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Oscillations in the reflectivity of a diffuse polymer layer. An analogy with the Ramsauer Townsend effect

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Abstract. — The reflectivity of a diffuse, finite layer of adsorbed polymers is examined. If the bulk solution is semi-dilute, the screening structure generates oscillations in the reflectivity function in the vicinity of total reflexion. The deviation with respect to the Fresnel law increases with the depth of the layer. In the limit of infinite depth the reflectivity function displays the discontinuity first predicted by Schack (Thesis, Munich 1986) and first observed by Guiselin (*Europhys. Lett.* **17** (1992) 57). In our approach, we make use of earlier results obtained by Morse and Feshbach in their interpretation of the Ramsauer-Townsend effect of slow electrons scattered by heavy atoms.

1. Introduction.

The reflectivity related to slowly varying concentration profiles has been the object of several theoretical predictions [1-4] and physical observations [5, 6]. As noted by Dietrich and Schack [1], the reflectivity function behaves in a singular manner, if the concentration profile of a binary system extends to infinity less rapidly than the inverse square power law of the distance. For instance, Schack [2] showed that an attractive interaction potential of the Coulomb type between the incoming radiation and the interface layer generates a discontinuity at total reflection edge. Guiselin [4] generalized this result to any power law with an exponent $\mu < 2$.

In reality a concentration profile is always finite, even though it may extend very far. This limitation is obvious. It corresponds to the fact that polymer chains are finite in the case of an adsorption layer, or that the temperature resolution in a demixion profile is finite. Under such circumstances the reflectivity function at total reflection edge is always of the Fresnel type. Thus the real situation is incompatible with the above mentioned theoretical prediction.

Of course, if the range of the profile is greater than a characteristic length [7] about 1μ , then the reflectivity function is expected to display a pseudo discontinuity which would be difficult to distinguish from a true discontinuity because of finite angular resolution effects. This is indeed what has been observed [5] in a neutron reflectivity experiment.

A different approach is to take explicitly into account the finite range of the concentration profile and to calculate the reflectivity function. The aim of the paper is to examine the finite size effect as such, and we show that interesting phenomena can be predicted.

We are greatly helped by the fact that similar problems have been solved in atomic physics. We refer in particular to the Ramsauer-Townsend effect, which describes the scattering of slow electrons by heavy atoms. Morse and Feshbach [8] assumed the range of the Coulomb interaction between incoming electrons and nucleus to be finite, because of the screening by the atomic electron shell. The introduction of screening shifts the energy of the system from the continuum to the discrete spectrum. If the energy of the incoming electron is low enough, quasi-bound states appear which are responsible for :

- a) oscillations in the cross section, and
- b) a vanishing cross section in the limit of infinite range and zero energy.

In the case of the adsorbed polymers in equilibrium with a semidilute bulk solution, there is a screening effect concerning the concentration profile. This effect is similar to that described above, but it fits much better to reality. We shall therefore transpose the formalism used in the description of the Ramsauer-Townsend effect to the reflectivity problem of long adsorbed polymer chains.

It is understood that the concentration profile of the layer follows a power law with an exponent $\mu < 2$ and that the interaction between the incoming radiation and the layer is attractive. For the case of a neutron beam, Bouchaud *et al.* [9] noted that the sign of the interaction potential can be chosen arbitrarily in organic systems, using the deuterium labelling technique. An attractive potential is obtained by deuterating the solvent in the polymer solution, and this is the situation investigated in this paper.

2. Concentration profiles of polymer chains in the vicinity of a wall.

We consider a polymer solution close to an adsorbing wall. The polymer volume fraction $\phi_p(z)$ decreases as the distance z from the wall increases. De Gennes [10] determined the concentration profile by scaling the screening length $\xi(z)$ with the distance z to the wall. The result is

$$\phi_p(z) = Az^{-\mu}$$

where A is a constant and μ an index related to the excluded volume exponent ν ($\mu = \frac{\nu d - 1}{\nu}$).

