sity in a neutral atom reveal that

$$\epsilon_{\max} - v_{\rm eff}(\infty) \leq -I , \tag{15}$$

where $v_{\rm eff}(\vec{r})$ is the effective potential in Eq. (12). From Eqs. (14) and (15) we can conclude that

$$v_{\rm eff}(\infty) = \lim_{r\to\infty} \delta E_{\rm xc}/\delta n(\vec{r}) \geq 0 . \tag{16}$$

By Eq. (2), $\mu = \lim_{r\to\infty}\{\delta T_s/\delta n(\vec{r}) + \delta E_{\rm xc}/\delta n(\vec{r})\}$ where $T_s[n]$ is the noninteracting kinetic energy,[2, 11, 12] and thus $\mu \geq \lim_{r\to\infty} \delta T_s/\delta n(\vec{r})$. All bounds are expected to be very tight[14] when N tends to Z from below.

The exchange-correlation functional $E_{\rm xc}[n]$ is not known explicitly except in various approximations. For separated LiH the local density approximation[2] displays no derivative discontinuity, and so it minimizes the energy incorrectly at the configuration $\mathrm{Li}^{+0.25}\mathrm{H}^{-0.25}$. The spin-restricted Hartree-Fock approximation leads to an even worse dissociation limit,[15] $\mathrm{Li}^{+0.45}\mathrm{H}^{-0.45}$.

All of our conclusions concerning atoms may be generalized to other electronic systems. In particular, the metal-insulator transition due to correlation is another example of a derivative discontinuity of $E_{\rm xc}$.

Discussions with L. J. Bartolotti have been beneficial. This work was supported in part by the National Science Foundation through grants to Tulane University and the University of North Carolina, and by the donors of the Petroleum Research Fund administered by the American Chemical Society.

---

[1] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[2] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[3] M. Levy and J. P. Perdew, Int. J. Quantum Chem. 21, 511 (1982), and references therein.

[4] R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, J. Chem. Phys. 68, 3801 (1978).

[5] E. P. Gyftopoulos and G. N. Hatsopoulos, Proc. Nat. Acad. Sci. U.S.A. 60, 786 (1968).

[6] M. Levy, Proc. Nat. Acad. Sci. U.S.A. 76, 6062 (1979).

[7] S. M. Valone, J. Chem. Phys. 73, 1344 (1980), and 73, 4653 (1980).

[8] P. Phillips and E. R. Davidson, in Proceedings of the Fourth International Congress on Quantum Chemistry (to be published).

[9] R. S. Mulliken, J. Chem. Phys. 2, 782 (1934).

[10] H. O. Pritchard and F. H. Sumner, Proc. Roy. Soc. London, Ser. A 235, 136 (1956).

[11] J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).

[12] M. Levy, Bull. Am. Phys. Soc. 24, 626, abstract EI16 (1979).

[13] J. F. Janak, Phys. Rev. B 18, 7165 (1978).

[14] M. M. Morrell, R. G. Parr, and M. Levy, J. Chem. Phys. 62, 549 (1975); M. Levy and R. G. Parr, J. Chem. Phys. 64, 2707 (1976); J. Katriel and E. R. Davidson, Proc. Nat. Acad. Sci. U.S.A. 77, 4403 (1980).

[15] H. F. King and R. E. Stanton, J. Chem. Phys. 50, 3789 (1969).

Direct Optical Observation of Interfacial Depletion Layers in Polymer Solutions

C. Allain, D. Ausserre, and F. Rondelez
Physique de la Matière Condensée, Collège de France, F-75231 Paris Cédex 05, France

(Received 22 July 1982)

The excitation of fluorescently labeled polymer coils by shallow optical evanescent waves permits measurement of the local monomer solute concentration in the vicinity of a nonadsorbing wall over controlled, submicroscopic distances. The existence of a depletion layer at the solid-solution interface is thus demonstrated directly for the first time. The results obtained on a 103 000-molecular-weight polystyrene sample dissolved in ethyl acetate are in agreement with the entropic repulsion model.

