X-Ray Measurements of Noncapillary Spatial Fluctuations from a Liquid Surface

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Off-specular diffuse x-ray scattering measurements on both pure water and a homogeneous Langmuir monolayer of poly-γ-benzyl-L-glutamate (PBLG) on water establish the validity of a proposed sum rule for scattering from capillary fluctuations on liquid surfaces. Excess scattering above the predicted capillary contribution is observed when the PBLG monolayer is compressed beyond its elastic limit. This is interpreted in terms of a second-layer inhomogeneity with a surface correlation length of ~1000 Å. Excess off-specular scattering can be used to probe interface correlation lengths from 100 Å to 1 μm. [S0031-9007(98)07353-0]

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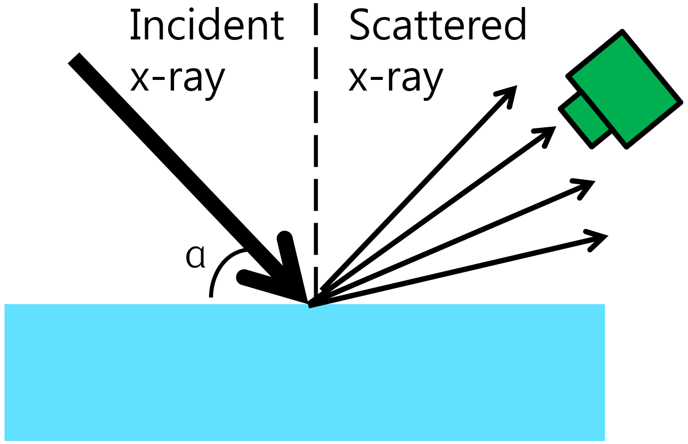
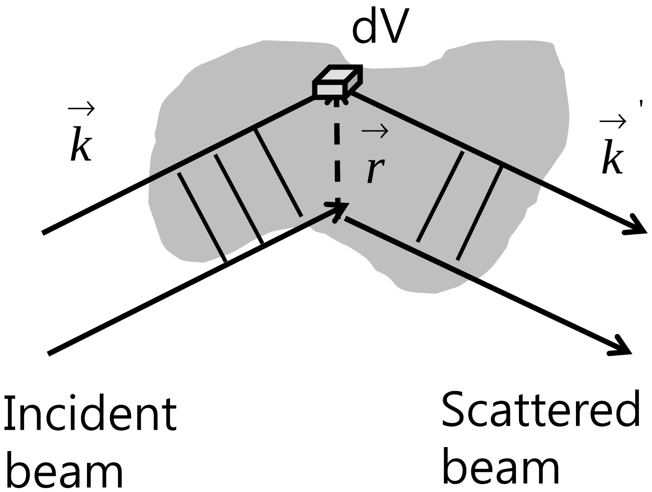


$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{(\text{number of scattered x-ray per second into } \Delta\Omega)}{(\text{Incident flux})(\Delta\Omega)}$$

$$= \frac{I_{SC}}{(I_0 / A_0)\Delta\Omega} = \frac{\left|E_{rad}\right|^2 R^2}{\left|E_{in}\right|^2}$$

$$\frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} \exp(-x^2 / 2\sigma^2) \exp($$



$$F = \int dV n(\vec{r}) \exp[i(\vec{k} - \vec{k}') \cdot \vec{r}] = \int dV n(\vec{r}) \exp[i(\vec{q}) \cdot \vec{r}]$$

$$\left(\frac{d\sigma}{d\Omega}\right) \propto \left[\int dV n(\vec{r}) \exp[i(\vec{k} - \vec{k}') \cdot \vec{r}]\right][C.C]$$

$$= N^2 \int_V d\vec{r} \int_V d\vec{r}\,' \exp[-i(\vec{q}) \cdot (\vec{r} - \vec{r}\,')]$$

