

Dynamic Scaling Behavior of Ballistic Coalescence

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Simulations of the two dimensional versions of a ballistic coalescence (or aggregation) model show significant deviations from the predictions of a mean-field scaling analysis. The growth exponents vary with density, due to multiple coalescence events. Kinetic theory combined with a self-similarity assumption leads to a hyperscaling relation between the exponents associated with the mass and the kinetic energy.

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Coalescence is a ubiquitous irreversible process controlling many nonequilibrium phenomena, such as nucleation and growth, droplet deposition, colloidal or micellar aggregation, polymerization, merging of vortices in turbulent flows, or the formation of planets by the aggregation of interstellar dust. Broadly speaking, particles coalesce upon collision; their motion between collisions is Brownian if they are mesoscopic, while it is essentially ballistic for macroscopic particles. Diffusion-limited aggregation (DLA) [1] is a widely studied schematic model for the former class of processes, whereas a very simple model for ballistic agglomeration (or aggregation) has more recently been put forward by Carnevale, Pomeau, and Young [2], who make a mean-field analysis of the asymptotic scaling governing particle growth.

In this model, spheres move freely in d -dimensional space; collisions are completely inelastic in the sense that two colliding spheres of initial masses and diameters (m_i, σ_i) , (m_j, σ_j) merge ("coalesce") into a single sphere of mass $m_{ij} = m_i + m_j$ and diameter

$$\sigma_{ij} = (\sigma_i^d + \sigma_j^d)^{1/d}. \quad (1)$$

The total momentum and the conjugate center-of-mass position are conserved during a collision, but the total kinetic energy decreases. After a time t , an initially monodisperse system of N_0 spheres (m_0, σ_0) will evolve into a polydisperse system characterized by a distribution of masses $f(m, t)$, a mean mass $\langle m \rangle(t)$, and a mean kinetic energy per particle $\langle \varepsilon_K \rangle(t)$; the total number of particles will have decreased to $N(t) = N_0 m_0 / \langle m \rangle(t)$. The model considered here differs in many aspects from random coalescence phenomena [3].

A simple scaling argument, making the implicit mean-field assumption that the momenta of all particles eventually merging into a single sphere are statistically uncorrelated, leads to the prediction that the mean mass increases asymptotically according to a power law and that $\langle \varepsilon_K \rangle(t)$ is constant in all dimensions, i.e., that the decrease of the total kinetic energy $K(t)$ (due to the inelastic character of particle collisions) is exactly compensated for by the decrease in the number of particles [2]:

$$\langle m \rangle(t) \propto t^\xi, \quad (2a)$$

$$K(t) \propto t^{-\delta}. \quad (2b)$$

The mean-field exponents are given by $\xi_0 = \delta_0 = 2d/(d+2)$. These predictions were confirmed by simulations carried out on 1D systems. Under weaker assumptions than those made in Ref. [2], Piasecki [4] showed that in the scaling regime the distribution of masses is a universal exponential distribution.

In this Letter, we examine the 2D version of the model. It is immediately clear that the spatial extension σ of the particles, which may be scaled out in 1D, becomes a relevant variable in $d \geq 2$. In particular, while coalescence is a purely binary process in 1D, multiple coalescence involving the simultaneous agglomeration of more than two particles into a single disk or sphere becomes possible in higher dimensions, particularly at higher densities. A convenient variable is the reduced density $n^* = \sum_i \sigma_i^2 / S$, where the sum runs over all particles in the domain of area S . In view of Eq. (1) it is clear that n^* is a conserved variable of the system (the packing fraction is constant). Only in the low-density limit $n^* \ll 1$ may one expect multiple coalescence events to play a negligible role, allowing a meaningful comparison with the behavior in 1D, and the predictions of mean-field scaling.

