Direct Visual Observation of Thermal Capillary Waves

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We studied the free fluid-fluid interface in a phase-separated colloid-polymer dispersion with laser scanning confocal microscopy and directly observed thermally induced capillary waves at the interface in real space. Experimental results for static and dynamic correlation functions validate the capillary wave model down to almost the particle level. The ultralow interfacial tension, the capillary length, and the capillary time are found to be in agreement with independent measurements. Furthermore, we show that capillary waves induce the spontaneous breakup of thin liquid films and thus are of key importance in the process of droplet coalescence.

At rest, the free interface between any two fluids, like that between a liquid and its vapor, appears to be smooth. Yet thermal motion inevitably gives rise to statistical fluctuations of the local interface position, leading to a rough interface. This phenomenon was first predicted by von Smoluchowski in 1908 (1); 5 years later, Mandelstam quantitatively described the interface roughness in terms of thermally excited capillary waves (2). These capillary waves have been studied with light (3) and x-ray scattering (4–8). They play an important role in modern theories of interfaces (9–11) and have been argued to be essential in the mesoscopic analog of the liquid-gas phase transition in atomic substances (12). The interface roughness is about 0.3 nm, whereas the correlation length is ~3 mm, resulting in extreme roughness–correlation length ratios of ~10<sup>12</sup>; such ratios are only accessible through scattering techniques. Here we exploit the scaling up of micrometer to nanometer techniques. Here we exploit the scaling up of micrometer to nanometer

The capillary wave spectrum, each Fourier component <i>h</i><sub>k</sub> of the interface displacement contributes according to the equipartition theorem

<i>⟨|h|<sup>2</sup>⟩ = k<sub>B</sub>T / 2γ / L<sup>2</sup> / k<sup>2</sup> + ξ</i><sup>2</sup> (1)

where <i>g</i> is Earth’s acceleration and Δρ is the mass density difference between the two phases. In molecular fluids, <i>γ</i> is on the order of 10 to 100 mN/m and Δρ is about 10<sup>−2</sup> to 10<sup>−5</sup> kg/m<sup>3</sup>. Therefore, the interface roughness is ~0.3 nm, whereas the correlation length is ~3 mm, resulting in extreme roughness–correlation length ratios of ~10<sup>12</sup>; such ratios are only accessible through scattering techniques. Here we exploit the scaling up of micrometer to nanometer techniques. Here we exploit the scaling up of micrometer to nanometer

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We used fluorescently labeled poly(methylmethacrylate) (PMMA) colloidal spheres (25) with radius <i>R</i> = 71 nm (obtained from static light scattering) and size polydispersity of less than 10%. The polymer was commercially available polystyrene (Fluka) with molecular weight <i>M</i><sub>w</sub> = 2 × 10<sup>6</sup> g mol<sup>−1</sup> (<i>M</i><sub>n</sub> / <i>M</i><sub>w</sub> < 1.2, where <i>M</i><sub>n</sub> is number-average molecular weight) and radius of gyration <i>R</i><sub>G</sub> ~ 44 nm [estimated from data in the literature (26)]. Thus, the size ratio, <i>R</i><sub>G</sub> / <i>R</i> = 0.6, was significantly large to obtain stable fluid-fluid demixing (27). Both species were dispersed in cis/trans-decalin, and because all densities were known, mass fractions could be directly converted to packing fractions of colloids, <i>ϕ</i><sub>c</sub> = 4/3π<sup>2</sup>π<sub>c</sub><sup>2</sup> / 3π<sub>c</sub><sup>3</sup> / 3π<sub>c</sub><sup>2</sup> and polymers, <i>ϕ</i><sub>p</sub> = 4/3π<sup>2</sup>π<sub>p</sub><sup>2</sup> / 3π<sub>p</sub><sup>3</sup> / 3π<sub>p</sub><sup>2</sup>, where <i>n</i><sub>c</sub> and <i>n</i><sub>p</sub> are the number densities of colloids and polymers, respectively. Samples were prepared by mixing colloid and polymer stock dispersions and diluting with decalin to control the overall packing fractions <i>ϕ</i><sub>c</sub> and <i>ϕ</i><sub>p</sub>. Large glass cuvettes (volume ~1 cm<sup>3</sup>) with very thin cover glass walls (0.17 mm) were used. A confocal scanning laser head (Nikon C1) was mounted on a horizontally placed light microscope (Nikon Eclipse E400). Each measurement was done after 1 day of equilibration. We checked that the system was well equilibrated by following the recovery of intensity after bleaching a space region in the gas and/or liquid phase. The recovery appeared to be governed solely through diffusion of particles without any indications of drift (e.g., through convection). Data sets were acquired at many different state points following several dilution lines. The underlying phase diagram is shown in Fig. 1.
Fourier-transforming Eq. 1 as $\bar{h}$ decreases. The microscopic records the fluorescence of excited dye within the colloids, hence the colloid-rich (liquid) phase appears bright and the colloid-poor (gas) phase appears dark. $I(x, z, t)$ is a direct measure of the local and instantaneous distribution of colloidal particles and provides the starting point for a statistical analysis. Because of the finite resolution (28), we can access length scales of $\sim 2R_c$; we neglect effects induced by the finite time needed to scan each frame, and we take $I$ as an instantaneous snapshot (justified by comparing the colloid self-diffusion time with the scanning time). Thus, the real-space pictures in Fig. 2 show the structure of a gas-liquid interface practically at the particle scale. We rely on the concept of a local interface between both phases. In the spirit of a Gibbs dividing surface, we define an interface position $h(x, t)$ such that in one column of vertical length $L_z$ the total intensity can be written as

