

Dense Cluster Formation during Aggregation and Gelation of Attractive Slippery Nanoemulsion Droplets

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Using time-resolved small angle neutron scattering, we have measured the wave-number-dependent structure factor $S(q)$ of monodisperse nanoemulsions that aggregate and gel after we suddenly turn on a strong, short-range, slippery attraction between the droplets. At high q , peaks in $S(q)$ appear as dense clusters of droplets form, and $S(q)$ increases strongly toward low q , as these dense clusters become locked into a rigid gel network, despite the fluidity of the films between the droplets. The long-time high- q structure of nanoemulsion gels formed by slippery diffusion-limited cluster aggregation is universal in shape and remarkably independent of the droplet volume fraction, ϕ .

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In diffusion-limited aggregation (DLA) [1], solid spherical particles are released one at a time far away from a growing cluster, diffuse through a viscous fluid, and stick rigidly to the cluster when they first encounter it. The attractive potential is extremely short in range, the well depth is much larger than the thermal energy, $k_B T$, and the particle volume fraction, ϕ , is extremely dilute. Once stuck to the cluster, particles do not rearrange due to the shear rigidity of the bonds. This classic picture leads to the well-known self-similar fractal aggregates of DLA. A different growth process at extremely dilute ϕ yields Eden clusters [2,3]. In Eden growth, individual particles are randomly placed at unoccupied sites adjacent to the surface of an existing cluster and are attached with shear-rigid bonds. Although Eden clusters have maximally dense cores, their surfaces can become quite tenuous. Eden growth has been used to describe nonequilibrium biological processes, such as tumor expansion [2], whereas DLA is typically associated with aggregation of colloids in solution.

For dilute $\phi \ll 1$, yet above the extreme limit of DLA, the structure of aggregates is strongly influenced by cluster-cluster bonding. When a strong short-range attractive force is suddenly activated in a homogenous suspension, neighboring fractal clusters aggregate together through diffusion-limited cluster aggregation (DLCA) [4]. Even at relatively low ϕ , many fractal clusters can combine to form percolating gels that span macroscopic dimensions with a well-defined characteristic length scale, ξ , between the cluster centers [5,6]. Both ξ and the fractal dimension d_f of the clusters have been measured using small angle light scattering in attractive systems of solid particles [5–7] and in microscale emulsions [8–10]. In reaction-limited cluster aggregation (RLCA) [11,12], a diffusing cluster may encounter another cluster many times before sticking with a single shear-rigid bond, resulting in a larger d_f than is observed for DLCA [12].

Although the structure of colloidal aggregates formed by shear-rigid bonds at dilute ϕ is well understood, the influence of alternative types of bonding, particularly slippery bonds, on the structure of aggregates has not been well explored. Theoretical investigations and simulations have begun to examine what happens during aggregation of spheres that are strongly attractive [13–20] yet may slip around their neighbors, as may be the case in aggregates of emulsion droplets. As the strength of the short-range attraction is increased, there is a crossover from equilibrium flocculation to irreversible percolating aggregation [18], whereby random bond formation between aggregates leads to a gel [13,16]. Moreover, rapid kinetic arrest can cause homogeneously dispersed particles to become jammed into a dense phase [21], reminiscent of a glass.

One key feature found in the most recent theoretical work is the appearance of peaks in the structure factor $S(q)$ at high wave number, q , corresponding to dense clusters [13,15]. The kinetics of the appearance of these high- q peaks after the activation of the attractive interaction have not been reported, although predictions exist for time-dependent cluster numbers [22]. The crossover in the low- q structure and dynamics between flocculation and percolating aggregation regimes has been explored experimentally through static and dynamic light scattering using a colloid-polymer system that creates a depletion attraction by excluded volume [23,24]. The formation of dense tetrahedral clusters as the primary rigid building blocks in the aggregation and gelation of emulsions has been hypothesized [25], but no clear experimental evidence for dense cluster formation has yet been seen.

