Resolving Paradoxes of Classical Nucleation Theory

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Abstract

We present a new model of homogeneous aggregation that contains the essential physical ideas of the classical predecessors, the Becker-Döring and Lifshitz-Slyozov models. These classical models, which give different predictions, are asymptotic limits of the new model at small (BD) and large (LS) cluster sizes. Since the new theory is valid for large and small clusters, it allows for a complete description of the nucleation process; one that can predict the creation of super-critical clusters at the Zeldovich nucleation rate, and the diffusion limited growth of large clusters during coarsening. By retaining the physically valid ingredients from both models, we explain the seeming incompatibilities and arbitrary choices of the classical models.

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I. INTRODUCTION

Nucleation refers to the aggregation of identical particles (monomers) into clusters. Its universality throughout physics, chemistry and biology is well known. References [1], [2], [3], [4], [5], [6], [7], [8], [9], [10] provide a lineup of the ‘usual’ (and some unusual) suspects. Also well known are the long-standing challenges that aggregation poses to modeling. Two classical models of aggregation due to Becker-Döring (BD) [11], and Lifshitz-Slyozov (LS) [7] are incomplete and mutually inconsistent.

In BD, clusters exchange particles with the surrounding monomer bath by a ‘surface reaction’, and it is assumed that the monomer bath around the clusters has uniform concentration. This is only possible with infinite diffusivity of monomers. While this description is asymptotically accurate for sufficiently small clusters, the uptake of monomers by large clusters is strongly controlled by the diffusivity. LS describes cluster growth and shrinkage controlled by diffusion of monomers. In LS, the monomer concentration at the surface of a cluster is a prescribed function of the local curvature, generally different from the ‘background’ concentration, far from clusters. Hence, monomer concentration about a large cluster is nonuniform, and there is diffusive transport of monomer into or away from the cluster. This physics of LS leads to a prediction for cluster growth that disagrees with BD. Furthermore, LS is ‘incomplete’, in that it does not describe the initial creation of clusters from pure monomer. While it is generally accepted that BD is a model for small clusters, and LS for large, several questions remain. How to interpolate between the two models? What is the characteristic size that separates ‘large’ from ‘small’? What physics governs the growth in the intermediate scale? What globally valid model encompasses the whole evolution of clusters, from an initial state of pure monomer to the asymptotic self-similar distribution of large cluster sizes?

The current paper presents a new model that retains the essential physical ingredients: the clusters gain and lose monomers by a surface reaction that depends on the cluster size and the monomer concentration seen on the surface. Monomers outside the cluster undergo diffusion with finite diffusivity. These ingredients give rise to a free boundary problem for the growth of a cluster that contains a new intrinsic cluster size, \( k^* \), in addition to the well known critical size, \( k_c \). The critical size, \( k_c \), separates shrinking clusters \( (k < k_c) \) from growing ones \( (k > k_c) \). The new cluster size, \( k^* \), indicates the importance of diffusion: the
new prediction for cluster growth asymptotes to BD for small clusters with $k \ll k_*$, and to LS for large clusters with $k \gg k_*$. In the former case, the diffusion effectively equates the surface density of monomer with the far-field density, thus, the surface reaction dictates the growth. In the latter case, growth is strongly limited by finite diffusivity. Furthermore, the new model of cluster growth interpolates between BD and LS for intermediate cluster sizes on the order of $k_*$.

The smooth interpolation between BD and LS is crucial for a global model of aggregation that describes the whole process, from the initial creation of clusters from pure monomer, to the late stage growth-attrition process called *coarsening*. The essential idea is simple: if $k_c \ll k_*$, as expected in most cases, standard BD describes the *nucleation* of super-critical ($k > k_c$) clusters and their growth while $k_c < k \ll k_*$. The super-critical clusters rapidly grow to sizes $k \gg k_*$, and their subsequent careers are described by LS.

Mathematically, we model this physics by a continuum approximation of the discrete kinetics. The continuum equations constitute a PDE signaling problem for the distribution $r(k, t)$ of large ($k \gg k_*$) clusters in the space of (continuous) cluster size $k$. At the lowest order of approximation, the cluster-size distribution satisfies an advection PDE, in which the growth rate ($\dot{k}$ vs. $k$) furnishes the advection velocity. The classical Zeldovich formula [12], which follows from BD, computes the creation rate of super-critical ($k > k_c$) clusters. Since we assume $k_c \ll k_*$, the Zeldovich formula gives rise to an effective source boundary condition on $k = 0$. The initial state of pure monomers is expressed by a zero initial condition, $r(k, 0) \equiv 0$. Information about the amount of small ($k < k_c$) clusters is not expressed directly in $r(k, t)$. Instead, using conservation of particles, we express the amount of sub-critical clusters using an integral of $r(k, t)$.

Our theory does not handle nucleation that happens with $k_c$ on the order of $k_*$. For this we suspect that a new theory is needed, one that considers the discrete and fluctuating nature of the monomer bath, and does not resort to the diffusion equation, which arises from mean-field averaging.

The paper is structured as follows. In section II we present a short summary of the classical microscopic aggregation theory (BD). We derive rate constants for attachment and dissociation of monomers from a cluster by using free energy and detailed balance arguments. The only difference from the classical theory is that it is based on the *surface* density of monomers, the density of monomers just outside the cluster, and does not assume that the
monomer density is homogeneous.

In section 3 we take into account the finite spatial diffusion of monomers. While still focusing on a single cluster, we connect the surface monomer density with a far-field monomer density, the nearly uniform concentration of monomers far from any cluster. This prescribes the growth rate of a cluster as a function of its size and the far-field monomer density. The standard assumption in diffusion limited aggregation is that the surface density corresponds to a critical cluster i.e., growing and shrinking are equally likely. This seems paradoxical for two reasons. First, the free energy of a cluster as a function of cluster size, \( k \), has its global maximum at \( k = k_c \). On the face of it, this seems to be an unstable equilibrium, but yet it is claimed that the cluster remains at the top of this equilibrium. In addition, if that is the value of the monomer density, how does the cluster grow or shrink?

This paradox is another artifact of assuming uniform monomer concentration as in BD. It is deconstructed at the end of section 3, by an asymptotic analysis which exposes the stabilizing role of finite monomer diffusion: If monomer concentration at the surface of a large (\( k \gg k_* \)) cluster has large deviation from the critical value described above, the surface reactions rapidly absorb or expel monomers. Consequently, due to finite diffusivity, the surface monomer concentration undergoes a collateral adjustment towards the critical value and the rapid reactions are turned off. The growth rate due to diffusion is much slower and dictates the evolution of large clusters.

In section IV we turn to the ensemble of all clusters. If the density of monomers is below a certain saturation value, an equilibrium exists, in which large clusters are extremely unlikely. For a ‘super-saturated’ ensemble, with monomer density exceeding the saturation value, clusters greater than a ‘critical cluster size’, \( k_c \), have a strong tendency to persist and grow. In this super-saturated case, there is no equilibrium; the distribution of clusters is continuously changing. Initially, there is nucleation, which is the creation of super-critical clusters. The calculation of the nucleation rate based on BD is reviewed here.

As stated before, this paper proposes a PDE signaling problem for the distribution of cluster sizes that quantifies the complete evolution of the aggregation process. Section 5 contains the assembly of the signaling problem from the component parts in sections 2–4. It has a peculiar nonlinearity, in which the advection velocity in the PDE and the boundary condition (BC) at \( k = 0 \) depend on the monomer density as a parameter. The monomer density can be written as an integral of the solution, and herein lies the nonlinearity.
The nonlinearity makes the task of solving the equations difficult enough to warrant placing it in a separate, forthcoming paper.

II. CLASSICAL BECKER-DÖRING MODEL

Becker-Döring theory (BD) imposes simplifying assumptions at the outset: The clusters are assumed to be uniformly distributed in a dilute ‘bath’ of monomers. This assumption is adjusted regarding the distribution of monomers in the next section, when we add diffusion. The clusters are assumed to change size only by losing or gaining one monomer at a time. Two large clusters do not fuse together nor does one cluster break into two. This can be justified heuristically by noticing that the density of the large clusters is much smaller than the (already small) density of monomers, thus the probability of two large clusters interacting is small. In addition, the mobility of the large clusters is much smaller than that of the monomers, so they are even less likely to stumble upon one another. Similarly, since the large clusters have a low mobility (relative to monomers) a cluster that breaks into two will, most likely, reconnect quickly, as the two parts remain close together.

Another important assumption is that the only governing parameter of a cluster is its size. The shape of the cluster is assumed to be fixed. This assumption can be weakened to require that clusters of same size have the same binding energy and the same surface area.

