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Elastocapillary coalescence: Aggregation and fragmentation with a maximal size

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Aggregation processes generally lead to broad distributions of sizes involving exponential tails. Here, experiments on the capillary-driven coalescence of regularly spaced flexible structures yields a self-similar distribution of sizes with no tail. At a given step, the physical process imposes a maximal size for the aggregates, which appears as the relevant scale for the distribution. A simple toy model involving the aggregation of nearest neighbors exhibits the same statistics. A mean-field theory accounting for a maximal size is in agreement with both experiments and numerics. This approach is extended to iterative fragmentation processes where the largest object is broken at each step.

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Aggregation and fragmentation are fundamental in a number of physical and manufacturing processes involving a broad range of object sizes: colloidal aggregation [1,2], polymerization [3] and polymer degradation [4], aerosols [5] and breath figures [6–8], mixing [9], formation of planets [10], ballistic aggregation [11,12], phase separation [13,14], vortex merging [15], and fragmentation by crushing [16,17] or by drying-induced stresses [18–20]. The formalism of Smoluchowski's coagulation equation [1] is still at the base of current theoretical effort, which focuses on scaling solutions to the equations of evolution for the distribution of object sizes, and on the convergence to these scaling solutions, either in fragmentation [21] or in aggregation [22,23]. Here we introduce aggregation and fragmentation processes with a maximal size. Our primary motivation is the experimental observation of the elastocapillary coalescence of flexible lamellas into bundles [24,25], which applies to macroscopic and microscopic systems. We showed that the maximal number of lamellas per bundle is determined by a balance between capillarity and elasticity. Here we study the size distribution of bundles, and we introduce a corresponding toy model which we simulate numerically and investigate analytically in a mean-field approach. As far as we are aware, we introduce the concept of a maximal size in the dynamics of aggregation. Eventually, by analogy, we study fragmentation with a maximal size. This type of process might apply to the aggregation of charged colloids [26] or to grinding [27].

Elastocapillary coalescence. Let us first describe the experimental system. A brush made of regularly spaced polyester strips is dipped into a wetting liquid, and then withdrawn quasistatically up to a height L. At small L, the lamellas remain straight [Fig. 1(a)], but at a first critical value of L, pairs of neighboring lamellas stick together, while some lamellas are left single between two pairs. A cascade of similar sticking transitions occurs when increasing L [Fig. 1(b)]: pairs of bundles merge into broader clusters. In contrast with usual time-dependent processes, the history of the transitions can be recovered directly from a single picture of the brush [Fig. 1(c)], as the withdrawal height L replaces time. In other words, the resulting hierarchical pattern can be viewed as the space-time diagram of either an aggregation or a fragmentation process (respectively, from top to bottom and from bottom to top). In [24], we found that for a given L, the maximum number of lamellas per bundle $N_{\max}$ is given by $N_{\max}^3 = 16/9[L^4/(dL_{ec})^2]$. It is a combination of three lengths: L, the separation between lamellas d, and the elastocapillary length $L_{ec}=(\kappa/\gamma)^{1/2}$ which is the scale at which capillary forces balance elastic bending forces (κ is the bending rigidity of the lamellae and γ is the surface tension of the liquid).

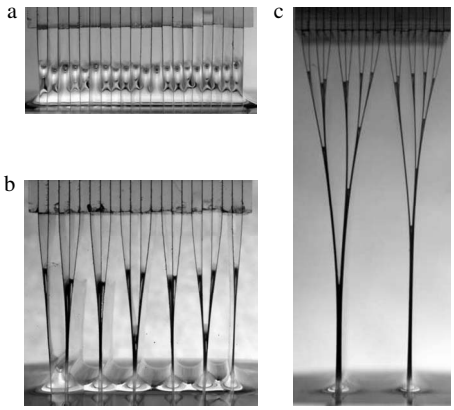

FIG. 1. Elastocapillary coalescence. Experiments with a brush made of flexible strips is progressively withdrawn from a bath of wetting liquid [24]. (a) Small withdrawal height L. (b) At higher L, bundles form successively. (c) Two bundles remain; if the vertical coordinate is replaced with time, this picture might be viewed as a space-time diagram for an aggregation process (from top to bottom) or a fragmentation process (from bottom to top).

