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Capillary waves in slow motion

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Capillary wave dynamics on glycerol surfaces has been investigated by means of x-ray photon correlation spectroscopy performed at grazing angles. The measurements show that thermally activated capillary wave motion is slowed down exponentially when the sample is cooled below 273 K. This finding directly reflects the freezing of the surface waves. The wave-number dependence of the measured time constants is in quantitative agreement with theoretical predictions for overdamped capillary waves.

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It is well known that thermally activated capillary waves decorate the surfaces of liquids.[1,2] Many x-ray scattering experiments that show the unambiguous ‘‘fingerprints’’ of capillary waves on liquid surfaces, such as power-law tails in the diffuse scattering or the dependence of the measured rms roughness on the instrumental resolution due to quasi-long-range correlations, have been performed in the past (see, e.g., Refs. 3–7). These experiments, however, have tested the *static* time-averaged structure rather than the dynamics of the surface fluctuations. Direct measurements of capillary wave fluctuations have been done extensively by dynamic light scattering[8,9] (DLS) (for a review, see the articles in Ref. 10 and references therein). For lateral length scales below 100 μm DLS may suffer from bulk scattering effects, making an unambiguous distinction between scattering stemming from the surface and from the liquid underneath almost impossible. It will be shown here that the accessible lateral length scales can be extended by almost two orders of magnitude toward smaller length scales if x rays instead of laser light are used as probe. For this purpose we have used the established fact that x-ray scattering becomes surface sensitive when applied under grazing incidence well below the critical angle of total external reflection. Thus, the resultant scattering is intrinsically free from bulk contaminations. In addition, x-ray scattering is unaffected by multiple scattering effects that may make the precise determination of the lateral wave vector difficult. The major drawback of x rays is the fact that conventional sources are essentially incoherent, which renders the direct measurement of dynamics impossible.

With high-brilliance third generation sources it has become possible to obtain intense x-ray beams possessing a high degree of coherence. Such beams are produced by selecting the coherent part of the impinging radiation from an otherwise incoherent beam using micrometer-sized pinholes. Both experiments and calculations have been carried out that demonstrate and explain the coherence properties of such beams (see, e.g., Refs. 11–13). In addition, photon correlation spectroscopy with coherent x rays (XPCS) has been successfully applied to study the dynamics in several colloidal and micelle systems.[14–17] The advantage of XPCS over DLS is that nontransparent samples can be investigated and larger wave-vector transfers may be achieved. Recently, XPCS has also been applied to study the dynamics of vertical fluctuations in free-standing smectic films.[18,19] Here we report the first successful application of XPCS to monitor lateral motions at surfaces. XPCS was applied under grazing incident and exit angles to measure the dynamics of capillary waves on the surface of the prototype glass-former glycerol.

The x-ray experiments were performed at the ID10A (Troika) beamline of the European Synchrotron Radiation Facility in Grenoble. The surfaces were illuminated with 8 keV radiation (wavelength $\lambda = 1.548$ Å) from a set of three undulators. The radiation was monochromatized by a Si(111) crystal with a wavelength bandpass of $\Delta\lambda/\lambda \approx 10^{-4}$ yielding a longitudinal coherence length $\xi_l = \lambda^2/\Delta\lambda$ of about 1 μm. A pinhole with a diameter of 12 μm was mounted 278 mm upstream from the sample in order to obtain a collimated and (partially) coherent beam. Typical transverse coherence lengths at the pinhole are 100 μm in the vertical and 10 μm in the horizontal direction. A guard slit in front of the sample was used to suppress the Fraunhofer fringes from the first pinhole. The data were collected with a scintillation counter at a distance 2368 mm downstream from the sample. A collimating aperture with an adjustable size of 15–100 μm was chosen in front of the detector. The time-autocorrelation functions were recorded with a digital ALV5000/E correlator. The setup is sketched in Fig. 1.