PACS numbers: 36.20.Ey, 68.45.-v

Interfacial phenomena are a field of growing physical interest and have generated a recent outburst of experimental work in various systems.[1] In most of these cases, the results were obtained in the vicinity of a phase transition, which has the advantage of scaling up the interfacial layer thickness.

The present work is devoted to dilute macromolecular solutions in the vicinity of an impenetrable, nonadsorbing wall. Such a system is amenable to experimental investigation because of the large size of the constituent objects and is relevant to such important research fields as colloid stabilization, gel permeation chromatography, biocompatibility, etc. Historically, Asakura and Oosawa[2] suggested long ago that the reduction of the configuration entropy of the flexible macromolecular coils in the neighborhood of the wall should lead to a strong steric repulsion and therefore to a decrease in the local solute concentration. We report here the first direct measurement of the overall thickness of the associated depletion layer.

Although several derivations have appeared in the literature[3-5] the numerical data of Feigin and Napper,[3] based on a combination of rotational-isomeric-state schemes and Monte Carlo procedures, contain all the essential features. The concentration of polymer $\varphi(z)$, which is zero at the wall, increases smoothly with the distance z from the solid surface and reaches the bulk concentration φ_B at a distance of the order of the root-mean-square end-to-end distance of the chains in free solution $\langle s^2\rangle^{1/2}$. The results are essentially independent of the detailed molecular structure of the chain and of local configurational restrictions due to valence lengths, valence angles, sterical requirements of constituent groups, etc. It is striking to note that they follow closely the analytical function $\varphi(z) = \varphi_B \tanh^2(\alpha z/\langle s^2\rangle^{1/2})$ with $\alpha \cong 2.20$ which is the profile established long ago by van der Waals for the interface between the coexisting fluid phases of a binary mixture.[6] A demonstration of this point for semidilute polymer solutions has been recently given by Joanny, Leibler, and de Gennes[7] in the framework of the mean-field theory.

Our optical technique is an extension of the total-internal-reflection methods[8] applicable to interfaces between an optically dense material (refractive index n_1) and a rarer one (refractive index n_2). The shallow evanescent wave, of wavelength λ_0, is used to excite fluorescently labeled solute molecules over controlled penetration depths

$$\Lambda = \frac{\lambda_0}{4\pi n_1}\frac{1}{(\sin^2\theta - n^2)^{1/2}}\,.$$

θ is the angle of incidence of the incident beam and is supposed to be larger than the critical angle $\theta_c = \sin^{-1} n$ (with $n = n_2/n_1$). n_1 corresponds to the solid material, n_2 to the solution. The value of n_2 is obtained from the refractive index of the pure solvent plus the contribution of the solute, via its specific refractive-index increment. The slight correction due to the existence of a nonuniform solute concentration profile will be neglected in all the following.

The total fluorescence intensity emitted by the solution is

$$I_F = AU_0\int_0^\infty \varphi(z)e^{-z/\Lambda}\,dz, \qquad (1)$$

where U_0 is the energy density at the solid boundary. For polarization in the plane of incidence,

$$U_0 = U_0'' = \frac{4\cos^2\theta}{n^2\cos^2\theta + n^{-2}\sin^2\theta - 1}\,.$$

Note that $U_0'' \to 0$ for $\theta \to 90°$ (see Fig. 1). A is a numerical factor including the collecting efficiency, the quantum yield of fluorescence, etc. If the concentration profile is uniform for all positive z $[\varphi(z) \equiv \varphi_{\text{bulk}}]$, then $I_F = I_F^{\text{ref}} = AU_0\Lambda\varphi_{\text{bulk}}$. If we take the ratio of these two fluorescence intensities, this yields immediately for a $\tanh^2(z/\chi)$ profile

$$\mathcal{R}(\theta) = p\int_0^\infty \tanh^2(z/\chi)c^{-pz/\chi}\,d(z/\chi), \qquad (2)$$

with $p = \chi/\Lambda$. χ is a characteristic length describing the thickness of the depletion layer. It is related to Γ, the Gibbs total surface excess,[9] by

$$\Gamma = \int_0^\infty [\varphi(z) - \varphi_B]\,dz = \varphi_B\chi.$$

The macromolecular chains used for this experiment were statistical copolymers of styrene and 9-methacryloyloxy methyl anthracene. Their anthracene molar content was 0.7%, as deter-

