Effective theories for Ostwald ripening

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1   Introduction

In this article we discuss the derivation and analysis of reduced models for a specific coarsening process which is known as Ostwald ripening. This phenomenon appears in the late stage of phase transitions, when – due to a change in temperature or pressure for example – the energy of the underlying system becomes nonconvex and prefers two different phases of the material. Consequently a homogeneous mixture is unstable and, in order to minimze the energy, it separates into the two stable phases. Typical examples are the condensation of liquid droplets in a supersaturated vapor and phase separation in binary alloys after rapid cooling.

With Ostwald ripening one usually denotes the case, when the composition of the mixture is such that one of the two stable phases has much smaller volume fraction than the other. Then the minority phase nucleates in form of many small droplets which first grow from a uniform background supersaturation. Once the latter is small, surface energy becomes the dominant part of the total energy and to minimize it particles start to interact via diffusional mass exchange to reduce their total surface area. As a consequence large particles grow, while smaller ones shrink and finally disappear.

Ostwald Ripening is a paradigm for statistical self-similarity in coarsening systems. Thie means that after a transient stage the particle number density evolves in a unique self-similar fashion, which is independent of the details of the initial data. The first quantitative description of this phenomenon was given by Lifshitz and Slyozov (1961) and Wagner (1961) and is nowadays known as the classical LSW-theory. In the regime where the volume fraction of the droplets is small they derive an equation for the particle number density based on the crucial assumption that in the dilute regime the interaction between particles can be expressed solely through a common mean-field. However, it has been established by a mathematically rigorous analysis that the long-time behavior within the LSW model is not a universal statistically self-similar one but on the contrary depends sensitively on the initial data. Hence, in order to overcome this shortcoming, one has to go beyond the mean-field assumption and take higher order effects such as screening induced fluctuations and particle collisions into account.

A number of different approaches to develop a corresponding theory can be found in the physics and metallurgical literature. However, the predictions based on the respective theories differ significantly and it seems that a more rigorous analysis could be helpful in resolving some of the open questions. It is the main goal of the present article to review corresponding progress on the understanding of first order corrections to the LSW theory. While we go along, we also point out some directions for future research, in particular where the combination of analytic and stochastic tools could be relevant.

For more background on results, which are not discussed in detail here, as well as for references to the applied literature, we refer to the review article (Niethammer et al., 2006).

2   Basic models and mean-field theories

2.1   The starting point: a simplified Mullins-Sekerka evolution

A basic model for diffusion controlled Ostwald ripening of spherical particles is a simplified Mullins-Sekerka type model which is appropriate in the case that particles have small volume fraction. In this model particles, called P_i, are distributed in a domain $\Omega \subset \mathbb{R}^3$ and are characterized by their immovable centers $X_i \in \Omega$ and their radii $R_i(t)$. Particles interact by diffusion, but in late-stage coarsening we can assume that mass exchange between particles is much faster than the growth of the interfaces. Hence we can use a quasi-steady approach, that is we assume that the potential u relaxes at each time instantaneously to equilibrium. This gives that for each time t the potential $u = u(x, t)$ solves

$$
\begin{aligned}
\Delta u &= 0 &&\text{in } \Omega \backslash \bigcup_i \overline{P_i} \\
u &= \frac{1}{R_i} &&\text{on } \partial P_i \,,
\end{aligned}
\tag{1}
$$

where Δ and later ∇ denotes derivatives with respect to the space variable x. The second equation in (1) is the well-known Gibbs-Thomson law which accounts for surface tension. To define the potential uniquely, we have to couple (1) with suitable boundary conditions on $\partial \Omega$. In the case that Ω is bounded, a natural assumption is to consider closed systems and require

$$
\frac{\partial u}{\partial \vec{n}} = 0 \qquad \text{on } \partial \Omega \,.
\tag{2}
$$

We can also consider the problem in the whole space $\Omega = \mathbb{R}^3$ in which case the appropriate boundary condition is a no-flux condition at infinity:

$$
|\nabla u| \to 0 \qquad \text{as } |x| \to \infty \,.
\tag{3}
$$

We easily convince ourselves that if all particles have the same size, the potential u is constant (indeed equal to the inverse radius of the particles).

However, if particles have different sizes, this induces gradients in the potential and these gradients drive the system towards a state of lower energy. The Gibbs-Thomson law in (1) implies that u is large at small particles which have large surface area compared to their volume, and small at large particles. Hence, mass diffuses from the small to the large particles. The growth rate of a particle is simply given by the total flux towards the particle, that is

$$\frac{d}{dt}\Big(\frac{4\pi R_i^3}{3}\Big) = \int_{\partial P_i} \frac{\partial u}{\partial \vec{n}}\, dS\,, \tag{4}$$

where here $\vec{n}$ denotes the outer normal to the particle.

It is not difficult to show that, if we start with a finite number of particles, which do not overlap, the problem (1)+(2) or (1)+(3) is well-posed (cf. (Dai and Pego, 2005a) for the case (3)) and depends Lipschitz-continuously on the initial radii of the particles. As a consequence, the full time-dependent system (1)-(4) is well-posed for short times. We can extend such a local solution up to a time when a particle vanishes or when two particles touch. In the first case we just eliminate the particle and continue with the remaining ones. In this way we obtain a continuous in time, piecewise smooth solution. In the second case, where particles touch, there is no way to extend the solution in a reasonable way. In fact, the simplifying assumption that particles are spherical is not a good approximation when particles are close.

However, we are interested in the dynamics of a large set of particles with small volume fraction, and we expect that the event that particles touch is rare if it occurs at all. Hence it is plausible that it does not have an influence on the global behavior of the system. As we shall see, the latter is true to leading order, but not if one is interested in higher order effects. We will return to this issue later in Section 4.

As long as the evolution is well-posed we easily verify that it preserves the total volume of the particles and decreases the surface energy. Indeed, we have

$$\frac{d}{dt}\sum_i R_i^3 = 0 \tag{5}$$

and

$$\frac{d}{dt}\sum_i R_i^2 = -\frac{\pi}{2}\int_\Omega |\nabla u|^2\, dx\,. \tag{6}$$

In contrast to other curvature driven evolutions, such as the mean curvature flow, the Mullins-Sekerka evolution (1)-(4) is nonlocal. More precisely, the evolution of the radius of one particle depends on all the other particles in the system, since all particles interact via the potential u. A priori the interaction range between particles is large due to the slow decay of the fundamental solution of Laplace's equation. The challenge is to derive the effective growth law of a particle in a sea of surrounding particles. We will see that a key aspect in the analysis will be to establish the screening effect which identifies the effective interaction range between particles (cf. Section 2.5).