Molecular dynamics-like simulations [5] were carried out on samples containing initially $N_0 = 5000, 30000$, or 10^5 identical disks (m_0, σ_0) in a square cell of area $S = L^2$ with periodic boundary conditions. As in the case of elastic spheres [6], the code treats binary encounters between disks sequentially and updates the table of collision times between all pairs of particles after each coalescence event. No rotations of disks about their centers are involved. An initial square lattice configuration was first allowed to melt and equilibrate by letting the system evolve according to elastic collision dynamics. The corresponding Boltzmann mean collision time $\tau_0 = (m_0 \sigma_0^2 / \pi k_B T_0)^{1/2} / 2n_0^*$ served as a natural time scale. Starting from the resulting fluidlike configuration, the system subsequently evolved under the fully inelastic dynamics, involving coalescence each time two disks come into

contact; multiple coalescence occurs whenever the larger disk resulting from a pair collision overlaps one or several neighboring disks. The instantaneous temperature T was determined from the instantaneous kinetic energy according to

$$k_B T(t) = \langle \epsilon_K \rangle(t) = K(t)/N(t), \quad (3)$$

where the instantaneous number of remaining particles also determines the mean mass $\langle m \rangle(t) = N_0 m_0 / N(t)$. Simultaneously, the mass and kinetic energy distribution functions $f(m, t)$ and $f(\epsilon_K, t)$ were monitored at regular time intervals. During the irreversible evolution, the collision mean-free path $l \propto l/n\langle \sigma \rangle = \langle \sigma \rangle / n^*$ increases as $\langle m \rangle^{1/2}$ which is expected to scale as $t^{\xi/2}$ (where the exponent ξ is not necessarily equal to the mean-field prediction). The system's evolution was monitored until $l \approx L$ since any subsequent evolution would be affected by finite size effects. Runs were carried out for reduced densities $10^{-3} < n^* < 0.8$ (note that close packing on a square lattice corresponds to $n^* = 1$).

In view of the earlier remark on multiple coalescence events, we present the results for the lowest density ($n^* = 10^{-3}$) first, where the percentage of events involving coalescence of more than two particles was found to be less than 0.5%. Log-log plots of the mean mass $\langle m \rangle$ and of the total kinetic energy K versus time are shown in Fig. 1. After an initial transient regime, a power law regime is clearly seen to extend over about two decades in time; as expected, this regime terminates roughly when $l \approx L$, and only about $1/n^*$ particles are left (here 10^3 from an initial 10^5). The exponents are found to be $\xi \approx 0.8$ for $\langle m \rangle$ and $\delta \approx 1.12$ for K . They differ significantly from the mean-field analysis, which predicts $\delta_0 = 1$ and $\xi_0 = 1$ for 2D. In particular, the kinetic energy per particle $\langle \epsilon_K \rangle(t)$ is not constant but scales like $t^{-0.32}$. These values are reasonably insensitive (deviations of 5% at most) to system size and initial conditions (we

have also used a square lattice initial condition with an exponential distribution of kinetic energies). We conclude that the assumptions underlying the mean-field scaling argument are valid in 1D [2], but do not apply in 2D (and most probably for any higher dimensionality).

The logarithm of the mass distribution $f(m, t)$ is plotted in Fig. 2 versus m at four stages of the irreversible evolution. The distribution is clearly exponential at each stage, thus confirming the prediction of Ref. [4], which may be shown in fact to be independent of dimensionality. Thus at all times $f(m, t) = F(t) \exp[-m/M(t)]$. The conservation of mass implies $\langle m \rangle = M$ in the limit where $f(m, t)$ can be considered as continuous. This is indeed confirmed by the simulations. Nevertheless, the effects of discretization are nonnegligible at the early stages and account for the difference observed between $\langle m \rangle$ and M defined from the slope in Fig. 2.

The normalized distribution function of kinetic energies, $f(\epsilon_K, t)$, also turns out to be exponential at all times to a high degree of accuracy. This is illustrated in Fig. 3, where the values of $\langle \epsilon_K \rangle(t) f(\epsilon_K, t)$ measured at 5 successive times are plotted versus $\epsilon_K / \langle \epsilon_K \rangle(t)$. The data are seen to collapse on a single master curve which is practically indistinguishable from an exponential, confirming that $f(\epsilon_K, t) = \tilde{f}(\epsilon_K / \langle \epsilon_K \rangle) / \langle \epsilon_K \rangle$, with $\tilde{f}(x) = \exp(-x)$. We conclude that at every stage of the evolution the system is characterized by a Boltzmann distribution of energies and hence appears to be constantly in a state of local

