Kinetically Induced Ordering in Gelation of Emulsions

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(Received 27 April 1992)

We report the formation of a solid gel network from purely liquid emulsion droplets. The gel remains rigid at droplet volume fractions as low as 10^{-3}. The gelation process is identified as diffusion-limited cluster aggregation. We find a surprising order in the gel structure. This ordering is induced by the aggregation kinetics, which result in an unexpected spatial correlation between the growing clusters, ensuring that the network is formed from clusters of nearly equal size and spacing.

PACS numbers: 82.70.Kj, 64.60.Ak, 82.70.Gg

Oil and water do not mix. However, upon addition of surfactant, mechanical energy can lead to the formation of an emulsion, a dispersion of one fluid in the second [1]. While an emulsion is thermodynamically unstable, the characteristic time for coarsening can be sufficiently long to allow the properties of these dispersions of soft spheres to be studied. These properties lead to many important technological uses for emulsions, ranging from foods to pharmacology and from coatings to cosmetics [2]. Moreover, emulsions with monodisperse droplets can be produced through fractionation, providing a marvelous model system for studying the properties of liquid dispersions [3]. The stability of these monodisperse emulsions is ensured by the short-range repulsive interaction between the droplets provided by the adsorbed surfactant layer at the interface. However, it is also possible to generate an additional attractive interaction between the droplets, while still avoiding destabilization through droplet coalescence. In less controlled, polydisperse emulsions, this leads to the formation of colloidal flocs, or creams, with indeterminate structure. By contrast, in monodisperse emulsions, a weak attraction leads to a thermodynamic phase transition between fluid and solid phases of the droplets [4]. A stronger attraction results in the deformation of the droplets when they adhere to each other [5], and the intrinsic liquid nature of the droplets might be expected to result in very different behavior from that observed with solid colloidal particles.

In this Letter, we demonstrate that, despite the intrinsic liquid nature of the droplets, these monodisperse emulsions can produce a connected, solid network, even at extremely low volume fractions. The rigidity of the tenuous network of liquid droplets must imply that the droplets do not slip, and permanent bonds can be formed between them. The emulsion gels exhibit an unexpected ordering in their structure, which possesses a very strongly delineated characteristic length scale, which is in sharp contrast with the structure of all gel networks investigated to date. This ordering in the structure results from the kinetics of the formation, which we show to be diffusion-limited cluster aggregation (DLCA) [6].

Our emulsion is comprised of droplets of silicone oil in water, stabilized by sodium dodecyl sulfate (SDS) [7]. Using the fractionated crystallization method [3], based on the fluid-solid equilibrium induced by SDS micellar depletion forces [8], we select a monodisperse dispersion of droplets with a radius of $a \approx 0.27$ μm. The water contains 10^{-2} M SDS, approximately the critical micelle concentration, and 0.5 M sodium chloride. For this concentration of salt, there is a sharp phase transition of this emulsion at 25 °C induced by the very strong temperature dependence of the droplet interaction. Above 25 °C, the droplets behave as a homogeneous, fluidlike dispersion, while below, a strong adhesion develops between the droplets, and a strongly nonequilibrium gelation transition is observed. Moreover, upon raising the temperature, the adhesion is removed and the phase transition reversed.

An example of the connected network formed by the emulsion droplets with $\phi = 5\times 10^{-3}$ is shown in Fig. 1(a). The network was formed using a cooling rate of 0.2 °C/sec from 40 to 15 °C. However, the structure is insensitive to the rate of quench because the onset of strong adhesion occurs in a very narrow temperature range of ~ 0.1 °C. While the network is clearly very tenuous, and is formed from purely liquid droplets, it is nevertheless a completely connected, rigid network. However, while the short-range structure of the network is highly disordered, there is a pronounced degree of order at larger length scales. This is apparent by the characteristic length scale in the network which can be seen in the lower magnification picture shown in Fig. 1(b). The clusters which form the network are clearly of nearly equal size and spacing. This picture represents a two-dimensional cut through the three-dimensional gel, due to the short depth of field of the microscope, which is comparable to the diameter of a single droplet. As a result, while the clusters do not appear to be connected, the full connectivity of the network is not visible in the picture, and the clusters are both immobile and rigid.

