Enhanced Kinetics and Free-Volume Universality in Dense Aggregating Systems

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Aggregation kinetics and cluster-size distributions are studied with off-lattice, diffusion-limited cluster-cluster simulations. With increased cluster crowding (occurring at late times) as measured by the normalized free volume, Ω, both the kinetics speeds up and the size distribution broadens. The exponents characterizing each, z and λ, respectively, are found to be universal functions of Ω. Moreover, the relation $z = (1 - \lambda)^{-1}$ continues to hold up to $\Omega = 0$ (the ideal gel point), implying mean-field kinetics still applies despite the crowding.

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Crowded states of dispersed particulate matter are ubiquitous in Nature and technology. Gels, colloidal emulsions, self-associating polymer networks, and aerogelation in soot aerosols are all examples of a transition to a crowded or packed state that show large scale connectivity across the macroscopic boundaries of the system [1–4]. They are found in far ranging contexts such as biological systems, the food industry, paints, air and wastewater treatment, and medical fields [5]. Percolation theory has been the most widely used model to describe these types of systems throughout the past 30 years [6]. More recently, studies of gels have pointed to similarities with the glass transition [7–10] and also linked to the more general concept of "jamming" [11,12]. However, these states are often the end result of the more general kinetic growth process of aggregation: the combination of small units to form larger clusters or aggregates [13]. Aggregation when dilute has been well understood since the early part of the past century [14]. However, the details of evolution from dilute to crowded is largely unknown. The purpose of this Letter is to provide a coherent description of aggregation from dilute to crowded, its surprising mean-field nature despite crowding, and its universality with free volume.

Models of aggregation have commonly fallen into three classes: (i) diffusion-limited cluster-cluster aggregation (DLCA); (ii) reaction limited cluster-cluster aggregation (RLCA); and (iii) ballistic limited cluster-cluster aggregation (BLCA) [15]. Common to all three classes, for solid particle aggregation, is the formation of fractal aggregates with fractal dimension $D_f < d$, the space dimension. The ratio of nearest-neighbor separation to the cluster radius of gyration scales in time as $R_{nn}/R_g \propto t^{-z(d-D_f)/dD_f}$, where $z > 0$ is the kinetic exponent (see below). As a result, the volume fraction occupied by the clusters increases throughout aggregation, and evolution to a crowded state is inevitable.

When dilute, aggregation kinetics is known to be governed by the Smoluchowski equation (SE), expressing the change in cluster concentration n_k for k monomers per cluster as [13,14,16]

$$\frac{dn_k}{dt} = \sum_{i=1}^{i=k-1} K(i, k-i) n_i n_{k-i} - n_k \sum_{i=1}^{\infty} K(i, k) n_i, \qquad (1)$$

where $K(i, j)$ is the aggregation kernel, or rate. The SE is a mean-field equation because it assumes that the probability of two clusters meeting is simply proportional to the product of their number densities; i.e., there are no spatial correlations between clusters. If K is a homogeneous function, $K(ai, aj) = a^{\lambda} K(i, j)$, where λ is the degree of homogeneity, the SE yields self-preserving scaling solutions for n_k [13,16]. For a wide variety of kernel functional forms, these may be written as [17]

$$n_k = M_1 s_p^{-2} \phi(x), \qquad (2)$$

where M_i is the ith moment of the size distribution and $s_p = M_p/M_{p-1}$ is a mean cluster size. The scaling function $\phi(x)$ in Eq. (3) is given by

$$\phi(x) = A x^{-\lambda} e^{-\alpha x}, \qquad x \gg 1, \qquad (3)$$

where $x = k/s_p$ is the scaled size $\alpha = p - \lambda$, and A is a normalization constant. Substituting (3) into the SE, one finds that the moments of the size distribution obey

$$M_i(t) = M_i(0)\left(1 + \frac{t}{t_c}\right)^{z(i-1)}, \qquad (4)$$

where t_c is a characteristic time and $z = (1 - \lambda)^{-1}$ is the kinetic exponent. Thus, if the aggregation kinetics is mean field, z and λ are tied together, linking the kinetics and the resulting size distribution.

