Shape Fluctuations of Interacting Fluid Droplets

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We study the thermally induced shape fluctuations of monodisperse emulsion droplets. The very small amplitude of these fluctuations is clearly resolved by diffusing wave spectroscopy and a theory is derived to describe the measured data. We measure the dependence of the fluctuations on droplet volume fraction ϕ, thereby directly probing the interplay between droplet interactions and droplet flexibility. The characteristic relaxation frequency of the fluctuations is found to decrease with increasing ϕ, while their amplitude increases.

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Interfaces between two fluids are subject to thermally induced fluctuations, or capillary waves. Their amplitude is controlled by the surface tension between the fluids Γ and is typically very small, of the order of 10 Å. Nevertheless, for flat interfaces, capillary waves have been observed using both light [1] and x-ray scattering [2]. The interfaces of fluid droplets will also be subject to thermal fluctuations, and these are of considerable importance. The properties of dispersions of liquid droplets, or emulsions, are dramatically different from dispersions of solid spheres as the volume fractions of the dispersed phase ϕ increases precisely because droplets are deformable, and the thermally induced fluctuations are the precursors to this deformation. Thus, the extra degrees of freedom introduced by these thermal fluctuations may have important consequences for the properties of emulsions as ϕ is increased. Unfortunately, however, the thermal fluctuations even of individual liquid droplets are extremely difficult to observe and have not been studied, and the consequences of increased volume fraction on these fluctuations is completely unknown.

Thermal fluctuations of other fluid dispersions have been studied; for example, thermal fluctuation of microemulsions [3,4] have been observed with neutron spin echo measurements, while those of liquid membranes have been observed with x-ray scattering [5], and those of vesicles have been directly observed with imaging [6]. In all these cases, the surface tension is essentially zero, so the fluctuations are controlled by the bending energy and are a significant fraction of the size of the structures, making them easier to observe. By contrast, for a fluid droplet with a larger value of Γ, the amplitude of the fluctuations is significantly reduced. The thermally induced increase in the surface area of a fluid droplet is $\Delta A \approx k_B T/\Gamma$, where k_B is Boltzmann's constant, and T is the temperature. For a typical surface tension of 10 dyn/cm, the increased area is only about 40 Å^2; for a 1 μm radius droplet, the corresponding deviation from sphericity is less than 0.1%. The relaxation time τ of these fluctuations is also short. If the viscosity of the droplet is much greater than that of the continuous phase, the relaxation time is $\tau \approx R\eta/\Gamma$; for $\eta = 0.1$ P and $R \approx 1$ μm, $\tau \approx 10^{-6}$ s. The combination of the very short time scale and the very small amplitude of the thermal fluctuations of emulsion droplets has, to date, precluded their observation.

In this Letter, we report the first observation of the thermal fluctuations of fluid emulsion droplets and present the significant finding that shape fluctuations are strongly affected by particle interactions. The relaxation frequency exhibits a linear decrease with increasing ϕ, while the amplitude of the fluctuations exhibits an unexpected increase with ϕ. Despite the very small amplitude of the fluctuations, we are able to measure them by exploiting two recent innovations. In order to have well-characterized dynamics, we use highly monodisperse emulsion droplets [7,8]. To measure the minute length scales, we use diffusing-wave spectroscopy (DWS), an extension of traditional dynamic light scattering to the multiple scattering limit which allows fluctuations on very small length scales to be probed [9]. We accomplish these measurements by generalizing DWS to account for fluctuations of the scattering form factor, in addition to the more familiar phase fluctuations.

Our samples are emulsions of silicone oil in water, stabilized with sodium dodecylsulphate. We use the technique of fractionated crystallization to yield highly monodisperse droplets with a mean radius of $R = 0.7$ μm, with an rms deviation of less than 5% [7]. The surface tension of the interfaces is 9.8 dyn/cm. We perform our DWS measurements in the transmission geometry using an expanded beam from an Ar^+ laser, which gives $k_0 = 16.3$ μm^{-1} for the incident wave vector in water. The detected light is collected from a point on the exit side of the 5 mm-thick sample cell. The transport mean free path l^* is determined independently by a static transmission measurement [9]. This information allows us to determine the dynamics of the individual emulsion droplets [10].

We might expect the dynamics of emulsion droplets to be the same as those of hard spheres. This is indeed the case for an emulsion made of a high viscosity oil, $\eta = 1000$ cP. This is illustrated in Fig. 1, where the open

circles represent $\langle \Delta r^2(t) \rangle$, the mean square displacement of an individual droplet. The data follow the curve predicted for hard spheres, shown by the solid line. By contrast, an emulsion made from a lower viscosity oil, $\eta = 12$ cP, exhibits distinct additional dynamics, as shown by the solid circles in Fig. 1. At early times, the data fall significantly higher than those expected for solid spheres; at later times, the data merge. Similar behavior is observed for all ϕ; Fig. 1 shows the data for $\phi = 0.35$. These additional dynamics result from the shape fluctuations; for the higher viscosity oil, the relaxation time τ is so long that any shape fluctuations are masked by the large displacements that occur during τ.

