PHYSICAL REVIEW E VOLUME 59, NUMBER 3 MARCH 1999

Comment on "Thermal fluctuations of the shapes of droplets in dense and compressed emulsions"

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(Received 9 July 1998)

The quasielastic differential cross section of light scattered from noninteracting emulsion droplets fluctuating in the shape is calculated. The result is compared with the shape fluctuation correlation function measured in the diffusing-wave spectroscopy experiments by Gang, Krall, and Weitz [Phys. Rev. E **52**, 6289 (1995)]. Assuming incompressible bulk fluids and the interfacial surfactant layer, we demonstrate that the experiments can be described more precisely than in the original paper. The time behavior of the calculated shape correlation function resembles better the observed one and its amplitude (as distinct from the discussed paper) almost exactly corresponds to the experimental value extrapolated to the zero volume fraction of the droplets in emulsion. [S1063-651X(99)14602-6]

PACS number(s): 68.10.−m, 82.70.Kj, 05.40.−a

In the work by Gang, Krall, and Weitz [1] the theory of diffusing-wave spectroscopy (DWS) was generalized by incorporating the effects of amplitude fluctuations in the scattering intensity. The DWS method was applied to the experimental study of thermally induced shape fluctuations of emulsion droplets, not detectable by conventional dynamic light scattering. From the generalization of the theory for DWS the contribution of the shape fluctuations was isolated and its dependence on ϕ (the volume fraction of the droplets in emulsion) was investigated. Although a good agreement was demonstrated between the theory for an isolated droplet and experimental values at low ϕ, the time dependence of the predicted shape fluctuation correlation function $F(t;0)$ differs notably from the experimental curve $F(t;\phi)$ obtained by extrapolation $\phi\to 0$, especially for larger t. The predicted value for the amplitude $F(0;0)$ was 52 Å^2 in contrast to the extrapolated experimental value 70 Å^2.

When the thickness d of the surfactant film on the droplet surface is negligible as in emulsions, $d/R\to 0$, where R is the equilibrium radius of the droplet, the quasielastic differential light scattering cross section per unit angle of the outgoing beam and per unit frequency $d\omega$ is determined in Born approximation by the correlator $\langle \varepsilon(\mathbf{Q},t)\varepsilon^*(\mathbf{Q},0)\rangle$, where $\mathbf{Q}$ is the wave-vector transfer and $\varepsilon(\mathbf{Q},t)$ is the Fourier transform of the dielectric constant, which is ε_1 in the droplet interior and ε_2 in its exterior [2]. The calculation of this correlator, assuming that the translational and other degrees of freedom are statistically independent, yields

$$\begin{aligned}\langle \varepsilon(\vec{\mathbf{Q}},t)\varepsilon^*(\vec{\mathbf{Q}},0)\rangle[3V(\varepsilon_1-\varepsilon_2)]^{-2}\exp(Q^2Dt)\\ = z^{-2}j_1^2(z)-z^{-1}j_0(z)j_1(z)\sum_{l=2}^{l_{\max}}\frac{2l+1}{2\pi}\langle a_{l0}^2\rangle\\ +\sum_{l=2}^{l_{\max}}\frac{2l+1}{4\pi}j_l^2(z)\langle a_{l0}(t)a_{l0}(0)\rangle, \qquad (1)\end{aligned}$$

where $j_l(z)$ are the spherical Bessel functions, $z=QR$, D is the self-diffusion coefficient of the droplet, and the sums appear due to the expansion of the instantaneous radius of the deformed droplet in spherical harmonics with the coefficients a_{lm}, as in Ref. [1]. The volume V of the droplet volume is conserved [1].

Apart from the second term, the right-hand side of Eq. (1) corresponds to the autocorrelation function of the scattering amplitude from Ref. [1]. Equation (1) must be averaged over the wave vectors which corresponds to DWS experiments [1]. We have performed the averaging both analytically, using properties of the Bessel functions, and numerically. The resulting cross section consists of the constant part σ_0 and the time-dependent part $\Delta\sigma(t)$; their combination corresponds to the measured function $F(t;\phi\to 0)=R^2\Delta\sigma(t;\phi\to 0)/\sigma_0$. For the experimental conditions and the parameters of the system studied in [1] (the wave number of the incident radiation $k_0=16.3\,\mu\mathrm{m}^{-1}$, the droplet radius $R=0.7\,\mu\mathrm{m}$, the surface tension coefficient of the surfactant layer $\Gamma=0.01\,\mathrm{J\,m}^{-2}$, and the temperature $T=298\,\mathrm{K}$), we have found the value for the shape correlation function amplitude of noninteracting droplets at $t=0$ to be $F(0;0)\cong 70.7\,\text{Å}^2$, in a very good agreement with the experiment.