Attempts [15,18–20] to study aggregation over the entire range from dilute to crowded have been limited to either (i) high monomer volume fractions where the system begins evolving already in a crowded state, or (ii) carried out for a limited time, and limited system size, with smaller volume fractions so that cluster crowding is yet to substantially modify the kinetic process. The present simulations strive to achieve a broad description by starting at small cluster volume fractions and letting

the system evolve to a crowded state. As mentioned above, all three aggregation classes will eventually reach a crowded state since $D_f < d$. For this reason, we consider here only the most common model, DLCA. We begin by randomly placing, off-lattice, up to 3×10^6 monomers in a cubic box of side length $L \leq 580$ monomer diameters. The simulation then proceeds by first randomly picking, with probability N_c^{-1}, a cluster of size N (number of monomers per cluster), where N_c is the number of clusters at time t. Invoking Stokes-Einstein–type diffusion, a cluster is moved, with probability N^{-1/D_o}, one monomer diameter in a randomly chosen direction, with $D_o = 1.8$, the well-known mass fractal dimension of diffusion-limited cluster-cluster aggregates [21]. Each time a cluster is picked, the time, measured in Monte Carlo steps per cluster, is incremented by N_c^{-1} regardless of whether the cluster has moved. If two clusters collide, and, hence, aggregate, the motion is adjusted in order to correct for any overlap between particles. The cluster number, size distribution along with its moments, free volume, and radius of gyration are monitored throughout the simulation. The free-volume calculation, normalized to the system volume, uses a reasonable estimate of the aggregate perimeter radius as $R_p = [(D_f + 2)/D_f]^{1/2} R_g$ [22], and is defined as

$$\Omega(t) = 1 - \frac{4\pi}{3}\left(\frac{D_f + 2}{D_f}\right)^{3/2} \sum_{i=1}^{N_n(t)} \left(\frac{(R_g)_i}{L}\right)^3. \qquad (5)$$

By defining the perimeter radius in this manner, analogous to a sphere of dimension $D_f = 3$, the free volume can pass through zero and become negative, thus marking the point of cluster interdigitation. For a system composed of equal size clusters, one can define a critical cluster size R_c, where clusters are just touching all of their neighbors, i.e., when $R_{nn}/R_p \rightarrow 2$, thus representing an ideal gel point. Note that this represents the point at which "gel-like" connectivity forms for a monodisperse cluster-size distribution. However, due to polydisperse cluster sizes, the true gel point is pushed to later times. For completeness, we have determined this point from our results as the time at which any cluster first spans the entire system.

Figure 1 shows results for the aggregation kinetics represented in terms of the inverse cluster number $N_c^{-1}(t)$ versus time t. From Eq. (5), $N_c^{-1}(t) = M_o^{-1}$ should be a power law in time with exponent z. For all values of monomer volume fraction, f_v, considered here, the slope of the log-log graph in Fig. 1 is initially unity ($z = 1$) in agreement with the expectations for a Brownian aggregation kernel with $\lambda = 0$. Subsequently, at later times, depending on the volume fraction f_v, the effective value of z (z_{kin}) increases, indicating acceleration of the aggregation kinetics. What is the reason for this acceleration as quantified by $z_{kin} > 1$?

A first-order correction can be made illustrating the importance of crowding to the deviation from $z_{kin} = 1$. Instead of defining the cluster number per unit system