To describe these new dynamics quantitatively, we must generalize the formalism for DWS to include fluctuations in the scattering *amplitude*, in addition to the phase fluctuations which result from translational motion. The analysis of the correlation function measured by DWS requires the calculation of the contribution of diffusive light paths comprised of a large number of scattering events; these are all represented by an angle-averaged scattering event [9]. Thus, to include the amplitude fluctuations, we write the normalized field correlation function for this q-averaged, single-scattering event as

$$g_1(t) = \frac{\langle b^*(q,t)b(q,0)\rangle_q}{\langle b^*(q,0)b(q,0)\rangle_q} \langle \exp\{-i\mathbf{q}\cdot\Delta\mathbf{r}(t)\}\rangle_q . \quad (1)$$

Here, the time dependent scattering amplitude is $b(q,t)$, and the brackets with the subscript q denote an ensemble and q average. Throughout we assume that the amplitude fluctuations are independent of the translational motion of the droplets; furthermore here we neglect spatial correlations. The amplitude fluctuations contribute an additional correlation function which is assumed to consist of a sum of a constant portion and a much smaller fluctuating portion. Performing the q average, we obtain

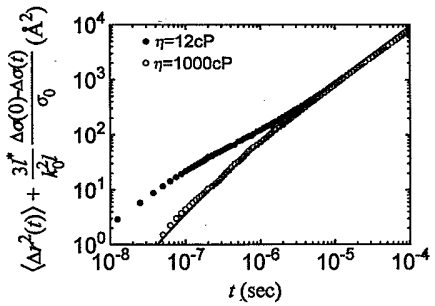

FIG. 1. Inverted correlation functions of monodisperse emulsions. The data are the sum of the mean square displacement and a term related to the correlation function of the fluctuating scattering amplitude. The solid points are for an emulsion with an oil viscosity of 12 cP, while the open points are for an emulsion with an oil viscosity of 1000 cP. The additional dynamics due to the shape fluctuations of the lower viscosity droplets are apparent. The solid line is the theoretical prediction for rigid spheres; it agrees well with the data for the viscous droplets.

$$g_1(t) = \left[\frac{\sigma_0 + \Delta\sigma(t)}{\sigma_0 + \Delta\sigma(0)}\right] \exp\left\{-\frac{k_0^2 l}{3l^*}\langle \Delta r^2(t)\rangle\right\}, \quad (2)$$

where σ_0 is the time independent total cross section, and $\Delta\sigma(t)$ is the correlation function of the fluctuating portion of $b(q,t)$, ensemble and q averaged. In addition, we have used the relationship, $\langle q^2\rangle_q = 2k_0^2 l/l^*$, where l is the scattering mean free path [11].

To calculate the correlation function for a diffusive path of length s, consisting of $n = s/l$ scattering events, we take the product of Eq. (2) n times [9]. Since $\Delta\sigma(t) \ll \sigma_0$, the first term can be approximated as an exponential, $\exp\{[\Delta\sigma(t) - \Delta\sigma(0)]/\sigma_0\}$; this ensures that the contribution of a single diffusive path is still linear in s, and allows the standard DWS analysis to be retained. Thus, the total DWS correlation function is a sum over the contributions of all paths, weighted by the probability that a photon follows the path, $P(s)$:

$$g_1(t) = \int P(s) \exp\left[-\frac{sk_0^2}{3l^*} \times\left(\langle \Delta r^2(t)\rangle + \frac{3l^*}{lk_0^2}\frac{\Delta\sigma(0) - \Delta\sigma(t)}{\sigma_0}\right)\right] ds . \quad (3)$$

Although we have neglected the effects of spatial correlations as ϕ increases, for the case of the relatively large particles used here, Eq. (3) can be generalized to include them. A q-averaged structure factor must be included to retain the form with $\langle \Delta r^2(t)\rangle$ [12]; however, because the shape fluctuations are not spatially correlated, the factor l^*/l within the square brackets must be evaluated in the limit of zero ϕ. Since $P(s)$ is known [9], this equation can be solved in exactly the same manner as is done for DWS from solid particles. The effects of the amplitude fluctuations are contained in the second term in the square brackets. It is clear from Eq. (3) that DWS probes the relative fluctuations of the cross section. Their contribution increases from zero at $t = 0$, like $\langle \Delta r^2(t)\rangle$, but saturates at long times. It is also clear why very small fluctuations can be detected; the signal arises from the sum of n independent amplitude fluctuations. These minute fluctuations would not be detectable without the advantage of the multiple scattering.