2.2 The leading order theory (LSW-theory)

Our goal is to derive from the Mullins-Sekerka model the BBGKY hierarchy for the number densities of particle radii and centers. The BBGKY hierarchy can be derived from the Liouville equation by averaging and describes the evolution of the N-particle distribution in terms of the $(N+1)$-particle distribution. To obtain a tractable system of equations one typically tries to truncate the hierarchy by a suitable closure hypothesis on the level of the one- or two particle number density. This procedure can often be justified if there is a small parameter in the system, such as in our case the volume fraction of the particles.

The formal identification of the leading order terms in the dilute regime is not difficult and goes back to the classical work by Lifshitz and Slyozov (1961) and Wagner (1961) (called nowadays the "LSW-theory").

If the particle size is much smaller than the typical distance between the nearest neighbors one can assume that the potential u is approximately constant in space away from the particles, that is $u \approx u_\infty(t)$. In other words, each particle P_i feels the influence of the other particles only through u_∞, also called a mean-field. We then solve for particle P_i

$$
\begin{aligned}
-\Delta u &= 0 && \text{in } \mathbb{R}^3 \backslash \overline{P_i} \\
u &= \frac{1}{R_i} && \text{on } \partial P_i \\
u &\to u_\infty && \text{as } |x| \to \infty \,,
\end{aligned}
\tag{7}
$$

whose solution is given by

$$
u(x,t) = u_\infty + \frac{1 - R_i u_\infty}{|x - X_i|} \,.
$$

Using this solution in (4) we obtain the simple law

$$
\frac{d}{dt}\Big(\frac{4\pi}{3} R_i^3\Big) = R_i u_\infty - 1 \,.
\tag{8}
$$

So far, we have not specified u_∞. In the above approximation we have not yet taken into account that the evolution preserves the total volume of the particles. This constraint determines u_∞ and implies that

$$
u_\infty = \frac{\sum_{i\,:\,R_i>0} 1}{\sum_i R_i} = \frac{1}{\text{mean radius}} \,.
\tag{9}
$$

We read off from (8)-(9) that the critical radius in this approximation is just the mean radius. Recall that in the coarsening picture, the critical radius typically increases, so that over time more and more particles start to shrink and finally disappear.

Based on (8) we can now derive an equation for the one-particle number density, that is the expected number of particles with radius R in $(R, R + dR)$, which we denote by $f_1 = f_1(R, t)$. Due to the translation invariance of the

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Mullins-Sekerka evolution f_1 is independent of the centers. The system (8)-(9) translates without further approximation into the following evolution law for f_1:

$$\partial_t f_1 + \partial_R \Big(\frac{1}{R^2} \left(R u_\infty(t) - 1 \right) f_1 \Big) = 0 \tag{10}$$

with

$$u_\infty(t) = \frac{\int_0^\infty f_1(R,t)\, dR}{\int_0^\infty R f_1(R,t)\, dR}. \tag{11}$$

2.3 Dynamic scaling and coarsening rates

Within the LSW model (10)-(11) we can investigate statistical self-similarity. In fact, we check that the equation has a scale invariance $R \sim t^{1/3}$ which is inherited from the Mullins-Sekerka evolution. It turns out that (10) has indeed self-similar solutions, but not only one but a one-parameter family of the form $f(R,t) = t^{-4/3} F_a(R/t)$ with $u_\infty = (at)^{1/3}$ and $a \in (0, \frac{4}{9}]$. All of the self-similar profiles have compact support, one is smooth, the other ones behave like power laws at the end of their support. LSW predict in their work that only the smooth self-similar solution is stable and is the unique scaling limit for the LSW model. As a consequence they obtain universal growth rates of the coarsening process, such as for example that the mean radius evolves as $\left(\frac{4}{9} t \right)^{1/3}$.

However, it has been rigorously established in (Niethammer and Pego, 1999) (see also (Carr and Penrose, 1998) for a related model and (Giron et al., 1998) for formal asymptotics) that the long-time behavior of solutions to the LSW model is not universal, but depends on the contrary sensitively on the initial data, more precisely on the behavior at the end of the support. Loosely speaking, if the data behave like a power law of power p, the solution converges to the self-similar solution with the same power law. The notion "to behave like a power law" is made precise, the technical term is that the data must be regularly varying with power p at the end of their support.

Before we continue to discuss how one could overcome this weak selection problem, let us digress to discuss a related issue, which is to establish coarsening rates, that is the growth rate of typical length scales, in general. While one can often predict coarsening rates via a dimensional analysis, a rigorous treatment has only recently become available. In (Kohn and Otto, 2002) a time averaged upper bound of the coarsening rate within the Cahn-Hilliard theory has been established via a lower bound on the decay rate of the energy density. The argument uses an energy-dissipation relation and a relation between the energy and a certain appropriate length scale. This technique has been shown to be quite robust and has been applied to a large variety of other coarsening problems (Kohn and Yan, 2004; Dai and Pego, 2005c), in particular also to the LSW model (Dai and Pego, 2005b; Pego, 2007). Naturally, pointwise upper bounds are much more difficult to obtain. For the relatively simple LSW model a first result has been obtained in (Niethammer and Velázquez, 2006a), where upper and even lower bounds on the coarsening rates have been established for data which are close to a self-similar solution. In general lower bounds cannot be

expected, since there are configurations for which coarsening does not occur (e.g. all particles with equal size in the LSW model) or is extremely slow (e.g. one-dimensional coarsening in the Cahn-Hilliard equation).

It would be extremely interesting to establish lower bounds for coarsening rates using probabilistic arguments, which characterize "typical" configurations, for which the system coarsens with the expected rate.

2.4   Questions around the LSW theory

We have seen that one problem in the LSW theory is the weak selection of self-similar asymptotic states, which suggests that some mechanisms are neglected in the LSW model.

Another shortcoming of the LSW model becomes apparent if one compares the predictions by LSW with experimental data. It turns out that the discrepancy is rather large: the constants in the coarsening rates are much larger and the size distributions are less narrow than predicted by the LSW theory.

It is usually argued in the applied literature that one disadvantage of the LSW theory is its mean-field nature which neglects the build up of correlations between particles, which are relevant already in the dilute regime. In other words, the LSW theory assumes that the interaction range of a particle is infinite and the contribution of all the other particles is given by a deterministic average, the mean-field. This picture however neglects screening, which implies that the interaction range of one particle is screened by its neighbors and hence finite, which leads to deviations of the effective mean-field from its average.