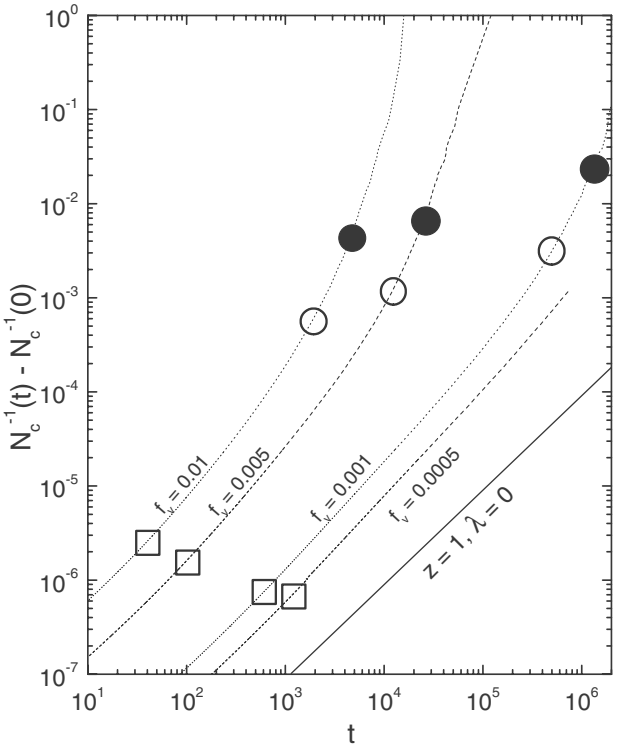

FIG. 1. Inverse cluster number as a function of time. Large open circles denote the ideal gel point. Large solid circles denote the true gel point. The large open squares correspond to $\langle N \rangle = N_m/N_c = 4$, where N_m is the total number of monomers in the system. The solid line represents the anticipated slope for dilute mean-field DLCA.

volume (L^3), we define it as per unit free volume, ΩL^3. This modified cluster number density is shown in Fig. 2 for $f_v = 0.005$. The factor of L^3 is a constant and has been left out for comparison with the uncorrected inverse cluster number. The "corrected" kinetics is now in rough accord with $z = 1$, up until $\Omega \approx 0.4$. This suggests that the enhanced kinetics results from aggregating clusters having less free volume in which to search for other clusters. Note that this correction is analogous to the free-volume correction of the ideal gas law to obtain the van der Waals gas law (with analogous limitations) and retains the mean-field nature of the kinetics.

We find that throughout aggregation the size distribution retains its scaling form but the scaling exponent evolves away from its dilute limit value, $\lambda = 0$. To determine λ, we calculate the polydispersity factor, $P = s_2/s_1$ [17], from simulation results. Utilizing the mean-field scaling form for large x represented by Eqs. (3)–(5), one can find $P \approx (2 - \lambda)/(1 - \lambda)$. Numerical integration suggests that the error in this functional form for P is only 4%–8%. λ is then determined by inversion of the above functional form and measured values for P. Figure 3 shows the size distribution exponent λ_{sd} obtained as a function of time. In all cases, there is an initial period where $\lambda_{sd} < 0$ for which the self-preserving distribution is yet to emerge from the initial monodisperse

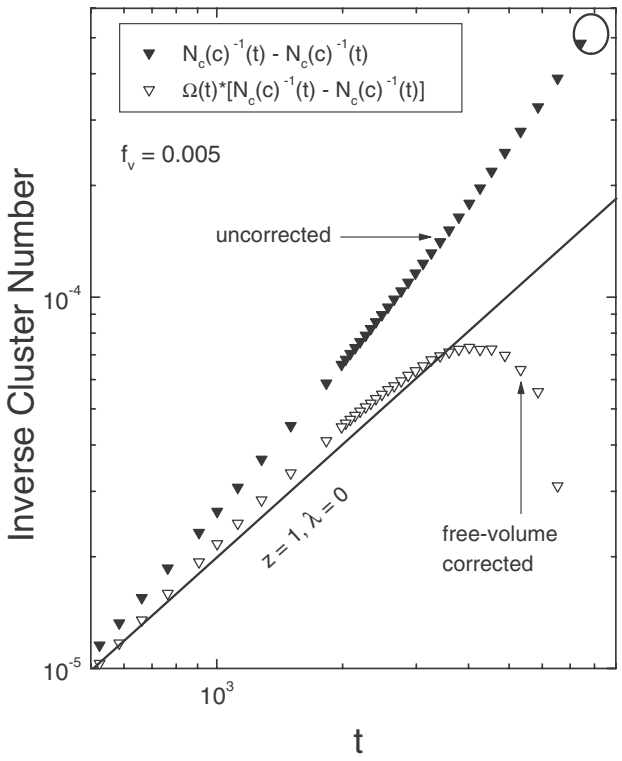

FIG. 2. Free-volume corrected inverse cluster number as a function of time. The large open circle denotes the ideal gel point. The solid line represents the anticipated result for dilute mean-field DLCA.