In this Letter, we examine the evolution of aggregate structures that form when a homogeneously stable dispersion of spheres in a viscous liquid is suddenly quenched, thereby creating strong and slippery short-range attractions between the spheres. We present time-resolved small angle neutron scattering (TR-SANS) measurements of the aggre-

gation of uniform spherical nanoemulsion droplets [26] that is induced by adding salt and quenching the temperature, T [8]. In this manner, we are able to quickly turn on a short-range central-force attraction that preserves a thin film of liquid between the droplets so that they neither coalesce nor stick together with a shear-rigid bond. Neutron scattering is well suited for revealing the interdroplet structure of bulk suspensions at high q . Changes in the time-dependent structure factor $S(q, t)$ show that a strong short-range slippery attraction leads to the initial formation of dense clusters, of which tetrahedra of four droplets are the primary rigid building blocks. These dense clusters aggregate to form rigid fractal cluster aggregates and gels. At long times, the final $S(q)$ is remarkably independent of ϕ . Our results motivate a universal picture of gels arising from a “slippery DLCA” process.

Silicone oil-in-water nanoemulsions stabilized by sodium dodecylsulfate (SDS) surfactant are synthesized using a high-pressure microfluidic device and size-fractionated through ultracentrifugation [26]. By contrast to equilibrium lyotropic phases known as “microemulsions,” nanoemulsions are long-lived metastable dispersions of nanoscale droplets of one liquid in another immiscible liquid. We use a nanoemulsion having an average radius $\langle a \rangle = 51$ nm and a polydispersity of 16%, as determined by fitting the scattered neutron intensity, $I(q)$, at $\phi = 0.005$ to a Schulz distribution of polydisperse hard spheres [27]. The nanoemulsions are diluted from $\phi = 0.57$, determined by evaporation, to the desired ϕ and volume ratio of $\text{H}_2\text{O}:\text{D}_2\text{O} = 1:1$ at fixed NaCl concentration of $C_{\text{NaCl}} = 0.67$ M and SDS concentration of $C_{\text{SDS}} = 10$ mM. This composition increases the scattering contrast and provides an easily accessible temperature, $T^* = 47^\circ\text{C}$, below which the slippery attraction becomes very strong. At the highest $\phi = 0.27$, 25% of incident neutrons are coherently scattered, 6.3% are doubly scattered, and 1.5% are multiply scattered in the worst case. To homogeneously disperse the droplets, we initially heat the nanoemulsion in a quartz banjo cell (1 mm path length) to $T = 90^\circ\text{C}$ and measure $I(q)$. To facilitate a rapid quench over a smaller temperature range, we cool to $T = 50^\circ\text{C}$, at which the droplets remain dispersed, and measure the prequench $I(q)$ over a 600 s duration. This prequench $I(q)$ is labeled “ $t = 0$ s;” it essentially matches $I(q)$ at $T = 90^\circ\text{C}$, and so, over the short time we wait, any residual small attraction that may be present at $T = 50^\circ\text{C}$ does not cause significant aggregation. We then rapidly quench to $T = 45^\circ\text{C}$, below T^* , to abruptly turn on the attractive interaction, and measure $I(q, t)$. The data collection interval is initially set at 100 s to capture the faster dynamics of the first stages of aggregation and is lengthened to 200 s and 300 s to obtain better statistics as the aggregation slows. Reported times represent the midpoint of the collection intervals, the first commencing when $T = T^*$. Short delays between intervals occur as data are saved; t includes these delays. Optical microscopy measurements of microscale droplets under the same ag-

gregation conditions confirm that bonds formed between liquid oil droplets are slippery, rather than shear rigid.

The TR-SANS intensity of an aggregating nanoemulsion at $\phi = 0.12$ is shown in Fig. 1. As the aggregation progresses, $I(q)$ rises at the lowest q , decreases at intermediate q , and forms striking primary and secondary peaks at high q . Visually, the emulsion forms a weak, yet rigid, gel. After about 30 minutes, $I(q)$ in the range we probe stops evolving, and the droplets remain locked into a static structure. Upon reheating, $I(q)$ matches that prior to quenching, with no evidence of coalescence.