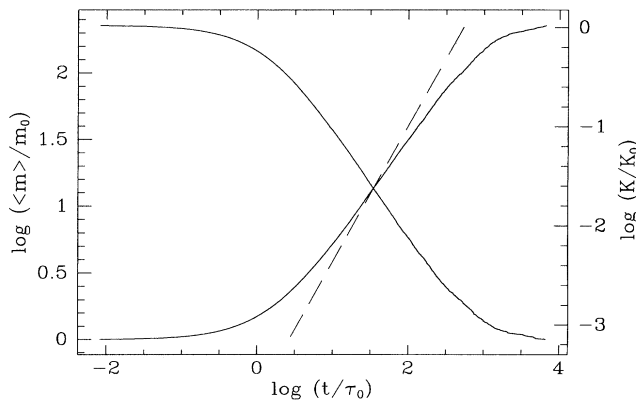


FIG. 1. Plots of $\log(\langle m \rangle / m_0)$ and $\log(K/K_0)$ vs $\log(t/\tau_0)$, where τ_0 is the Boltzmann mean collision time at $t = 0$. The dashed line represents the slope of $\log(\langle m \rangle / m_0)$ vs $\log(t/\tau_0)$ according to the mean-field result, with exponent ξ_0 . Initial conditions: fluidlike configuration of $N_0 = 99\,856$ hard disks, with $n^* = 10^{-3}$.

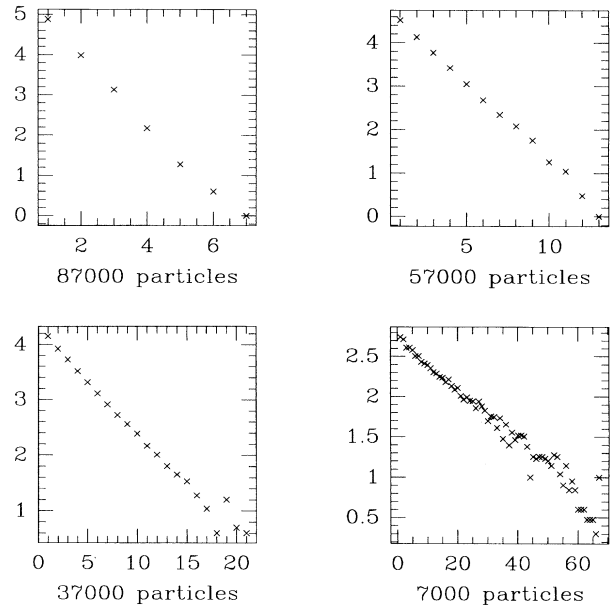


FIG. 2. Successive snapshots for a given initial condition of $\log f(m, t)$ vs m at four different times, when there are $N(t)$ particles left. Initial conditions: $N_0 = 99\,856$ and $n^* = 10^{-3}$. Here $f(m, t)$ is the number of particles of mass m (in multiples of m_0) present in the system at time t . The results shown are highly representative of the behavior observed for all initial conditions which were sampled.

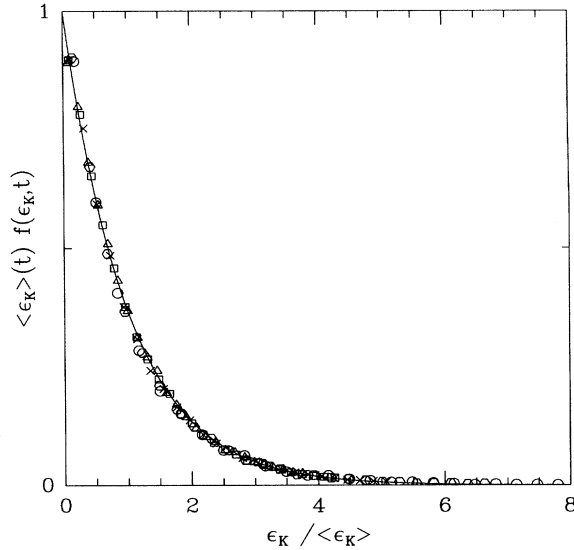


FIG. 3. Plots of $\langle \epsilon_K \rangle f(\epsilon_K, t)$ vs $\epsilon_K / \langle \epsilon_K \rangle$ for $N_0 = 99\,856$ and $n^* = 10^{-3}$ [$f(\epsilon_K, t)$ is the density probability of finding a particle with kinetic energy ϵ_K]. The symbols correspond to $N(t) = 87\,000$ (triangles), $67\,000$ (squares), $47\,000$ (crosses), $27\,000$ (hexagons), and $17\,000$ (circles) particles left. The full curve represents $\tilde{f}(x) = \exp(-x)$.

thermodynamic equilibrium. Moreover, if the initial velocity distribution function is chosen to be uniform rather

than exponential, the Boltzmann distribution is rapidly recovered in the course of the irreversible evolution.