There is a cut off at large distances of the order R and a cut off z_0 at distances of the order of an atomic size. Here we are interested in the effect of the cut off at large distance on the reflectivity, at total reflectivity edge.

Two characteristic situations occur according to the importance of the bulk volume fraction $\phi_b = \lim_{z \rightarrow \infty} \phi_p(z)$.

2.1 DILUTE POLYMER SOLUTION : $\phi_b \rightarrow 0$. — The cut off is related to the finite size R of the chains. We expect an exponential cut off

$$\phi_p(z) = \frac{A}{(z + z_0)^\mu} \quad z < R \quad (1)$$

$$\phi_p(z) = \frac{A}{(R + z_0)^\mu} \exp(-z/R) \quad R < z. \quad (2)$$

2.2 SEMIDILUTE SOLUTION WITH OVERLAP. — The volume fraction at which the coils begin to overlap in the bulk solution is ϕ_b^* . Here $\phi_b \geq \phi_b^*$, and as a consequence the polymer volume fraction becomes constant for $z > \xi_b = R(\phi_b/\phi_b^*)^{-1/\mu}$

$$\phi_p(z) = \frac{A}{(z + z_0)^\mu} \quad z < \xi_b \quad (3)$$

$$\phi_p(z) = \frac{A}{(\xi_b + z_0)^\mu} \quad \xi_b < z. \quad (4)$$

A monomer can approach the interface at a distance smaller than ξ_b only if it belongs to an adsorbed polymer chain. Similarly, an electron scattered by an isolated atom sees the charge of the nucleus only if it approaches the nucleus at a distance smaller than the electron shell radius.

Situation 2.2 illustrates the screening effect. We shall see that the reflectivity profiles at total reflection edge differ substantially in 2.1 and 2.2.

3. Interaction potential between incoming radiation and interface structure.

When a radiation of wavevector k falls on a flat surface at an angle θ , the stationary state of the collision process is given by the equation :

$$\frac{d^2\psi}{dz^2} + (k^2 \sin^2 \theta - V(z)) \psi = 0 \quad (5)$$

where for a binary incompressible system made of polymers (p) and solvent (s)

$$\begin{aligned} V(z) &= 4 \pi \left[\frac{b_p}{v_p} \phi_p(z) + \frac{b_s}{v_p} (1 - \phi_p(z)) \right] \\ &= 4 \pi \frac{b_s}{v_s} [1 + \gamma \phi_p(z)] \end{aligned} \quad (6)$$

b is the (monomer) collision amplitude and v the molecular volume. Here

$$\gamma = \frac{b_p}{v_p} \frac{v_s}{b_s} - 1 \quad (7)$$

is a *negative* quantity, because we choose a deuterated solvent and a non-deuterated polymer. As a result $V(z)$ is an increasing function of z . It has the appearance of a truncated well, and this is the origin of several interesting phenomena at total reflection edge. Another way of writing (5) consists in introducing the refraction index

$$n^2(z) = 1 - V(z)/k^2. \quad (8)$$

Then

$$\frac{d^2\psi}{dz^2} + k^2 n^2(z) \psi - k^2 \cos^2 \theta \psi = 0 \quad (9)$$

is the equation for the stationary state of electromagnetic s waves. Explicit expressions for $V(z)$ in (6) are obtained by inserting equations (1) to (4) of the volume fractions $\phi_p(z)$. We require here that the index of the adsorbed molecules be greater than the index of the solvent.

4. Standard form.

In order to study reflectivity at total reflection edge, it is useful to introduce the following decomposition

$$V(z) = \Delta V(z) + V_{\infty} \quad (10)$$

where

$$V_{\infty} = \lim_{z \rightarrow \infty} V(z). \quad (11)$$

We write :

$$\ell^{\mu-2} = 4 \pi \frac{b_s}{v_s} |\gamma| A > 0. \quad (12)$$

In situation 2.2.

$$V_{\infty} = 4 \pi \frac{b_s}{v_s} - \frac{\ell^{\mu-2}}{(\xi_b + z_0)^{\mu}} = V_{\infty}^I + V_{\infty}^{II} \quad (13)$$

and

$$\Delta V(z) = -\ell^{\mu-2} \left[\frac{1}{(z + z_0)^{\mu}} - \frac{1}{(\xi_b + z_0)^{\mu}} \right], \quad z < \xi_b \quad (14a)$$

$$= 0 \quad \xi_b < z. \quad (14b)$$

The interaction is a screened interaction.