X-ray scattering cross section and surface roughness

$$\left(\frac{d\sigma}{d\Omega}\right) = N^2 b^2 \int_V d\vec{r} \int_V d\vec{r}\,' \exp[-i(\vec{q})\cdot(\vec{r}-\vec{r}\,')],\, b = \frac{e}{mc}$$

$$= N^2 b^2 \frac{1}{(\vec{q}\cdot\vec{z})^2} \int_S (d\vec{S}\cdot\vec{z}) \int_S (d\vec{S}\,'\cdot\vec{z}) \exp[-i(\vec{q})\cdot(\vec{r}-\vec{r}\,')]$$

Gauss theorem

$$\frac{d\sigma}{d\Omega} = \frac{N^2 b^2}{q_z^2} \int\int_{S_0} dx\, dy \int\int_{S_0} dx'\, dy' \exp\{-iq_z[z(x,y)-z(x',y')]\} \exp\{-i[q_x(x-x')+q_y(y-y')]\}$$

From assumption that $z(x,y)-z(x',y')$ is a function of relative position $(x-x', y-y')$ and it has Gaussian distribution centered zero,

X-ray scattering cross section and surface roughness

$$\langle \exp(iqx) \rangle = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} \exp(-x^2/2\sigma^2)\exp(iqx)dx = \exp(-q^2\sigma^2/2)$$

$$\langle x^2 \rangle = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} \exp(-x^2/2\sigma^2)x^2 dx = \sigma^2$$

$$\Rightarrow \langle \exp(iqx) \rangle = \exp(-q^2 \langle x^2 \rangle / 2)$$

Bakker-Hausdorff theorem

$$\frac{d\sigma}{d\Omega} = \frac{N^2 b^2}{q_z^2} L_x L_y \int\int_{S_0} dX\, dY\, e^{-q_z^2 g(X,Y)/2} e^{-i(q_x X + q_y Y)} .$$

(In rectangular illumination area)

X-ray scattering cross section and surface roughness

$$g(X,Y) = 2\langle z^2\rangle - 2\langle z(X,Y)z(0,0)\rangle \ .$$

$$C(X,Y) \equiv \langle z(X,Y)z(0,0)\rangle = \sigma^2 - \tfrac{1}{2}g(X,Y)$$

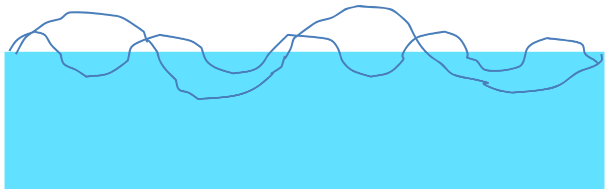
$S(\vec{q}) = \dfrac{1}{Nb^2 L_x L_y}\left(\dfrac{d\sigma}{d\Omega}\right)$ is then,

$$S(\mathbf{q}) = \frac{1}{q_z^2} e^{-q_z^2\sigma^2} \int\int_{S_0} dX\, dY\, e^{q_z^2 C(X,Y)} e^{-i(q_x X + q_y Y)} \ .$$

$$S_{\mathrm{spec}}(\mathbf{q}) = \frac{4\pi^2}{q_z^2} e^{-q_z^2\sigma^2} \delta(q_x)\delta(q_y)$$

$$S_{\mathrm{diff}}(q) = \frac{2\pi}{q_z^2} e^{-q_z^2\sigma^2} \int_0^\infty dR\, R F(q_z,R) J_0(q_r R) \qquad F(q_z,R) \equiv e^{q_z^2 C(X,Y)} - 1$$

Capillary wave and roughness



in liquid surfaces, many harmonic waves called 'capillary wave' exist and they give surface roughness

$$\zeta(\vec{S}) = \sum_{q} \alpha(\vec{q}) \exp(i\,\vec{q}\cdot\vec{S})$$

So, surface energy due to height variation is,

$$w = \iint_A dS\left[\int_0^{\zeta(\vec{S})} dz(\rho^l - \rho^g)mgz + \gamma\left(1 + \left(\frac{d\zeta(\vec{S})}{dx}\right)^2 + \left(\frac{d\zeta(\vec{S})}{dy}\right)^2\right)^{1/2}\right]$$

$$\simeq \gamma A + \frac{1}{2}\sum_{q_1}\sum_{q_2} \alpha(q_1)\alpha(q_2)\iint_A dS \exp(i(\vec{q}_1 + \vec{q}_2)\cdot\vec{S})[(\rho^l - \rho^g)mgz - \gamma\,\vec{q}_1\cdot\vec{q}_2]$$

$$= \gamma A\{1 + \frac{1}{2}\sum_{q>0} \alpha(q)\alpha(-q)[2a^{-2} + q^2],\ a^2 = 2\gamma / mg(\rho^l - \rho^g)$$