To derive the kinetic model of nucleation we introduce the essential quantitative ingredients: energy, free energy, and the rate constants of transitions between configurations.

A. Energy and Free Energy

FIG. 1: A schematic cubic crystal surrounded by the monomer bath.
The energy of cubic cluster with \( k \) monomers is

\[
\varepsilon_k \sim 3\varepsilon(k - k^{\frac{2}{3}}).
\]  

(1)

Here \( \varepsilon \) is the binding energy of a single bond between two adjacent particles, the energy needed to break it.

While the clusters are not assumed to be simple cubes, the general structure of the binding energy is expected to remain. Thus, we assume that there is a bulk energy constant, \( \alpha > 0 \), and a surface energy constant, \( \sigma > 0 \), such that the energy of a \( k \)-cluster is

\[
\varepsilon_k \sim k_B T(\alpha k - \frac{3}{2}\sigma k^{\frac{2}{3}}), \text{ for } k \gg 1,
\]

(2)

where, \( k_B T \) is the Boltzmann factor. The factor of \( \frac{3}{2} \) is added in hind-foresight, as it makes some formulas cleaner. Equation (2) is only true asymptotically for large clusters. For small clusters, the separation between ‘bulk’ and ‘surface’ is artificial, and we do not expect (2) to be quantitatively accurate. In particular, \( \varepsilon_1 = 0 \) since the binding energy is the change in the energy from the unbound state and a cluster with one particle is unbound.

Next we consider the free energy costs to create a \( k \)-cluster from the monomer bath. The bath is characterized by the density \( \rho_1 \) of monomer, measured in units of \( \frac{1}{v} \), where \( v \) is the volume of each monomer. In other words, \( \rho_1 \) is the volume fraction occupied by monomers.

The free energy cost to create a \( k \)-cluster from the monomer bath is

\[
g_k = -\varepsilon_k - k_B T k \log \rho_1 \\
\sim -k_B T \left( (\alpha + \log \rho_1)k - \frac{3}{2}\sigma k^{\frac{2}{3}} \right), \text{ for } k \gg 1.
\]

(3)

Here, \( k_B T \log \rho_1 \) is the chemical potential of a monomer in the bath. Rewriting the \( k \gg 1 \) asymptotic form of the free energy gives insight into the existence of a critical monomer density, \( \rho_s \equiv e^{-\alpha} \). We call \( \rho_s \) the saturation density of monomers. Setting \( \alpha = \log \frac{1}{\rho_s} \) in (3) gives

\[
g_k \sim k_B T \left( \frac{3}{2}\sigma k^{\frac{2}{3}} - k \log \frac{\rho_1}{\rho_s} \right).
\]

Thus, when \( \rho_1 < \rho_s \) the free energy increases with \( k \), allowing for an equilibrium. When \( \rho_1 > \rho_s \), the free energy attains its maximum at the critical cluster size \( k_c \).

\[
k_c \sim \left( \frac{\sigma}{\log \frac{\rho_1}{\rho_s}} \right)^{\frac{3}{2}}, \text{ as } \rho_1 \to \rho_s^+.
\]

(4)

We investigate the implications of this critical value later.
B. Kinetics and Detailed Balance

FIG. 2: The exchange of particles between a cluster and the monomer bath. $c_k \rho_1$ is the rate at which a monomer gets added to the cluster, and $d_k$ is the rate at which monomers leave.

To study the rate of change in the cluster size we need to model the allowed reactions. BD allows two types of reactions: (1) A monomer in the bath can join the cluster; (2) A particle on the surface of the cluster can dissociate from it and enter the bath. Mathematically, the two reactions are modeled as independent Poisson processes. Let us call the rate at which particles leave a $(k + 1)$-cluster $d_k$, and the rate at which particles join a $k$-cluster $c_k \rho_1$. We work under the assumption that the solution is dilute, that is, $\rho_1 \ll 1$. It is reasonable to expect that in the dilute limit, the growth rate is proportional to $\rho_1$. Thus, we include $\rho_1$ in the growth rate, $c_k \rho_1$, so that both $c_k$ and $d_k$ are independent of $\rho_1$.

Initially we assume a uniform $\rho_1$, so it is a global parameter. When we add diffusion, we are a little more careful and take $\rho_1$ to be the density at the surface of the cluster.

Since the dissociation happens on the boundary of the cluster, we expect $d_k$ to be proportional to the surface area, which, in turn, is proportional to $k^{2/3}$,

$$d_k = \omega k^{2/3}.$$  \hspace{1cm} (5)

Here, $\omega$ includes a per-particle dissociation rate and a geometric factor.

A standard detailed balance argument relates $c_k$ to $d_k$. Let $\rho_1$ be the value of monomer density so that a $k$-cluster is in equilibrium with the monomer bath. That is, the cluster has no net tendency to grow nor shrink, hence, the adsorption rate, $\rho_1 c_k$, should match the emission rate, $d_k$. The physical requirement for the equilibrium is that the free energy is unchanged when a monomer is taken from the bath and added to the cluster,

$$g_{k+1} - g_k = -\varepsilon_{k+1} + \varepsilon_k - k_B T \log \rho_1 = 0.$$
hence,
\[ \rho_1 = e^{\frac{\varepsilon_k - \varepsilon_{k+1}}{k_B T}}. \]

The detailed balance relation between \( c_k \) and \( d_k \) is therefore,
\[ c_k = e^{\frac{\varepsilon_{k+1} - \varepsilon_k}{k_B T}} d_k. \] (6)

We use the adsorption and emission rates, \( c_k \rho_1 \) and \( d_k \), to derive a kinetic equation for the expected change in size of a cluster. In a small time span \( \delta t \), the expected change in cluster size, \( \delta k \), is:
\[ \langle \delta k \rangle = (c_k \rho_1 - d_k) \delta t. \] (7)

Using the model for the binding energy of large clusters (2) and relation (6) between \( c_k \) and \( d_k \), equation (7) can be rewritten as
\[ \langle \delta k \rangle \sim \omega \left( \frac{\rho_1 - \rho_s}{\rho_s} k^\frac{3}{2} - \sigma k^\frac{1}{2} \right) \delta t, \text{ for } k \gg 1. \]

In the appendix we show that if the variance in \( k \) is much smaller than \( \langle k \rangle \) initially, it will remain so, as long as \( \langle k \rangle \) is bounded away from the critical size \( k_c \) in (4). In this case we approximate the evolution of \( k(t) \) for a given cluster as deterministic, and governed by the ODE
\[ \dot{k} = \omega \left( \eta k^\frac{3}{2} - \sigma k^\frac{1}{2} \right). \] (8)

Here, \( \eta \) is the super-saturation, defined by
\[ \eta = \frac{\rho_1 - \rho_s}{\rho_s}. \] (9)

The super-saturation in (9) is generally a function of time, due to the exchange of particles between clusters and the monomer bath. By conservation of the total particle density, the average value of \( \rho_1 \), and hence \( \eta \), is determined from the densities of all clusters with \( k \geq 2 \).

Within the framework of BD, which assumes that the monomer density is uniform, we simply set \( \eta \) to this average value, and, in this sense, (8) is the BD prediction for cluster growth. However, if the diffusivity of monomers is finite, the density of monomers seen at the surface of the cluster will be different from the average value far away. We propose that (8) holds generally, with \( \eta \) equal to the value of super-saturation seen at the surface of the cluster.

Equations (8) and (9) expose the kinetic significance of the saturation density \( \rho_s = e^{-\alpha} \), and the critical cluster size \( k_c \) in (4), which we rewrite using \( \eta \),
\[ k_c \sim \left( \frac{\sigma}{\eta} \right)^3, \text{ as } \eta \to 0^+. \] (10)
If the surface value of $\rho_1$ is less than $\rho_s$, all the clusters shrink, regardless of $k$. For $\rho_1 > \rho_s$, i.e. $\eta > 0$, the critical size, $k_c$, separates growing, *super-critical* clusters ($k > k_c$) from shrinking, *sub-critical* ones ($k < k_c$).

It should be noted that while the expected change in size of sub-critical clusters is negative, there is a small probability for a sub-critical cluster to grow and become super-critical. The rate at which this happens is estimated by the Zeldovich formula, to which we come back in section IV. First we add finite diffusion of monomers to the model and see how it affects the growth rate.

\[ k v = \frac{4\pi}{3} a^3. \]  

The monomer density is assumed to be radially symmetric (with the cluster centered at the

**III. ADDING MONOMER DIFFUSION**

Diffusion is the usual model of transport for monomers in the bath. For a finite diffusion coefficient, $D$, the exchange of particles between a cluster and the bath directly outside of it leads to non-uniform monomer density. Hence, the monomer concentration, $\rho_1$, is a function of position and time that satisfies the diffusion PDE.