To obtain the evolution of the structure factor, in Fig. 2 we divide the measured intensities by the prequench scattering intensity: $S(q) = I(q)/F(q)$, where $F(q) \approx I(q, T = 50^\circ\text{C})$. Thus, S measures the effective structural changes between aggregating and dispersed droplets. Towards low q , S increases strongly to a value many times greater than unity. At intermediate $q \approx 0.003 \text{ \AA}^{-1}$, S forms a deep minimum. At higher q , distinct peaks and minima indicative of spatial correlations between neighboring droplets, as in a concentrated emulsion [28], appear. Although the peaks do not increase much above unity, indicating that the residual polydispersity in our droplet size distribution is playing a role, the deepening of the minima over time clearly indicates the formation of significant nearest neighbor correlations.

We have characterized the temporal dependence of the primary features in $S(q)$. The low q value of S , $S_L(t)$, increases as the larger length scale “surfaces” of the aggregate structure grow [Fig. 3(a)]. The minimum value of S , $S_{\text{min}}(t)$, decreases, reflecting the reduction in scattering from individual isolated droplets and the crossover to the low- q tail in the scattering from large aggregates

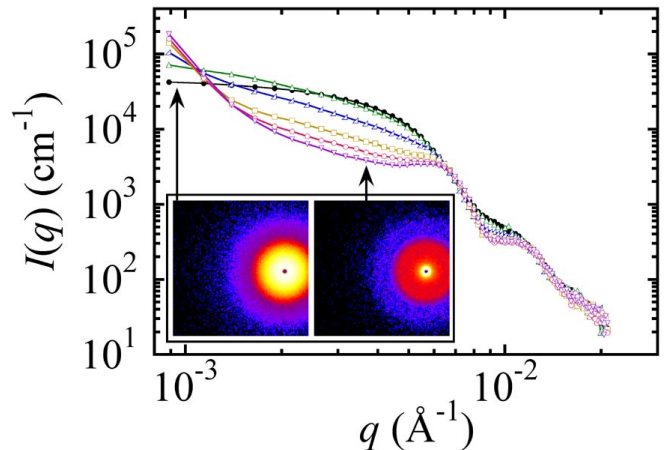


FIG. 1 (color online). Scattered neutron intensity from aggregating nanoemulsions as a function of wave number, $I(q)$, for a series of times, $t = 0$ (●), 239 (△), 482 (◁), 724 (□), 968 (○), and 2100 s (▽), following an abrupt quench from 50°C to 45°C . The oil droplets have an average radius $\langle a \rangle = 51 \pm 8$ nm and a volume fraction $\phi = 0.12$. Lines guide the eye. Inset: 2D scattering intensity patterns before the quench (left) and at the longest time (right). Arrows indicate the related $I(q)$.

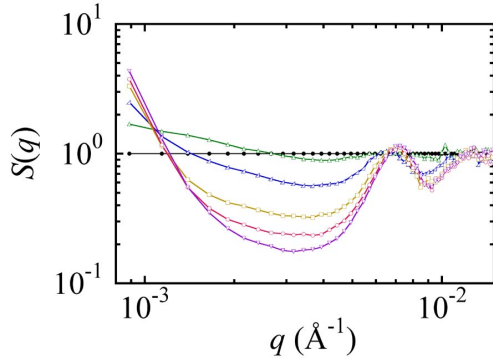


FIG. 2 (color online). Temporal evolution of the structure factor as a function of wave number, $S(q, t)$, of aggregates of attractive nanodroplets. Symbols are defined in Fig. 1.

[Fig. 3(a)]. The high- q minimum of S between the cluster peaks, $S_{\text{cm}}(t)$, is indicative of local correlations between neighboring droplets [Fig. 3(b)]; $S_{\text{cm}}(t)$ reaches a time-independent plateau more quickly than either $S_{\text{min}}(t)$ or $S_L(t)$. This is sensible, since $S_{\text{min}}(t)$ and $S_L(t)$ both depend on the diffusion of larger length scale structures.