The glycerol (from Fluka No. 49770, purity always better than 99.5%) was put into an evacuated inner sample cell. This cell was cooled by a constant flow of liquid nitrogen. A film of approximately 4.5 mm thickness was filled into an aluminum trough of 140 mm diameter. The size of the trough was chosen such that a large flat area of glycerol is obtained in the middle that is unaffected by the meniscus at the border. Furthermore, the entire footprint of the impinging radiation should fit onto the sample surface in order to maximize

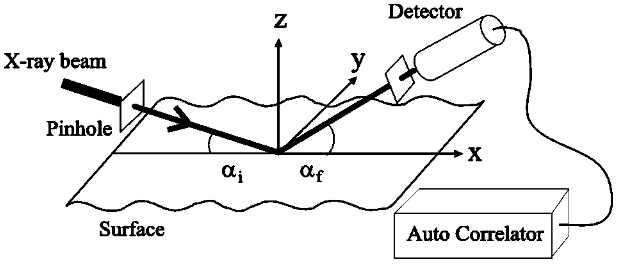

FIG. 1. Sketch of the setup for a surface XPCS experiment.

the reflected intensity and to avoid parasitic scattering from the sample container. The inner cell was evacuated to about 10 mbar and isolated against possible temperature variations introduced from the outside by a vacuum ($p<10^{-5}$mbar) that was maintained during the experiments. The temperature stability of this setup was better than 0.02 K over several hours. A second outer cell was directly attached to the evacuated flight path on the detector side. The sample was cooled down to the desired temperature with a cooling rate of approximately 1 K/min. Each time the data collection was started one hour after reaching the respective temperature.

The glycerol surfaces were illuminated under the grazing incident angle of $\alpha_i=0.075°$ well below the critical angle of total reflection $\alpha_c=0.170°$ for 8 keV radiation. Thus, the penetration depth $\Lambda=\lambda/(2\pi\alpha_c)$ of the radiation was always restricted to the topmost 80 Å of the sample. X-ray reflectivity and diffuse scattering experiments are sensitive to the electron density contrast. This contrast is very large at the surface compared with the liquid material underneath. Hence, for incident angles below the critical angle the scattering is dominated by contributions stemming from the surface rather than from the bulk. For larger α_i the situation may become more complicated. In addition, at very small incident angles absorption is minimized in the sample and the 12-μm-sized beam is spread over an area of about 9 mm. Both effects prevent the sample from being radiation damaged.

The scattered radiation was detected under different exit angles α_f within the scattering plane. Hence the lateral and perpendicular components of the wave-vector transfer, q_x and q_z, are given by $q_x=(2\pi/\lambda)(\cos\alpha_f-\cos\alpha_i)$ and $q_z=(2\pi/\lambda)(\sin\alpha_f+\sin\alpha_i)$. From the q_x value the lateral length scale x_0 that is probed may be easily obtained by $x_0=2\pi/q_x$. In our study length scales in the region 5 μm $<x_0<150$ μm were tested.

Dynamics can be measured in a photon correlation spectroscopy experiment by evaluating the normalized time-correlation function $g_2(\tau)=\langle I(t+\tau)I(t)\rangle_t/\langle I(t)\rangle_t^2$ where $I(t)$ is the observed intensity in a detector.[10] We found that all of our data can be perfectly described by the exponential form

$$g_2(\tau)=g_0\exp(-\tau/\tau_0)+1, \qquad (1)$$

with $0\leqslant g_0\leqslant 1$ and a time constant τ_0. The constant g_0 depends on the degree of coherence of the incident beam and the degree of ensemble averaging for the incident and scattered beams.

Figure 2 shows a correlation function $g_2(\tau)$ that has been obtained for a lateral length scale of $x_0=56$ μm and an opening of 30 μm×30 μm of the exit aperture in front of the detector. The temperature of the glycerol surface was $T=253$ K. For comparison the time-correlation function of the monitor signal is also plotted in Fig. 2. Oscillations at shorter times than those shown in Fig. 2 are due to the incident beam. Between $\tau=0.1$ ms and $\tau=100$ ms a well-defined correlation function is visible. A fit of Eq. (1) to the data (solid line in Fig. 2) yields the time constant $\tau_0=17.9$ ms and a contrast of $g_0=0.405$. The maximum value for the contrast in our measurements was $g_0=0.695$.