To add diffusion to the BD model, we make a couple of additional assumptions. The cluster is taken to be spherical, filled with monomers, each taking volume $v$. Thus, the number of particles in the cluster, $k$, and the radius of the cluster, $a$, are related by

\[ k v = \frac{4\pi}{3} a^3. \]
Thus, the density, \( \rho_1(r, t) \), satisfies the radially symmetric diffusion PDE in \( \mathbb{R}^3 \)

\[
\partial_t \rho_1 = \frac{D}{r^2} \partial_r (r^2 \partial_r \rho_1) \quad \text{in } r > a,
\]

(12)

There are two BC at \( r = a \): one is the kinetics due to BD as in equation (8). That is, \( \rho_1(a, t) \) is related to \( k \) and \( \dot{k} \) by

\[
\dot{k} = \omega \left( \eta(a, t) k^{2/3} - \sigma k^{1/3} \right),
\]

(13)

where,

\[
\eta(a, t) = \frac{\rho_1(a, t) - \rho_s}{\rho_s}
\]

is the super-saturation seen at the surface of the cluster.

The second BC results from conservation of particles. The particles that are added to the cluster can come from two possible sources: particles in the solution surrounding the cluster, which join the cluster as it engulfs them, and particles added by the diffusive flux. This can be put in a simple equation:

\[
\dot{a}(1 - \rho_1(a, t)) = D(\partial_r \rho_1)(a, t) = D\rho_s(\partial_r \eta)(a, t).
\]

(14)

Finally, there is a BC at \( \infty \): the monomer concentration has the asymptotically uniform value \( \rho_\infty \) far from the clusters,

\[
\rho_1 \to \rho_\infty \text{ as } r \to \infty.
\]

(15)

In the context of the full aggregation problem, \( \rho_\infty \) is generally a function of time, which follows from overall conservation of particles. Equations (11–15) constitute a free boundary problem (FBP) for \( a(t) \) and \( \rho_1(r, t) \) in \( r > a \).

The analysis of the FBP begins by identifying suitable non-dimensional variables. We assume that the local super-saturation

\[
\eta(r, t) \equiv \frac{\rho_1(r, t) - \rho_s}{\rho_s}
\]

is uniformly small in \( r > a \). Hence, we introduce \( \varepsilon \) as a gauge parameter for \( \eta(r, t) \) and we replace \( \eta(r, t) \) in (11–15) by \( \varepsilon \eta(r, t) \). The analysis of the FBP is based on an \( \varepsilon \to 0 \) limit process. However, we do not yet take the \( \varepsilon \to 0 \) limit. It remains to determine the scaling of the other variables \( k, r, a \) and \( t \) with \( \varepsilon \). These follow from simple physical balances: in
the ‘kinetic’ BC \((13)\), \(\eta(r,t)\) has order of magnitude \(\varepsilon\), so the two terms of the RHS balance when \(k\) has magnitude \((\sigma \varepsilon)^3\). Notice that this is the critical cluster size \((10)\) for \(\eta = \varepsilon\). The scalings of \(\eta\) and \(k\) are recorded in the scaling table.

| Variable | \(\eta\) \(\quad k\) \(\quad a, r\) \(\quad t\) |
|----------|-----------------|-----------------|-----------------|
| Unit     | \(\varepsilon\) \((\frac{\varepsilon}{\sigma})^3\) \(\frac{\varepsilon}{\sigma} v^{1/3}\) \(\frac{\sigma}{\varepsilon^2}\) |

The unit of \(r\) and \(a\) is the radius of a cluster with \(k = \((\frac{\sigma}{\varepsilon})^3\)\) particles. The unit of \(t\) is chosen to balance the LHS of the BC \((13)\) with the two terms on the RHS.

The equations of the non-dimensional FBP that follow from \((11–15)\) are

\[
k = \frac{4\pi}{3} a^3, \quad (16)
\]

\[
\partial_t \eta = \frac{D}{\omega v^{2/3}} \frac{1}{r^2} \partial_r (r^2 \partial_r \eta), \quad \text{in} \ r > a, \quad (17)
\]

\[
\dot{k} = \eta(a,t) k^{2/3} - k^{1/3}, \quad (18)
\]

\[
\dot{\alpha} \left(1 - \rho_s (1 + \varepsilon \eta(a,t)) \right) = \frac{D}{\omega v^{2/3}} \frac{\varepsilon \rho_s}{\sigma} (\partial_r \eta)(a,t) \quad (19)
\]

\[
\eta \rightarrow \eta_{\infty} \text{ as } r \rightarrow \infty. \quad (20)
\]

Here, \(\eta_{\infty}\) is the asymptotically uniform value of \(\eta(r,t)\) as \(r \rightarrow \infty\). The characteristic time of its variation is assumed to be comparable to or larger than the unit of time \(\frac{\sigma}{\varepsilon^2}\) from the scaling table.

The dimensionless constant \(\frac{D}{\omega v^{2/3}}\) can be interpreted as a ratio of characteristic times for two different physical processes. Recall that \(\frac{1}{\omega}\) is the characteristic time for a monomer on the surface of a cluster to dissociate into the solution. The ratio \(\frac{v^{2/3}}{D}\) is the characteristic time for a monomer to diffuse a distance comparable to its own size. The conventional assumption is that the “dissociation time” is much longer than the “diffusion time,” so that

\[
\frac{1}{\omega} \gg \frac{v^{2/3}}{D} \iff \frac{D}{\omega v^{2/3}} \gg 1.
\]

In this limit, the diffusion equation \((17)\) reduces to a radial Laplace equation

\[
\partial_r (r^2 \partial_r \eta) = 0.
\]

The solution with \(\eta = \eta_{\infty}\) as \(r \rightarrow \infty\) is

\[
\eta(r,t) = \eta_{\infty} + (\eta(a,t) - \eta_{\infty}) \frac{a}{r}. \quad (21)
\]
The time dependence of $\eta$ is implicit due to the time-dependence of its values at $r = a$ and $r = \infty$.

In the dilute limit, with $\rho_s \ll 1$, the conservation equation (19) reduces to

$$\dot{a} = \frac{D}{\omega v^{2/3}} \frac{\varepsilon \rho_s}{\sigma} (\partial_r \eta)(a, t).$$

Substituting $\eta$ from (21), this becomes

$$a \dot{a} = \frac{D}{\omega v^{2/3}} \frac{\varepsilon \rho_s}{\sigma} \left( \eta_\infty - \eta(a, t) \right). \quad (22)$$

Equation (22) can be converted into an equation for $\dot{k}$ using (16). This gives

$$\dot{k} = \varepsilon \mu (\eta_\infty - \eta(a, t)) k^{1/3}, \quad (23)$$

where $\mu$ is the dimensionless constant:

$$\mu = (3 \cdot 16 \pi^2)^{1/3} \left( \frac{D}{\omega v^{2/3}} \right) \left( \frac{\rho_s}{\sigma} \right).$$

Since $\mu$ is a product of a large number, $\frac{D}{\omega v^{2/3}}$, and a small number, $\frac{\rho_s}{\sigma}$, it can be large or small. We therefore entertain any value of $\mu$.

The two equations for $\dot{k}$, (18) and (23), involve the super-saturation at the surface of the cluster, $\eta(a, t)$. Solving for $\dot{k}$ and $\eta(a, t)$ gives

$$\dot{k} = \frac{\eta_\infty k^{2/3} - k^{1/3}}{1 + \frac{k^{1/3}}{\varepsilon \mu}}, \quad (24)$$

$$\eta(a, t) = \frac{\eta_\infty + \frac{k^{1/3}}{\varepsilon \mu}}{1 + \frac{k^{1/3}}{\varepsilon \mu}}. \quad (25)$$

ODE (24) indicates a second characteristic cluster size besides $k_c$. In units of $(\frac{\sigma}{\varepsilon})^3$ this cluster size is

$$k_* = (\varepsilon \mu)^3.$$

In the original variables, $k_*$ is a combination of basic physical constants:

$$k_* = (\sigma \mu)^3 = (3 \cdot 16 \pi^2) \frac{D^3 \rho^3_s}{\omega^3 v^2}. \quad (26)$$

Notice that for $k \ll k_*$ equation (24) asymptotes to BD. For $k \gg k_*$, the asymptotic form of (24) is

$$\dot{k} \sim \varepsilon \mu \left( \eta_\infty k^{1/3} - 1 \right). \quad (27)$$
Restoring original units, (27) becomes
\[ \dot{k} = d \left( \eta_\infty k^{\frac{2}{3}} - \sigma \right), \quad d = (3 \cdot 16\pi^2)^{\frac{1}{3}} \frac{D\rho_s}{v^{\frac{2}{3}}}, \tag{28} \]
which is the standard result for diffusion limited growth (DLG) [7]. Equation (25) shows how the surface value of super-saturation differs from the uniform value, \( \eta_\infty \), far from the cluster. Notice that it is a function of \( k \). We convert it into an equation for \( s_k \), the value of monomer density seen at the surface of a \( k \)-cluster (again, in original units):
\[ s_k = \rho_s \left( 1 + \eta_\infty + \frac{\mu}{1 + k^{1/3} \sigma} \right). \tag{29} \]
This will be important, when we examine the whole ensemble of clusters, and formulate evolution equations for cluster densities.