It is the goal of Velázquez (2000) to investigate whether these discrete effects in the mean-field and similarly in the data change the weak-selection criterion of the LSW model over the relevant time scales, that is as long as a sufficiently large number of particles is still present. However, the analysis is restricted to a regime, in which screening effects are not relevant. It turns out that in this regime, stochastic effects do not essentially modify the effective dynamics as described by the LSW model and thus do not provide a selection mechanism.

Before we continue to give an overview of further attempts to access the effect of finite volume fraction on Ostwald ripening, we describe screening in Section 2.5 and review results on the rigorous derivation of the LSW model from the Mullins-Sekerka evolution in Section 2.6.

2.5   Screening

The screening effect, described above, can be most easily understood by referring to electrostatics. We briefly recall the argument which gives us the scaling of the screening length in terms of the parameters of the system.

To that aim we consider a point charge at $X_0 \in \mathbb{R}^3$ surrounded by conducting balls $P_i = B(R_i, X_i)$ which are uniformly distributed according to a number density ρ, have volume fraction $\varepsilon \ll 1$ and average radius $\langle R \rangle$. The point charge at X_0 creates an electric field and a corresponding potential G and thus induces a negative charge on $\partial B(R_i, X_i)$. This induced charge roughly equals

$-4\pi R_i G(X_i)$, where $4\pi R_i$ is the capacity of a single ball in $\mathbb{R}^3$. In a dilute system capacity is approximately additive which implies that the total negative charge density is approximately given by $-4\pi\langle R\rangle\rho G$. Hence the effective electric potential satisfies

$$-\Delta G = \delta_{X_0} - 4\pi\langle R\rangle\rho\, G \qquad \text{in } \mathbb{R}^3,$$

and thus

$$G(x) = \frac{1}{4\pi|x-X_0|} e^{-\frac{|x-X_0|}{\xi}}, \tag{12}$$

where the "screening length" ξ is given by

$$\xi = \frac{1}{\sqrt{4\pi\langle R\rangle\rho}}. \tag{13}$$

Formula (12) shows that the presence of the balls has the effect that the effective range of the electric potential is limited to ξ, whereas the electric potential in a system without balls is just $\frac{1}{4\pi|x-X_0|}$ and decays slowly. Notice that the number of particles within the screening range is $\xi\rho^{1/3}$ which according to (13) equals $\langle R\rangle^{-1/2}\rho^{-1/6} \sim \varepsilon^{-1/6}$. Hence, in the dilute regime, the number of particles within the screening range is still large and becomes infinite as $\varepsilon \to 0$.

For further reference, we also note another relevant scaling, the ratio between typical radius and screening length, which is $\langle R\rangle/\xi \sim \varepsilon^{1/2}$.

2.6 Rigorous derivation of the LSW theory

The rigorous derivation of the LSW model from the Mullins-Sekerka evolution as $\varepsilon \to 0$ is by now rather complete. It is treated in a series of papers (Niethammer, 1999; Niethammer and Otto, 2001; Niethammer and Velázquez, 2004a,b) which deal with different assumptions on the data respectively. First, the simplest case was treated in (Niethammer, 1999), where the system size is smaller than the screening length. More precisely, one starts with $N_\varepsilon \gg 1$ well-separated particles in - say - the unit box with volume fraction $\varepsilon \ll 1$, that is $\rho = N_\varepsilon$ and $N_\varepsilon\langle R\rangle^3 = \varepsilon$. That the system size (here equal to one) is smaller than the screening length means in view of (13) that $\lim_{\varepsilon\to 0}\langle R\rangle N_\varepsilon \to 0$ as $\varepsilon \to 0$. In this regime it is established in (Niethammer, 1999) that the solution of the Mullins-Sekerka problem converges to the (unique) solution of the LSW model. (Well-posedness of the LSW model is established in (Niethammer and Pego, 2005); see also (Laurençot, 2002).)

In the case that the system is of the order of the screening length or larger one obtains an inhomogeneous extension of the LSW model (Niethammer and Otto, 2001). Most interesting and natural is the case that the system size is much larger than the screening length. This implies that when rescaling the system with respect to the natural length scale, the screening length, one obtains a homogenization problem in an unbounded domain. As a consequence energy-type estimates are not useful in the analysis. One important step in the

analysis of (Niethammer and Velázquez, 2004a,b,c) is the result (Niethammer and Velázquez, 2006b) which establishes that the fundamental solution of the microscopic problem decays exponentially w.r.t. the screening length. This allows to "localize" the homogenization procedure in (Niethammer and Velázquez, 2004a,b). While in previous work it has been assumed that initially particles are well-separated so that they cannot touch during the evolution, Niethammer and Velázquez (2004b) treat the case of initially randomly distributed particles. In this case particles might overlap and the evolution is defined by merging these particles in a larger one and continue. To justify this procedure it is important to show that very small fraction of particles can overlap and that this does not affect the macroscopic evolution law for the remaining particles. This result rules out corrections on the zero order level due to a stochastic nature of the data.

The result by Niethammer and Velázquez (2006b) should also turn out to be useful in further related investigations. In fact, the Mullins-Sekerka evolution has not yet been considered in the setting, where infinitely many particles distributed in the whole space, e.g. according to a homogeneous Poisson process. Even if one handles collision of particles in some way, global existence of a solution to this problem is not obvious, since if locally screening is very weak there could be a mass flux from infinitely far away leading to the finite time blow up of the radius of one particle. We expect, however, that if particles are initially uniformly distributed, such that there is a uniform - in a sense which has to be made precise - screening length, such a scenario does not take place and that the evolution is well-posed.

3 Scaling of the first order correction: a cross-over due to screening

In order to derive a perturbative theory to the LSW model which takes nonzero volume fraction into account we first have to identify the correct expansion parameter, or in other words, the scaling of the first order correction. In this chapter we review a result which rigorously establishes such a scaling. The analysis combines a variational viewpoint with elementary probability.

In the applied literature there had been a controversy about the size of the scaling of the first order correction, since numerical simulations for finite systems predicted an error of order $\varepsilon^{1/3}$, whereas theories for infinite systems predicted an error of order $\varepsilon^{1/2}$. This was first to some extent resolved by numerical simulations in (Fradkov et al., 1996), which show a cross-over from $\varepsilon^{1/3}$ to $\varepsilon^{1/2}$ when the system size becomes larger than the screening length. We will now discuss in some detail a result, which proves a refined version of this observation.