To obtain the time dependence of the function $F(t;0)$ we need the decay rates ω_l for the modes of fluctuation of the deformed droplet, which enter the correlators

$$\langle a_{l0}(0)a_{l0}(t)\rangle=\frac{k_BT}{\Gamma R^2}\frac{\exp(-\omega_l t)}{(l-1)(l+2)}. \qquad (2)$$

The expression used in [1] for ω_l in the overdamped limit of the shape fluctuations of droplets neglects the viscosity of the fluid outside the droplet ($\eta=12\,\mathrm{cP}$ for the oil droplets studied in [1] is an order of magnitude higher than the viscosity of the solvent, η'). Moreover, it corresponds to the limit when the surfactant film on the droplet surface is highly compressible, $G=-n_s\partial\Gamma/\partial n_s\to 0$, where n_s is the concentration of the molecules in the layer [3]. Recently [4] we showed that when the surface compressibility $1/G$ is finite, the overdamped mode of the shape fluctuations splits into

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*Electronic address: lisy@kosice.upjs.sk two modes that depend on the modulus G. The dispersion laws for both the modes were found analytically and differ from ω_l used in [1]. We applied these analytical expressions to fit the experimental data of Ref. [1] for the function $F(t;\phi)$ at low $\phi=0.07$ when the emulsion droplets are expected to interact weakly. We have found that an agreement with the experiment requires large G, about 1 Jm^{-2} or larger (this means that the surfactant film is almost incompressible, which is the usual assumption in the literature [5]). For larger G the curves $F(t;0)$ become indistinguishable since the decay rates ϖ_1 practically do not depend on G [4],

$$\varpi_l \approx \frac{\Gamma}{R}\left[\frac{2l+3}{l(l+2)}\eta + \frac{2l-1}{(l-1)(l+1)}\eta'\right]^{-1}, \qquad (3)$$

in agreement with the formula found in Ref. [6]. The scattering function is not influenced by the second relaxation mode whose decay rate is much higher than ϖ_l. Equation (3) now takes into account also the dependence on the viscosity of the solvent (water). The difference between ϖ_l and ω_l [1] affects the time behavior of the correlation functions (2) and thus the function $F(t;0)$. Figure 1 presents the calculation of $F(t;0)$, which includes the modes up to $l=30$ (the contributions from the higher l modes are negligible). The theoretical curve agrees very well with the experimental data taken from Ref. [1] for the low droplet volume fraction $\phi=0.07$. Note that in Ref. [1] the ϕ-dependent experimental data were scaled onto the theoretical correlation function $F(t;0)$ for noninteracting droplets. The scaling implies that particle interactions bring about the enhancement and slowing down of shape fluctuations without altering the spectrum of deformation modes. Our calculations suggest that this scaling should be slightly changed. In [1] the experimental curves collapse to one curve $F(\omega(\phi)t;\phi)/f(\phi)$, where the scaling function for the relaxation rate was proposed in the form $\omega(\phi)=\Gamma(\eta R)^{-1}(1-a\phi)$ with $a=0.78$, and $f(\phi)=\Delta\sigma(0;\phi)/\Delta\sigma(0;0)=1+C\phi(1-\phi/2)/(1-\phi)^3$ with $C=0.2$. The decrease of our theoretical curve $F(t;0)$ with t is more strong than in [1], which corresponds to the experiment. As a consequence, $\omega(\phi)$ must be smaller (the constant a larger) than determined in [1]. On the other hand, the value $C=0.2$ is too small to obtain the correct magnitude from our $F(0;0)$. For $\phi=0.07$ we found that C should be approximately 1.7.

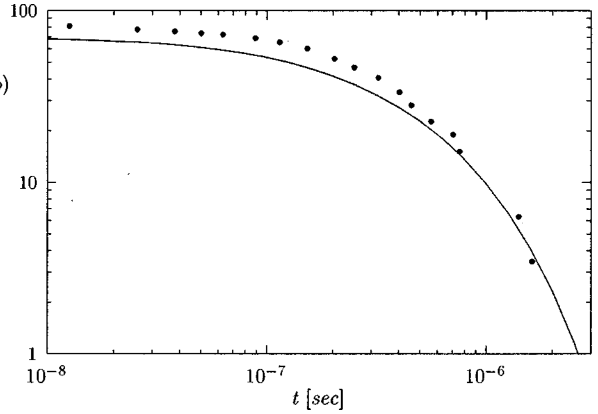

FIG. 1. Theoretical (——) shape correlation function of noninteracting droplets compared with the experimental curve (dark circles) [1] for the low droplet volume fraction $\phi=0.07$. The value $F(0;0)\cong 70.7$ Å^2 coincides with that obtained in Ref. [1] by extrapolation of experimental data to $\phi=0$.

In conclusion, our calculations within the Gang, Krall, and Weitz theory of DWS show that their experiments on emulsions can be described by the theory more precisely than in the original paper [1]. The discussed work opens new possibilities for investigations of systems of particles with internal dynamics, particularly the ensembles of liquid droplets exhibiting high interfacial flexibility, as it is in case of microemulsions or vesicles. This comment supports the applicability of the DWS method as a dynamical probe of emulsions.

The authors acknowledge financial support from VEGA, Slovak Republic (Grant No. 1/4387/97).

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