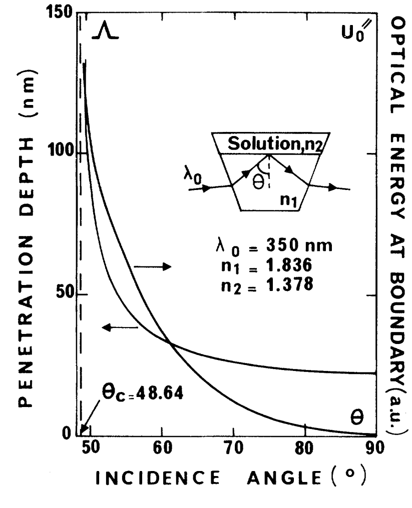

FIG. 1. Left ordinate: Penetration depth Λ of the optical evanescent wave vs incidence angle θ at the solid-solution interface. $\theta > \theta_c$, where θ_c is the critical angle for total internal reflection. Right ordinate: Variation with θ of the optical energy density U_0'' present in the interfacial plane, for polarization of the incident light beam in the plane of incidence.

mined from ultraviolet spectroscopy. The number $\bar{M}_n$ and weight $\bar{M}_w$ molecular averages were 62×10^3 and 103×10^3, respectively, according to gel permeation chromatography. Pure 9-methyl anthracene purchased from Merk was used for the calibration measurements. The copolymers were then dissolved in ethyl acetate, a fairly good solvent of polystyrene. Its low refractive index of $n_2 = 1.375$ is favorable for our total-optical-reflection method.

The experimental setup is described schematically in the inset of Fig. 1. The 350.7-nm line of an Ar^+ laser was used because it corresponds to one of the absorption maxima of anthracene. The total reflection takes place at the interface between the top surface of the Dove-shaped prism (Corning Glass D 88-47, $n_1 = 1.836$ at 350 nm) and the solution. The prism surface was polished to λ and its local roughness was 50 Å. To avoid possible adsorption of the polymer onto the glass, the surface silanol sites were previously deactivated by chemically grafting a monolayer of tri-chloro octadecyl silane with a procedure described by Sagiv.[10] By adjusting the incidence angle θ between θ_c and $\theta_c + 8°$, Λ was then varied between ∞ and 40 nm (see Fig. 1). The angular precision was better than 1 arc min. The fluorescence of the solution excited by the evanescent wave was detected with a low-dark-count phototube (Hamamatsu, R 649) used in the photon counting mode. A set of filters cut out all but a band of 30 nm between 410 and 440 nm centered in the fluorescence spectra of anthracene. Typically, for an incident light power of 1 mW and for a 1% (by weight) copolymer solution, the detected fluorescence light dropped from 2×10^5 counts/sec at the critical angle to 10^4 counts/sec 8° away, while the stray light level due to the residual prism fluorescence stayed approximately constant at 2×10^3 counts/sec.

The fluorescence intensity has been measured as a function of incident angle θ for 1% copolymer solutions in ethyl acetate. Mixtures of free anthracene molecules and homopolymer polystyrene chains have also been studied in the same solvent and at the same respective concentrations. They provide a reference set of data since, in this case, no depletion is expected to occur for the anthracene molecules. The ratio of the two measured intensities $\mathcal{R}(\theta) = I_F/I_F^{\mathrm{ref}}$ is presented in Fig. 2 (lower curve) for each angle. It starts from 1 close to the critical angle of $\theta_c = 48.64°$ and decreases monotonically to 0.91 at $\theta_c + 8°$. To evaluate the reproducibility of the method, we have also taken the ratio of data obtained on two nominally identical reference solutions. The results are shown as the upper curve of Fig. 2. Values centered around unity are obtained over the whole angular range. The typical data spread is ±0.02. Last, we have checked on a two times more concentrated copolymer solution that the results are independent of concentration. This is consistent with the fact that, for sufficiently dilute solutions, the chains are noninteracting.