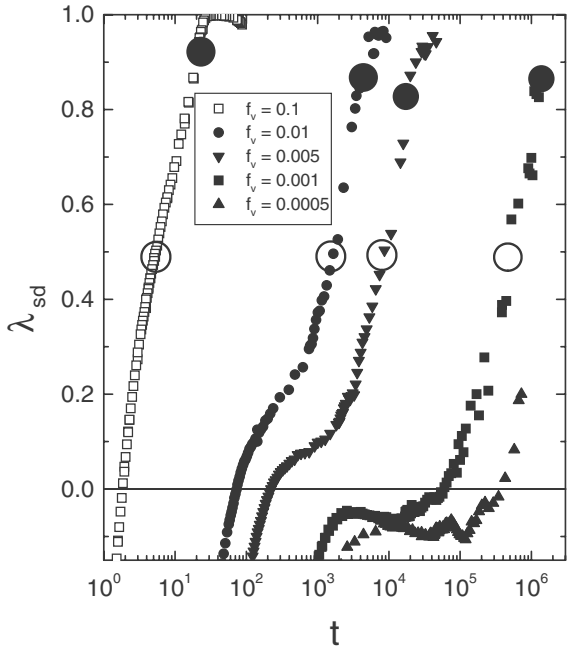

FIG. 3. Size distribution exponent, λ_{sd}, as a function of time. Large open circles denote the ideal gel point. Large solid circles denote the true gel point.

distribution. When $f_v \leq 10^{-3}$, $\lambda_{sd} \approx 0$ holds for some time once the self-preserving nature is obtained, indicating archetypical DLCA over this regime. As time evolves, λ_{sd} eventually becomes larger than zero. When $f_v > 10^{-3}$, λ_{sd} shows only a slight inflection near $\lambda_{sd} = 0$ and then quickly rises. Two questions now arise: First, are λ_{sd} from the size distribution and z_{kin} from the kinetics still tied together via $z = (1 - \lambda)^{-1}$ as required by the mean-field SE? Second, since crowding is implicated as the cause of the deviation from mean-field behavior, can it act as a viable descriptor of both z_{kin} and λ_{sd} in the crowded state?

To answer these questions, we first convert λ_{sd} to $z_{sd} = (1 - \lambda_{sd})^{-1}$ which can be compared to z_{kin}. We then plot both z_{kin} and z_{sd} in Fig. 4 against the normalized excluded (occupied) volume $(1 - \Omega)$. We see that both of these quantities follow the same functionality with Ω up to the ideal gel point where $\Omega = 0$. The near equality, $z_{kin} \simeq z_{sd}$, implies the remarkable fact that mean-field SE still holds despite the great crowding that is occurring. Furthermore, the same functionality with Ω, despite the wide range of time and monomer volume fractions, implies that the free volume is a universal descriptor of the aggregation in a concentrated system.

Beyond the ideal gel point, z_{sd} becomes larger than z_{kin} but each remains universally related to Ω, which is now negative, indicating interdigitation of aggregates. This behavior continues up to the presence of the first system-spanning cluster and finally the end of aggregation. The inequality of exponents implies that mean-field theory does indeed break down beyond the ideal gel point.

What is the reason for the coordinated increase in z_{kin} and λ_{sd} for a concentrated system up to the ideal gel point? To lend insight to this question, we have also studied the simulated kinetics of liquid drop sols. Liquid drops coalesce keeping the dimensionality of the aggregate equal to three, and, hence, the free volume, once decided by the initial concentration, remains fixed during aggregation. We find that the kinetic exponent z_{kin} remains fixed throughout the simulation for a particular value of concentration, hence, for a particular value of Ω. With increasing initial concentration, Ω decreases and z_{kin} increases (see Fig. 4). This universal behavior strongly supports the concept that crowding is the only factor for an enhanced kinetics. Cluster morphology and impending gelation are of no consequence. With this, and the apparent validity of the mean-field SE, we propose that crowding alters the Brownian aggregation kernel in some manner to increase its homogeneity λ. This modification of λ then carries into both the size distribution and the kinetics in the usual, mean-field manner.