Introducing the « internal » wave vector

$$Q^2 = [k^2 \sin^2 \theta - V_{\infty}] \quad (15)$$

equation (5) is written explicitly as

$$d^2 \psi / dz^2 + [Q^2 + V_{\infty}] \psi = 0 \quad z < 0 \quad (16a)$$

$$d^2 \psi / dz^2 + Q^2 \psi - \Delta V(z) \psi = 0 \quad 0 < z < \xi_b \quad (16b)$$

$$d^2 \psi / dz^2 + Q^2 \psi = 0 \quad \xi_b < z. \quad (16c)$$

Expression (16) is the standard form for the stationary state equations. We are interested in the vicinity of $Q = 0$, which is the total reflection edge.

5. The Morse and Feshbach approach.

In the bulk solution ($z > \xi_b$), the « energy » $k^2 \sin^2 \theta$ of the incident radiation is compared to V_{∞} . this leads to the definition of the internal wave vector Q (15). In the interval $0 \leq z \leq \xi_b$, the referential can be chosen differently. As a matter of fact, Morse and Feshbach noticed, in their analysis of the scattering of an electron by a heavy atom, that the constant term in the perturbation $\Delta V(z)$ (14a) should be subtracted from V_{∞} . In dimensionless units this term is written

$$\beta^2 = \frac{\ell^{\mu-2} \xi_b^2}{(\xi_b + z_0)^{\mu}} \quad (17)$$

and we set

$$(K\xi_b)^2 = \beta^2 - (Q\xi_b)^2 = \left(4\pi \frac{b_s}{v_s} - k^2 \sin^2 \theta\right) \xi_b^2. \quad (18)$$

In case 2.2 of semi-dilute bulk solutions this quantity changes sign according to the value of the « energy » $k^2 \sin^2 \theta$. We note that in case 2.1 of dilute solutions, $K^2 = -Q^2$, and is always negative.

Then, from (16b)

$$\frac{d^2\psi}{dz^2} - K^2 \psi + \frac{\beta^2(1 + z_0/\xi_b)^\mu \xi_b^{\mu-2}}{(z + z_0)^\mu} \psi = 0 \quad 0 < z < \xi_b. \quad (19)$$

For $K^2 > 0$, the solution of equation (19) corresponds to the stationary state of radiation trapped in a potential well. In this situation « quasi » bound states are expected and these will cause reflectivity minima. However, because the perturbation $\Delta V(z)$ is a slowly increasing function, the spectrum of states is continuous in the limit $\xi_b \rightarrow \infty$, and this yields another characteristic behaviour of the reflectivity function.

In this paper, we look for analytical solutions to this problem. They can be obtained in some particular cases, such as for $\mu = 1$ which corresponds to polymer solution in Θ conditions.

We introduce dimensionless variables

$$Y = 2K\xi_b \left(\frac{z}{\xi_b} + \frac{z_0}{\xi_b} \right) \quad (20)$$

$$\mathcal{K}(\mu) = \beta^2 \frac{1 + (z_0/\xi_b)^\mu}{(2K\xi_b)^{2-\mu}} \quad (21)$$

and we set $\mathcal{K}(1) = \mathcal{K}$.

Equation (19) is written

$$\frac{d^2\psi}{dY^2} - \frac{\psi}{4} + \frac{\mathcal{K}}{Y} \psi = 0. \quad (22)$$

Solutions are the Whittaker functions $M_{\mathcal{K}, 1/2}(Y)$ and $W_{\mathcal{K}, 1/2}(Y)$. The function ψ is a combination of such functions, the weights are determined by the boundary conditions.