Capillary wave and roughness

$$w = \gamma A\{1 + \frac{1}{2}\sum_{q>0} \alpha(q)\alpha(-q)[2a^{-2} + q^2],\ a^2 = 2\gamma / mg(\rho^l - \rho^g)$$

Probability of a given amplitude , $\alpha(q)$ is proportional to

Boltzmann factor $\exp(-w/kT)$

$$\Rightarrow \langle \zeta^2 \rangle = \sum_{q>0} \langle \alpha(q)\alpha(-q) \rangle = \frac{kT}{\gamma A} \sum_{q>0} (2a^{-2} + q^2)^{-1} = \frac{kT}{4\pi\gamma} \ln[\frac{1 + 2(\pi a / l)^2}{1 + 2(\pi a / L)^2}]$$

$$, q_{\min} = 2\pi / L \text{ and } q_{\max} = 2\pi / l$$

$$\Rightarrow \boxed{\langle \zeta^2 \rangle = \frac{kT}{4\pi\gamma} \ln[\frac{1 + 2(\pi a / l)^2}{1 + 2(\pi a / L)^2}] \simeq \frac{kT}{2\pi\gamma} \ln[q_{\max} / q_{\min}] = \sigma^2{}_{cap}}$$

Capillary wave and roughness

$$g(R) = A + B\ln(R) \quad (R \text{ in Å}).$$?

$$S(q) = \frac{2\pi}{q_z^2} e^{-q_z^2 A/2} \int_0^\infty dR\, R R^{-Bq_z^2/2} J_0(q_r R)$$

$$= \frac{2\pi}{q_z^2} e^{-q_z^2 A/2} \frac{2^{1-\eta}}{q_r^{2-\eta}} \frac{\Gamma(1-\eta/2)}{\Gamma(\eta/2)},$$ where, $\eta = (kT/2\pi\gamma)q_z^2$

If temperature, surface tension, and q_{xy} are given, intensity of scattered x-ray can be calculated.

Experiment

X-ray experiments were carried out using the Harvard/BNL liquid surface spectrometer [27] on Beamline X22B at the National Synchrotron Light Source ($\lambda = 1.55$ Å). For both XR and OSDX, the center of the detector (NaI scintillator) slits lies in the incident plane ($2\theta = 0$). For XR, the reflected intensity at $\beta = \alpha$ (or $q_{xy} = 0$) is measured as a function of $q_z = (4\pi/\lambda)\sin(\alpha)$, while OSDX was measured as a function of β at fixed α. For both measurements the background was eliminated through subtraction of intensities from identical scans taken with 2θ offsets of $\pm 0.3°$. The results were normalized to the incident intensity and analyzed in terms of the theoretical predictions for the difference $\Delta I/I_0 \equiv \{I(2\theta = 0) - (1/2)[I(+0.3°) + I(-0.3°)]\}/I_0$ [20]. The rectangular detector slits, located $L = 621$ mm from the sample center, of (height H) $\times$ (width W) give an angular resolution of $\delta\beta = H/L$ and $\delta(2\theta) = W/L$. The slit sizes in mm were $(H, W) = (2.5, 3.0)$ for XR, (1.1, 3.0) for β scans on water, and (1.0, 3.0) for β scans on PBLG films.