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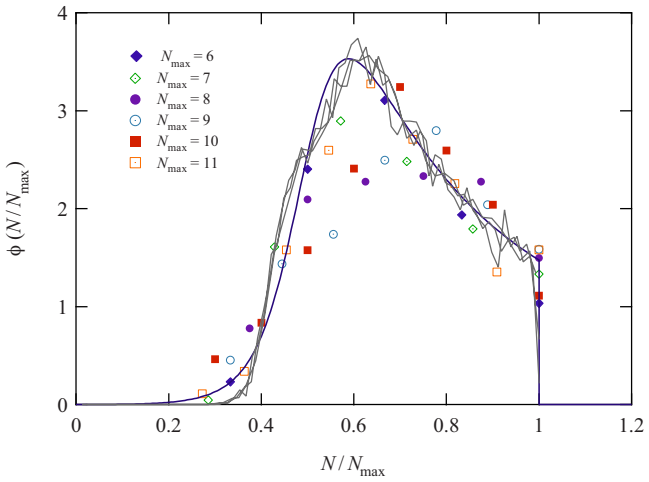

FIG. 2. (Color online) The scaling function for the statistics of sizes (proportional to the probability distribution function). If $n(N,N_{\max})$ is the number of bundles (particles) of size N when the maximal size is $N_{\max}$, $N_{\max}^2 n(N,N_{\max})/N_{\text{tot}}$ is plot as a function of $N/N_{\max}$. Experimental data (symbols) for $N_{\max} \in (6,11)$; toy model results starting with 10^6 particles after 9.5×10^5, 9.7×10^5, and 9.9×10^5 iterations (nonsmooth lines); solution of the mean-field model for $\Pi \simeq 0.56$ (smooth line).

In an ideal cascade, all bundles would coalesce by pairs so that they would all have the same size at a given L, following a geometric series $1,2,4,8,\ldots,2^m,\ldots$. This is not the case at all in the experiment where a broad size distribution is observed. For a given withdrawal length L or equivalently for a given maximum size $N_{\max}$, we counted the number $n(N,N_{\max})$ of clusters of size N in a brush of N_{tot} lamellas. The existence of a cascade process suggests a self-similar distribution of the form

$$n(N,N_{\max}) = \frac{N_{\text{tot}}}{N_{\max}^2}\phi(N/N_{\max}), \tag{1}$$

where ϕ is a scaling function unknown at this stage. The power-law dependence $1/N_{\max}^2$ is a consequence of the conservation of the total number of lamellas through the cascade. In fact ϕ is proportional to the probability of finding a cluster of given reduced size $N/N_{\max}$. This self-similar form allows the approximate collapse of experimental data (Fig. 2).

A toy model with aggregating particles. Particles of mass (or size) 1 are initially evenly distributed on a line, with a separation 1 between two consecutive particles; the position of each particle is then perturbed with a small random number—we chose 1% of the interparticle spacing and checked that the results are insensitive to this choice. The following elementary process is then iterated at each time step t: the two neighboring particles (masses m_1 and m_2) with the smallest interspacing are merged and replaced with a particle of mass m_1+m_2 located at their center of mass. The simulation also results in a cascade of sticking transitions (schematic in Fig. 3) and leads to a broad size distribution of clusters. Because of geometry and the sticking rule, clusters of mass M appear only after all possible smaller sizes are

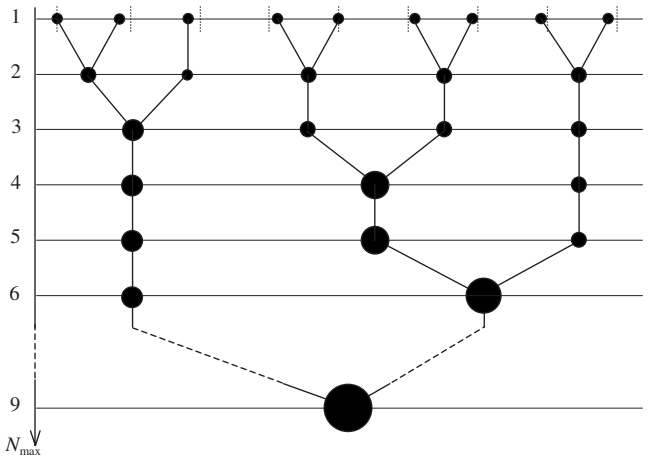

FIG. 3. A sketch of the toy model. It starts with approximately evenly spaced particles. The iteration rule is that, successively, the two neighbors with the smallest interspacing are merged, imposing the conservation of the center of mass (see text).

formed, so that we also obtain a process with maximal size. As in experiments, we define a maximal mass $M(t)$ for the clusters. Let $n(m,t)$ be the number of particles of mass m at time t. The distribution of masses can be rescaled according to

$$n(m,t) = \frac{M_{\text{tot}}}{M(t)^2}\phi(m/M(t)), \tag{2}$$

M_{tot} being the total mass in the system. After a number of iterations of the order of $0.9N_{\text{tot}}$, the distributions obtained from the toy model collapse on the same curve (Fig. 2), which is close to the experimental data.