### A. Physical Meaning of \( k^* \)

We show that \( k^* \) is the characteristic size of clusters for which finite diffusion induces a significant relative difference between \( \eta_\infty \) and \( \eta(a, t) \). That is, \( \delta\eta \equiv \eta_\infty - \eta(a, t) \) is comparable in magnitude to \( \eta_\infty \). A simple examination of two physical balances is sufficient. First, the cluster’s growth rate balances the diffusive influx of monomers. This is expressed by
\[ \dot{k} = a^2 D \frac{\langle \omega \rangle}{a} \frac{\delta\eta}{a}. \tag{30} \]
Here, the equality means ‘order of magnitude balance’. In the RHS, \( \frac{\omega}{v} \delta\eta \) is the difference between monomer densities at \( \infty \), and on the surface, expressed in the conventional unit of \( 1/volume \). For quasi-static diffusion, the diffusion zone about the cluster of radius \( a \) has thickness \( a \), so \( \left( \frac{\langle \omega \rangle}{a} \delta\eta \right) \) estimates \( \langle \partial_r \rho_1 \rangle(a, t) \) and the influx of monomers per unit area into cluster is estimated by multiplying this by \( D \). Finally, multiplying by the area, proportional to \( a^2 \), gives the cluster growth rate, \( \dot{k} \).

Second, the magnitude of \( \dot{k} \) as dictated by the surface reactions is
\[ \dot{k} = \omega \eta k^{\frac{2}{3}}. \tag{31} \]
Enforcing the equivalence of (30) and (31) and using \( k = \nu a^3 \) (order of magnitude equality again), we find
\[ \frac{\delta\eta}{\eta} = \frac{\omega v^{2/3}}{D\rho_s} k^{\frac{2}{3}} \left( \frac{k}{k^*} \right)^{\frac{1}{3}}. \]
We see that \( \delta\eta \) is comparable to \( \eta \) when \( k \) is comparable to \( k^* \).
B. Critique of DLG and its ‘paradox’

We briefly examine the ‘traditional’ derivation of ODE (27) for DLG, within the framework of the non-dimensional free boundary problem (16–20). Given \( \eta(a, t) \), equation (23) gives the growth rate of the cluster that follows from diffusive flux of monomers. In the traditional analysis of DLG, \( \eta(a, t) \) is chosen so that the cluster is in equilibrium with the monomer bath that surrounds it. Under the current non-dimensionalization, this ‘critical nucleus’ BC reads

\[
\eta(a, t) = k^{-\frac{1}{3}}. 
\]

(32)

Substituting (32) for \( \eta(a, t) \) in (23) leads directly to the ODE (27).

By inspection, we see that the traditional equations (27, 32) arise by taking the \( \varepsilon \mu \to 0 \) limit of (24, 25) with \( k \) fixed. The alternative limit process, \( \frac{k}{k_*} \to \infty \) with \( k_* = \varepsilon \mu \) fixed is more physical: the value of \( \varepsilon \mu \) is set by material properties and initial conditions, and we expect that clusters eventually grow to sizes \( k \gg k_* \). We have already seen that the ODE (24) for \( k \) converges to the DLG result in this limit, but the expression (25) for the surface value of monomer density does not converge to the DLG boundary condition (32). Instead,

\[
\eta(a, t) \sim (1 + \mu \eta_\infty)k^{-\frac{1}{3}},
\]

(33)

which has an additive term \( \mu \eta_\infty \) in the prefactor of \( k^{-1/3} \) not present in (32). A mathematical critique of the ‘critical nucleus’ boundary condition (32) is simple; it results from formally neglecting \( \dot{k} \) in the LHS of the ‘surface kinetics’ boundary condition (18). In our result, \( \dot{k} \) balances the RHS, even in the limit \( \frac{k}{k_*} \to \infty \), resulting in (33).

Recall that the ‘critical nucleus’ boundary condition in traditional DLG looks paradoxical because the ‘cluster sits on top of a free energy maximum’. A ‘lazy’ deconstruction might say: “Nothing to explain, the critical nucleus boundary condition is simply incorrect in the (more physical) limit \( \frac{k}{k_*} \to \infty \) with \( k_* \) fixed.” Another easy explanation looks at the free energy. The free energy (3) refers to a simple cluster surrounded monomers of uniform density, whereas the actual kinetics we consider involves a non-uniform density \( \rho_1(r, t) \) in \( r > a \). The actual free energy takes into account the functional dependence of \( \rho_1(r, t) \) in \( r > a \). These remarks indicate that the ‘paradox’ in its original form is naïve. Nevertheless, it points to some physics that is not expressed in the quasi-static model (24, 25) of cluster growth as it stands.
Suppose that we place a cluster of size $k$ into a uniform monomer bath that has the ‘wrong’ monomer density, not equal to the surface value $s_k$ given in (29). In order for our model to be plausible, the surface value of $\rho_1$ should rapidly relax to $s_k$ in (29). We now show that the full free boundary problem (16–20) implies such a relaxation transient.

C. The Stability of the Free Boundary Problem

The relaxation transient is characterized by a balance of the time and space derivatives in the diffusion PDE (12). Hence the characteristic time of the relaxation transient is

$$t_r \equiv \frac{a^2}{D}, \quad (34)$$

where $a$ is the cluster radius. The relative change of the cluster radius in this characteristic time is small: from (14), $\dot{a}$ has the order of magnitude $\frac{D\rho_1}{a}$. Hence, the relative change of radius in time $t_r$ has magnitude $\varepsilon \rho_a$. The small relative change in cluster radius means that the cluster radius is asymptotically constant during the relaxation transient, and it remains to derive from the full free boundary problem (11–15) a reduced boundary value problem for $\eta(r, t)$ in $r > a$, with $a$ fixed. We use the previous units in the scaling table for all variables except time $t$. For $t$ we use $t_r$ in (34) with $a$ replaced by the characteristic cluster radius, $\frac{\sigma}{\varepsilon^{1/3}}$. The reduced boundary value problem is

$$\begin{align*}
\partial_t \eta &= \frac{1}{r^2} \partial_r (r^2 \partial_r \eta) \quad \text{in} \ r > a, \\
\lambda (\partial_r \eta)(a, t) &= \eta(a, t) - k^{\frac{1}{3}}, \\
\eta(r, t) &\to \eta_{\infty} \quad \text{as} \ r \to \infty,
\end{align*} \quad (35-37)$$

in the limit $\varepsilon \to 0$, and $\lambda \equiv (\frac{\lambda}{\rho_1})^{\frac{1}{3}} \varepsilon \mu$ fixed. The far-field super-saturation, $\eta_{\infty}$, is assumed to vary on a characteristic time much longer than $t_r$, so $\eta_{\infty}$ is effectively constant.

The time-independent solution of (35–37) for $\eta(r, t)$ is (21) with $\eta$ on $r = a$ given by (25). We show that this time-independent solution is asymptotically stable. We notice that

$$E \equiv \frac{\lambda}{2} \int_a^\infty r^2 (\partial_r \eta)^2 \, dr + \frac{a^2}{2} \left( \eta(a, t) - k^{\frac{1}{3}} \right)^2 \quad (38)$$

is a Lyapunov functional for equations (35–37). The time derivative of $E$,

$$\dot{E} = -\lambda \int_a^\infty r^2 \eta_t^2 \, dr,$$
is found by time-differentiation of (38), integration by parts, and use of the PDE (35) and BC (36). Since $E$ is positive definite, and $\dot{E} \leq 0$, it follows that $\eta(r, t)$ converges to the time-independent solution. We conclude that if the surface monomer concentration is initially different from the quasi-static value (25), it relaxes to it in characteristic time $t_r$.