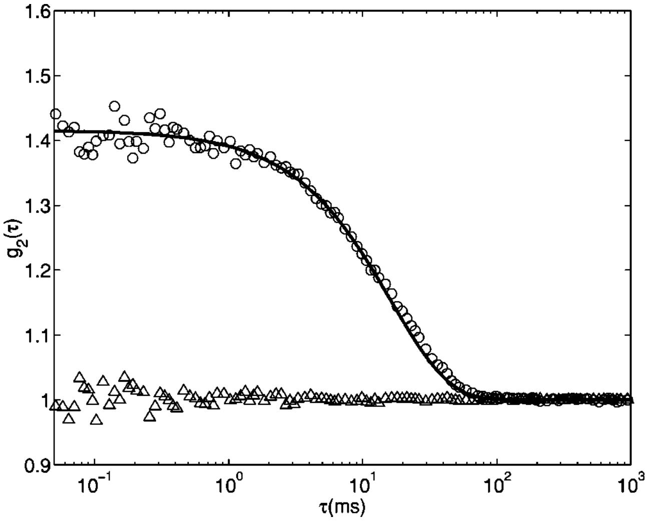

FIG. 2. Intensity-intensity correlation function $g_2(\tau)$ from a glycerol surface at $T=253$ K (open circles). The length scale that was probed is $x_0=56$ μm. The correlation function of the monitor signal is given by the open triangles. The solid line is a fit according to $g_2(\tau)=g_0\exp(-\tau/\tau_0)+1$ from which the two parameters g_0 (contrast) and τ_0 (time constant of overdamped capillary waves) are obtained.

Figure 3 shows the observed time constants τ_0 as a function of the lateral length scale x_0 for different temperatures T. A linear relationship between τ_0 and x_0 is evident for all T. The slope of the curves depends almost exponentially on the temperature. This is shown in Fig. 4 where the measured ratio τ_0/x_0 is plotted versus T on a logarithmic scale. Figure 4 directly reflects the slowing down of the motion on the glycerol surfaces with decreasing temperature.

Figures 3 and 4 can be understood quantitatively by the capillary wave theory for viscous liquids published by

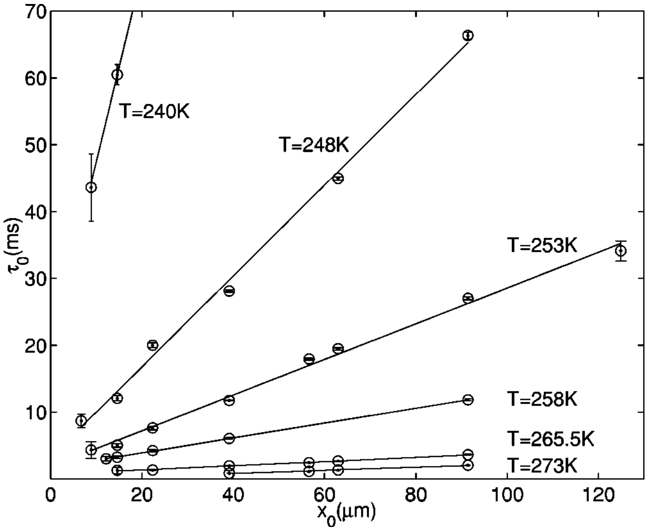

FIG. 3. Measured time constants τ_0 vs the lateral length scale x_0 as given by the detector positions for various temperatures T. For the sake of clarity not all data are shown.

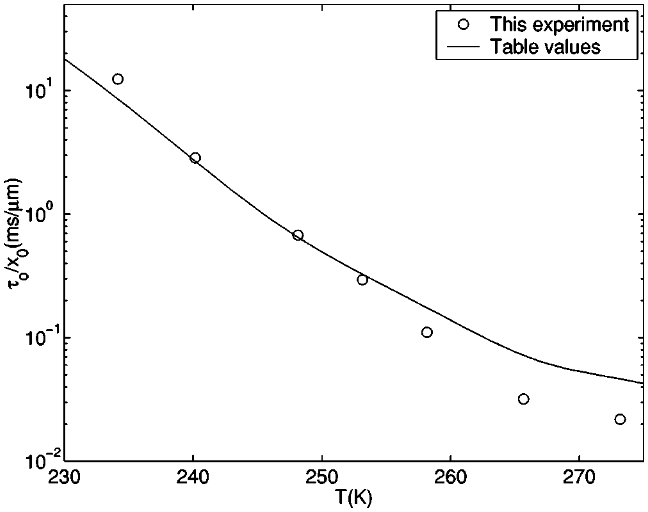

FIG. 4. Ratio τ_0/x_0 as obtained from the slopes in Fig. 3 and additional data (open circles). The solid line was calculated with published data for the viscosity $\eta(T)$ and surface tension $\gamma(T)$ according to $\tau_0/x_0 = \pi^{-1}\eta(T)/\gamma(T)$. This curve has been smoothed for clarity.