A mean-field theory. We build here a coalescence process using kinetic equations [1,23]. Consider a large collection of particles progressively aggregating. We use the mass m of a particle and the time t as mathematical representations of the size of a bundle and of the withdrawal height L, respectively. Let $n(m,t)dm$ be the density of particles of mass larger than m and smaller than $m+dm$. The evolution equation for $n(m,t)$ reads

$$\frac{\partial n}{\partial t}(m,t) = \frac{1}{2}\int dm_1 dm_2 [K(m_1,m_2)n(m_1,t)n(m_2,t) \times \delta(m_1+m_2-m)] - \int dm_1 K(m,m_1)n(m,t)n(m_1,t), \tag{3}$$

where δ is Dirac's distribution. The first integral corresponds to the creation of particles of mass m through coalescence of particles of mass m_1 and m_2 with a rate $K(m_1,m_2)$, whereas the second integral stands for the anihilation of particles of mass m through coalescence with a particle of mass m_1. The crucial question is how to define the kernel K. In classical aggregation theory [23], this kernel is constant. Here, since only bundles of size $N_{max}(L)$ are created at a withdrawal height L, we take the maximum mass in the system as a given increasing function of time $M(t)$ and we set

$$K(m_1,m_2) = \frac{2}{\Pi \int dm\, n(m,t)} \delta[M^{-1}(m_1+m_2) - t]. \quad (4)$$

This δ function is the novelty here; it corresponds to the fact that the two particles (masses $m_{1,2}$) can coalesce if and only if the sum of their masses is equal to the maximal mass $M(t)$. If each particle could interact with the same probability with any other particle, there would be no prefactor in the equation above. For particles distributed on a line, any particle can interact with one of its two neighbors among $N_{\text{clusters}} = \int dm\, n(m,t)$ clusters. However, the aggregation dynamics imposes that particles cannot be ordered arbitrarily, e.g., the sum of the masses of two neighboring particles cannot be smaller than the maximal mass $M(t)$; otherwise they would have merged before. Here we assume the existence of a well-defined probability Π such that the number of possible neighbors is not N_{clusters} but ΠN_{clusters}, hence a probability $2/(\Pi N_{\text{clusters}})$ of coalescence. Π will be used as a fitting parameter in order to account for spatial correlations.

We look for self-similar solutions of Eqs. (3) and (4) in the scaling form (2). This leads to

$$\Pi \int_0^1 \phi(\xi_1) d\xi_1 \left(\phi(\xi) + \frac{1}{2}\phi'(\xi) \right) = \phi(\xi)\phi(1-\xi) - \frac{1}{2}\delta(\xi-1) \int_0^1 \phi(\xi_1)\phi(1-\xi_1) d\xi_1. \quad (5)$$

It also appears that the dependence of the maximal mass $M(t)$ on time is unimportant. The decomposition $\phi(\xi) = \phi_e(\xi - 1/2) + \phi_o(\xi - 1/2)$, where ϕ_e and ϕ_o are even and odd functions, respectively, transforms Eq. (5) into a system of ordinary differential equations with an integral constraint

$$2\Pi \int_0^{1/2} \phi_e(u_1) du_1 \left[\frac{1}{2} u \phi_e'(u) + \frac{1}{4}\phi_o'(u) + \phi_e(u) \right] = \phi_e^2(u) - \phi_o^2(u), \quad (6)$$

$$\frac{1}{4} u \phi_o'(u) + \frac{1}{2} u \phi_o'(u) + \phi_o(u) = 0. \quad (7)$$

A solution to this system can be found for each value of $\phi_e(0)$ [note that by parity $\phi_o(0)=0$]. Due to the definition of the scaling function, if $\phi(\xi)$ is a solution of Eqs. (6) and (7) then $\lambda\phi(\xi)$ is also a solution, so that one might choose $\phi_e(0)$ to ensure the normalization $\int \xi\phi(\xi) d\xi = 1$, which corresponds to the scalings (1) and (2). The value $\Pi \simeq 0.56$ gives the best agreement with the numerical data as shown in Fig. 2.

Thus we showed that the elastocapillary coalescence can be described as an aggregation process, where the maximal size is the key ingredient and sets the typical size of bundles or masses. In particular, the distribution has no tail as ϕ vanishes above 1.