We note that this derivation is independent of the nature of the amplitude fluctuations, not only shape fluctuations, but other phenomena, such as rotational motion of aspherical particles, can also result in a similar contribution. Moreover, the DWS data can be inverted and the translational and amplitude contributions separated. The scaled form of the theory [10], which appears in Fig. 1 as the solid curve, allows us to take into account the effects of hydrodynamic and particle interactions on the translational dynamics. We therefore can obtain separately the fluctuating cross section, as influenced by interactions. We plot $R^2\Delta\sigma(t)/\sigma_0$ for $\phi = 0.35$ in Fig. 2; we multiply the normalized fluctuating cross section by R^2 to give the correlation function of the fluctuations of the droplet

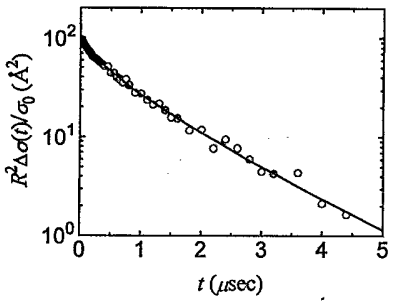

FIG. 2. Correlation function of the fluctuations of the droplet radius for an emulsion with $\phi = 0.35$. The solid line is the theoretical prediction.

radius. We note that the data exhibit a distinctly nonexponential decay.

Similar behavior is found for all other droplet volume fractions. Surprisingly, the shape of the correlation function is independent of ϕ; all the data can be scaled onto a single master curve. This behavior enables us to quantify the effects of particle interactions on shape fluctuations in terms of the required ϕ-dependent scalings that collapse the data. We find that the characteristic frequency of the decay decreases with increasing volume fraction; as shown by the open triangles in Fig. 3, the decrease is approximately linear in ϕ. By contrast, we find that the amplitude of the shape fluctuations increases significantly with ϕ; this is shown by the solid circles in Fig. 3.

To describe the correlation function of the fluctuating shape quantitatively, we expand the instantaneous radius of the drop in spherical harmonics [13]. Each independent deformation mode creates an excess area given by $k_BT/2\Gamma$. Together with the conservation of volume, this condition determines the amplitude of the expansion coefficients. Each mode relaxes independently with an exponential decay rate ω_l that must be calculated in the overdamped, or low Reynolds number, limit [14,15]. We obtain

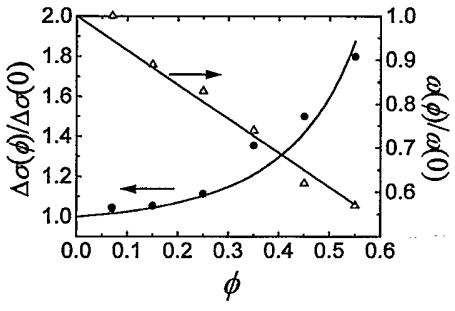

FIG. 3. The ϕ dependence of the characteristic frequency (open triangles) and the fluctuating amplitude (solid circles). Both quantities have been reduced by their extrapolations to zero volume fraction. The solid line is a fit to a linear decay, with a coefficient of 0.78; the dashed line is a fit to a simple model which attempts to include the effects of interactions between the droplets.

$$\Delta\sigma(t) = \frac{k_BT}{4\pi\Gamma R^2}\sum_{l=2}\frac{2l+1}{l(l+1)-2}g_l\exp(-\omega_l t), \quad (4)$$

with

$$\omega_l = \frac{l(l+2)(2l+1)\,\Gamma}{2(2l^2+4l+3)\,\eta R}. \quad (5)$$

In general, ω_l depends on the viscosities of both fluids [16]; here we have assumed that the viscosity of the oil is much greater than that of the water. Note that asymptotically $\omega_l \sim l$, reflecting the fact that the dynamics are driven by surface tension; by contrast, $\omega_l \sim l^3$, when the dynamics are driven by the interfacial rigidity [13]. The scattering cross section for each mode is calculated within the Rayleigh-Gans (RG) approximation [3],

$$g_l = \pi\int_0^\pi \sin\theta(1+\cos^2\theta)[3j_l(x)]^2\,d\theta, \quad (6)$$

where $x = 2k_0R\sin(\theta/2)$, and where we have omitted an optical constant which is canceled in the normalization by σ_0. The coefficients g_l depend only on k_0R and become negligible when $l \gg k_0R$, since the length scale of the features described by such modes is much smaller than the wavelength of the radiation. This behavior sets a natural cutoff mode $l_{\max}$ for the expansion; we find that the series converges for $l_{\max} \approx 20$. Because of their large mismatch in index of refraction, the RG approximation is not strictly valid for these droplets, and Mie theory, suitably generalized to treat nonspherical scatterers, should be used instead. However, the average cross section σ_0 calculated within the RG approximation differs by less than 0.5% from that calculated from Mie theory. Moreover, the value for g_2 estimated by differentiating the scattering-intensity pattern calculated with Mie theory is within 10% of the RG value. Thus, we conclude that the RG approximation is sufficiently accurate.