6. Reflectivity functions for neutrons and electromagnetic (s waves).

The reflectance for neutrons and electromagnetic s waves is written [11]

$$r_s = \frac{1 - W_s}{1 + W_s} = r_s[\beta, Q\xi_b] \quad (23)$$

where

$$W_s = \frac{1}{ik \sin \theta} \frac{\psi(z=0)}{\psi'(z=0)} \quad \text{and } \psi(z) \text{ is solution of (22).}$$

The reflectivity is

$$R_s = |r_s|^2 = R_s[\beta, Q\xi_b]. \quad (24)$$

The transmission is

$$T_s = 1 - R_s. \quad (25)$$

Analytical calculations of T_s are displayed in figures 1 and 2.

7. Discussion.

7.1 EXISTENCE OF RIDGES. — We have plotted the transmission $T_s[\beta, Q\xi_b]$ against the reduced interaction β and the reduced wavevector $Q\xi_b$, for two values of the parameters (ℓ^{-1}, V_∞^1) (Figs. 1a, 1b). The transmission displays a characteristic oscillatory structure in the domain $\beta > \text{veo}$. We observe that ℓ^{-1} and V_∞^1 only modify the magnitude of the oscillations. In this manner we check that the numbers β and $Q\xi_b$ are the good parameters. Each maximum in the transmission corresponds to a quasi bound state of the potential well (Eq. (22)). The periodicity is given by $\beta_n = 0.6 n \pi$ ($n = 1, 2, \dots$).

In the domain $\beta < Q\xi_b$, the quantity K^2 in equation (19) is negative and no bound state can occur. Indeed, no oscillations are seen in this domain (Fig. 1b). It is also of interest to note that the condition $\beta_1 = 0.6 \pi$ corresponds to the Bohr Sommerfeld quantization rule

$$\int_0^{z_1} dz \, 4 \pi \left[\frac{b_s}{v_s} |\gamma| \Delta\phi(z) \right]^{1/2} = \frac{3}{4}$$

from which we derive $(z_1 \sim \xi_b)_1$, the length at which the first resonance occurs [6].

The ridges seen in figures 1a, 1b have an intrinsic width. This width can be related to a life time of the incoming particle in the well. For this, we consider the states corresponding to the ridges as bound, but non-stationary.

Along the reduced energy axis, the width is $\Delta\beta = 0.2$ when we take $\ell^{-1} = 5 \times 10^{-3} \text{ \AA}$, $V_\infty^1 = 10^{-2} \text{ \AA}^{-2}$. With $\xi_b = 10^4 \text{ \AA}$, the wavevector width is $\Delta k = 2 \times 10^{-5} \text{ \AA}^{-1}$. The lifetime $\tau = \frac{2m}{(\Delta k)^2 \hbar}$ is then 10^{-4} s . Smaller values of ℓ^{-1} and V_∞^1 yield longer lifetimes.

Along the reduced wave vector axis the width is slightly larger, but of the same order of magnitude.

7.2 THE STIFFENING EFFECT. — Figure 2 helps us to understand the manner in which the reflectivity profile becomes singular as $\xi_b \rightarrow \infty$. Here we represent the transmission of the system divided by the equivalent Fresnel transmission :

$$T_F = \frac{4 Q\xi_b}{\xi_b k \sin \theta} \left[1 + \frac{Q\xi_b}{\xi_b k \sin \theta} \right]^{-2} \quad (26)$$

If we consider T_F as a function of « $Q\xi_b$ », the slope at the origin is $\frac{4}{\xi_b V_\infty^{1/2}}$. On the other hand, the transmission T for the case of polymer layers is also linear in « $Q\xi_b$ », but with a different slope. Thus, the quantity $\frac{T}{T_F} (\beta, Q\xi_b = 0)$ displayed in figure 2 is the ratio of the 2 slopes. We note that this quantity increases with β , i.e. with the range ξ_b . When $\xi_b \rightarrow \infty$, $\frac{T}{T_F} (Q\xi_b = 0)$ diverges. The reflectivity discontinuity is the result of this divergence. An alternative interpretation of this limit may be given in terms of eigenmodes of equation (22). As