More dramatic evidence of this surprising order is obtained by measuring the scattered light intensity as a function of the scattering wave vector $I(q)$ at small angles. Initially, when $T > 25$ °C, the angular dependence of the scattered intensity is roughly uniform, and the speckle spots flicker, reflecting the motion of the droplets.

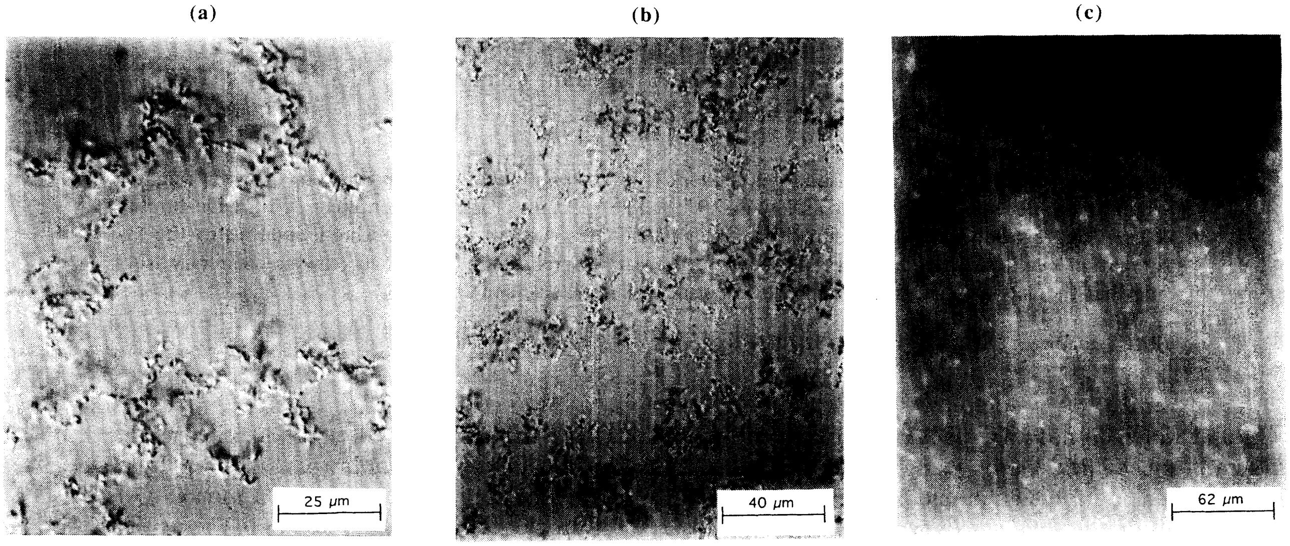

FIG. 1. Photographs of a gel formed from an emulsion with $\phi=5\times10^{-3}$, showing (a) the random, tenuous structure of the network at short length scales, and (b) the characteristic spacing of the roughly equally sized clusters that make up the network at larger length scales. The growing clusters before gelation are shown in (c).

As the temperature of the sample is decreased below 25 °C and the clusters begin to form, the scattered intensity increases dramatically. Moreover, a ring of increased intensity develops almost immediately. As the clusters continue to grow, the intensity of the ring increases, the peak shifts towards smaller angles, and the width of the ring shrinks. This behavior is evident by the scattering data obtained at different times during the growth process of the same sample, plotted in Fig. 2. Ultimately, the flickering of the speckle spots ceases completely, indicating that the droplets are no longer moving and that they have formed a rigid network. The scattering from this network is shown by the solid line in Fig. 2. It exhibits a peak at $q_m=0.3$ μm^{-1}, corresponding to the characteristic length of ~20 μm observed for the network in Fig. 1(b).