3.1 Set-up and assumptions

Our starting point here is the monopole approximation of (1), (3),(4). In fact, it has been established in (Dai and Pego, 2005a), that the monopole approximation

is exact for a variant of (1), (3),(4), where the Gibbs-Thomson condition is averaged, instead of the Stefan condition (4).

In the monopole approximation we use the ansatz $u(x,t) := -\sum_i \frac{V_i}{|X_i - x|}$ for a solution of (1), where $\{V_i\}_i$ are the growth rates of the particle volumes, that is $V_i := \frac{d}{dt}[\frac{4\pi}{3} R_i^3] = 4\pi R_i^2 \frac{dR_i}{dt}$. Using the Gibbs-Thomson condition in (1) gives to leading order the following linear system of equations

$$\frac{1}{R_i} = u_\infty - \frac{V_i}{R_i} - \sum_{j \neq i} \frac{V_j}{d_{ij}}, \tag{14}$$

where $d_{ij} := |X_i - X_j|$ is the distance between particle centers and u_∞ is such that

$$\sum_i V_i = 0. \tag{15}$$

We consider from now on a fixed distribution of $n \gg 1$ particles centers $\{X_i\}_i$ in a sphere of volume n (that is the number density ρ satisfies $\rho \sim 1$) which satisfies certain regularity assumptions listed below. The particle radii $\{R_i\}_i$ are identically and independently distributed according to a distribution with compact support and mean volume ε. Within this setting the screening length is given by $\xi \sim \frac{1}{\sqrt{\langle R \rangle}} \sim \varepsilon^{-1/6}$ and hence the screening length is smaller, resp. larger, than the domain size if $\xi \ll n^{1/3}$ or $\xi \gg n^{1/3}$ – in other words if $\varepsilon n^2 \gg 1$ or $\varepsilon n^2 \ll 1$ – respectively. We call these regimes supercritical and subcritical respectively.

In the following we estimate the deviation of the joint distribution $\{X_i, R_i, V_i\}_i$ from $\{X_i, R_i, V_i^{LSW}\}_i$, where the $\{V_i\}_i$ are determined according to (14) and $\{V_i^{LSW}\}_i$ are the LSW growth rates, given by the truncation of (14)

$$\frac{1}{R_i} = u_\infty^{LSW} - \frac{V_i^{LSW}}{R_i} \quad \text{and} \quad \sum_i V_i^{LSW} = 0. \tag{16}$$

Such an analysis is also called "Snapshot"-analysis, since we only estimate the difference in the rate of change of the system at a given time.

The quantity we consider in the following will be the relative deviation in the rate of change of energy, which is another convenient measure for the coarsening rate. More precisely we consider $\frac{\dot{E}^{LSW} - \dot{E}}{|\langle \dot{E}^{LSW} \rangle|}$, where E is the interfacial energy of the particles, i.e. $E = \frac{1}{2n} \sum_i R_i^2$, and its rate of change is

$$\dot{E} = \frac{1}{n} \sum_i \frac{V_i}{R_i},$$

while

$$\dot{E}^{LSW} = \frac{1}{n} \sum_i \frac{V_i^{LSW}}{R_i},$$

with V_i^{LSW} given by (16). Since the energy is decreasing, $\dot{E}$ is always negative. Likewise $\dot{E}^{LSW}$ is always negative, but we expect the difference $\dot{E}^{LSW} - \dot{E}$ to

be negative for most realizations, since the LSW theory should underestimate the rate at which E is decreasing.

For the analysis we need the following regularity assumptions on the distribution of $\{X_i\}_i$. The first one ensures a certain uniformity in the distribution. We assume in the supercritical case, i.e. when the system size is much larger than the screening length, that each subdomain of size of order ξ, contains at least of the order of $\varepsilon^{-1/2}$ particles. This assumption can be shown (at least if $\varepsilon \leq \frac{1}{\ln n^5}$, cf. (Niethammer and Velázquez, 2004b)) to be satisfied with probability converging to one as $n \to \infty$.

The second assumption is less natural. We assume that the minimal distance between particles is of the order of the mean nearest neighbor distance, that is $\min_{j \neq i} d_{ij} \geq c_0 > 0$. This assumption is not satisfied with probability close to one. The number of particles which violate this assumption is small and one might expect that the inclusion would not destroy our result. It would be very interesting to establish a corresponding result rigorously, or show, on the contrary, that the above assumption is relevant.

One consequence of these two assumptions on the distribution of particle centers is that we can approximate discrete sums by the corresponding integrals, an approximation we use frequently in the proofs.

3.2 The result

The main result in (Hönig et al., 2005b) is that for a fixed distribution of particle centers satisfying our regularity assumptions we have with high probability (with respect to the radius distribution)

$$-\frac{\dot{E} - \dot{E}^{LSW}}{|\langle \dot{E}^{LSW} \rangle|} \sim \left\{ \begin{array}{ll} n^{-1/3} \varepsilon^{1/3} & \text{for} \quad n \ll \varepsilon^{-1/2} \\ \varepsilon^{1/2} & \text{for} \quad n \gg \varepsilon^{-1/2} \end{array} \right\}. \tag{17}$$

Notice that this is a qualitative statement about the entire distribution, not just its expected value, which is usually considered in numerical simulations. Furthermore it makes the dependence on n precise and gives a proper cross-over, that is the scalings agree in the case that $n \sim \varepsilon^{-1/3}$.

In the following $\langle \cdot \rangle$ denotes the expected value with respect to the joint probability measure P of the variables $\{R_i\}_i$.

Theorem 3.1 *((Hönig et al., 2005b), Theorem 2.2) (The super-critical regime)*
If $n \ll \varepsilon^{-1/2}$ and $\varepsilon \leq \varepsilon_0$ we have with high probability that

$$-C \varepsilon^{1/2} \leq \frac{\dot{E} - \dot{E}^{LSW}}{|\langle \dot{E}^{LSW} \rangle|} \leq -\frac{1}{C} \varepsilon^{1/2},$$

that is for all $\delta > 0$ there exists a constant $C = C(\delta)$ such that

$$P\left(\left\{-C \varepsilon^{1/2} \leq \frac{\dot{E} - \dot{E}^{LSW}}{|\langle \dot{E}^{LSW} \rangle|} \leq -\frac{1}{C} \varepsilon^{1/2}\right\}^c\right) \leq \delta.$$

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Theorem 3.2 *((Hönig et al., 2005b), Theorem 2.1) (The sub-critical regime)*
If $n \ll \varepsilon^{-1/2}$ and $\varepsilon \leq \varepsilon_0$ we have with high probability that

$$\frac{\dot{E} - \dot{E}^{LSW}}{|\langle \dot{E}^{LSW}\rangle|} \geq -C \, n^{-1/3} \, \varepsilon^{1/3}.$$

Furthermore

$$\frac{\langle \dot{E} - \dot{E}^{LSW}\rangle}{|\langle \dot{E}^{LSW}\rangle|} \leq -\frac{1}{C} \, n^{-1/3}\varepsilon^{1/2}.$$

Remark: Notice that in the sub-critical regimes we only succeed to derive a lower bound, whereas we obtain an upper bound only for the expected value. It is not surprising, that subcritical systems have less good self-averaging properties than supercritical systems and, in fact, a recent rigorous result by Conti et al. (2006) shows, that for any $M > 0$ there is a finite probability $\rho_M > 0$ such that $(\dot{E} - \dot{E}^{LSW})/|\langle \dot{E}^{LSW}\rangle| > M$.