We have examined the aggregation of slippery droplets for the same temperature quench over $0.05 \leq \phi \leq 0.27$. In Fig. 4, the long-time $I(q, t \rightarrow \infty)$ for four different ϕ have been rescaled onto a universal master curve. Although the initial structure factors are different, the shape of $I(q, t \rightarrow \infty)$ is nearly independent of ϕ , as shown by the excellent overlap of the rescaled intensities. The inset of Fig. 4 shows the universal $S(qa)$, representing the ϕ -averaged intensities divided by the form factor. The first cluster peak, corresponding to droplets bonded with their nearest neighbors, slightly above $qa \approx \pi$, is easily seen, and, as qa decreases, S goes through a minimum and then a sharp rise as it approaches a fractal scaling law. This structure is the hallmark of dense clusters of slippery spheres that have attractively jammed into a fractal gel at intermediate ϕ . The cluster peaks at high q are stronger than those seen with x-ray scattering from aggregates of gold colloids which form shear-rigid bonds [29].

Our observations of nanoemulsion aggregation support the following scenario called slippery DLCA. In both slippery and classic DLCA, the short-range attraction is much greater than $k_B T$, so bonds between pairs of spheres are never broken once they have formed. In classic DLCA, the rearrangement of bonds within a cluster is not allowed, since all bonds are shear rigid. However, for slippery DLCA, the relative positions of the centers of the spheres within aggregates can change subject to the constraint that the center-to-center distances between pairs of bonded spheres remain fixed. In the early stages of slippery DLCA, these internal degrees of freedom disappear as more spheres are added and more bonds form, yielding dense rigid building blocks that will bond rigidly with other small clusters [Figs. 5(a)–5(d)]. This can be seen by considering small clusters of N particles, holding the centers of $N - 1$ particles fixed, and considering the mo-

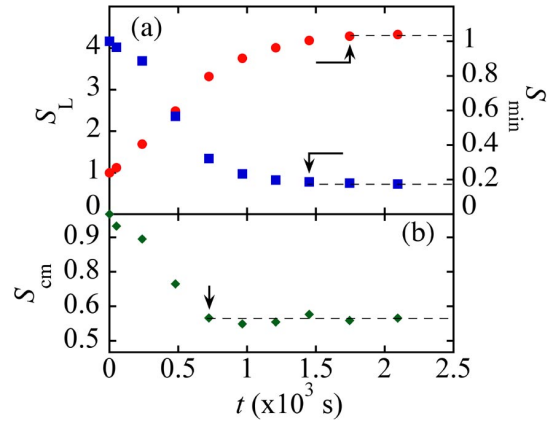


FIG. 3 (color online). Time-dependent behavior of the key features in the structure factor, $S(q)$: (a) magnitude of S at the lowest q measured, $S_L(t)$ (●); minimum value of S , $S_{\text{min}}(t)$ (■); and (b) value of S at the first cluster minimum at higher q , $S_{\text{cm}}(t)$. Arrows mark the onset of saturation, and dashed lines indicate long-time values.

tion of the remaining sphere. For a dimer ($N = 2$), the center of the free sphere can trace out a spherical shell. For a trimer ($N = 3$), any linear configuration will collapse into a dense equilateral trimer under thermal agitation. The center of the third sphere can trace out a circle centered about the axis of the two fixed spheres. For a tetramer ($N = 4$), any noncompact configuration will collapse into a dense equilateral tetrahedron. When three spheres are fixed, the center of the fourth one is constrained to a point, and no internal rearrangement is possible. Thus, even when bonds are slippery, a fundamental rigid building block, the dense tetramer, can be formed at very early stages in the aggregation. The dense tetramer presents four dimpled triangular faces to any other cluster that might encounter it. When one tetramer diffuses into another, typically only one slippery bond forms at first, and thermal agitation will rotate and translate the joined clusters until they lock together rigidly, forming a total of six new bonds. Three