While the pronounced peak in the scattered intensity is clear evidence of some form of order at larger length scales, at shorter length scales the structure must be substantially more disordered. In fact, for the droplets to span space at such low volume fractions, the structure on shorter length scales is most likely fractal. Examination of the two-dimensional cut through the three-dimensional network shown in Fig. 1(a) qualitatively confirms this. The structure in this plane is very random and tenuous, consisting of disordered, but essentially one-dimensional, arms of droplets, which are disconnected. This immediately suggests that the fractal dimension of the image plane is less than 1. Thus, the fractal dimension of the network itself, d_f, which is obtained by adding 1 to the fractal dimension of the image plane, is less than 2. To quantify this, we measure the fractal dimension of the network on short length scales from a series of high magnification pictures, such as the one shown in Fig. 1(a). Using a box-counting technique [9], we measure $d_f\approx1.9\pm0.2$, where the error represents an estimate of the uncertainty in identifying the droplets in the image. These observations are supported by our scattering measurements, as shown by the inset in Fig. 2, which is a logarithmic plot of the data at high q. Although we do not measure the intensity at sufficiently large q, a power-law

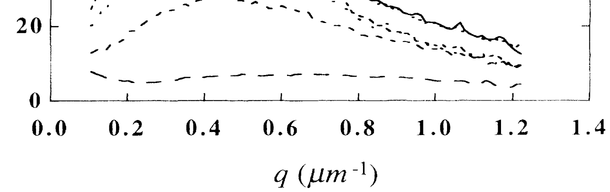

FIG. 2. Scattered light intensity from an emulsion with $\phi=5\times10^{-3}$ as the gel is formed. Starting from the lowest intensity data, the times for each set are 5, 90, 150, 240, 360, and 600 sec after the phase transition begins. The solid line is the data from the final gelled state. Inset: The high-q data from the gel plotted logarithmically, illustrating the fractal structure at short length scales.

decay is nevertheless observed for $q > q_m$, and, from the exponent, a fractal dimension of $d_f \approx 1.6 \pm 0.2$ is obtained, in reasonable accord with the value determined from the image analysis. Thus, we conclude that the structure of the network at short length scales is fractal with $d_f \sim 1.8$.

The observation of this fractal structure at shorter length scales suggests that the emulsion network results from diffusion-limited cluster aggregation of the droplets [6,10]. This aggregation process occurs when there is no repulsion between particles in a dispersion, allowing them to stick to one another immediately upon collision due to their diffusive motion, which limits the rate of their aggregation. At low volume fractions, DLCA results in the formation of clusters of nearly equal size, and with $d_f \approx 1.85$. Because they are fractal, the density of the clusters decreases as their size increases, and hence the volume fraction of clusters ϕ_c must increase. As ϕ_c approaches 1, the clusters are separated by their average diameter, and gelation must occur. The cluster volume fraction is $\phi_c \approx (R/a)^3\phi/N_R$, where the number of droplets in the average cluster of radius R is given by its fractal structure, $N_R \sim (R/a)^{d_f}$. Setting $q_m \sim 1/R$, and letting $\phi_c = 1$, we obtain $q_m \sim a\phi^{1/(3-d_f)}$. Since we measure $d_f \sim 1.8$, we expect that $q_m \sim \phi^{0.83}$. To test this, we use light scattering to measure q_m as ϕ is varied using different cell thicknesses to avoid multiple scattering and to ensure that $2\pi/q_m$ is less than the cell thickness. We show the results in a logarithmic plot in Fig. 3. For $\phi \leq 0.01$, we do indeed observe power-law scaling with an exponent of 0.88 ± 0.05, obtained from the fit to the data shown by the solid line, consistent with DLCA. At higher ϕ, we observe a clear deviation from the predicted scaling behavior. Since DLCA models the kinetics only at low ϕ, it cannot be expected to describe the initial cluster formation at high ϕ.