### IV. EVOLVING DISTRIBUTION OF CLUSTER SIZES

The kinetics equation (24) requires $\eta_{\infty}$, the super-saturation far from any cluster. To find $\eta_{\infty}$ we look at the joint evolution of all the clusters, each assumed to follow the dynamics in (24). The clusters are coupled by the combined effect they have on the monomer density, and consequently, on the super-saturation.

Let $\rho_k(t)$ be the average spatial density (in units of $\frac{1}{v}$) of $k$–clusters at time $t$. Assuming that the total particle density has a fixed value, $\rho$, the $\rho_k$ satisfy a particle conservation equation. Since a $k$-cluster is made of $k$ particles, the total particle density, $\rho$, must satisfy

$$\rho = \sum_{k=1}^{\infty} k \rho_k. \quad \text{(39)}$$

With the help of (39), the space averaged super-saturation can be rewritten as a function of the cluster densities $\rho_k$ with $k \geq 2$:

$$\frac{\rho_1 - \rho_s}{\rho_s} = \frac{\rho - \rho_s}{\rho_s} - \frac{1}{\rho_s} \sum_{k=2}^{\infty} k \rho_k. \quad \text{(40)}$$

In the dilute limit with inter-cluster distances much greater than cluster radii, we expect that the super-saturation is asymptotically uniform, throughout most of the monomer bath far from clusters. In this case, that asymptotically uniform value, $\eta_{\infty}(t)$, should be well approximated by the spatial average (10),

$$\eta_{\infty} = \frac{\rho - \rho_s}{\rho_s} - \frac{1}{\rho_s} \sum_{k=2}^{\infty} k \rho_k. \quad \text{(41)}$$

We turn to the evolution of the densities. The $\rho_k$ obey kinetic equations associated with the reactions

$$k\text{-cluster} + \text{monomer} \rightleftharpoons (k+1)\text{-cluster}.$$  

The equations are

$$\dot{\rho}_k = j_{k-1} - j_k, \quad \text{(42)}$$
for \( k \geq 2 \), where the discrete flux \( j_k \) is the net rate of creation of a \((k+1)\)-cluster from a \( k \)-cluster,

\[
j_k \equiv c_k s_k \rho_k - d_k \rho_{k+1}. \tag{43}
\]

As before, \( d_k \) is the rate constant for shedding a monomer from the surface of a \((k+1)\)-cluster. For \( k \gg 1 \) it has the asymptotic behavior \( d_k \sim k \sigma \), proportional to surface area. The prefactor \( c_k s_k \) of \( \rho_k \) in \( 43 \) is the rate constant for adding a monomer. Recall that \( s_k \) is the value of monomer density seen at the surface of a \( k \)-cluster, given by \( 29 \), and \( c_k \) is related to \( d_k \) by the detailed balance condition \( 6 \). A more explicit formula for \( j_k \) displaying the \( k \)-dependence of surface monomer concentration and detailed balance is

\[
j_k = d_k \left( e^{\frac{s_k-1}{k \mu}} s_k \rho_k - \rho_{k+1} \right). \tag{44}
\]

Equations \( 42, 44 \) can be summarized as discrete advection-diffusion equations,

\[
\dot{\rho}_k + D^- \left[ d_k \left( 1 - e^{\frac{s_k-1}{k \mu}} s_k \right) \rho_k - d_k D^+ \rho_k \right] = 0 \quad \text{for} \quad k \geq 2. \tag{45}
\]

Here \( D^+, D^- \) are, respectively, the forward and backward difference operators. In these equations, the surface monomer density \( s_k \) contains the super-saturation \( \eta_\infty \) as a parameter, and \( \eta_\infty \) is connected to the \( \rho_k \) according to \( 41 \). So we see explicitly how the cluster densities are coupled to each other via the super-saturation. The \( k \)-dependence of \( s_k \) induced by the finite diffusivity of monomers is the essential difference from classical BD. We recover classical BD by taking \( \mu \to \infty \), which in turn results from \( \frac{D}{\omega v^2} \to \infty \). Then \( s_k \) in \( 29 \) reduces to \( \rho_s(1 + \eta_\infty) \), which is the uniform value of \( \rho_1 \) assumed in classical BD.

A. Equilibrium

Equilibria are time independent densities, \( \tilde{\rho}_k \), so that all the fluxes \( j_k \) are zero, and the sum \( 39 \), which gives the total particle density, is convergent. Setting \( j_k = 0 \) in \( 44 \) gives a recursion relation that determines \( \tilde{\rho}_k \) from \( \rho_1 \),

\[
\tilde{\rho}_k = \rho_1^k e^{\frac{s_k}{k \mu}}, \quad \text{for} \quad k \geq 2. \tag{46}
\]

Here, we used \( s_k = \rho_1 \) for all \( k \), since \( \rho_1 \) should be uniform in the equilibrium case. Substituting these \( \tilde{\rho}_k \) into \( 39 \) gives,

\[
\rho = \rho(\rho_1) \equiv \sum_{k=1}^{\infty} k \rho_1^k e^{\frac{s_k}{k \mu}}. \tag{47}
\]
Hence, equilibria exist for monomer densities \( \rho_1 \) so that this series converges. For large values of \( k \), the binding energy can be written as

\[
\varepsilon_k \sim k_B T \left( \alpha k - \frac{3}{2} \sigma k^{2/3} \right)
\]

Therefore, convergence happens for

\[
\rho_1 \leq e^{-\alpha} = \rho_s.
\]

In other words, equilibria exist only if the super-saturation is non-positive. The largest value of total particle density for which there is equilibrium is obtained by setting \( \rho_1 = \rho_s \) in (47). We denote this critical particle density by \( \rho_c \),

\[
\rho_c = \rho(\rho_s).
\]

(48)

Since \( \rho_s \ll 1 \), the first few terms of the series give a close approximation of \( \rho_c \).

**B. Zeldovich Nucleation Rate**

For positive super-saturation \( \eta \), there is the critical cluster size \( k = k_c \), for which the free energy cost to assemble a \( k \)-cluster from dissociated monomers is maximized. In the small super-saturation limit \( \eta \to 0^+ \), and \( k \gg 1 \), it follows from (3) and (9), that

\[
g_k \sim k_B T \left( \frac{3}{2} \sigma k^{2/3} - \alpha \eta \right),
\]

(49)

and that the free energy cost (in units of \( k_B T \)) of the critical cluster is asymptotic to

\[
g \equiv \max_k g_k \sim \frac{\sigma^3}{2 \eta^2}.
\]

For small super-saturation, the free energy cost is high, and an analogy with the famous Arrhenius rate suggests that super-critical nuclei with \( k > k_c \) are produced at a rate proportional to the exponential \( e^{-g} \). Since this proposed creation rate is exponentially small as \( \eta \to 0 \), one might expect that after some initial transient, quasi-static but non-equilibrium values of \( \rho_k \) are established for \( k \) on the order of \( k_c \), in which the discrete fluxes \( j_k \) in (43) are asymptotically equal to a uniform value \( j \). This \( j \) is the creation rate of super-critical nuclei, proportional to \( e^{-g} \). These essential ideas of nucleation kinetics are set forth in a famous paper of Zeldovich, on the nucleation of vapor bubbles for under pressurized liquid [12].
starting point is a discrete system of kinetic ODE’s like BD, but he first passes to a PDE limit of the ODE’s and calculates the nucleation rate from the PDE. Here, we implement the essential Zeldovich ideas, but within the framework of the discrete BD ODE’s.

We work in the limit \( k_c \ll k^* \), so for \( k \) on the order of \( k_c \) there is negligible difference between the surface value, \( s_k \), of monomer density in (29), and the uniform value, \( \rho_1 \), far from clusters. We show this: in equation (29) for \( s_k \), we see that \( s_k \sim \rho_1 (1 + \eta_\infty) = \rho_1 \) if \( \frac{1}{\mu} \ll \eta_\infty \) and \( k^{1/3} / \sigma \mu \ll 1 \). For \( k_c = (\sigma / \eta_\infty)^3 \) in (10) and \( k^* = (\sigma \mu)^3 \) in (26), we find \( \frac{k_c}{k^*} = \left( \frac{1}{(\mu \eta_\infty)^3} \right) \).

So, \( \frac{k_c}{k^*} \ll 1 \) implies \( \frac{1}{\mu} \ll \eta_\infty \). Furthermore, for \( k \) on the order of \( k_c \), \( k^{1/3} / \sigma \mu \) is on the order of \( \left( \frac{k_c}{k^*} \right)^{1/3} \ll 1 \).