3.3 Sketch of proof

In the following we present the main ideas of the proof of Theorem 3.1.

We first perform the natural rescaling, by rescaling radii with respect to their typical size $\varepsilon^{1/3}$ such that (14) becomes

$$\frac{1}{R_i} = u_\infty - \frac{V_i}{R_i} - \varepsilon^{1/3} \sum_{j \neq i} \frac{V_j}{d_{ij}}, \tag{18}$$

where again u_∞ is such that $\sum_i V_i = 0$. Recall that the radii are distributed according to a distribution with compact support. Thus, after rescaling we can assume that $R_i \leq C_0$ for some $C_0 > 0$.

Variational formulation:

A key idea in the proof of Theorem 3.1 is that the deviation in the rate of decrease of the energy can be formulated variationally. First we observe that the solution of (18) can also be characterized as a minimizer of

$$\min_{\{W_i\}_i; \sum_i W_i = 0} \left\{ \frac{1}{n} \sum_i \frac{1}{2R_i} W_i^2 + \varepsilon^{1/3} \frac{1}{n} \sum_i \sum_{j \neq i} \frac{W_i W_j}{2d_{ij}} + \frac{1}{n} \sum_i \frac{W_i}{R_i} \right\}.$$

and the solution $\{V_i\}_i$ satisfies

$$\frac{1}{n} \sum_i \frac{1}{2R_i} V_i^2 + \varepsilon^{1/3} \frac{1}{n} \sum_i \sum_{j \neq i} \frac{V_i V_j}{2d_{ij}} + \frac{1}{n} \sum_i \frac{V_i}{R_i} = \frac{1}{n} \sum_i \frac{V_i}{2R_i} = \frac{1}{2} \dot{E}.$$

Hence

$$\dot{E} - \dot{E}^{LSW} = \min_{\{W_i\}_i, \sum_i W_i = 0} \left\{ \frac{1}{n} \sum_i \frac{1}{R_i} W_i^2 \right.$$

$$\left. + \varepsilon^{1/3} \frac{1}{n} \sum_i \sum_{j \neq i} \frac{W_i W_j}{d_{ij}} + \frac{1}{n} \sum_i \frac{2W_i}{R_i} - \frac{1}{n} \sum_i \frac{V_i^{LSW}}{R_i} \right\}.$$

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and after some elementary manipulations, recalling $V_i^{LSW} = \frac{R_i}{\overline{R}} - 1$ with $\overline{R} := \frac{1}{n} \sum_i R_i$, we find

$$\dot{E} - \dot{E}^{LSW} = \min_{\{W_i\}_i; \sum_i W_i} \left\{ \frac{1}{n} \sum_i \frac{1}{R_i} \left(W_i - V_i^{LSW} \right)^2 + \varepsilon^{1/3} \frac{1}{n} \sum_i \sum_{j \neq i} \frac{W_i W_j}{d_{ij}} \right\}. \tag{19}$$

Hence our goal will be to show that for any $\delta > 0$ there exists a constant $C = C(\delta)$ such that

$$P\left(\left\{ -C \leq T \leq -\frac{1}{C} \right\}^c \right) < \delta, \tag{20}$$

where

$$T := \min_{\{W_i\}_i; \sum_i W_i} \left\{ \varepsilon^{-1/2} \frac{1}{n} \sum_i \frac{1}{R_i} \left(W_i - V_i^{LSW} \right)^2 + \varepsilon^{-1/6} \frac{1}{n} \sum_i \sum_{j \neq i} \frac{W_i W_j}{d_{ij}} \right\}.$$

Notice that this is exactly the statement in Theorem 3.1, since our scaling is such that $|\langle \dot{E}^{LSW} \rangle| = O(1)$.

The variational formulation has the advantage that, first, we get rid of the nonlocal term u_∞, which is not explicit, and, second, that we can obtain an upper bound by constructing a suitable test function $\{W_i\}_i$.

The upper bound:

In the supercritical case, that is the case when the system size is much larger than the screening length ξ, our intuition is, that the system separates into many small subsystems of size of order ξ. With this idea in mind we divide our system into subsystems of order ξ and use the LSW construction in each subsystem j, that is $W_i := \frac{R_i}{\overline{R}_{[j]}} - 1$, where $\overline{R}_{[j]}$ means that we take the average over subsystem j. This construction indeed gives the desired upper bound. The computations are somewhat tedious but straightforward (see (Hönig et al., 2005b) for details).

The lower bound:

We now turn to the mathematically most interesting part, which is the lower bound for T. We write $T = T_0 + T_1$ with

$$T_0 := \varepsilon^{-1/2} \frac{1}{n} \sum_i \frac{1}{R_i} \left(W_i - V_i^{LSW} \right)^2, \qquad T_1 := \varepsilon^{-1/6} \frac{1}{n} \sum_i \sum_{j \neq i} \frac{W_i W_j}{d_{ij}},$$

that is, T_0 is the "good" positive part, and what we need to show is that T_1 can be split in terms which can be absorbed in T_0 and other terms which are bounded in weak-L^1, that is we aim to show that $|T_1| \leq \frac{1}{2} T_0 + \tilde{T}$, where $\tilde{T}$ is bounded in weak-L^1. (We say that T is bounded in weak-L^1 if there exists exists a constant C such that $P(|T| \geq M) \leq C/M$ for all $M > 0$.)

- *Replace V_i^{LSW} by $\frac{R_i}{\langle R \rangle} - 1$:*

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In a first step we replace in T_0 the term V_i^{LSW} by $L_i := \frac{R_i}{\langle R \rangle} - 1$. This has the advantage that $\langle L_i \rangle = 0$ and $\langle L_i L_j \rangle = 0$ for $i \neq j$. It is not difficult to show that the error which is made by this replacement is bounded in the supercritical regime, which ensures that $\overline{R}$ is a good approximation of $\langle R \rangle$. We omit the details here.