Simple scaling arguments can be invoked to pinpoint limiting cases of the functional form of the kernel, and, hence, determine the homogeneity when crowded. The rate at which two clusters collide, K, is proportional to their relative cross-sectional area A and relative velocity, v, yielding $K \propto Av$, consistent with the units of $[L^3/t]$. In the dilute limit, R_g is the only relevant length scale in the system. Thus, for Brownian diffusion $v \propto D/R_g$, where D is the diffusion coefficient, giving $K \propto DR_g$,

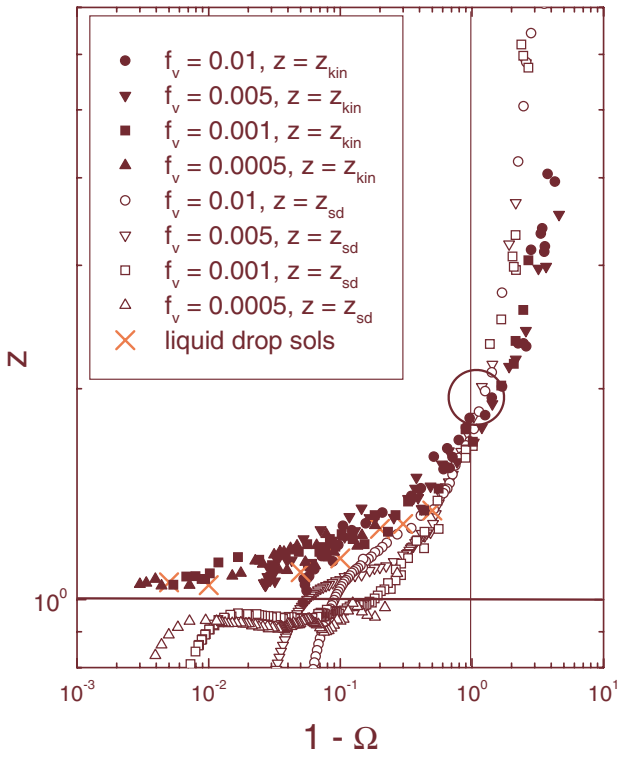

FIG. 4 (color online). z_{kin} and z_{sd} as a function of excluded (occupied) volume. Large open circles denote the ideal gel point. The results for liquid drop sols are shown as large crosses. Note that $z = 2$ at the critical point when $\Omega = 0$.

originally derived by Smoluchowski [14] in a more rigorous fashion. Since $D \propto 1/R_g$, K is constant and $\lambda = 0$. As the system continuously gets crowded, R_{nn} eventually becomes a relevant length scale with respect to any given cluster's motion. When this happens, at some intermediate time regime, one can estimate the characteristic velocity v as $v \propto D/R_{nn}$. This makes $K \approx N^{0.2}$, hence, $\lambda = 0.2$ consistent with simulation results in the intermediate regime. At the ideal gel point, the overall motion is "ballisticlike" since any cluster motion prior to a collision is small relative to its size. The cluster velocity is then given through the equipartition of energy as $v \propto N^{-1/2}$. In such a crowded state, a cluster sees the "fingerlike" detail of a neighboring fractal aggregate and the cross-sectional area must be replaced by the surface area, $A_s \propto N$. Thus, the kernel crosses over to $K \propto N^{1/2}$, yielding $\lambda = 0.5$, consistent with simulation results at the ideal gel point (see Fig. 3), irrespective of the initial volume fraction.

In conclusion, we present first results of the kinetics for an aggregating system which evolves from dilute to concentrated. The dynamical evolution of the system obeys typical DLCA-type kinetics at early times with a constant kinetic exponent, $z_{kin} = 1$ and size distribution exponent $\lambda_{sd} = 0$. Subsequently, crowding of clusters occurs and the kinetics can be described by a continuously evolving exponent, z_{kin}. We find that: (i) both exponents, z and λ, characterizing the kinetics and size distribution, respectively, show universal behavior with free volume, independent of the initial volume fraction. (ii) Remarkably, the relationship between z and λ maintains its mean-field nature. However, once the clusters become strongly interdigitated, beyond the ideal gel point, mean-field theory does indeed fail.

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