Next, the effect of increasing the density n^* was investigated. As n^* increases, multiple coalescence events become more frequent. The number of particles out of the initial set which, by the end of the run, have participated in such events rises from 0.5% at $n^* = 10^{-3}$ to 70% at $n^* = 0.8$, so that multiple coalescence becomes predominant at the higher densities. Examination of the time dependence of $\langle m \rangle$ and K clearly exhibits a scaling regime at each density, but the exponents ξ and δ are found to depend on n^* . As shown by the results listed in Table I, ξ increases gradually up to values close to 1 while δ decreases to practically 1. These values are close to the mean-field predictions ($\xi_0 = \delta_0 = 1$), and it may be speculated that the rise in multiple coalescence events leads to a more efficient randomization of the momenta of the particles about to collide, thus validating the key assumption in the mean-field analysis.

A scaling law relating the dynamical exponents ξ and δ may be derived from the first equation of the BBGKY (Bogoliubov-Born-Green-Kirkwood-Yvon) hierarchy relating the one and two particle distribution functions $f^{(1)}(m, \mathbf{v}, t)$ and $f^{(2)}(m_1, \mathbf{v}_1, m_2, \mathbf{v}_2, \sigma_{12}, t)$, where $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ is the distance between the centers of the two colliding particles of diameters σ_1 and σ_2 . Taking into account coalescence events, the relation between $f^{(1)}$ and $f^{(2)}$ reads, for a spatially homogeneous and isotropic fluid in d dimensions,

$$\begin{aligned} \frac{\partial f^{(1)}(m, \mathbf{v}, t)}{\partial t} = S_t(d) \int dm_1 dm_2 d\mathbf{v}_1 d\mathbf{v}_2 |\mathbf{v}_1 - \mathbf{v}_2| \sigma_{12}^{d-1} \\ \times \left[\delta(m - m_1 - m_2) \delta\left(\mathbf{v} - \frac{m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2}{m}\right) - \delta(m_1 - m) \delta(\mathbf{v}_1 - \mathbf{v}) \right. \\ \left. - \delta(m_2 - m) \delta(\mathbf{v}_2 - \mathbf{v}) \right] f^{(2)}(m_1, \mathbf{v}_1, m_2, \mathbf{v}_2, \sigma_{12}, t). \end{aligned} \quad (4)$$

This evolution equation is exact only in the low-density limit where all events can be considered to be binary ($n^* \ll 1$). The dimensionless prefactor $S_t(d)$ is the total cross section of a particle of unit diameter ($S_t = 1, 2$, and π in one, two, and three dimensions, respectively). Making an assumption of self-similarity, we introduce two fundamental exponents ξ and γ to renormalize masses and velocities by t^ξ and t^γ in the asymptotic regime; distances scale accordingly like $t^{\xi/d}$. The self-similarity assumption for $f^{(1)}$ then translates into

$$f^{(1)}(m, \mathbf{v}, t) = \frac{1}{t^{\alpha_1}} \tilde{f}^{(1)}\left(\frac{m}{t^\xi}, \frac{\mathbf{v}}{t^\gamma}\right), \quad (5)$$

where $\tilde{f}^{(1)}$ is a time-independent scaling function and $\alpha_1 = 2\xi + d\gamma$ is due to conservation of the total mass. Similarly, the self-similarity assumption for $f^{(2)}$ implies

$$\begin{aligned} f^{(2)}(m_1, \mathbf{v}_1, \mathbf{r}_1, m_2, \mathbf{v}_2, \mathbf{r}_2, t) \\ = \frac{1}{t^{\alpha_2}} \tilde{f}^{(2)}\left(\frac{m_1}{t^\xi}, \frac{\mathbf{v}_1}{t^\gamma}, \frac{m_2}{t^\xi}, \frac{\mathbf{v}_2}{t^\gamma}, \frac{|\mathbf{r}_1 - \mathbf{r}_2|}{t^{\xi/d}}\right). \end{aligned} \quad (6)$$