In (44), we replace \( s_k \) by \( \rho_1 \), and \( j_k \) by \( j \), to obtain a recursion equation that determines \( \rho_k \) for \( k \geq 2 \) from \( \rho_1 \). We write it as

\[
\frac{\rho_k}{\rho_1} - \frac{\rho_{k+1}}{\rho_{k+1}} = \frac{j}{d_k} e^{\frac{g_k}{3 \sigma \mu}}.
\]

(50)

Here, \( g_k \) is the free energy cost of a \( k \)-cluster, given in (49), and \( \tilde{\rho}_k \) denotes the solution (46) of the homogeneous recursion relation with \( j = 0 \), and \( \tilde{\rho}_1 = \rho_1 \). For positive super-saturation \( \eta \), \( \tilde{\rho}_k \to \infty \) as \( k \to \infty \), and we expect that the \( \rho_k \) in (51) have \( \frac{\rho_k}{\rho_1} \to 0 \) as \( k \to \infty \). Summing (50) over \( k \) gives a formula for \( j \). On the LHS, we get a telescoping sum with value

\[
\frac{\rho_1}{\rho_1} - \lim_{k \to \infty} \frac{\rho_k}{\rho_k} = 1 - 0 = 1.
\]

Hence,

\[
1 = j \sum_{k=2}^{\infty} \frac{1}{d_{k-1}} e^{\frac{g_k}{3 \sigma \mu}}.
\]

(51)

In the RHS, \( g_k \) decreases linearly with \( k \) as \( k \to \infty \), so the series converges. In the small super-saturation limit \( \eta \to 0^+ \), we expect that the sum on the RHS is dominated by terms with \( k \) near \( k_c \sim \left( \frac{2}{\eta} \right)^3 \), where \( g_k \) attains its maximum. The relevant approximation to \( g_k \) as \( \eta \to 0^+ \) and \( k \) is on the order of \( k_c \) is given by (49). Also, \( d_k \sim \omega k^{2/3} \) as in (5). Hence, (51) has the asymptotic approximation

\[
1 = \frac{j}{\omega} \sum_{k=2}^{\infty} k^{-\frac{2}{3}} e^{\frac{3}{2 \sigma \mu^2} - k \eta}.
\]

(52)

The final step is the approximation of the sum by an integral, and evaluation of the \( \eta \to 0^+ \) limit by the saddle point method. This leads to the approximation of \( j \),

\[
j \sim \omega \sqrt{\frac{\sigma}{6 \pi}} e^{-\frac{\sigma^3}{2 \pi^2} \eta}.
\]

(53)
V. ADVECTION SIGNALING PROBLEM

We examine the aggregation process, starting from a super-critical density of particles, $\rho > \rho_c$, all in the form of monomers at time $t = 0$. That is,

$$\rho_1(0) = \rho > \rho_c, \quad \rho_k(0) = 0 \text{ for } k \geq 2.$$ 

There is an initial transient, called ignition, in which the first supercritical clusters appear. A detailed analysis of the ignition transient appears in a paper by Bonilla et al. \cite{13}. Here we give a brief summary. First, sub-critical ($k < k_c$) clusters are created with quasi-static densities close to the values $\tilde{\rho}_k$ in (46). Of course, the value of $\rho_1$ becomes less than $\rho_1(0) = \rho$, since these sub-critical clusters are created from monomers. Hence, the appearance of the sub-critical quasi-static densities is accomplished by the decrease of super-saturation from an initial value of $\eta(0) = \frac{\rho - \rho_s}{\rho_s}$ to a smaller value, which we denote by $\eta_*$. In appendix A.2, we show that $\eta_*$ is related to $\rho - \rho_c$ by

$$\rho - \rho_c \sim \eta_* \rho_s \rho' (\rho_s)$$

as $\rho \to \rho_c^+$. Here, $\rho = \rho(\rho_1)$ is the equilibrium relation (47) between $\rho_1$ and $\rho$ for $0 < \rho_1 \leq \rho_s$. Figure 4 is a visualization of the relation (54) between $\eta_*$ and $\rho - \rho_c$. The ‘completion’ of the quasi-equilibrium in $1 \leq k < k_c = \left( \frac{\rho_s}{\eta_*} \right)^3$ is accompanied by the appearance of the first super-critical clusters with $k > k_c$. The rate of creation rises from zero to the Zeldovich rate in (53) with $\eta = \eta_*$. We assume $\eta_*$ is so that $k_c \ll k_*$, so the Zeldovich rate indeed applies.

Now our focus shifts to the evolving distribution of the super-critical clusters. The model we present here has three physical ingredients. Two of them are the growth of the clusters, and their creation. Both processes contain the super-saturation as a parameter, and the remaining ingredient is the connection of super-saturation to the distribution of cluster sizes.

First, growth. We expect a predominance of super-critical clusters with $k \gg k_*$ that undergo diffusion limited growth. Here is the heuristic argument for not resolving size scales comparable to $k_*$ or smaller: once a cluster achieves super-critical size, with $\frac{k - k_c}{k_*} \gg \eta^2$ (see the appendix A.1) it continues to grow nearly deterministically, as shown in section 3. Since the Zeldovich rate is exponentially small in $\eta$, an exponentially long time elapses before the super-saturation shows an significant decrease below the effective initial value,
FIG. 4: The darkened curve is the graph of \( \rho(\rho_1) \) in \( 0 \leq \rho_1 \leq \rho_s \). The dashed line is its linear interpolation into \( \rho_a > \rho_s \). It intersects \( \rho = \rho_1(0) > \rho_c \) at \( \rho_1 = \rho_s(1 + \eta_*) \). The arrow labeled \( i \) represents the decrease of \( \rho_1 \) during ignition, and the arrow \( a \) represents the decrease during the subsequent aggregation process.

\( \eta_* \), established during ignition. In this exponentially long time, we expect the super-critical clusters to grow to sizes \( k \gg k_\ast \), the regime of diffusion limited growth.

We assume that the characteristic cluster size \( \bar{k} \) corresponding to significant variations of the densities \( \rho_k \) for \( k \gg k_\ast \gg 1 \) is itself much larger than \( k_\ast \), and this motivates a continuum limit,

\[
\rho_k(t) \sim r(k, t). \tag{55}
\]

Here, \( r(k, t) \) is a smooth function of its arguments, with the characteristic scale \( \bar{k} \) of \( k \) much larger than \( k_\ast \). Substituting (55) for \( \rho_k \) into the discrete advection-diffusion equations (45) and using the assumed largeness of \( \bar{k} \), it follows that \( r(k, t) \) asymptotically satisfies the advection PDE,

\[
\partial_t r + \partial_k (u r) = 0. \tag{56}
\]

Here, the advection velocity \( u = u(k, \eta) \) is identified from ODE (28) for diffusion limited growth. We have,

\[
u(k, \eta) = d \left( \eta k^\frac{3}{2} - \sigma \right), \tag{57}\]

where \( \eta = \eta(t) \) is the ‘background’ super-saturation, far from any cluster.

Next, creation. In the analysis according to Zeldovich, recall that the discrete flux \( j_k \) in
is asymptotically uniform for $k$ on the order of $k_c$, with value $j$ given by (53). Here, we make the stronger assumption that the range of $k$ with the asymptotically uniform value $j$ of $j_k$ extends to a scale of $k$ much larger than $k_*$ but smaller than the characteristic cluster size $\bar{k}$ associated with the continuum limit (55). In this case, we expect an asymptotic matching between the continuum limit of $j_k$, given by

$$j_k \sim u(k, \eta) r(k, t),$$

and the uniform value, $j$, of $j_k$, in some overlap domain of cluster sizes $k$ much larger than $k_*$, but much smaller than $\bar{k}$. Since $k \gg k_* \gg k_c = (\frac{\sigma}{n_*})^3$ in the overlap domain, the dominant component of $u$ in (57) is $d \eta k^{1/3}$ and (58) reduces to

$$j_k \sim d \eta k^{1/3} r(k, t).$$

in the overlap domain. Hence, we propose the effective boundary condition (BC)

$$d \eta k^{1/3} r(k, t) \rightarrow j = \omega \sqrt{\frac{\sigma}{6\pi}} e^{-\frac{\sigma^3}{2k^2}} \text{ as } k \rightarrow 0. \quad (59)$$

If $\eta = \eta(t)$ is known, the advection PDE (56) and creation BC (59) lead to a simple determination of $r(k, t)$, starting from the initial condition of pure monomer, $r(k, 0) \equiv 0$ in $k > 0$.

