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Capillary waves on a poly(vinylacetate) surface studied by off-specular diffuse X-ray scattering

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Summary

The waves excited in thermal equilibrium on the surface of a liquid show up in X-ray scattering experiments in a diffuse component with center at the specular beam. They can be studied with the aid of a Kratky-camera carrying out rocking-scans. Results obtained for poly(vinylacetate) agree with the theoretical prediction. Evaluation of the data yields the surface tension.

Introduction

If a X-ray beam is directed onto the surface of a solid or liquid under a grazing angle, a reflected (‘specular’) beam is observed as in the case of a normal mirror. Up to a critical angle one finds total reflection of the beam. After having crossed this angle the intensity of the specular beam decreases sharply in accordance with Fresnel’s law $I \sim 1/q^4$ ($\vec{q}$ giving the scattering vector). For an ideally plane surface only this specular beam would be found, however, such surfaces do not exist. There are always surface waves (‘capillary waves’) excited by thermal forces [1] and they lead to a roughening. As a consequence the intensity distribution measured in a scattering experiment becomes modified. There arises a scattering also in off-specular directions, and it is accompanied by a corresponding weakening of the intensity of the specular beam. Theoretical analysis directly relates the diffuse off-specular scattering to the mean-squared amplitudes of the capillary waves [2] [3] [4]. As these are determined by the surface tension γ only, the latter may be deduced from the data.

Experiments may be simply carried out with the aid of a Kratky camera, after the installation of a rotation device. By ‘rocking’ the sample surface around the direction of the specular beam, keeping the detector position constant, the scattering originating from the capillary waves is registered. In our experiments, we chose poly(vinylacetate) as an example.

Experimental

We employed a Kratky camera where the usual sample holder was replaced by a device which enabled a thin film placed on a glass substrate to be rotated about the specular position. Motions of both the detector and the rotating device were under computer control. Details are given elsewhere [5]. Measurements were conducted using the CuK_α–radiation of a rotating anode X-ray generator.

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The rocking motion of the sample holder scans the intensity distribution in the direction q_ρ, perpendicular to the surface normal, for a fixed value of the parallel scattering vector component q_z. Fig. 1 shows this measurement geometry.

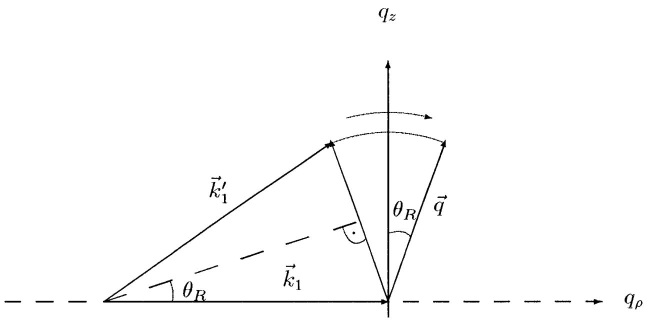

Figure 1: Motion of the scattering vector during a rocking scan. q_z and q_ρ are reciprocal space coordinates parallel and perpendicular to the surface normal ($\vec{k}_1$ and $\vec{k}'_1$: wave vectors of the primary and scattered beam; θ_R: Bragg reflection angle)

Thin films of poly (vinylacetate) (PVac) with a molecular weight M_w = 30.000 were obtained by spin-coating a solution directly onto the glass slide. Spinning frequencies were in the range of 3.000 turns/min, using solutions with a concentration of 10 mg/ml. Film thicknesses were in the range of 20 - 40 nm. Most measurements were carried out at ambient temperature just below the glass-transition (T_g = 28°C). Samples had to be below T_g in order to avoid a flowing away in the generally oblique positions.

Thermally excited capillary waves

The thermal motion in liquids generally leads to fluctuations of the surface level around the average position. Theory shows that the motion may be described as a superposition of surface waves having wave vectors κ_j which vary in the two dimensions of the surface. Waves with different wave vectors are decoupled and therefore excited independently. For each wave separately, excitation is associated with an increase of the free energy per unit area of surface. For an amplitude A_j the free energy increase of the wave with wave vector κ_j is given by

$$\frac{\Delta F}{a} = \frac{1}{2}(\rho g + \gamma \kappa_j^2) A_j^2 \tag{1}$$

Here ρ is the density and γ denotes the surface tension (a: surface area, g = 9.81 in sec^{-2}). The first contribution describes the increase in potential energy in the gravitational field, the second originates from the increase of the surface area due to the sinusoidal height fluctuations. Scattering intensities may be related to the mean-squared amplitudes of the capillary waves. These follow from Boltzmann statistics as

$$\langle A_j^2 \rangle = \frac{k_B T}{\gamma a} \left[\frac{\rho g}{\gamma} + \kappa_j^2 \right]^{-1} \tag{2}$$

