(\phi) t]^{1/3}$. The values for the coarsening rate obtained by the fits to fig. 2 are given as a function of $\phi$ in fig. 3, in which the numerical values for $K$ are compared with various theoretical predictions. One can see that the theories of TKE, MR, and Marqusee well explain the data at small volume fractions, while our theory continues to work well at somewhat larger volume fractions.

Comparisons of theoretical predictions for the scaled distribution function $g(z)$ in $D = 3$ with simulations and an experimental measurement [12] are presented in fig. 4, and in $D = 2$ in fig. 5. Different symbols correspond to distribution functions at different times as noted in the caption. Scaling is confirmed by the universal curve to which the data from different times collapse. Again, one can see that the theories of TKE, MR, and Marqusee well explain the data at small volume fractions, while our theory continues to work well at somewhat larger volume fractions. The good fit of Ardell’s theory in $d = 2$ is accidental, since the coarsening rate is not well described by that theory.

It should be noted that the main difference between our theory and the perturbation theories is the inclusion of terms to all orders in $\phi$ in our mean-field theory. The perturbation theories and ours give essentially the same result to leading order in the expansion in $\sqrt{\phi}$. However, our numerical data indicates that higher-order volume fraction effects, beyond this order, are important for volume fractions as low as 1%.

5. Conclusions

In summary, modern approaches to the theory of Ostwald ripening have advanced to the point where one now has a quantitative understanding of this phenomena. The theories reviewed here can be tested experimentally by many methods. In particular, this would allow the study of the importance of effects which have been neglected here. It is impossible to say with certainty what those effects might be. Perhaps correlations will be of importance, but we
Fig. 2. Results of our numerical simulations for the time evolution of average droplet size $(\bar{R}^3(t) - \bar{R}^3(0))$ vs. $t$ for (a) $\phi = 0, 0.01$ and $0.05$ in $D = 3$; (b) $\phi = 0.01, 0.05$ and $0.10$ in $D = 2$. The straight lines indicate that the time evolution of the average droplet radius is consistent with $\bar{R}(t) = [\bar{R}^3(0) + K(\phi) t]^{1/3}$, allowing us to estimate the coarsening rate $K(\phi)$.

rather suspect it is our starting point itself which will have to be modified. For example, in the nucleation of a solid from a liquid, we expect stress and strain effects to be important, which have been neglected from our starting point.
Fig. 3. Plots of coarsening rates $K$ vs. $\phi$ in (a) $D = 3$, and (b) $D = 2$. In (a) $(K(\phi)/K(0) \text{ vs. } \phi)$, the dotted, dashed, long-dashed, dash-dotted, and solid lines correspond respectively to results of MR [16], TKE [7], Ardell [13], Mardar [17], and us, denoted YEGG. The lines for MR and TKE are almost superimposed. The symbols correspond to our simulation results. In (b) $(K(\phi) \text{ vs. } \phi)$, dotted, dashed, long-dashed, and solid lines correspond respectively to results of Ardell [13], Marqusee [19], ZG [20], and us, denoted YEGG. The symbols represent our simulation results.

* Here, we only present TKE's mean-field results, called the drift-term approximation by them.
Fig. 4. Comparisons of the distribution functions $g(z)$ between different theories, our simulations, and an experiment is displayed in $D = 3$ for $\phi = 0.01$ in (a); for $0.05$ in (b). The symbols (except the solid circles) are simulation results. The different symbols correspond to different times when the number of remaining droplets $N = 600, 500, 400$ and $300$. The dotted, long-dashed, dash-dotted, and solid lines are the respective predictions of MR [16], TKE [7], Ardell [13], Mardar [17], and us, denoted YEGG ([21,22] in $D = 3$), where the lines for MR and TKE superimpose. In (b), the solid circles are the experimental distribution function at very late times [12] for $\phi \sim 0.05$. 
Fig. 5. Plot of the scaled normalized distribution function $g(z)$ vs. the scaled radius $z = R/R$ for $D = 2$. Dotted, dashed, and solid lines correspond respectively to Marqusee [19], Ardell [13], and us, denoted YEGG [21,22]. Circles, squares, and triangles give the scaled normalized distribution functions from the simulation, corresponding respectively to different times when the number of remaining droplets $N = 500$, 400, and 300, for $\phi = 0.01$ in (a); for $\phi = 0.05$ in (b).
Acknowledgements

We thank Mohamed Laradji for collaboration on some of the work reviewed here. This work was supported by the Natural Sciences and Engineering Research Council of Canada and le Fonds pour la Formation de Chercheurs et l'Aide à la Recherche de la Province de Québec.

References