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GLANCING INCIDENCE NEUTRON SCATTERING

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Résumé - On examine des comportements singuliers de la réflectivité au voisinage de
la réflexion totale, pour des profils de concentration lentement décroissant. Les
contraintes expérimentales sont discutées.

Abstract - We discuss an approach to the neutron glancing incidence experiment
by polymer interfaces: Singular properties at total reflection edge are
confronted to experimental possibilities

1. Introduction : Different approaches to the reflectivity experiment

Specular reflection of a neutron beam occurs when the beam hits a flat interface,
materializing a change \( \Delta n \) of refractive index. The difference \( \Delta n \) between vacuum and
condensed matter being very small (\( \Delta n \approx 10^{-6} \)), the reflected beam intensity is sizeable
only at grazing angles of incidence. However, one advantage of experiments with neutrons,
is the relative ease with which \( \Delta n \) can be modulated when the interface compounds are
organic (deuteration).

The reflectivity experiment allows to investigate the structure of the interface.
We call \( z \) the distance to the interface. Traditionally two types of analysis are made.

a) Determination of a systematic index variation \( \Delta n(z) \) in the direction orthogonal to the
surface.

The function \( \Delta n(z) \) is for instance associated with a concentration profile in a binary
solution, one of the component being preferentially adsorbed at the interface. This is the
situation /1/ which we discuss in sections 2 and 3. We shall be interested in the
correspondence between \( \Delta n(z) \) and the reflectivity function \( R(k \sin \theta) \), where \( k \) is the
incident wave vector and \( \theta \) the angle of incidence. In particular, we consider the total
reflection edge $k \sin \theta \rightarrow k \sin \theta_c$, at which the radiation penetration diverges.

b) Determination of the surface roughness

The liquid air interface is subject to capillary wave fluctuations and to liquid-vapour roughness. The effect of such fluctuations on the reflectivity curve $R(k)$ can be approximated /2, 3/ by an attenuation factor

$$\frac{R(k)}{R_F(k)} = \exp - \frac{k^2 A}{2}$$

where $A$ is a characteristic square amplitude and $R_F(k)$ is the Fresnel reflectivity function. The quantity $A$ is given in terms of capillary length and cut off for the capillary wave. In absence of a cut off, a detailed calculation /2/ shows that $R(k)$, in the asymptotic range $k/k_c \gg 1$, deviates essentially from the Fresnel law

$$R_F(k) = \frac{k_c^4}{4k^4}$$

When the liquid is a polymer solution, there is an added roughness at the air interface caused by the persistence length of the polymer chain. Such effects have recently been observed by E.M. Lee, E.A. Simister and R. Thomas /4/.

Comparison between (1) and (2) indicates that roughness effects are relatively more important at large wave vectors $k$.

c) There are other approaches in the reflectivity experiment aimed at a better resolution of the detailed structure: study of the diffuse scattering away from specular reflection, polarization analysis, etc. We also mention the possibility to introduce labelling patterns in the sample, in order to study specifically the contribution of partial structure factors to the reflectivity.

d) From a given $\Delta n(z)$ function it is possible to derive a reflectivity function $R(k)$, for instance by computer simulation. The reverse problem is solved in some cases, when the Born approximation /2/ or the distorted wave approximation /2/ are valid. However, their validity breaks down near total reflection ($k/k_c = 1$). Dietrich and Schack /6/ have pointed out the existence of singular behaviours of the reflectivity function at total reflection edge. These singularities directly reveal the nature of the asymptotic behaviour of the index increment function, $\Delta n(z)$. Experimental investigation of the reflection edge ($k/k_c \gg 1$) is therefore of great interest. Naturally, the cross over to the evanescent wave situation ($k/k_c \ll 1$) should also be considered /7/.

There are however difficulties, mostly related to the fact that the experimental situation is not as simple as the theoretician would like.

2. Concentration profiles of polymer solutions

Polymer solutions near an interface have interesting structure properties which have been studied /9, 10/ since the years 1980. We give here some results of interest.
a) In the case of a strongly absorbing interface, if the bulk concentration is negligible, the concentration of infinitely long polymers decreases away from the surface like $z^{-d-1/\nu}$.

b) A universal behaviour /11/ is predicted in the limit of dilute solutions in a good solvent. The polymer concentration $C(z)$ writes (in Å$^3$ units):

$$C(z) = A(0.476/R_0^2)^{1/2}z^{-d-1/\nu}$$

where $A \approx 2/\pi^2$ and where $R_0^2$ is the square radius of gyration.

c) The finite size of polymer chains imply a cut off $z_{\text{max}}$ in the concentration profile. This cut off plays an essential part in the interpretation of experiments /8/.

All these facts are now well known. Our aim is to report on the correspondence between the asymptotic behaviour of the (infinitely long) polymer concentration profiles and the singular behaviour of the reflectivity at total reflection edge. The problem is of interest by itself and in relation to the one dimensional Schrödinger equation.