Experimental data

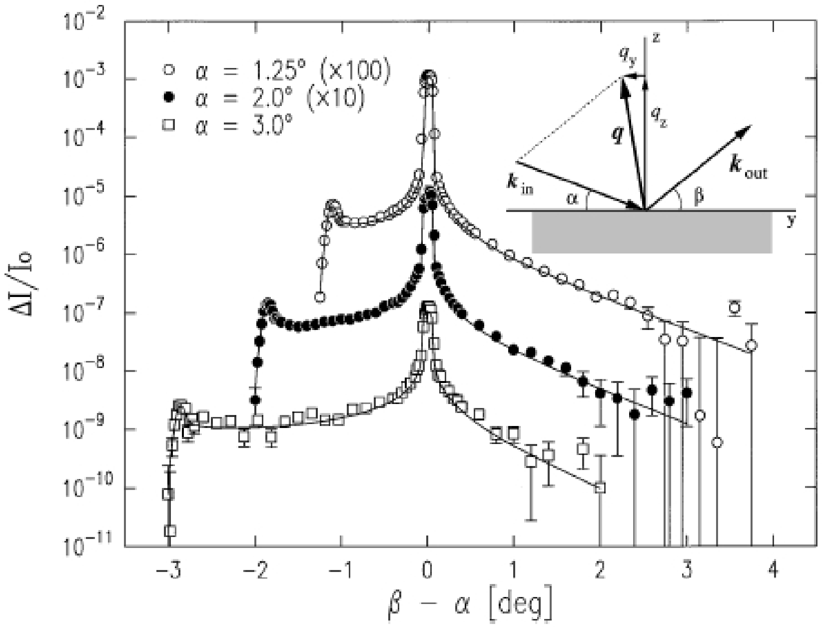


FIG. 1. Measured normalized intensity $\Delta I/I_0$ as a function of $\beta - \alpha$ at fixed α for a bare water surface. The solid lines are theoretically expected curves. The inset is a schematic for the incident-plane ($2\theta = 0$) scattering geometry used in the XR and OSDX.

$$q_z = \frac{2\pi}{\lambda}[\sin(\alpha) + \sin(\beta)], \text{ and}$$

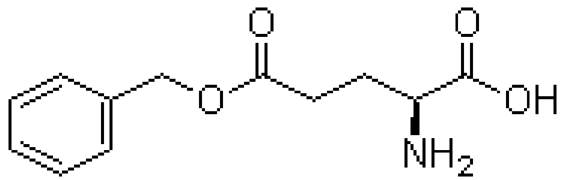
$$q_{xy} = \frac{2\pi}{\lambda}[\cos^2(\alpha) + \cos^2(\beta) - 2\cos(2\theta)\cos(\alpha)\cos(\beta)]$$

$$\frac{1}{A_0}\left(\frac{d\sigma}{d\Omega}\right)_0 = \frac{N}{q_z^2}|\Phi_0(q_z)|^2 \frac{2\pi\eta}{q_{xy}^2}\left(\frac{q_{xy}}{q_{\max}}\right)^\eta, \quad (1)$$