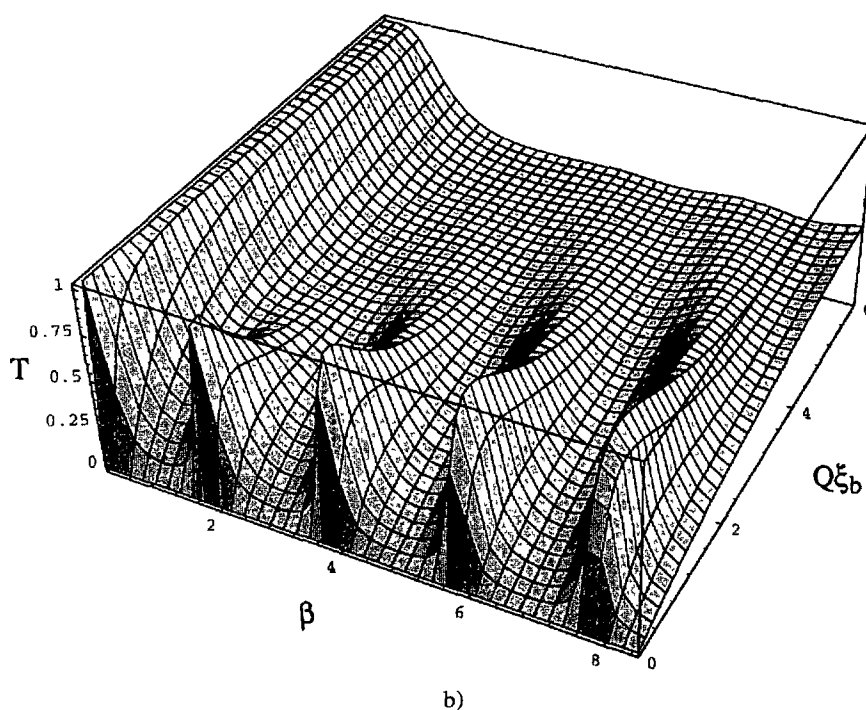
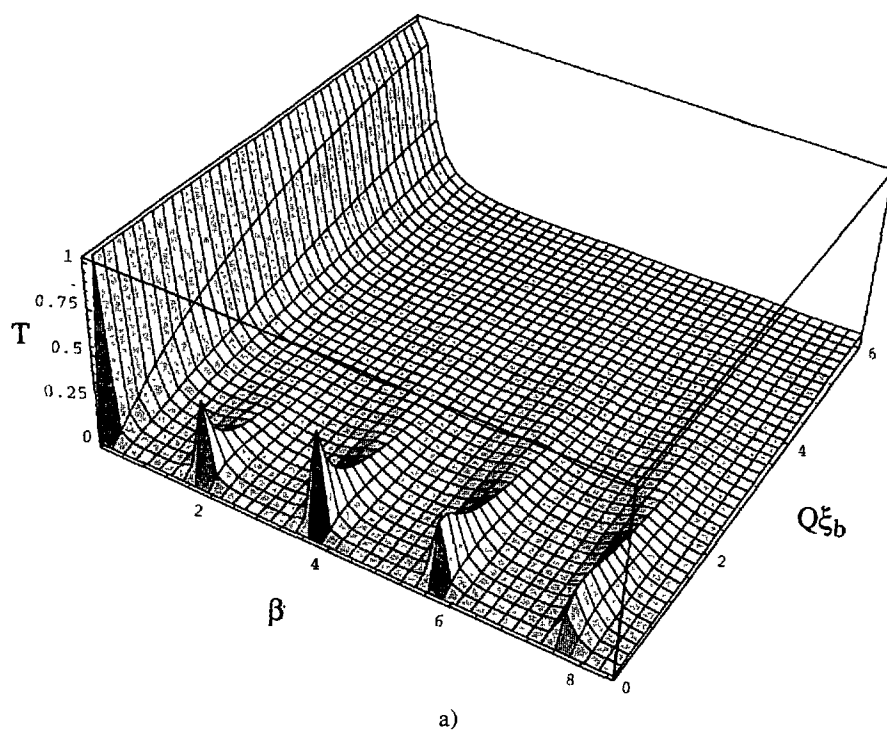