Scattering law

Rocking scans monitor the intensity distribution in the q_x, q_y-plane at a certain fixed q_z. The scattering law can be derived in a straightforward way and is given by the following expression for the scattering cross section

$$\frac{d\sigma}{d\omega} = r_o^2 \frac{\rho_e^2}{q_z^2} e^{-q_z^2 \sigma_h^2} \left\{ 4\pi^2 \delta(q_x)\delta(q_y) + q_z^2 \frac{k_B T}{\gamma} \frac{1}{\rho g/\gamma + q^2} \right\} \tag{3}$$

The first term with the product of two δ-functions represents the specular beam; the second term describes the diffuse scattering associated with the capillary waves. The intensity measured at a certain q relates to the contribution of capillary waves with $q = \kappa$ only, being determined by their amplitude. It is interesting to calculate the total intensity of both the specular beam and the diffuse scattering. The result of the calculation is

$$\int_{q_x, q_y} \left\{ 4\pi^2 \delta(q_x)\delta(q_y) + q_z^2 \frac{k_B T}{\gamma} \frac{1}{\rho g/\gamma + q^2} \right\} \mathrm{d}q_x \mathrm{d}q_y = e^{q_z^2 \sigma_h^2} \tag{4}$$

Here

$$\sigma_h^2 = \sum_j \langle A_j^2 \rangle \tag{5}$$

gives the total mean-squared height fluctuation (r_e: classical electron radius, ρ_e: electron-density of the liquid). According to the result the integrated intensity is constant; the loss of intensity in the specular beam shows up in the diffuse scattering. Therefore, the surface roughening just leads to a redistribution of the scattering within the q_x, q_y-plane.

To discuss the experimental results one has additionally to account for

- the continuous transition of the local density from the bulk value down to zero, usually represented by an error function with width σ_z^2
- the incomplete transition of the primary beam into the sample and of the scattered beams out of the sample, to be described by the amplitude transmission coefficients $T(\alpha)$ and $T(\beta)$ (α and β denote the entrance and the exit angle)
- the slit-smearing of the Kratky camera amounting to an integration of the intensity along q_y (we also substitute q_x by q_ρ)
- the finite angular resolution of the detection system which may be specified by a resolution function ø (q_ρ) (usually a Gaussian with the given width).

Introducing all these factors into Eq. (3) yields

$$I^* = r_\circ^2 \frac{\rho_e^2}{q_z^2} e^{-q_z^2\sigma_z^2} e^{-q_z^2\sigma_h^2} \cdot \int_{q'_\rho} (4\pi^2\delta(q'_\rho) + q_z^2 \pi \frac{k_B T}{\gamma} \frac{1}{\sqrt{\rho g/\gamma + q'^2_\rho}})|T(\alpha)|^2 |T(\beta)|^2 \phi(q'_\rho - q_\rho) \mathrm{d}q'_\rho \qquad (6)$$

Fig. 2 shows for illustration the result of model calculations carried out for three different values of γ. The central peak arises from both the specular beam and the central part of the diffuse scattering when carrying out the convolution with the resolution function. There follows a decay on both sides which is essentially given by the power-law

$$I^* \sim \frac{1}{\sqrt{\rho g/\gamma + q_\rho^2}} \approx \frac{1}{q_\rho} \qquad (7)$$

As a third characteristic feature one notes an intensity enhancement at both edges. It originates from a corresponding behavior of the transmission coefficients. The feature is known as 'Yoneda-peak' and shows up just at those positions where either the incoming or the outgoing beam meets the critical condition, i.e. encounters the surface under the critical angle [6].

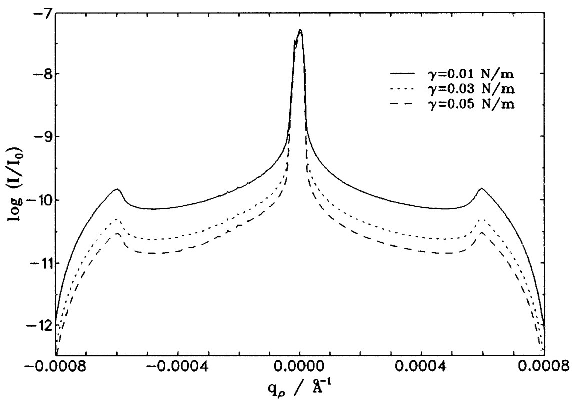

Figure 2: Model curves for rocking scans (q_z = 1nm^{-1}, δq_ρ = 5 • 10^{-6} nm^{-1}, T = 273K)