Fitting with model well matched with experimental data

Experimental data

Poly benzyl-L-glutamate monolayer / water interface



benzyl-L-glutamate

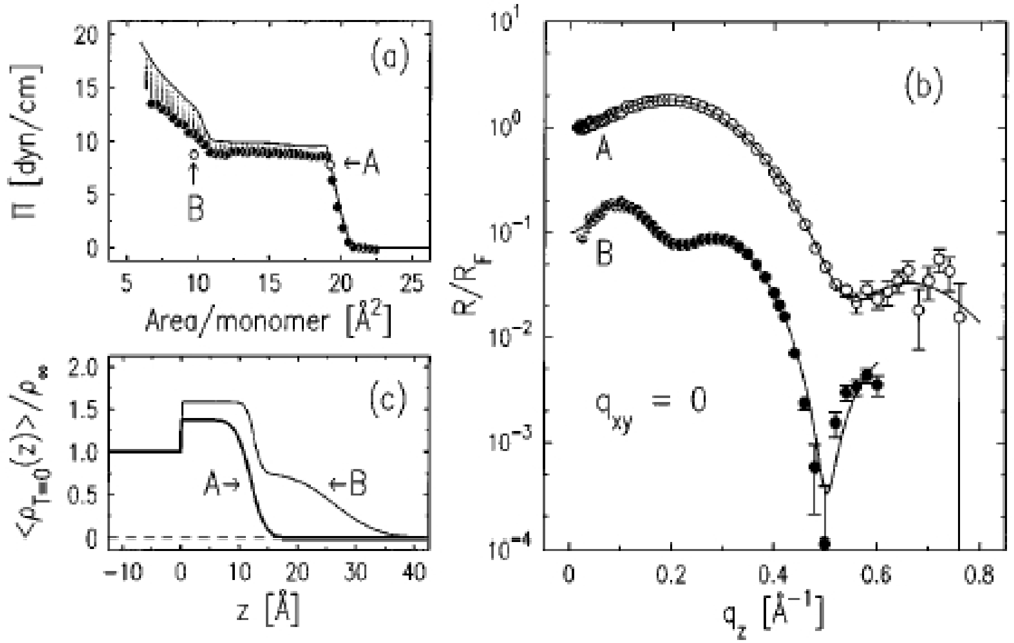


FIG. 2. (a) Π-A isotherms for PBLG films at $T = 23\,^\circ\mathrm{C}$, showing a continuous scan (—) and a relaxation scan (●), in which the film is relaxed at given A until $\Delta\Pi$ over 5 min is <0.05 dyn/cm. (b) Normalized reflectivity R/R_F at points A and B in (a). Fits (—) are based on Eq. (1), detector resolutions, and average local electron densities in (c), where $q_{\max} = 0.5$ Å^{-1} is assumed.

Forming bilayer was confirmed by p-A isotherm and x-ray reflectivity

Experimental data

OSDX data about PBLG monolayer /water interface can be fitted with model but collapsed layer shows big difference. (factor of 2)