It remains to connect $\eta(t)$ to $r(k, t)$. In the particle conservation identity (49), we now distinguish between sub-critical and super-critical clusters sizes. That is,

$$\rho = \sum_{1 \leq k \leq k_c} k \rho_k + \sum_{k_c < k} k \rho_k.$$ 

The sub-critical sum is approximated by substituting quasi-equilibrium values (46) for $\rho_k$ based on super-saturation $\eta$,

$$\rho_k \sim \tilde{\rho}_k = (1 + \eta)^k \rho^s e^{\frac{\sigma}{k_B T}},$$

and then taking the limit $\eta \rightarrow 0$. The details here are a re-run of the calculation in appendix A.2. We get

$$\sum_{k=1}^{k_c} k \rho_k \sim \rho_c + \eta \rho_s \rho'(\rho_s).$$

The super-critical sum is approximated by the integral,

$$\int_0^\infty k r(k, t) \, dk.$$
Here, the lower limit is \( k = 0 \) and not \( k_c \), because the characteristic scale, \( \hat{k} \), of \( k \) in \( r(k,t) \) is much larger than \( k_c \). Thus, the conservation identity (17) takes the asymptotic form

\[
\rho \approx \rho_c + \eta \rho_s \rho_s' + \int_0^\infty \hat{k} r(k,t) \, dk.
\]

(60)

Notice that if \( r \equiv 0 \), which corresponds to negligible super-critical clusters, (60) reduces to (54) with \( \eta = \eta_s \). Hence, \( \eta(t) \) has the effective initial condition \( \eta(0) = \eta_s \).

In summary, the signaling problem for \( r(k,t) \) consists of the advection PDE (56), the creation BC (59), and the functional dependence of the super-saturation, \( \eta \) on \( r(k,t) \) in (60). This signaling problem is nonlinear because \( \eta \), as a functional of \( r \), appears in the advection PDE and, in addition, in the exponential creation rate in the BC.

VI. CONCLUSIONS

The discrepancy between the two accepted model of nucleation—the surface reaction model derived by Becker and Döring, and the diffusion limited growth model due to Lifshitz and Slyozov—has now been resolved. Our new model, in which clusters interact with diffusing monomers by a surface reaction, predicts both models as limit cases. Although it provides a growth rate for clusters of all sizes, from small to large, its limiting behaviors are of special interest for us. In the limit of small clusters, the BD model emerges, and we can derive the Zeldovich creation rate of super-critical clusters using the BD kinetics. In the limit of large clusters, the diffusion limited growth model emerges, from which we derive the same evolution PDE for the density function, \( r(k,t) \), as LS.

Not all our findings corroborate the classical assumptions and results. We find that the ‘common wisdom’ about the monomer density at the cluster surface is wrong. In the classical DLG model, the surface density is chosen so that the surface reaction is in equilibrium. In our model, the balance between the surface reaction and diffusion leads to a surface monomer density substantially different from the ‘equilibrium’ value. Despite this, the new model still predicts the same growth rate as the classical DLG model (for large clusters).

Another piece of ‘common wisdom’ is that BD pertains to small clusters and DLG to large ones. In our model, there is a new characteristic cluster size, \( k_* \), that separates small \( (k \ll k_*) \) from large \( (k \gg k_*) \). This is useful in providing definite predictions for the validity of the model. For example, since nucleation happens around the critical size \( k_c \), and the
Zeldovich creation rate assumes the small cluster limit of the model, the validity of the Zeldovich formula requires $k_c \ll k_*$. The case where $k_c$ is of the same order or larger than $k_*$ is not covered by the current paper nor by classical Zeldovich nucleation theory. A separate investigation is required for this case, one that goes beyond or treatment of the monomer bath as a smooth ‘mean field’ and really accounts for its discrete and fluctuation nature.

The monomer density around the cluster satisfies the diffusion equation and a mixed boundary condition at the surface of the cluster. To calculate the flux of the monomers into or out of the cluster, our model assumes that the monomer density in the vicinity of the cluster is a quasi-static solution of the diffusion equation. We show that the quasi-static ‘surface’ value of monomer concentration in our model is stable: starting from general initial conditions, the concentration of the monomer bath rapidly relaxes to the quasi-static approximation.

The preceding insights are codified in a signaling problem for the cluster size distribution. It consists of an advection PDE consistent with diffusion limited growth, and a BC consistent with the Zeldovich creation rate. The PDE and BC contain the super-saturation as a parameter. The super-saturation, in turn, is a function of the cluster size distribution as dictated by the overall conservation of particles. Hence, the full signaling problem is non-linear. In particular, the Zeldovich creation rate is exponentially small as the super-saturation goes to zero. Therefore, accounting for small corrections to the monomer density is important, especially in the initial stage when new clusters are being created.

Given an initial condition of pure monomers, quasi-static densities are formed during the ignition phase [13], whereby small, sub-critical clusters are created from the monomers. The ignition transient is a precursor to the nucleation of super-critical clusters. Therefore, once the nucleation ‘has ignited’, the monomers density is lower than the its original value, prior to the ignition transient. The signaling problem starts from an effective IC that explicitly accounts for the loss of monomers during ignition. This is especially relevant in our case, where the monomer-density is close to the saturation density, $\rho_s$, and the dependence of the PDE and BC on the monomer density is very strong.

Such is the state of the theory. We now conclude the conclusion by a small trespass into the domain of accountability: do the material parameters of real aggregation processes cooperate with the various assumptions of the modeling? We start with the characteristic cluster size $k_*$, most conspicuously present in our model. We examine physical constants
associated with an aqueous solution of calcium carbonate, CaCO$_3$. Its solubility is rather small, so the basic requirement of ‘diluteness’ is satisfied. Admittedly, CaCO$_3$ dissolves into positive (Ca$^{2+}$) and negative (CO$_3^{2-}$) ions, which is not reflected in our aggregation model with identical particles. But we are examining crude order of magnitude estimates, so will not be distracted by the inconvenience, and we formally consider a positive-negative ion pair as a ‘monomer.’

Formula (26) for $k^*$ contains molecular volume $v$, the saturation density of monomer $\rho_s$, the diffusion coefficient $D$ of monomer in solution, and the dissociation rate constant $\omega$. Estimates of $v$, $\rho_c$, and $D$ are readily found in a chemical handbook [14]. We use $\rho_c$ as an order of magnitude estimate of $\rho_s$. The dissociation rate, $\omega$, is much more elusive. Here, we indulge in the activation energy model similar to Kelton’s, in his review of glass-crystal transitions [2]. The model is summarized by the formula

$$\omega = \frac{D}{v^{2/3}} e^{-\beta}, \quad (61)$$

Here, $v^{2/3}D$ is the characteristic time for a monomer to diffuse a distance comparable to its own size, and $\beta$ is an ‘activation energy of dissociation’, in units of $k_B T$. Inserting (61) for $\omega$ into (26), we find

$$\begin{align*}
    k^* &= (3 \cdot 16 \pi^2) \left(e^\beta \rho_s\right)^3, \\
    \text{or, using } \rho_s &= e^{-\alpha}, \\
    k^* &= (3 \cdot 16 \pi^2) e^{3(\beta-\alpha)}. \quad (62)
\end{align*}$$

Formula (61) has other applications for us, besides the estimate (62) of $k^*$. For instance, recall that the quasi-static limit of the FBP (21) is based on the ‘diffusion time’ $v^{2/3}D$ much smaller than the dissociation time $\frac{1}{\omega}$, so we required $\frac{D}{\omega v^{2/3}} \gg 1$. From (61) we get

$$\frac{D}{\omega v^{2/3}} = e^\beta, \quad (63)$$

and so an activation energy $k_B T \beta$ on the order of a few $k_B T$ is sufficient.

Next, we examine the criterion $\frac{k}{k^*} \ll 1$ for the validity of the Zeldovich nucleation rate. Using (10, 62), we find this implies a bound on the super-saturation,

$$\eta \gg \sigma e^{\alpha-\beta}.$$
Using the crude ‘cube’ model of bonding energy \(1\) we estimate \(\sigma\) by, \(\sigma \approx \frac{2}{3} \alpha\) so the criterion on the supersaturation becomes

\[
\eta \gg \alpha e^{\alpha - \beta}.
\]  

(64)

A lower bound on the super-saturation might seem like a problem, as we expect \(\eta\) to asymptote to zero in the long-time limit of an aggregation process. However, significant nucleation occurs at an early and relatively brief phase, so (64) should apply for the initial super-saturation. In late stage coarsening, \(\eta\) is much smaller than the RHS of (64), but significant nucleation is not happening then.