- *Introduce cut-off length $\hat{\xi} := \delta \xi$:*

  Next, we introduce a length $\hat{\xi} := \delta \xi$, where $\delta > 0$ is a small number, which will be chosen appropriately. We split the kernel

  $$\frac{1}{d_{ij}} = \frac{e^{-d_{ij}/\hat{\xi}}}{d_{ij}} + \frac{1 - e^{-d_{ij}/\hat{\xi}}}{d_{ij}}$$

  into a far-field and near-field respectively, a splitting motivated by the screening effect and also used for example in the Ewald summation method. Accordingly we split

  $$T_1 = \varepsilon^{-1/6} \frac{1}{n} \sum_i \sum_{j \neq i} \frac{e^{-d_{ij}/\hat{\xi}}}{d_{ij}} W_i W_j \; + \; \varepsilon^{-1/6} \frac{1}{n} \sum_i \sum_{j \neq i} \frac{1 - e^{-d_{ij}/\hat{\xi}}}{d_{ij}} W_i W_j$$

  $$=: T_{11} + T_{12} \,.$$

- *The "far-field" term:*

  It turns out that the far-field term T_{12} is the simpler one to estimate. We split again

  $$T_{12} := \varepsilon^{-1/6} \frac{1}{n} \sum_i \sum_j \frac{1 - e^{-d_{ij}/\hat{\xi}}}{d_{ij}} W_i W_j \; - \; \varepsilon^{-1/6} \frac{1}{n\hat{\xi}} \sum_i W_i^2$$

  $$=: T_{121} - T_{122} \,.$$

We see that T_{121} is positive, since the kernel is even and is the Fourier transform of a positive measure and hence a function of positive type according to Bochner's theorem.

On the other hand

$$T_{122} = \varepsilon^{-1/6} \frac{1}{n\hat{\xi}} \sum_i \big(W_i - L_i + L_i \big)^2$$

$$\leq 2\varepsilon^{-1/6} \frac{1}{\hat{\xi}} \Big(\frac{1}{n} \sum_i (W_i - L_i)^2 + \frac{1}{n} \sum_i L_i^2 \Big)$$

$$\leq C \varepsilon^{-1/6} \frac{1}{\hat{\xi}} \big(\varepsilon^{1/2} T_0 + \frac{1}{\overline{R}^2} \big)$$

since $R_i \leq C_0$ and since $\frac{1}{n} \sum_i L_i^2 \leq C \frac{1}{\overline{R}^2}$. Recall that $\xi \sim \varepsilon^{-1/6}$ and hence

$$T_{122} \leq \frac{C}{\delta} \big(\varepsilon^{1/2} T_0 + \frac{1}{\overline{R}^2} \big) \,.$$

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Using large deviation theory one can show that the expected value of all moments of $\overline{R}^{-1}$ are bounded. Hence, once we have chosen δ, we can choose e.g. $\varepsilon \leq \delta^2$ such that and T_{122} is bounded by $C\delta T_0$ plus a term which is bounded in weak-L^1.

- *The "near-field" term:*

  It remains to estimate the near-field term T_{11}. We write

  $$T_{11} = \varepsilon^{-1/6}\frac{1}{n}\sum_i \sum_{j\neq i}\frac{e^{-d_{ij}/\hat{\xi}}}{d_{ij}}\big(W_i - L_i\big)\big(W_j - L_j\big)$$

  $$+ 2\varepsilon^{-1/6}\frac{1}{n}\sum_i \sum_{j\neq i}\frac{e^{-d_{ij}/\hat{\xi}}}{d_{ij}}L_j\big(W_i - L_i\big) + \varepsilon^{-1/6}\frac{1}{n}\sum_i \sum_{j\neq i}\frac{e^{-d_{ij}/\hat{\xi}}}{d_{ij}}L_i L_j\,.$$
  $$\tag{21}$$

  The first term on the right hand side can be estimated by a kind of convolution argument and turns out to be smaller than $C\varepsilon^{1/3}(\hat{\xi})^2 T_0 \leq C\delta T_0$. We denote the second term in (21) by T_{112} and have with

  $$Z_i^2 := \sum_{j\neq i}\sum_{k\neq i}\frac{e^{-\frac{d_{ij}}{\xi}}}{d_{ij}}\frac{e^{-\frac{d_{ik}}{\xi}}}{d_{ik}}L_j L_k$$

  that

  $$\big|T_{112}\big| \leq \varepsilon^{-1/6}\Big(\frac{1}{n}\sum_i \big(L_i - W_i\big)^2\Big)^{1/2}\Big(\frac{1}{n}\sum_i Z_i^2\Big)^{1/2}\,.$$

  As before we argue that $\frac{1}{n}\sum_i \big(L_i - W_i\big)^2 \leq C\varepsilon^{1/2}T_0$. Furthermore, due to $\langle L_j L_k\rangle = 0$ for $j \neq k$, we have

  $$\langle Z_i^2\rangle = \sum_{j\neq i}\frac{e^{-\frac{2d_{ij}}{\xi}}}{d_{ij}^2}\langle L_i^2\rangle \leq C\xi\,,$$

  where the last inequality follows from our regularity assumptions on the distribution of particle centers which allow to approximate sums by the corresponding integrals. Thus, we obtain

  $$\begin{aligned} P\big(|T_{112}| \geq M\big) &\leq \frac{1}{M}\langle|T_{112}|\rangle \\ &\leq \frac{1}{M}\varepsilon^{-1/6}\varepsilon^{1/4}\sqrt{T_0}\sqrt{\xi} \\ &= \frac{1}{M}\varepsilon^{-1/6+1/4-1/12}\sqrt{\delta T_0} \\ &\leq \frac{C}{M}\big(\delta T_0 + 1\big)\,, \end{aligned}$$

  which says that T_{112} is bounded in weak-L^1.

  The third term in (21) can be handled similarly, we omit the proof here.

- *Summary:*

  Collecting the above computations we have

  $$T \geq (1 - C\delta)T_0 + \tilde{T}_1$$

  with $P\big(|\tilde{T}_1| \geq M\big) \leq \frac{C}{M}$. Choosing δ sufficiently small finishes the proof of the lower bound.