Fig. 1. — a) Transmission (s wave) plotted against β and $Q\xi_b$, for $\ell^{-1} = 4 \times 10^{-5} \text{ \AA}^{-1}$, $V_{\infty}^I = 7 \times 10^{-5} \text{ \AA}^{-2}$ and $z_0 = 2 \text{ \AA}$. b) Same function for $\ell^{-1} = 5 \times 10^{-3} \text{ \AA}^{-1}$, $V_{\infty}^I = 10^{-2} \text{ \AA}^{-2}$ and $z_0 = 2 \text{ \AA}$.

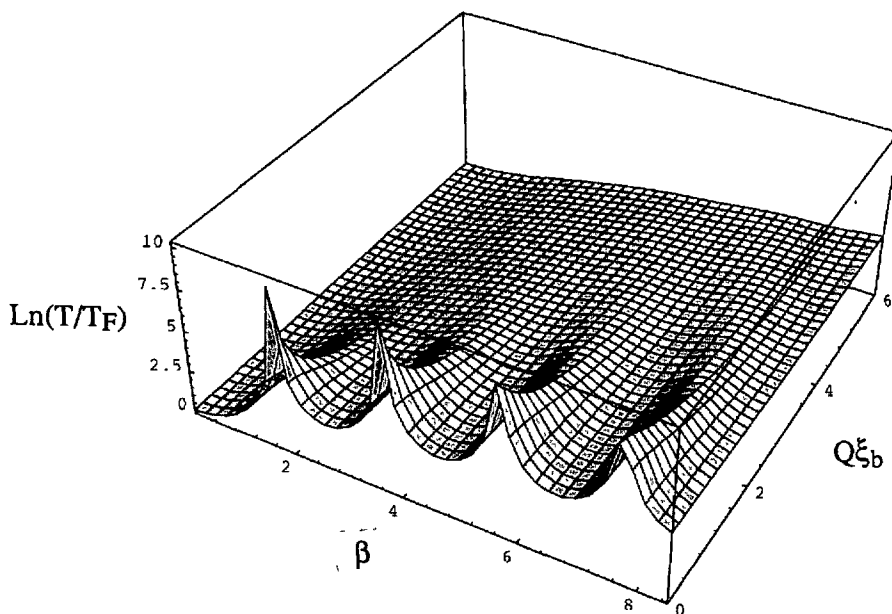


Fig. 2. — Ratio of the transmission (s wave) to the equivalent Fresnel Transmission ($\ell^{-1} = 0$). At $Q\xi_b = 0$, the plot displays the ratio of the slopes associated with formula (25) and (26) respectively. Analytical result, parameters as in figure 1a.

long as ξ_b is finite, there exists a discrete spectrum of « pseudo » bound levels. When the « energy » K corresponds to the top bound level, a resonance occurs and the reflectivity drops. As $\xi_b \rightarrow \infty$, the discrete spectrum becomes continuous and the top bound level coincides with the value $K = 0$. The discontinuity is related to the existence of a non-evanescent wave [4] at $K = 0$.

7.3 THE CASE OF A RECTANGULAR WELL. — We may compare the polymer problem to the equivalent classical case of discontinuous potentials $\Delta V(z) = V_2 < V_\infty$, as illustrated by the succession of a rectangular well of width ξ_b and an infinite slab.

For this arrangement, the ratio of the transmissions is, in the limit $Q\xi_b = 0$:

$$\lim_{Q\xi_b \rightarrow 0} \frac{T}{T_F} = \frac{1}{1 + \left(\frac{V_\infty - V_2}{k^2 \sin^2 \theta} - 1 \right) \sin^2 \beta} \quad (27)$$

This function is only weakly oscillating and does not exhibit any steady increase. The steady increase of T/T_F with β , or stiffening effect, is a consequence of the smooth transition between $\Delta V(z)$ and V_∞ in the polymer case.