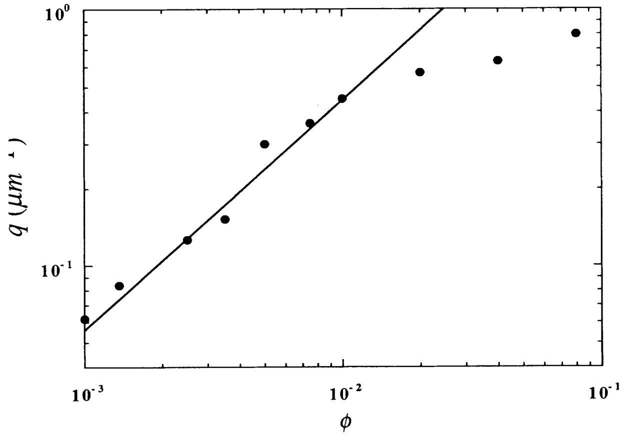

FIG. 3. The dependence of q_m on ϕ, showing the scaling behavior for $\phi \leq 0.01$. The solid line shows a fit to the data at low ϕ, and has a slope of 0.85, as expected for a fractal structure at short length scales.

For low ϕ, the characteristic length scales develop long before the final gelled state is reached, as evidenced by the ring exhibited by the light scattering pattern obtained at the very early stages of the aggregation process. For example, after the clusters have grown for about 1 min, the scattered intensity exhibits a peak at $q \approx 0.45\ \mu m^{-1}$, as shown by the second lowest curve in Fig. 2. At this stage, the clusters have only grown to a size of a few droplets, as shown by the microscope image of the emulsion obtained at the same time, shown in Fig. 1(c). The peak in the scattered intensity corresponds to a length scale of roughly 14 μm, which is significantly larger than the average size of the clusters, measured directly from the picture to be roughly 2 μm. Instead, the characteristic length scale of the light scattering must reflect the average cluster spacing, and this is consistent with the spacing observed in Fig. 1(c).

The surprising spatial correlation between the positions of the growing clusters develops almost immediately when the aggregation commences. Thus the aggregation mechanism itself must spontaneously induce this characteristic length scale, which persists throughout the aggregation process until gelation occurs. This suggests that the kinetics of the aggregation process induces an effective repulsion between the clusters, which is responsible for the ordering. Support for this picture is obtained by observing the gelation process under the microscope. As the temperature is decreased below the transition, the droplets stick to one another as soon as they collide. The diffusion of the larger clusters is markedly slower than that of the individual droplets. As a result, the larger clusters appear to engulf all the isolated droplets and smaller clusters surrounding them, and a very distinct depletion zone develops around each cluster. Moreover, each cluster is nearly the same size. This depletion zone appears to act as an effective repulsion, causing the spatial correlation to develop between the clusters. The spatial correlation persists, and the gel that is ultimately formed is comprised of nearly equally sized and spaced clusters.

Similar correlations between clusters growing by a diffusion-limited mechanism are observed in other systems. In a recent study [11] of DLCA of polystyrene colloids with $\phi \approx 3 \times 10^{-4}$, a peak in the scattering intensity due to spatial correlations between the clusters was also observed, and was attributed to a process analogous to spinodal decomposition. In fact, spinodal decomposition has been hypothesized as a general mechanism which describes a wide variety of aggregation processes in colloids with attractive interactions [12]. A peak in the scattered intensity was also reported [13] for a colloidal suspension of hard spheres undergoing a fluid-crystal transition at $\phi \approx 0.52$. These results were also ascribed to the development of a depletion zone around the growing crystallites. Finally, a peak in the scattering intensity was also observed [14] for the growth of clusters of glass formed by the addition of nucleation centers in the molten glass.

This was ascribed to a depletion zone of material, and was modeled as an effective repulsive interaction between the growing clusters.