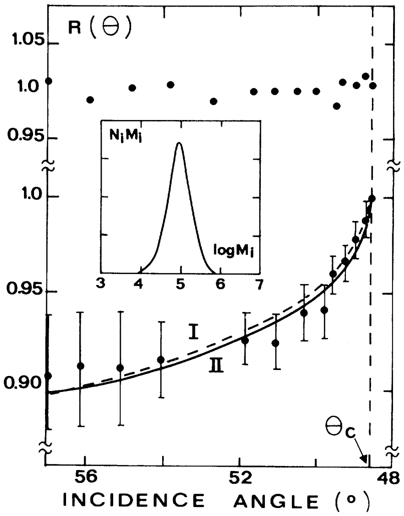

FIG. 2. Lower plot: Variation with the incidence angle θ of the ratio $\mathcal{R}(\theta)$ for the fluorescent intensities emitted by two polymer solutions of identical concentrations but one composed of free anthracene mixed with polystyrene chains and the other of anthracene-bound copolymer polystyrene chains. The dashed and solid curves are fits by a $\tanh^2(z/\chi)$ concentration profile, respectively, without (I) and with (II) inclusion of the sample polydispersity described in the inset. Upper plot: Same but for two identical solutions of free anthracene mixed with polystyrene chains. Deviations from unity give an estimate of the precision of the method.

We will now show how the variation of $\mathcal{R}(\theta)$ with θ can be interpreted in terms of a depletion layer at the solid-solution interface. First of all, ratios less than unity mean that the density of fluorescent chromophores in the illuminated volume is smaller when they are attached to the polymer chains than when they are unbound. Second, the monotonous decrease of $\mathcal{R}(\theta)$ as θ is increased indicates that the difference between the local monomer densities in the interfacial layer and the bulk solution becomes more pronounced as regions closer to the solid wall are progressively probed. On the other hand, since $\mathcal{R}(\theta)$ varies by no more than 10% over the angular range investigated, this means that the depletion layer is a relatively small fraction of the penetration depth of the evanescent wave. This remark enables us to make a Taylor expansion of $\mathcal{R}(\theta)$ in Eq. (2) to second order in $p=\chi/\Lambda$. $R_\Lambda(p)=1-p+(\ln 2)p^2+o(p^3)$. It is interesting to note that a step-function profile of identical total surface excess would give a very close expression $R_\Lambda(p)=1-p+\frac{1}{2}p^2$. A least-squares fit to the experimental data gives an optimized χ value of 4.5 nm. Neglect of the p^2 term would give $\chi=4.2$ nm and a 25% decrease in the fit quality. The slight difference between the two χ values is evidence that the quadratic term is but a small correction in the Taylor expansion and justifies our approximation. We can also check that p is always much less than unity, even at large experimental angles where Λ is minimum. Under our conditions $\Lambda_{\text{min}}=40$ nm and therefore $p=p_{\text{max}}\simeq 0.1$.

In order to see if this experimental value of χ is meaningful, we can now try and relate it to the molecular dimensions of the polymer coils. It is easy to show that $\chi=\langle s^2\rangle^{1/2}/\alpha$. This yields $\langle s^2\rangle^{1/2}\simeq 10$ nm. For polystyrene chains with $M_w=103\,000$, the radius of gyration R_G and the end-to-end mean distance $\langle s^2\rangle^{1/2}$, which are proportional to each other by a factor of the order of $7^{1/2}$, can be estimated to be 11 and 27–29 nm, respectively.[11] Our result is therefore closer to R_G than to $\langle s^2\rangle^{1/2}$. This point would have to be checked more systematically in future experiments on chains of various molecular weights.