TABLE I. Evolution of the exponents ξ and δ with the initial reduced density n^* [ξ_{th} is evaluated from the hyperscaling relation (9) and the measured δ]. The weight of multiple coalescence is also shown: The percentage is the ratio (number of particles disappearing in multiple coalescence events)/ N_0 .

| n^* | δ | ξ | ξ_{th} | Multiple coalescence |
|-------|----------|-------|-------------------|----------------------|
| 0.001 | 1.12 | 0.8 | 0.88 | 0.029% |
| 0.01 | 1.12 | 0.86 | 0.88 | 0.23% |
| 0.05 | 1.10 | 0.90 | 0.90 | 1.23% |
| 0.5 | 1.03 | 0.95 | 0.97 | 26% |
| 0.8 | 1.0 | 1.0 | 1.0 | 66% |

Since, in the limit $|\mathbf{r}_1 - \mathbf{r}_2| \rightarrow \infty$, $f^{(2)}$ factorizes according to

$$f^{(2)}(m_1, \mathbf{v}_1, \mathbf{r}_1, m_2, \mathbf{v}_2, \mathbf{r}_2, t) \rightarrow f^{(1)}(m_1, \mathbf{v}_1, t) f^{(1)}(m_2, \mathbf{v}_2, t), \quad (7)$$

it follows that $\alpha_2 = 2\alpha_1 = 4\xi + 2d\gamma$. Requiring that the scaling assumptions (5) and (6) are compatible with Eq. (4) immediately leads to the following hyperscaling relation:

$$\xi = d(\gamma + 1). \quad (8)$$

Since according to Eq. (5) the total kinetic energy $K(t)$ scales like $t^{2\gamma}$, the exponent δ in Eq. (2b) is given by $\delta = -2\gamma$, so that the scaling relation (8) may be reexpressed as

$$\delta - \delta_0(d) = \frac{2}{d} [\xi_0(d) - \xi]. \quad (9)$$

This relation is trivially satisfied by the mean-field exponents in all dimensions. It is satisfied within statistical errors by the values of ξ and δ deduced from our 2D simulations in the low-density limit as shown in Table I. For higher densities, the mean-field prediction turns out to be reasonably well obeyed; hence the numerical exponents agree better with the scaling relation. Finally, one might expect to deduce a further expression between ξ and γ from the conservation of total momentum. But since the scaling assumptions (5) and (6) only hold in the center-of-mass frame, this does not yield any new relation.

The results presented in this Letter show that the ballistic coalescence model has a nontrivial dynamical behavior in 2D, characterized by power laws in the asymptotic regime, with density-dependent exponents which differ significantly from mean-field predictions, particularly at low densities. Extensions of the simulations to higher dimensions will be very demanding on computer resources due to the need to consider large systems. Qualitative differences are expected if the mass-diameter relation $\sigma \propto m^{1/d}$, which in the language of polymers corresponds

to collapsed chains (provided σ is regarded as the radius of gyration), is generalized to allow for "swelling." In such a model $\sigma \propto m^\nu$, where ν could be taken equal to its Flory value $\nu = 3/(d + 2)$, i.e., $\nu = \frac{3}{4}$ in 2D. An immediate generalization of the mean-field argument of Ref. [2] then predicts a faster increase of the mean mass characterized by the exponent $\xi_0^f = 2(d + 2)(12 - 3d)$, equal to $\frac{3}{4}$ (rather than 1) in 2D. Similarly, the reduced density n^* (or packing fraction), which is conserved when $\sigma \propto m^{1/d}$, increases with time as $t^{4(d-1)/(12-3d)}$ for Flory chains. This clearly leads to an increase of multiple coalescence events in the course of time. One might then expect that, in any dimension $d > 1$, after a certain time, the remaining particles will coalesce into a single particle in a final "catastrophic" event. Preliminary simulations carried out on 2D systems indeed confirm this scenario which we are presently exploring in more detail. We also plan to investigate the situation where the motion of particles between collisions leading to coalescence is Brownian rather than ballistic, since the former is more appropriate for the modeling of polymerization.

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