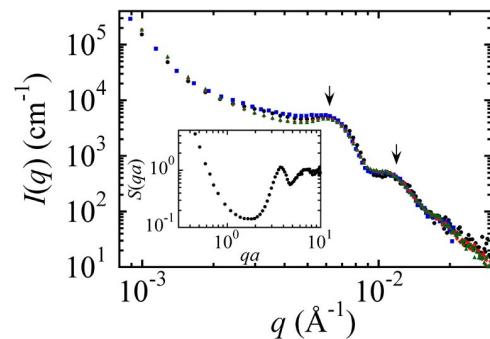


FIG. 4 (color online). Long-time scattering intensity, $I(q, t \rightarrow \infty)$, for droplet volume fractions, $\phi = 0.05$ (●), 0.12 (■), 0.20 (◆), 0.27 (▲). The data at lower ϕ have been rescaled onto a master curve with absolute intensity corresponding to $\phi = 0.27$. Cluster peaks are evident at high q over a wide range of ϕ (arrows). Inset: the universal structure factor as a function of dimensionless wave number, $S(qa)$.

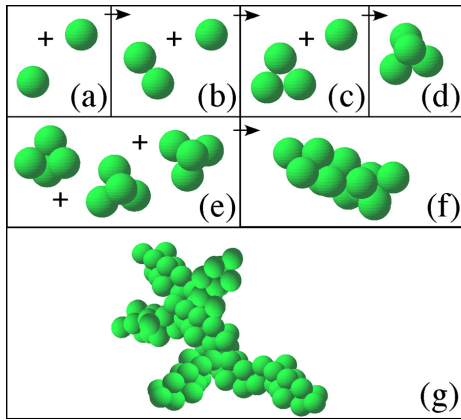


FIG. 5 (color online). Slippery aggregation of spheres and clusters after the sudden onset of a short-range, central-force, non-shear-rigid attraction: (a) monomers diffuse and aggregate to form a dimer (b). A dimer and a monomer aggregate to form a trimer (c). A trimer and a monomer (or two dimers) aggregate to form a tetramer (d). Tetramers (e) are the minimal clusters of larger scale aggregates that are stable against thermal fluctuations (i.e., shear-rigid) and form extended, nonspherical structures (f), even fractal aggregates. At sufficiently large concentrations, the aggregates can form extended networks and even attractively jammed gels (g).

basic configurations are possible: right-handed and left-handed chiral (e.g., when a monomer of one tetramer first locks into a dimple of another tetramer), and, rarely, non-chiral (e.g., when two tetramers aggregate face to face). Thus, small dense clusters combine to create rigid oblong clusters [Figs. 5(e) and 5(f)].

As slippery DLCA continues, oblong clusters bond to create large rigid fractal clusters that can join to fill space and gel [Fig. 5(g)]. These large clusters can interact in a more complex manner and their corrugated surfaces may interlock without perfect tetrahedral bond formation, but the dominant particle-scale motif is the tetrahedron. It is remarkable that such large-scale tenuous and rigid structures can be made through an aggregation process that involves only strong slippery bonds. These clusters and gels do not collapse into dense flocs or crystals under thermal agitation, since this would require breaking many bonds with energies far in excess of $k_B T$, but a stronger external agitation (e.g., shear) could cause a collapse.

The structures of attractive nanoemulsions are qualitatively consistent with slippery DLCA, in which small dense clusters of droplets rigidly combine to form fractal aggregates and gels. The final static structure of a gel of slippery droplets can be decomposed into a shear-rigid framework that is primarily comprised of tetrahedra that may share common triangular faces. By contrast, dense clusters would not be found in the more tenuous particulate aggregates formed through classic DLCA. Moreover, in slippery DLCA, bonds are not permitted to break once they have formed; this is fundamentally different than models such as RLCA. The peaks in $S(q)$ at high q , correspond to dense droplet clusters and are in good qualitative agree-

ment with predictions given in recent simulations and theory of attractive spheres. If these predictions can be modified to include a small size polydispersity, it will be possible to quantitatively compare our measurements with them in order to determine the average coordination number. Slippery DLCA could also be important for solid particulate systems in which attractions, such as depletion, cause particles to become strongly bound in a deep secondary minimum, thereby creating slippery bonds that preserve a thin film of liquid between solid particles.

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