Numerical evaluation of \(k_*\), or the RHS of (64) require actual values of \(\alpha\) and \(\beta\). It is relatively easy to find \(\alpha\), as we have \(\alpha = -\log \rho_s\) and \(\rho_s\) is essentially the volume fraction of monomer in saturated solution. For instance, from the data in [14], we find that \(2.44 \times 10^{-4}\)cm\(^3\) of solid CaCO\(_3\) is soluble in 100cm\(^3\) of water at room temperature. The volume of the solution is nearly 100cm\(^3\) so the volume fraction occupied by Ca\(^{2+}\), CO\(_3^{2-}\) is (roughly) \(\rho_s = 2.44 \times 10^{-6}\), and our estimate of \(\alpha\) is \(\alpha \approx 12.9\). The bad news is that we do not know \(\beta\) any better than we know \(\omega\) in the first place, so we cannot do primia-facie evaluations of \(k_*\) nor the RHS of (64).

Our policy is to use (64) to obtain bounds on \(\beta\) for which our model is valid. For instance, we have seen that the quasi-static approximation requires \(\beta \gg 1\). In addition, our whole analysis is based on small super-saturation, so \(\eta \ll 1\). This is compatible with (64) only if

\[
\alpha e^{\alpha - \beta} \ll 1.
\]  

(65)

Starting with \(\alpha = 12.9\), we find the LHS is unity if \(\beta - \alpha = 2.56\), but if we increase the activation energy, \(\beta\), by \(3k_B T\) we get \(\beta - \alpha = 5.56\) and the LHS of (65) is \(0.061 \ll 1\). Inserting the value of \(\beta - \alpha = 5.56\) into (62) for \(k_*\) results in \(k_* \approx 8.3 \times 10^9\).

Our estimate of \(k_*\) does not really use values of \(D\) and \(v\) because the combination \(\frac{D^3}{v^2}\), which appears in the formula (26) is absorbed by the Kelton formula (61) for \(w\). Again we ‘turn the equations around’: using physical values of \(D, v,\) and \(\rho_s\), and our ‘made up’ estimate of \(k_*\), we work backwards to \(w\). From the Handbook of Chemistry and Physics [14], we find that the diffusion coefficients of Ca\(^{2+}\) and CO\(_3^{2-}\) are \(.792 \times 10^{-5}\)cm\(^2\)/s and \(.9.23 \times 10^{-5}\)cm\(^2\)/s. So, as a crude estimate we put \(D \approx 10^{-5}\)cm\(^2\)/s. The nucleous volume of solid CaCO\(_3\) is \(v = 4.51 \times 10^{-26}\)cm\(^3\). Inserting these values of \(D\) and \(v\) into (26), along with the previously determined \(\rho_s\) and \(k_*\) we obtain the estimate of \(w, w \approx 2 \times 10^6\)s\(^{-1}\).
VII. ACKNOWLEDGMENTS

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APPENDIX A: APPENDIX

1. Deterministic Cluster Growth According to BD

Here we determine the domain of $k$ in which the average change in the cluster size $\langle \delta k \rangle$ is a good approximation to the actual change in cluster size. BD assumes that the cluster grows and shrinks by means of discrete, independent Poisson processes. The cluster gains monomers at a rate $c_k \rho_1$ via the adsorption process, and via the emission process it loses monomers with rate $d_k$. Therefore, the average change in size over a short interval $\delta t$ is

$$\langle \delta k \rangle = \langle k(t + \delta t) - k(t) \rangle = (c_k \rho_1 - d_k) \delta t,$$

provided that $\delta t$ is small enough so that

$$|c_k \rho_1 - d_k| \delta t \ll k. \quad (A1)$$

Since the two controlling process are assumed to be independent Poisson processes, the mean square deviation of $k$ from the average is

$$\langle (\delta k - \langle \delta k \rangle)^2 \rangle = (c_k \rho_1 + d_k) \delta t$$

The process can be considered deterministic if the deviation is much smaller than the expected change, so

$$\sqrt{c_k \rho_1 + d_k \sqrt{\delta t}} \ll |(c_k \rho_1 - d_k) \delta t|. \quad (A2)$$

Combining inequalities (A1) and (A2) we get a condition on $\delta t$

$$c_k \rho_1 + d_k \ll |(c_k \rho_1 - d_k)|^2 \delta t \ll |c_k \rho_1 - d_k| k.$$

We can find $\delta t$ which satisfies this condition if

$$c_k \rho_1 + d_k \ll |c_k \rho_1 - d_k| k. \quad (A3)$$
This does not hold for every value of \( k \). In particular, we notice that for \( k = k_c \) the RHS is zero. Hence, the \( k(t) \) that can be approximated as deterministic must be bounded away from \( k_c \).

For \( k \gg 1 \) in \((A3)\) we insert the approximations \((5, 6)\) for \( d_k \) and \( c_k \), and then examine its asymptotic form as \( \eta \to 0^+ \). The result is

\[
\left(2 + \eta \left(1 - \left(\frac{k}{k_c}\right)^{-\frac{1}{3}}\right)^{\eta}\right) \ll \eta \left|1 - \left(\frac{k}{k_c}\right)^{-\frac{1}{3}}\right| k. \tag{A4}
\]

For clusters with \( k \gg k_c \), this condition is satisfied trivially for \( \eta \ll 1 \). For \( k \) on the order of \( k_c \), we need to dig a little deeper.

Since we are looking at the \( \eta \to 0 \) limit, we look at the leading order terms of \((A4)\)

\[
\frac{2}{\eta k} \ll \left|1 - \left(\frac{k_c}{k}\right)^{\frac{1}{3}}\right| .
\]

For \( k \) near \( k_c \) we expand the RHS around \( k = k_c \). Keeping the leading order terms of the Taylor series of the RHS, we find an explicit condition for the evolution of clusters to be treated deterministically: \( k \) must be bounded away from \( k_c \) according to

\[
\frac{6}{\eta} \ll |k - k_c| .
\]

As \( \eta \to 0 \), the excluded domain grows. On the other hand, its size relative to \( k_c \sim \left(\frac{\sigma}{\eta}\right)^3 \) shrinks to zero:

\[
\frac{6\eta^2}{\sigma^3} \ll \left|\frac{k - k_c}{k_c}\right| .
\]

Therefore, we see that for small super-saturation the evolution of clusters can be treated deterministically, for all but a vanishingly small domain around \( k_c \).

2. Effective Super-Saturation, \( \eta \), After Ignition

It has previously been shown that an initial condition of pure monomer leads to a transient ‘ignition’ phase in which quasi-static densities of sub-critical clusters are created \([13]\). Since these sub-critical clusters are made of monomers, after the ignition transient the monomer density will be lower than the original value, prior to the ignition. We compute the value \( \eta_* \) of super-saturation after the formation of the \( k < k_c \) quasi-static densities, but before significant depletion by super-critical clusters.
The starting point if the sum \((39)\) truncated to \(k \leq k_c\) because the contribution from super-critical clusters is insignificant:

\[
\rho = \sum_{1 \leq k \leq k_c} k \rho_k.
\]

Since the sub-critical cluster densities are quasi-static, we approximate them by the equilibrium densities \((40)\), and the corresponding approximation of the sum is

\[
\rho = \sum_{1 \leq k \leq k_c} k \rho_1^k e^{-\frac{\varepsilon_k}{kT}}.
\]

Recalling the definition of the super-saturation, \((9)\), \(\rho_1 = \rho_s(1 + \eta)\), and taking the two-term expansion as \(\eta \to 0^+\), we find

\[
\rho \sim \rho_c + \eta \sum_{1 \leq k \leq k_c} k^2 \rho_s^k e^{-\frac{\varepsilon_k}{kT}}.
\]

The sum on the RHS can be obtained by differentiating the series representation \((47)\) of \(\rho(\rho_1)\), setting \(\rho_1 = \rho_s\), multiplying by \(\rho_s\), and then truncating to \(k \leq k_c\). The derivative series converges at \(\rho_1 = \rho_s\), so for \(\eta \to 0\) (and hence for \(k_c \to \infty\)), the sum is asymptotic to \(\rho_s \rho'(\rho_s)\). Hence,

\[
\rho \sim \rho_c + \eta \rho_s \rho'(\rho_s),
\]

and so,

\[
\eta = \frac{1}{\rho'(\rho_s)} \frac{\rho - \rho_c}{\rho_s}.
\]

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