Fragmentation with a maximal size. As an extension, we now introduce fragmentation processes with a maximal size. We consider a collection of fragmenting particles. At each step the largest particle is broken. This is the analog of forming clusters with the maximal size in the processes introduced above. Keeping the same notations, the general kinetic equation for the mass density $n(m,t)$ reads

$$\frac{\partial n}{\partial t}(m,t) = -n(m,t) \int_0^m dm_1 K(m_1, m-m_1) + 2\int_m^\infty dm_1 K(m, m_1 - m) n(m_1,t). \quad (8)$$

The first term in the right-hand side corresponds to all fragmentation events of a particle of mass m into two particles of mass m_1 and $m_1 - m$. The last term corresponds to all creation events of a mass m from the fragmentation of a mass m_1. The dynamics is that the largest mass is broken into two masses m_1 and m_2. The size probability of the fragments is $p[m_{1,2}/(m_1+m_2)]$ (p must be symmetric with respect to 1/2). This is achieved by imposing the maximum mass $M(t)$ as a decrasing function of time and a reaction rate in the form

$$K(m_1,m_2) = \frac{1}{m_1+m_2} p\left(\frac{m_1}{m_1+m_2} \right) \delta[t - M^{-1}(m_1+m_2)]. \quad (9)$$

We look for solutions of Eqs. (8) and (9) in the scaling form (2). This leads to an ODE for ϕ which solution reads

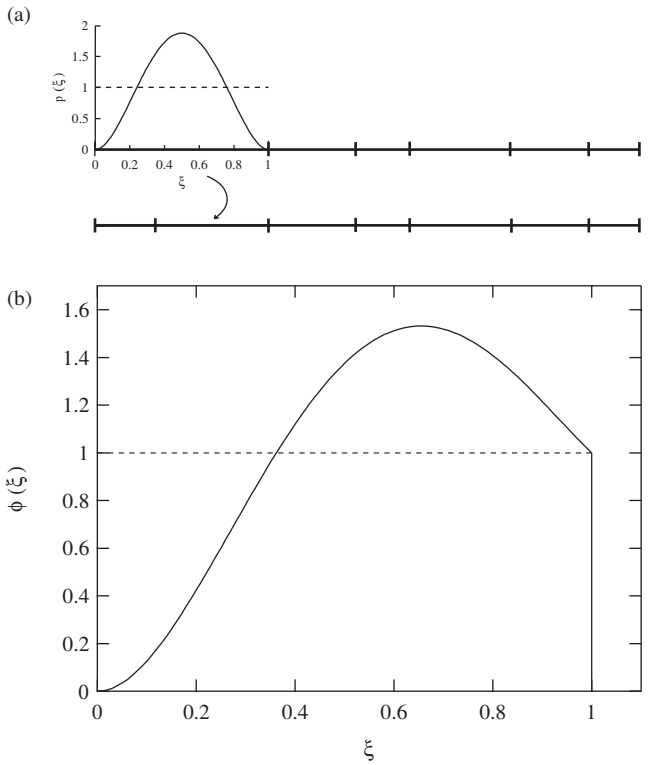

FIG. 4. The fragmentation model. At each step, the largest segment (length ℓ) is cut into two fragments of lengths $u\ell$ and $(1-u)\ell$ with a probability $p(u)$. (a) A uniform cutting probability (dashed line) or a peaked one $[p(u) = 30u^2(1-u)^2$, continuous line]. (b) Corresponding scaling function for the statistics of lengths: uniform cutting (dashed line) and peaked cutting (continuous line).

$$\phi(\xi) = \frac{2}{\xi^2}\int_0^{\xi} \xi_1 p(\xi_1) d\xi_1, \tag{10}$$

with the normalization $\phi(1)=1$. Again, if the cutting probability is uniform $[p(\xi)=1]$, then the size distribution is uniform (Fig. 4). To obtain distributions which are qualitatively similar to those of the fragmentation process, one must take a probability $p(\xi)$ that is peaked when the two fragments have the same size (maximum for $\xi=1/2$). For instance, for $p(x)=30\xi^2(1-\xi)^2$, Eq. (10) yields $\phi(\xi)=\xi^2(15-24\xi+10\xi^2)$, which is plotted in Fig. 4.

Conclusion. We introduced the concept of maximal size in both aggregation and fragmentation processes. This approach was inspired by the elastocapillary coalescence experiments and it allowed us to retrieve the experimental results. It might be relevant to grinding [27]: if solid blocks are crushed in between two parallel jaws, the largest block is first broken. In the case of the aggregation of charged colloids [26], a maximal size seems to be imposed by a competition between coalescence and electrostatic repulsion. The minimal ingredients included in our contribution should warrant robustness and possible generalization to other physical systems.

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