$$\int_0^{L_z} dz I(x, z, t) = I_{\text{gas}}(x)h(x, t) + I_{\text{liq}}(x)[L_z - h(x, t)]$$

where $I_{\text{gas}}(x)$ and $I_{\text{liq}}(x)$ are the average bulk intensities in the gas and liquid phase, respectively, and are taken to be functions of $x$ to account for the microscope objective properties. In practice, integrals in the notation are sums over pixels, and we have checked that the results of the subsequent analysis do not depend sensitively on the precise definitions of $I_{\text{gas}}$ and $I_{\text{liq}}$. The resulting “height” function $h(x, t)$ describes the interface position quite accurately. From top to bottom in Fig. 2 we approach the critical point, and both the capillary waves and density fluctuations increase while the density difference between the two phases decreases.

For each frame the average interface position is $\bar{h}(t) = \langle h(x', t) \rangle$, in which the angle brackets denote averages over primed quantities. The time-dependent height-height correlation function is constructed as

$$g_\delta(x, t) = \langle [h(x', t') - \bar{h}(t')][h(x' + x, t') + t] - \bar{h}(t')\rangle$$

The corresponding static correlation function, $g_0(x) = g_\delta(x, t = 0)$, is obtained (5) by Fourier-transforming Eq. 1 as

$$g_\delta(x) = \frac{k_B T}{2\pi \gamma} K_0(x/\xi)$$

where $K_0$ is the modified Bessel function of the second kind as a function of $x/\xi$. Equation 6 holds for distances $x$ larger than a small-distance cutoff on the order of the particle size. Capillary wave theory in the overdamped regime (29, 30) predicts modes with wave vector $k$ to decay according to $\exp[-\tau(\gamma k + g_\delta(x)/k)]$. Introducing $k = \xi k$, the dynamical correlation function at fixed position, $g_\delta(t) = g_0(x = 0, t)$, can be expressed as

$$g_0(t) = \frac{k_B T}{2\pi \gamma} \int_0^\infty dk \frac{\exp[-(k + k^{-1})t/\tau]}{1 + \tau}$$

where $\tau$ is as given in Eq. 3 with $\eta = \eta_{\text{colloidal}} + \eta_{\text{gas}}$, the sum of the viscosities of the (colloidal) liquid and gas phase (29, 30).
Equations 6 and 7 describe the experimental data points very well, as can be clearly seen in Fig. 3, A and B, for various state points with only two physical parameters ($\gamma$, $\xi$ in the static case and $\gamma$, $\tau$ in the dynamic case). Results for the interfacial tension, capillary length, and capillary time are displayed in Fig. 3, C to E, respectively. The relation of these quantities through Eq. 3 allows for an independent check of the consistency of our measurements. For example, for state point I, $\gamma = 100$ nN/m, $\xi = 15\mu$m, and $\eta_{\text{liq}} + \eta_{\text{gas}} = (30 + 12.6)$ mPars, leading via Eq. 3 to a capillary time of 6 s. From the dynamical correlation function we find
RNA-Mediated Metal-Metal Bond Formation in the Synthesis of Hexagonal Palladium Nanoparticles

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RNA sequences have been discovered that mediate the growth of hexagonal palladium nanoparticles. In vitro selection techniques were used to evolve an initial library of ~10^{14} unique RNA sequences through eight cycles of selection to yield several active sequence families. Of the five families, all representative members could form crystalline hexagonal palladium platelets. The palladium particle growth occurred in aqueous solution at ambient temperature, without any endogenous reducing agent, and at low concentrations of metal precursor (100 micromolar). Relative to metal precursor, the RNA concentration was significantly lower (1 micromolar), yet micrometer-size crystalline hexagonal palladium particles were formed rapidly (7.5 to 1 minutes).

Biomineralization achieves exquisite control over crystal type and hierarchical materials self-assembly with protein biopolymer templates. RNA molecules are also highly structured biopolymers. Given the landmark discovery of in vitro selection (1, 2) and the use of these techniques to discover RNA catalysts that mediate a variety of organic reactions (3–10), we sought to determine whether RNA could serve as a template for inorganic–particle growth. Here we report examples of individual RNA sequences that mediate metal-metal bond formation to create novel inorganic materials.

Conventional methods for controlling metal-metal bond formation and crystal growth primarily use synthetic polymers. Archetypical examples are the formation of cubic silver and palladium particles using poly(acrylate) (11) or poly(vinylpyrrolidone) templates (12). Smaller multidentate ligands such as trisodium citrate can be used to control crystal shape as well—for example, in the photoinduced conversion of silver nanoparticles to triangular prisms (13).

In attempts to mimic natural biomineralization, proteins and polypeptides have been studied extensively as templates for materials synthesis (14–17). Belcher et al. have used phase display techniques to mine for peptides that can bind selectively to various semiconductor crystal faces (18). Knowledge of peptide-surface binding affinity was then used to engineer a virus that could bind and organize semiconductor nanocrystals into well-ordered thin-film assemblies (19). Much less research has focused on the interactions between materials

References and Notes
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