4 Approaches to extend the LSW model

In this section we review different approaches to derive extensions to the LSW model which take nonvanishing volume fraction into account. The theories we present now are not derived in full rigor, which due to the complexity of the problem can also not be expected. The first approach, described in Section 4.1, has been derived by establishing several building blocks rigorously. The model is also self-consistent for small times. However, it turns out not to be self-consistent for large times. Another approach, which overcomes this difficulty is presented in Section 4.2. Section 4.3 finally discusses an ad-hoc model which takes encounters of particles into account.

4.1 BBGKY hierarchy to capture correlations

The first attempt to derive a corresponding theory was done in (Marqusee and Ross, 1984), where an evolution of the one-point statistics under the assumption of independently and identically distributed particles is derived. However, it is obvious that the assumption of statistical independence is not preserved up to the relevant order $O(\varepsilon^{1/2})$ by the evolution and thus this theory is not self-consistent.

A more advanced theory has been developed by Marder (1987) who takes the build up of correlations into account. Let us briefly discuss, why one expects a faster coarsening process due to correlation effects. Consider a system which has undergone coarsening and suppose you find a large particle. The likely reason for it being large is that it is surrounded by smaller than average particles. Because of that fact the large particle can also grow faster than predicted by the LSW mean-field theory. Equally, smaller than average particles shrink faster than predicted by the mean-field theory, and one should obtain larger coarsening rates than within the LSW model.

In order to access correlations Marder (1987) derives the evolution of the two-point statistics up to an error $o(\varepsilon^{1/2})$. Starting from the monopole approximation he generates the BBGKY hierarchy for the particle number densities, computes the growth rates which appear as coefficients in these equations and truncates the hierarchy on the level of two-particle statistics by a closure hypothesis.

The goal of Hönig et al. (2005a) was to find a new method to identify the conditional expectations of particle growth rates under a more natural closure hypothesis than Marder's.

The assumption in (Hönig et al., 2005a) is that the joint probability distribution of $\{(R_i, X_i)\}_{i \geq 1}$ satisfies a cluster expansion. More precisely, if $f_1(R_1, t)$ and $f_2(R_1, R_2, X_1, X_2, t)$ denote the one- and two-particle number densities respectively, it is assumed, with $g_2(R_1, R_2, X_1, X_2, t) := f_1(R_1)f_1(R_2)$ $-f_2(R_1, R_2, X_1, X_2, t)$, that $\frac{g_2}{f_1 f_1} = O(\varepsilon^{1/2})$ and that higher order correlations are of order $o(\varepsilon^{1/2})$ and can henceforth be neglected.

Under this assumption Hönig et al. (2005a) derive that f_1, f_2 satisfy the Liouville equations

$$
\begin{aligned}
&\frac{\partial f_1}{\partial t} + \frac{\partial}{\partial R_1}\Big(\frac{1}{R_1^2}\left\langle V_1 \,|\, 1\right\rangle f_1\Big) = 0\,,\\
&\frac{\partial f_2}{\partial t} + \frac{\partial}{\partial R_1}\Big(\frac{1}{R_1^2}\left\langle V_1 \,|\, 1,2\right\rangle f_2\Big) + \frac{\partial}{\partial R_2}\Big(\frac{1}{R_2^2}\left\langle V_2 \,|\, 1,2\right\rangle f_2\Big) = 0\,,
\end{aligned}
\tag{22}
$$

where $\left\langle V_1 \,|\, 1\right\rangle, \left\langle V_1 \,|\, 1,2\right\rangle$ denote the expected growth rates of particles conditioned on size and position of particle (R_1, X_1) and (R_1, X_1, R_2, X_2) respectively. These are given by

$$
\begin{aligned}
\left\langle V_1 \,|\, 1\right\rangle &= \Big(1 + \frac{R_1}{\xi}\Big)(R_1 u_\infty - 1 - \delta u_1) + o(\varepsilon^{1/2}), &(23)\\
\left\langle V_1 \,|\, 1,2\right\rangle &= \Big(1 + \frac{R_1}{\xi}\Big)(R_1 u_\infty - 1 - (\delta u_1 + \delta u_2))\\
&\quad + \frac{R_1}{d_{12}} e^{-\frac{d_{12}}{\xi}}(1 - R_2 u_\infty) + o(\varepsilon^{1/2})\,, &(24)
\end{aligned}
$$

where for $i = 1, 2$

$$
\delta u_i = \int \frac{e^{-\frac{|y - X_1|}{\xi}}}{|y - X_1|}\big(1 - R u_\infty\big)\frac{g_2(R_i, X_i, R, y)}{f_1(R_i)}\, dR\, dy
\tag{25}
$$

and δu_i have relative size of order $O(\varepsilon^{1/2})$. The mean field u_∞ is implicitly determined by volume conservation, which is expressed by the condition $\left\langle V_1\right\rangle = 0$.

Notice that the terms R_1/ξ and R_1/d_{12}, etc. are terms which have typically size of order $\varepsilon^{1/2}$ due to (13). Hence, we recover in (23) to leading order the LSW theory.

We also observe that (24) has the expected structure. The second term on the right hand side describes how a particle (R_2, X_2) affects the growth rate of particle (R_1, X_1). If it is larger than average, the growth rate of particle (R_1, X_1) is smaller than predicted by LSW, if it is smaller than the growth rate of particle (R_1, X_1) increases. The effect is more relevant the closer particle (R_2, X_2) is to particle (R_1, X_1) and can be neglected if the distance between two particles is larger than the screening length ξ.

Nevertheless, it turned out that the model (22)-(25), despite its complexity, is still not satisfying. First, even though this is not demonstrated rigorously, it seems that the model contains no mechanism to select a unique self-similar

solution. Furthermore, and most important, the model is not self-consistent for large times, more precisely it fails for the largest particles in the system. The argument for the latter is basically as follows. Suppose one solves (22)-(24) for uncorrelated initial data, where $f_1(R_1, 0)$ has compact support. Consequently, the support of $f_2 = f_2(R_1, R_2, X_1, X_2, 0)$ is also compact in R_1 and R_2. However, the evolution of R_1 and R_2, determined by (24), depends on space due to the term $e^{-d_{12}/\xi}/d_{12}$ in (24). Therefore, particles R_1 and R_2 which are at a distance smaller than ξ evolve differently from particles R_1 and R_2 which are at a distance much larger than ξ. As a consequence also the support of f_2 in R_1 and R_2 varies in space and we obtain regions in the variables (R_1, R_2, X_1, X_2) where f_2 identically vanished but $f_1(R_1)$ and $f_1(R_2)$ not and consequently g_2 is of the order $f_1(R_1)f_1(R_2)$ which violates the cluster expansion.