Levich[20] and later by Jäckle and Kawasaki[21] for the simple case of sinusoidal surface waves. The first rigorous treatment for thermally excited waves was given by Bouchiat and Meunier.[22] Their result is similar to that given by Levich for the parameter space that is addressed in the present work. A discussion of the dispersion relation for capillary waves on the surface of a viscous liquid yields

$$\Gamma = 2\,\nu q^2 \tag{2}$$

as damping constant for propagating waves with frequency $\omega_0(q) = q^{3/2}\sqrt{\gamma/\rho}$, where ν and ρ are the kinematic viscosity and the density of the liquid, respectively. Here, the tiny effect of gravity has already been neglected. For highly viscous liquids such as glycerol the damping of the surface waves is so large that all propagating modes become unstable. Thus, for high viscosities so-called overdamped capillary waves are expected with a damping term[8,20,22]

$$\Gamma = q\,\frac{\gamma(T)}{2\,\eta(T)}, \tag{3}$$

where the dynamic viscosity $\eta(T)$ and the surface tension $\gamma(T)$ are temperature dependent quantities. Equation (3) may be translated via $\Gamma = 1/\tau_0$ and $q = 2\pi/x_0$ into a linear equation for the relaxation time τ_0 and the probed length scale x_0

$$\tau_0 = \frac{1}{\pi}\,\frac{\eta(T)}{\gamma(T)}\,x_0. \tag{4}$$

Since $\gamma(T)$ changes by less than a factor of 2 in the temperature range of our experiment (234 K$\leqslant$T$\leqslant$273 K) the exponential increase of the ratio $\eta(T)/\gamma(T)$ with decreasing temperature is caused by the strong temperature dependence of the viscosity. The line in Fig. 4 is calculated with $\eta(T)$ values published in the literature[23] and $\gamma(T)$ values obtained from reflectivity data.[24] The good agreement between the XPCS results and the literature values confirms our assumption of overdamped capillary waves on glycerol surfaces. Although our probed lateral length scales are still quite large we note that the dynamics of capillary waves on viscous liquids has not been measured before over such a large range to our knowledge. We extend the results published so far by almost two orders of magnitude toward smaller length scales. In addition, a large temperature range was coverd in order to monitor *in situ* the freezing of the surface waves. Figures 3 and 4 directly reflect that the quasi-long-ranged surface motion due to overdamped capillary waves starts to freeze on a time scale of seconds at temperatures of 230 K, i.e., far above the calorimetric glass transition temperature $T_G = 186$ K.[25] For $T = 198$ K, still well above T_G, the surface motion was so slow that no time constant could be detected for any length scale. This means that the surface was already static on a time scale of hours as suggested by Eq. (4).

In summary, we have presented a measurement of capillary wave *motion* by *x-ray* scattering. XPCS was applied under grazing angles to detect overdamped capillary waves on glycerol surfaces in the most direct and unambiguous manner. The damping due to the high viscosity of glycerol is responsible for the relatively slow motion that could be detected in our measurements. Our results suggest that the surface fluctuations of viscous liquids freeze on a time scale of hours far above the calorimetric glass transition temperature. However, it is important to note that this finding can be totally explained by the fact that long-range correlations are probed at a liquid/gas interface. Equation (4) has been confirmed by our measurements by using the *bulk* viscosity $\eta(T)$. This means that the calorimetric glass transition temperature T_G at the surface, which reflects the microscopic motion of the liquid in the bulk, is *not* altered at glycerol surfaces. This finding is of decisive importance for the future interpretation of glass transition data, since it has been speculated recently that T_G may be different at the surface and in the bulk of viscous polymeric liquids.[26,27]

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