The pronounced peak in the scattering intensity, and the characteristic length scale in the structure which it reflects, is unique to gelation by a DLCA process. The structure of other gels, formed either from colloidal particles [15] or from cross-linked polymers [16], is also characterized by a single length scale, ξ, which reflects the average distance between loops or cross-links. However, the scattering from these gels exhibits a structure factor that is well described by an Ornstein-Zernicke form: It decreases as a power law in q above $q\xi=1$, but is constant for smaller q. All other colloidal gelation processes studied to date have entailed reaction-limited cluster aggregation [17], which results in a very broad, power-law cluster mass distribution. A similar broad, power-law cluster mass distribution is expected for other gelation processes that can be modeled as a percolation process [18]. These broad cluster distributions presumably preclude the formation of a network with a dominant length scale.

We conclude by noting that spatial correlations between the DLCA clusters have not been recognized in previous theoretical treatment of DLCA, which considered much lower ϕ, suggesting a reappraisal of the theory at higher ϕ is merited. Moreover, further experimental work, particularly the characterization of the gelation dynamics, would be of great interest, and is currently in progress. Finally, we emphasize what is perhaps the most remarkable feature of these gels: They are formed from an emulsion, and a rigid, solid network is produced from dispersions of liquid droplets with volume fractions of less than 1%. However, the origin of the adhesion responsible for these random solid structures, and the persistence of the droplet integrity, without coalescence, remains an open question.

We thank Bernard Cabanne for helpful suggestions.

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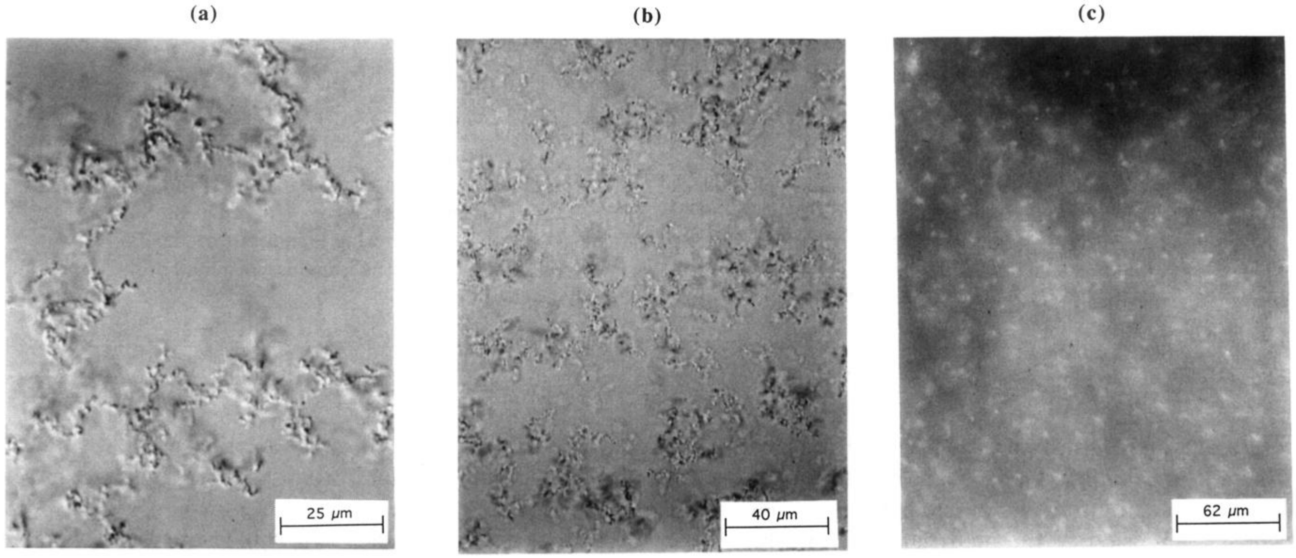

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