Results

Measured rocking curves largely agree with the theoretical predictions. Fig. 3 shows the scattering intensity distribution for three different values of q_z. As expected, the range of diffuse scattering is limited by the Yoneda-peaks on both sides; their distance

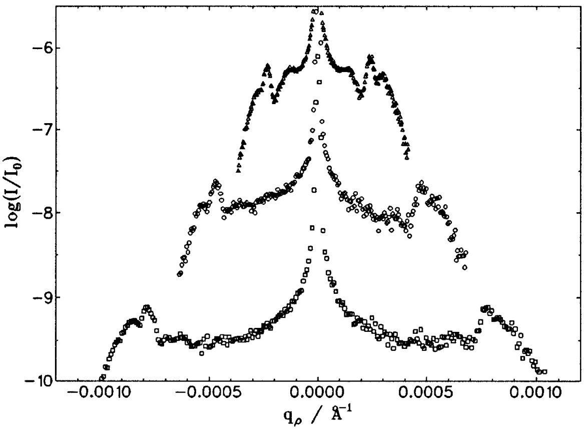

Figure 3: Rocking curves obtained for a surface of PVAc at different values of q_z (from above: 0.62, 0.78, 0.96 nm^{-1})

increases with q_z. Surprisingly, the Yoneda-peaks show a fine structure. At present we cannot offer an explanation for this behavior.

Fig. 4 puts the focus on the ranges between the central maximum and the Yoneda-peaks. As demonstrated by the log-log plots in the figure we have indeed a power-law behavior with $I^* \sim 1/q_\rho$.

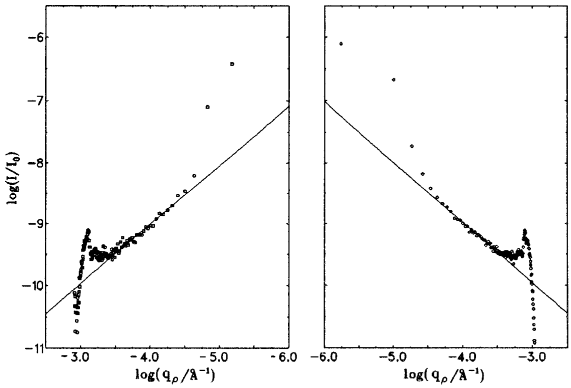

Figure 4: Demonstration of power-law behaviour $I^* \sim 1/q_\rho$

As a third result, Fig. 5 displays a measured rocking curve (q_z = 0.78 nm^{-1}) compared to a fit on the basis of Eq. (6). Except for the region around the Yoneda-peaks we find a good agreement. The fitting procedure yields the surface tension γ, here with a value γ = 0.034 Nm^{-2}. This comes very near to literature data: (γ = 0.0365 Nm^{-2} at 30 °C [7]).

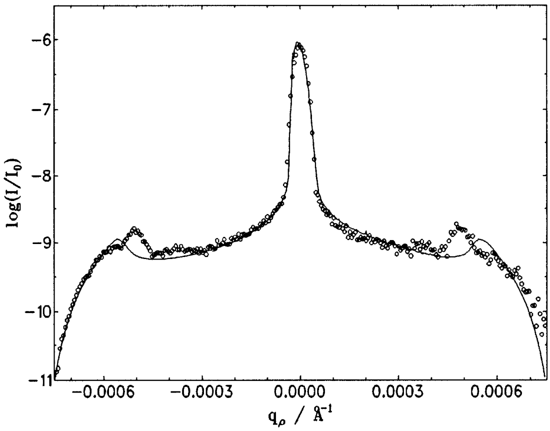

Figure 5: Rocking-curve measured for a PVAc-surface at q_z = 0.78 nm^{-1}, compared to an adjusted theoretical curve

In conclusion, we learned that the roughening of the surface of a polymer by capillary waves may be studied quantitatively employing a modified Kratky camera.

References

[1] J.S. Rowlinson and B. Widom (1988) *Molecular Theory of Capillarity*

[2] S.K. Sinha, E.B. Sirota, S. Garoff, and H.B. Stanley (1988) *Phys.Rev.B* 38:2297

[3] M.K. Sanyal, S.K. Sinha, K.G. Huang, and B.M. Ocko *(1991) Phys.Rev.Lett.* 66:2108

[4] J. Daillant and O. Belorgey (1992) *J.Chem.Phys.* 97:5824

[5] H. Elben and G. Strobl (1993) *Macromolecules* 26:1013

[6] Y. Yoneda (1963) *Phys.Rev.* 131:2010

[7] J. Brandrup and E.H. Immergut (1975) *Polymer Handbook*