These expressions apply only to an isolated droplet, However, since we find the shape of our data to be independent of ϕ, we can describe interactions by inserting two ϕ-dependent scaling factors $\Delta\sigma(\phi)/\Delta\sigma(0)$ and $\omega(\phi)/\omega(0)$ in the right sides of Eqs. (4) and (5). The solid line through the data in Fig. 2 illustrates the fit so obtained for $\phi = 0.35$. The agreement is excellent. The nonexponential decay clearly reflects the contribution of the different modes. The fit is noticeably poorer if fewer modes are included; this is true at all ϕ. Quantitative agreement between the theory and the experiment should be obtained when the ϕ-dependent characteristic frequency $\omega(\phi)$ and amplitude $\Delta\sigma(\phi)$ are extrapolated to zero volume fraction. Our extrapolated value of $\omega(0)$ is identical to the predicted value of $\Gamma/\eta R = 1.2$ MHz. Similarly, the extrapolated value of the amplitude ratio $R^2\Delta\sigma(0)/\sigma_0$ is 70 Å^2, while the predicted value is $(k_BT/4\pi\Gamma\sigma_0)\Sigma(2l+1)g_l/[l(l+1)-2] = 52$ Å^2. The remaining discrepancy may reflect the error introduced by the RG approximation.

The ϕ dependence of both the frequency and the amplitude must reflect the consequences of the interactions between the droplets, and these are not, as yet, well understood theoretically. The normalized characteristic frequency is well represented by a linear behavior, $\omega(\phi)/\omega(0) = 1 - 0.78\phi$. The most likely origin of this behavior is the ϕ dependence of the effective viscosity of the emulsion. A similar linear form was recently predicted (for the $l = 2$ modes only), but the predicted coefficient is 1.4 [17]. However, this theory was restricted to the case of equal viscosities of the oil and water, which may account for the discrepancy.

The increase of the amplitude of the shape fluctuations with ϕ is more surprising. It may reflect the effects of collisions between the droplets, which become increasingly likely as ϕ increases; because the droplets are flexible, these collisions may result in additional deformations. If these are relatively localized, a large number of spherical harmonics will be required to describe the deformation, and a nonexponential relaxation will result. We therefore model the consequences of collisions by introducing a contribution to the amplitude proportional to the fraction of the droplets that, at any instant, are colliding with a neighbor. This fraction we estimate as $\phi g(2, \phi)$, where $g(2, \phi)$ is the pair correlation function at contact. The dashed line through the data in Fig. 3 is a fit of $\Delta\sigma(\phi)/\Delta\sigma(0)$ to the functional form $1 + C\phi g(2, \phi)$ with $g(2, \phi) = (1 - \phi/2)/(1 - \phi)^3$ as holds for hard spheres [18]. Good agreement is found with $C = 0.2$, suggesting that droplets in collision deform an extra amount that is about 0.2 times the deformation exhibited by an isolated droplet. We emphasize, however, that while this model gives reasonable agreement with the data, it is nevertheless only a crude approximation. More generally, it should be possible to regard these increased shape fluctuations as the consequence of the osmotic pressure of flexible spheres. The expression $1 + C\phi g(2, \phi)$, with $C = 4$ and $g(2, \phi)$ as given above, is in fact the ratio of the full osmotic pressure of a hard-sphere suspension to the kinetic part nk_BT, where n is the number density [18]. This observation suggests that $\Delta\sigma(\phi)/\Delta\sigma(0)$ may be related to the reduced osmotic pressure of the suspension of flexible droplets. Further theoretical work is clearly required to determine the underlying physics of this surprising behavior.

The flexibility of fluid droplets is one of their most distinguishing features; it controls many of their unique properties. The shape fluctuations studied here directly probe this flexibility. Moreover, as the volume fraction increases, these shape fluctuations can lead to significant modifications of the properties of the interacting droplets. In particular, they may make a significant contribution to the onset of an elastic shear modulus, which occurs as ϕ is increased sufficiently to permanently deform the droplets. The increasing effects of interactions on the shape fluctuations may provide new insight into this important problem. Finally, the techniques reported here may provide a new method for probing the stability of emulsions: shape fluctuations may be a critical precursor of coalescence, one of the key mechanisms by which emulsions are destroyed.

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