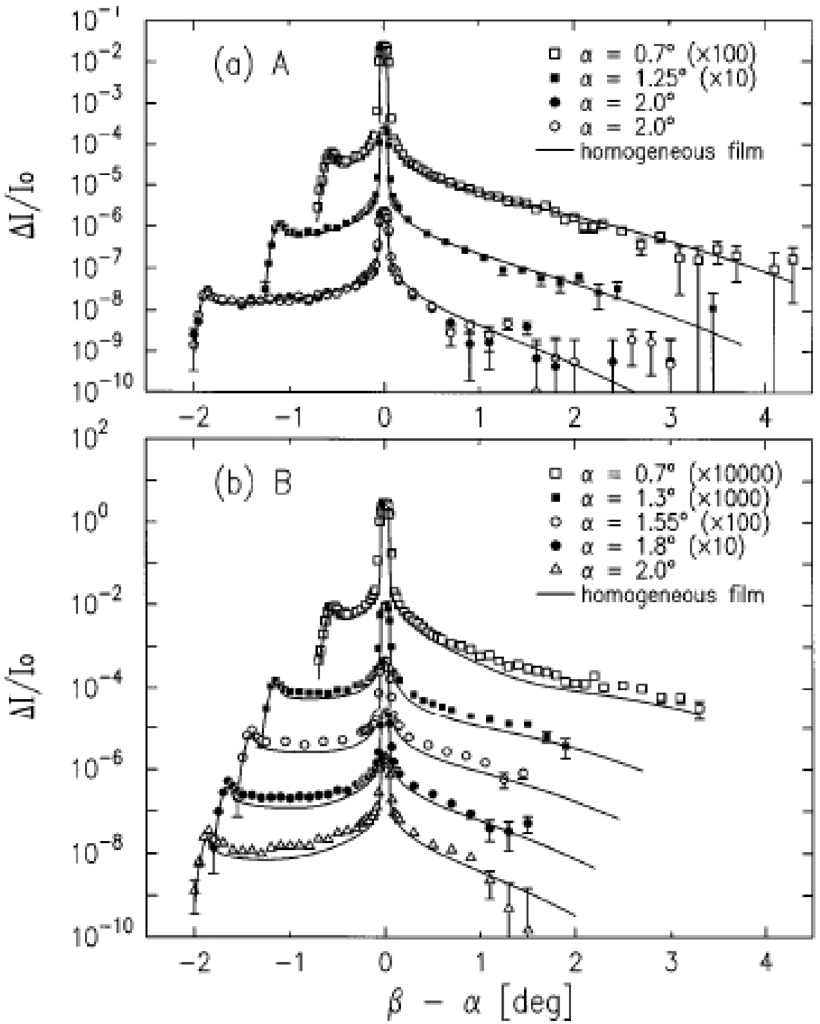


FIG. 3. Measured $\Delta I/I_0$ vs $\beta - \alpha$ for PBLG (a) monolayer at A and (b) bilayer at B in Fig. 2(a). The solid curves (—) theoretically expected for *homogeneous* PBLG films are based on Eq. (1), detector resolutions, and $\langle \rho_{T=0}(z) \rangle$ in Fig. 2(c).

Experimental data

$$\frac{1}{A_0}\left(\frac{d\sigma}{d\Omega}\right)_1 \cong \frac{N\phi_2^2 e^{-\sigma_2^2 q_z^2}}{2\pi}\int_{q'_{xy}<q_{\max}} d^2\mathbf{q}'_{xy} \times \frac{\eta}{q'^2_{xy}}\left(\frac{q'_{xy}}{q_{\max}}\right)^{\eta} C_2(\mathbf{q}_{xy}-\mathbf{q}'_{xy}), \qquad (2)$$

Height fluctuation in second layer was considered

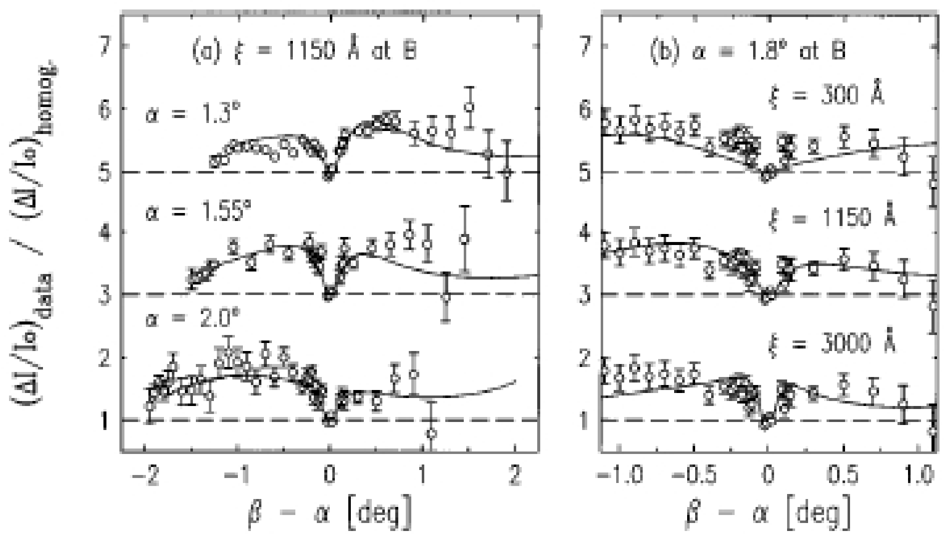


FIG. 4. The ratio of measured $\Delta I/I_0$ to the homogeneous contribution in Fig. 3(b) for the PBLG bilayer at B. The fits (—) in (a) are based on an inhomogeneous model Eq. (2) with roughness $\sigma_2 = 2.2$ Å and correlation length $\xi = 1150$ Å for the second layer/gas interfacial height fluctuations. The solid curves in (b) correspond to the $\Delta I/I_0$ ratio calculated for three different values of ξ.

Conclusion

- capillary wave contribution to surface roughness can be considered and separated from data

- Unlike pure water and PBLG monolayer cases, PBLG bilayer shows big difference from fitting.

- And, by using additional non-capillary fluctuation model data was fitted with various coherence length