7.4 EFFECT OF THE BOUNDARY CONDITIONS. — We compare the 2 finite size effects (described in Sect. 2) on the transmission functions at a given value of the interactions $\beta = 1.89 = \beta_1$. These functions are calculated here by numerical integration of equation (5). For an exponential cut-off in dilute bulk solutions (Eq. (2)), the plot of the transmission against reduced wave vector in figure 3a displays a monotonic variation.

On the contrary, in figure 3b, the plot of the transmission corresponding to semi-dilute solutions shows a pronounced oscillation, which in some way amplifies the reflectivity jump theoretically obtained in the limit $\xi_b \rightarrow \infty$. This is the effect of screening by the bulk solution ($\phi_b > \phi^*$, case 2.2) analogous to the screening effect of the Coulomb interaction in the Ramsauer Townsend effect.

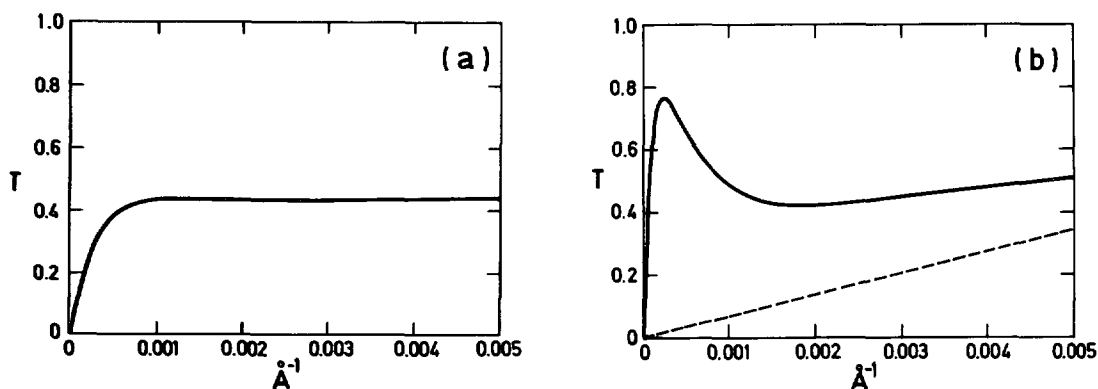


Fig. 3. — Transmission (s wave) for $\beta = \beta_1 = 1.89$ plotted against Q , for two types of boundary conditions at $z = \xi_b$ (ℓ^{-1} and V_∞^I as in Fig. 1b). Here $\xi_b = 720 \text{ \AA}$. 3a) Exponential cut-off (Eq. (2)). 3b) Screening cut-off, as for figure 1b (Eq. (4)). The equivalent Fresnel transmission curve is at the bottom. The discontinuity in the limit $\xi_b \rightarrow \infty$ is obtained by extrapolation, at $Q = 0$, the asymptotic behaviour. (Result of a numerical integration of Eqs. (5) and (6), kindly given to the author by Guiselin.) Figure 3b is a cut of figure 1b along $\beta = 1.89$.

The absence of oscillations in the case of 2.1 of dilute solutions is related to the fact that K^2 in equation (18) is always negative when the concentration of polymers is zero in the bulk. The exponential factor in equation (8), although significant [12] by itself, is here irrelevant. It can be argued that the discontinuous slope at $z = \xi_b$ in equation (3) is unphysical. Indeed, this slope must be continuous: in other words, there are a few monomers belonging to non-adsorbed chains, at distances $z < \xi_b$. Similarly, the electron polarizes slightly the atom before entering the shell. These effects are however second order.