3. Singularities at total reflection edge

The reflectivity $R$ of a radiation is derived from the "Schrödinger" equation

$$\left(\frac{\partial^2}{\partial z^2} + k^2 \sin^2 \theta - V(z)\right) \psi(z) = 0$$

where $z=0$ defines the interface, $\theta$ is the angle of incidence for the incoming wave of vector $k$.

The radiation interaction potential $V(z)$ is related to the index increment $\Delta n(z)$

$$V(z) = \frac{\Delta n^2}{k^2}$$

and to the concentration profile. In the limit $z \to \infty$, the solution $\psi(z)$ of (4) represents an outgoing wave. The reflectivity $R$ is then given by:

$$R(k \sin \theta) = \left| \frac{k \sin \theta - \psi'(0) \frac{i}{\psi(0)} \right|^2$$

Let us now discuss equation (4), considering the monomer volume fraction

$$\psi(z) = N \nu_p C(z)$$

where $N$ is the number, $\nu_p$ the partial volume of a monomer. Then
where $b_i$ are the scattering amplitudes associated respectively to a monomer (i-p) and to a solvent molecule (i-s).

a) Factorization

We assume $V(z)$ to be continuous and different from zero, for $z > 0$. It is then useful to rescale the energy $k^2 \sin^2 \theta$ such as

$$k^2 = k^2 \sin^2 \theta - \lim_{z \to 0^+} V(z) \quad (8)$$

The quantity

$$\Delta V(z) = V(z) - \lim_{z \to 0^+} V(z)$$

factorizes into

$$\Delta V(z) = 4\pi \gamma \left( \frac{b_s}{v_p} \right) \Delta \Phi(z) \quad (9)$$

where

$$\Delta \Phi(z) = \Phi(z) - \lim_{z \to 0^+} \Phi(z)$$

and

$$\gamma = \left( \frac{b_p}{v_p} \right) \left( \frac{v_s}{b_s} \right) - 1 \quad (10)$$

Equation (4) writes

$$\left( \frac{\partial^2}{\partial z^2} + k^2 - \Delta V(z) \right) \psi(z) = 0 \quad (11)$$

The quantity $\gamma$ can be modulated by deuteration of the solvent or the solute. This is the important experimental fact /1/. If the polymer is deuterated, $\gamma > 0$ and the adsorbed polymer layer acts as a barrier with respect to the neutron beam. On the contrary, if the solvent is deuterated, $\gamma < 0$ and the layer acts as a well.

b) Singularities

The reflectivity function $R(K)$ displays singular behaviours in the vicinity of

$$k^2 \sin^2 \theta |_c = \lim_{z \to 0^+} V(z) \quad (12)$$

defining the onset on total reflection, $R(0) = 1$. Consider the case of the infinitely long polymer chain adsorbed at an interface. Combining (3), (6) and (9), we have

$$\Delta V(z) = 4\pi \gamma b_s \left( \frac{v_p}{v_s} \right) \left( \frac{0.476}{R_c^2} \right)^{1/2} / z^{\mu} \quad (13)$$
where \( \mu = d \cdot 1/v - 1.3 \) for good solutions.

Typically, for polydimethyl-siloxane in toluene,

\[
\Delta V(z) \approx \gamma \times 2.5 \times 10^{-5}/z^\mu
\]

where \( z \) is written in Å units.

There are two situations of interest, according to the sign of the parameter \( \gamma \).

1) \( \gamma < 0 \) : the well

The behaviour of the reflectivity function is singular when the interaction potential decreases slowly enough, i.e. \( \mu < 2 \) in (13). O. Guiselin has proved /12/ that, in such conditions, \( R(K) \) is discontinuous at \( K = 0 \) (see Fig.1). This fact can also be inferred /13/ from (5) and from the WKB approximation to the solution of equation (11)

\[
\psi(z) = \left( K^2 + |\Delta V(z)| \right)^{1/4} \exp \int_0^z dy \left( K^2 + |\Delta V(y)| \right)^{1/2}
\]

Fig.1. Case of potential well. Calculated discontinuity of the reflectivity curve and preliminary experimental results obtained with PDMS in deuterated toluene.

\[
\gamma = \frac{K}{k_c \sin \theta} \cdot \sqrt{k^2/k_c^2 - 1} \text{(see (12) for the definition of } k_c) \]

- result of a computer simulation /14/, eq.(14) and (10) with \( \gamma = -1 \) and \( z_0 = 4 \text{ Å} \).
- experimental result

--- Fresnel reflectivity : \( R(\gamma) = \frac{\sqrt{Y^2 + 1} - Y}{\sqrt{Y^2 + 1} + Y} \)

--- Schematic representation of the reflectivity curve associated with \( \Phi(z) = \frac{A}{(z + z_0)^2} \)

The experimental problem is to reduce cut off and resolution effects. This is achieved by testing solutions with longer chains, with improved optical resolution.
Namely, the quantity \( \lim_{K \to 0} \left[ \text{Im} \frac{\psi'(0)}{\psi(0)} \right] \) does not vanish, and this causes the discontinuity in \( R(0) \).