4.2 Boundary layers due to fluctuations

For the reasons described in the previous section one cannot assume that correlations are small around the largest particles and hence a uniform cluster expansion approach cannot be successful. The onset of correlations for the largest particles has instead to be described by a suitable boundary layer, that is a small region in the space of radii on which the number densities vary rapidly. A corresponding model has been derived in (Niethammer and Velázquez, 2007). The analysis is quite elaborate and also the resulting model is complicated to state in full detail. We confine ourselves here to describe the most important aspects.

The main idea in the derivation of the model is that we do not start from an expansion on the level of the number densities, but instead on the level of the trajectories of particles. This allows for a closure relation using Taylor's expansion in order to express f_2 by f_1 and $\partial_R f_1$.

One aspect is however very similar to the analysis of Hönig et al. (2005a). A key idea in the computation is always to describe a system of particles through the ones in a system where a particle has been removed. This is a version of Schwarz alternating method.

The resulting model has the following form:

$$\partial_t f_1 + \partial_R \left(\frac{1}{R^2} \big(R u_\infty - 1 \big) f_1 \right) = \varepsilon^{1/2} \, \partial_R \Big(D(R) \, \partial_R f_1 \Big) \qquad (26)$$

where the function $D = D(R)$ acts as a kind of diffusion coefficient and is determined via a complicated nonlocal integral equation. We refer for details to (Niethammer and Velázquez, 2007); the most relevant property of D however is, that it is positive and has the appropriate scaling such that (26) has a scale invariance.

Let us emphasize again, that the right hand side is seemingly a higher order term due to the factor $\varepsilon^{1/2}$. However, this is only true where f_1 is not small. For largest particles, where f_1 is small, the right hand side of (26) becomes of the same size as the left hand side.

By formal asymptotic expansion it is also established in (Niethammer and Velázquez, 2007) that a unique self-similar solution to (26) exists. This is a perturbation of the LSW self-similar solution with a Gaussian tail. Thus, the boundary layer provides a possible solution to the selection problem within the LSW theory. The induced correction to the mean particle size of order $\varepsilon^{1/4}$. Notice, that the latter does not contradict our scaling analysis in Section 3. For short times we have that the correction terms are of order $\varepsilon^{1/2}$. This does not say, however, what order of size of correction we can expect in a self-similar regime.

4.3   The LSW model with encounters

A different approach from the ones described in the last two sections has been suggested already in (Lifshitz and Slyozov, 1961). As we have already mentioned, particles may collide during their evolution and merge into a larger particle. At first glance, this effect seems to be of higher order than correlations, since the number of particles per unit volume which are involved in collisions is of order $\rho\varepsilon$ and as a consequence the correction of the LSW model due to collisions should have relative size of order ε.

A model which takes this effect into account has already been suggested in (Lifshitz and Slyozov, 1961). To state it it is more convenient to change variables from radius R to volume $v := R^3$. After rescaling time by a constant, the LSW law $\dot{R} = \frac{1}{R^2}(Ru_\infty - 1)$ reads in the volume variable $\dot{v} = v^{1/3}u_\infty - 1$ and the LSW model for the density of volumes g (defined by $g(v)\,dv = f_1(R)\,dR$) is given by

$$\partial_t g + \partial_v\big((v^{1/3}u_\infty - 1)g\big) = 0\,.$$

Introducing self-similar variables via $x := \frac{v}{t}$, $F(x,\tau) := t^2 g(v), \tau = \ln t$ and $\lambda = u_\infty t^{1/3}$ we obtain the equation in self-similar variables as

$$\partial_\tau F - x\partial_x F - 2F + \partial_x\big((x^{1/3}\lambda - 1)F\big) = 0\,. \tag{27}$$

To account for collisions, or "encounters" as the phenomenon is called by Lifshitz and Slyozov, a coagulation term is added on the right hand side which is of the form

$$\frac{1}{2}\int_0^x K(y, x-y)F(x-y)F(y)\,dy \,-\, F(x)\int_0^\infty K(x,y)F(y)\,dy\,. \tag{28}$$

Since merging particles basically add their volume (this is not completely correct, since at the same time they still interact with the other particles, but sufficient for our purpose), it is assumed that K is additive and grows proportional to $x + y$ as $x, y \to \infty$. For simplicity we set $K(x,y) := x + y$. To summarize, after normalizing to $\int xF(x)\,dx = 1$, self-similar solutions for the LSW model with encounters are given by the equation

$$-x\partial_x F - 2F + \partial_x\big((x^{1/3}\lambda - 1)F\big)$$
$$= \varepsilon\Big(\frac{x}{2}\int_0^x F(x-y)F(y)\,dy - xF(x)\int_0^\infty F(y)\,dy - F(x)\Big)\,. \tag{29}$$

Naively, one would expect that since the order of the right hand side is $O(\varepsilon)$ collisions are not as relevant as correlations and fluctuations which are of order $O(\varepsilon^{1/2})$. However, all particles can encounter other particles and thus two colliding particles of medium size produce a large particle which then dominates the long-time behavior. Hence, for the large-time behavior encounters could be more relevant than fluctuations and correlations.

This conjecture is supported by an asymptotic analysis by Lifshitz and Slyozov (1961). Assuming that there exists a fast decaying solution to (29), they find that the correction of the growth rate of the particles is of order is of order $\frac{1}{|\ln \frac{1}{\varepsilon}|^2}$ and hence much larger than the correction induced by fluctuations.

It is still open, however, whether the analysis in (Lifshitz and Slyozov, 1961) is correct, since is is not obvious that exponentially fast decaying solutions to (29) exist at all. In fact, we know from the pure coagulation equation that such a solution only exists for $\varepsilon = 1$. The situation here might be of course completely different. Preliminary computations by Herrmann et al. (2007) suggest, that for small ε there are both, algebraically decaying solutions, as well as an exponentially decaying one. If this turns out to be correct, it is reasonable to expect, that solutions to the time dependent problem with compactly supported data converge to the self-similar solution with exponential decay and the correction to the mean radius is indeed of order $\frac{1}{|\ln \frac{1}{\varepsilon}|^2}$.

To summarize, even though the model including encounters is set up only ad hoc and is not derived from the Mullins-Sekerka evolution, which would be another challenging task, the enormous effect on the mean radius and hence the coarsening rate suggests that encounters are in fact more relevant for the long-time self-similar dynamics than fluctuations. The explanation lies in the kinetic character of the collision term, that the fraction of particles which are transported to the super-critical regime is of order ε, whereas the diffusive correction due to fluctuations in (26) only involves the few largest particles.

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