The effect of sample polydispersity can be easily accounted for when the Taylor expansion is used. In first approximation, we assume that each fraction of the molecular weight distribution (N_i chains of molecular weight M_i) behaves independently. Therefore R_Λ is written as

$$R_\Lambda=\frac{\sum_i N_i M_i[1-p_i+(\ln 2)p_i^{\,2}]}{\sum_i N_i M_i},$$

where $p_i=\chi_i/\Lambda$ and $\chi_i=\alpha^{-1}\langle s_i^{\,2}\rangle^{1/2}\sim M_i^{\,3/5}$ (for good solvents). The actual molecular distribution measured by gel permeation chromatography is shown in the inset of Fig. 2. The theoretical R_Λ can then be fitted to the data points to yield

$$\langle\chi_i\rangle_w=\sum_i N_i M_i \chi_i/\sum_i N_i M_i=4.7\text{ nm}.$$

It is immediately apparent that polydispersity does not seriously distort our determination of χ.

In conclusion, we have demonstrated the possibility of measuring depletion-layer thicknesses in polymer solutions close to a solid boundary. Detailed analysis of the concentration profile should be possible with high-molecular-weight solutes ($\bar{M}_w>10^6$) which have dimensions large compared with the minimum penetration depth of the evanescent wave. The experimental technique is well suited in all cases where the surface excess is small and is therefore complementary to ellipsometry. Extensions to anisotropic media are possible by use of the polarization properties of the evanescent wave. The method could also prove interesting for measurement of local velocities in fluid flows.

We thank Dr. Mikeš, of the Macromolecular Institute, Prague, for the generous supply of the anthracene-labeled polystyrene. We acknowledge helpful discussions with J. F. Joanny and H. Hervet. Physique de la Matière Condensée is an équipe de recherche associée au Centre National de la Recherche Scientifique (No. 542).

---

[1] C. Frank and S. E. Schnatterly, Phys. Rev. Lett. 48, 763 (1982); D. Beyssens and S. Leibler, J. Phys. (Paris), Lett. 43, 133 (1982); O'D. Kwon, D. Beaglehole, W. W. Webb, B. Widom, J. W. Schmidt, J. W. Cahn, M. R. Moldover, and B. Stephenson, Phys. Rev. Lett. 48, 185 (1982); U. T. Höchli and H. Rohrer, Phys. Rev. Lett. 48, 188 (1982).

[2] S. Asakura and F. Oosawa, J. Chem. Phys. 22, 1255 (1954).

[3] R. I. Feigin and D. H. Napper, J. Colloid Interface Sci. 74, 567 (1980), and 75, 525 (1980).

[4] E. Di Marzio and M. McCrackin, J. Chem. Phys. 43, 539 (1965).

[5] E. F. Casassa, Macromolecules 9, 182 (1976), and references therein.

[6] J. D. van der Waals, Z. Phys. Chem. 13, 657 (1894).

[7] J. F. Joanny, L. Leibler, and P. G. de Gennes, J. Polym. Sci., Polym. Phys. Ed. 17, 1073 (1979). Starting from their Eqs. (2)–(19) and writing $\psi_1=\psi_0$ in the case of a single wall (i.e., for $D\to\infty$ one should reach the bulk value ψ_0) we get

$$\tfrac{1}{6}a^2(\partial\psi/\partial Z)^2=\tfrac{1}{2}v(\psi^2-\psi_0^{\,2})^2.$$

A simple integration yields $\psi=-\psi_0\tanh(z/\sqrt{2}\xi)$ where ξ is a characteristic length $=a/(6vc_0)^{1/2}$. Since $\varphi=|\psi^2|$ we obtain the expected result $\varphi(z)\propto\tanh^2(z/\sqrt{2}\xi)$.

[8] G. J. Müller, in *Multichannel Image Detectors*, edited by Y. Talmi, American Chemical Society Symposium Series No. 102 (American Chemical Society, Washington, D.C., 1979), p. 239; J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1962).

[9] See, for example, A. W. Adamson, *Physical Chemistry of Surfaces* (Wiley, New York, 1976).

[10] J. Sagiv, J. Am. Chem. Soc. 102, 92 (1980).

[11] J. P. Munch, S. Candau, J. Herz, and G. Hild, J. Phys. (Paris) 38, 971 (1977).