7.5 FEASIBILITY. — A test of the predicted transmission function (Fig. 1) consists in measuring T_s as a function of the reduced wavevector ($Q\xi_b$), at different values of the reduced interaction β in the vicinity of the first oscillation $\beta = 1.89$. In order to vary β it is sufficient for instance to vary the bulk concentration ϕ_b . We first examine the values of the parameters which meet the above condition, i.e.

$$\frac{\ell^{-1} \xi_b}{1 + z_0/\xi_b} = \ell^{-1} \xi_b = 3.6. \quad (28)$$

We evaluate, in the case of a neutron radiation

$$\ell^{-1} = 4 \pi \frac{b_s}{v_s} |\gamma| A.$$

For a deuterated solvent, $\frac{b_s}{v_s}$ is typically $6 \times 10^{-6} \text{ \AA}^{-2}$. The coupling with a non-deuterated solute gives $|\gamma| \approx 1$. With $A = 2 \text{ \AA}$, we have $\ell^{-1} = 1.5 \times 10^{-4} \text{ \AA}^{-1}$. In order to satisfy condition (28), the screening length is $\xi_b = 6 \times 10^3 \text{ \AA}$. For this we need polymer chains with an end-to-end distance R at least of order $6 \times 10^3 \text{ \AA}$! It will be difficult to meet this requirement with synthetic polymers. An alternative system is a solution of single DNA strands in water plus added salt, at the interface solution air.

Exploring the concentration range $\phi_b \geq \phi^*$ one should be able to detect a sharp increase of the initial slope as $\phi_b \rightarrow \phi^*$.

A high resolution in wave number k is necessary to measure the effect predicted in figure 2a, i.e. close to resonance. The reflectivity minimum occurs at $Q\xi_b = 0.4$,

$$(k^2 \sin^2 \theta - V_\infty)^{1/2} = \frac{4}{\xi_b} = 10^{-4} \text{ \AA}.$$

With neutron beams, such a high resolution is for instance possible at the ILL facility, using ultra cold neutrons.

8. Conclusion. .

Introducing the boundary condition based on the screening effect of the semi-dilute bulk solution, we make the following prediction for the reflectivity (transmission) of an adsorbed polymer layer at a planar interface :

- 1) the reflectivity (transmission) function displays ridges along the wave number axis, at periodic values of the interaction parameter between radiation and layer,
- 2) the extension of the ridges along the wave number axis is finite and increases with the interaction parameter.
- 3) the deviation with respect to the Fresnel law at total reflection edge increases with the interaction parameter.

Property 1) follows from the potential well in the interaction between radiation and polymer layer. (The index of the adsorbed layer should be greater than the index of the solvent).

Properties 2) and 3) are related to the particular nature of the well, characterized by a slowly varying function which generates singular behaviours, in particular in the limit of infinite interaction.

These results may be used to test boundary conditions far away from the interface. Surprisingly, the oscillations are only generated by the continuous semi-dilute profile.

The combination of 1), 2) and 3) is not an isolated case. The Ramsauer effect in the scattering of slow electrons by heavy atoms is described in similar terms, and there are probably effects of the same type at other spatial scales.

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References

- [1] DIETRICH S. and SCHACK R., *Phys. Rev. Lett.* **58** (1987) 140.
- [2] SCHACK R., Thesis, Munich (1986).
- [3] JANNINK G., FARNOUX B. and DES CLOIZEAUX J., *J. Phys. Colloq. France* **50** (1989) C7-67.
- [4] GUISELIN O., *J. Phys. France* **50** (1989) 3407.
- [5] GUISELIN O., *Europhys. Lett.* **17** (1992) 57.
- [6] GUISELIN O., JANNINK G. and DES CLOIZEAUX J., *Makromol. Chemie, Makromol. Symp.* **62** (1992) 19.
- [7] This length is derived from the Bohr-Sommerfeld rule (P. G. de Gennes, private communication).
- [8] MORSE P. and FESHBACH H., *Methods of Theoretical Physics*, vol. II (MacGraw Hill, New-York, 1955).
- [9] BOUCHAUD E., FARNOUX B., SUN X., DAOUD M. and JANNINK G., *Europhys. Lett.* **2** (1986) 315.
- [10] DE GENNES P. G., *Macromolecules* **14** (1981) 1637.
- [11] CHARMET J. C. and DE GENNES P. G., *J. Opt. Soc. Am.* **73** (1983) 1977.
- [12] LIU A. J. and FISHER M. E., *Phys. Rev. A* **40** (1989) 7202.