This behaviour is remarkable, because it occurs only if the potential \( ∆V(z) \) extends to infinity and decreases slower than \( z^{-2} \). In all other situations, \( R(K) \) is continuous at \( K=0 \). For instance, if \( z > z_{\text{max}} \) the potential \( ∆V(z) \) is zero, the solution \( \psi(z) \) \((z > z_{\text{max}})\) to equation (11) is simply a plane wave. One can then easily show:

\[
\lim_{K \to 0} \left[ \text{Im} \frac{\psi'(0)}{\psi(0)} \right] = 0
\]

and as a result, \( \lim_{K \to 0} R(K) = 1 \).

For this, we write: \( \Psi(K,z) = \Psi_1(K,z) + iK\Psi_2(K,z) \) where \( \Psi_1, \Psi_2 \) are two solutions such that:

\[
\Psi_1(K,z_{\text{max}}) = 1, \quad \Psi_1(K,z_{\text{max}}) = 0
\]

and

\[
\Psi_2(K,z_{\text{max}}) = 0, \quad \Psi_2(K,z_{\text{max}}) = 1
\]

When \( K \to 0, \Psi_1(K,z) \) and \( \Psi_2(K,z) \) have well defined limits. The quantity \( \Psi(0,z) = \Psi_1(0,z) \) is real, and this holds true for \( \Psi'(0,z)/\Psi(0,z) \).

2) \( γ > 0 \): the barrier

The transmission

\[ T(K) = 1 - R(K) \]

evaluated \( /6/ \) in the WKB approximation gives

\[
\lim_{K \to 0} T(K) = \exp \left( 2i(\mu) B^{1/\mu} K^{2(1/2 - 1/\mu)} \right)
\]

where (see (14))

\[
B = γ \times 2.5 \times 10^{-5} \, \text{Å}^{\mu - 2}
\]

and

\[ I(1.3) = 1.2 \]

For such small values of \( B \), the argument of (15) is of the order of .1, if \( K \approx K_0, 10^{-7} \text{Å}^{-1} \). Practically, the interval \((0, K_0)\) can then only be explored with a long wavelength radiation, as for instance in light scattering experiments. Reflectivities measured with a neutron beam gave \( /1/ \) for \( γ > 0 \) an unexpected result, indicating the existence of a deep but rather dilute polymer layer \( /15/ \).

c) Cut off and resolution effects

In a real experiment, the polymer chains are finite and the radiation interaction potential \( ∆V(z) \) displays a cut off at about \( z_{\text{max}} \approx R_0 \). Existence of a cut-off in \( ∆V(z) \) removes the singular behaviour described above: \( R(K) \) has in fact a dependence similar to the Fresnel law (A detailed calculation of \( R(K,z_{\text{max}}) \) was recently made by A. Johner \( /16/ \)). However, trends towards the singular behaviour should be observed, when the experiment is made with longer and longer chains.
Another difficulty is introduced by the finite resolution of the reflectometer, which also has the effect to wash out the singularities.

d) Detailed investigations

Labelling the polymer chains in form of pseudo triblocks

\[ \text{DHD} \]

where D indicates deuterated, H non deuterated, allows to specifically observe the contribution of tails (or loops and trains) to the concentration profile. Consider namely the expression of the radiation interaction potential

\[ V(z) = 4\pi \left( b_s + (b_{P_0} - b_s) \varphi_0(z) + (b_{P_H} - b_s) \varphi_H(z) \right) \]  

(17)

Matching the labelled scattering length \( b_{P_0} \) or unlabelled scattering length \( b_{P_H} \) with the solvent scattering length \( b_s \), allows to focus either on tails or on loops and trains.

4. Concluding remarks

The vicinity \( K > 0 \) of the reflectivity curve contains direct evidence of the asymptotic behaviour of the interaction potential. If cut off and resolution effects are mastered, the experiment associated with the potential well and the reflectivity discontinuity should give direct evidence of the slow decay predicted for the concentration profile of adsorbed polymers. Another possibility is to consider the total reflection edge from the side of evanescent waves \( (K^2 < 0) \). The penetration depth

\[ \Lambda = \frac{1}{k} \sqrt{\frac{1}{\cos^2 \theta - \lim_{z \to \infty} V(z)}} \]  

(18)

diverges as the grazing angle \( \theta \) of the incident beam tends to the critical value \( \theta_c \) (see (12)).

Here, the appropriate experiment /7/ consists in using evanescent light waves to excite fluorescent groups attached to polymer chains. The measured quantity is the fluorescent intensity

\[ I(p) \sim \int_0^\infty dz \ e^{-pz} \Delta \varphi(z) \]  

(19)

where \( \frac{1}{p} = \Lambda \)

and where \( \Delta \varphi(z) \) is the concentration profile.

Singularities associated with the profile \( \Delta \varphi(z) \) appear here in the limit \( p = 0 \). In this case /17/

\[ I(p) \propto p^{2-1/\nu} e^{z_0 p} \Gamma(1/\nu - 2, z_0 p) \]  

(20)

Experimental results /7/ agree qualitatively with this behaviour, in the limit \( p \to 0 \).
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