Of butterflies and terraces

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Ten years ago at a modest spallation-neutron source at Argonne National Laboratory, a "gizmo" was installed which was later christened a *reflectometer*. The popularity of the "gizmo" spread like wildfire: now virtually all neutron sources possess at least one of them. Some are graced by splendid names: CRISP and SURF at Rutherford, TOREMA at Jülich, DESIR in Saclay and EVA in Grenoble. With the exception of SPEAR of Los Alamos, that touch is not followed in the United States; the beautiful data of Majkrzak and Satija at NIST (and Larry Passell at Brookhaven) come from "beam hole #8" or something of that sort. Why such a popularity? Because its function, the determination of the depth profile in thin films and at surfaces, turns out to be useful in a number of scientific fields. The notion itself is easy to understand. On top of that, the instrument is relatively cheap and friendly to the users. Perhaps the time has come to make an assessment of the success of reflectometry. Did this come out to be a new, solid tool or rather an ephemeral fashion that meteorically rose, to bite the dust soon after? Did I hear somebody quote it "the EXAFS of the '90s"? Is it just a settled technique or rather, with the new neutron sources that are promised to us with their hefty neutron flux, will new twists become available?

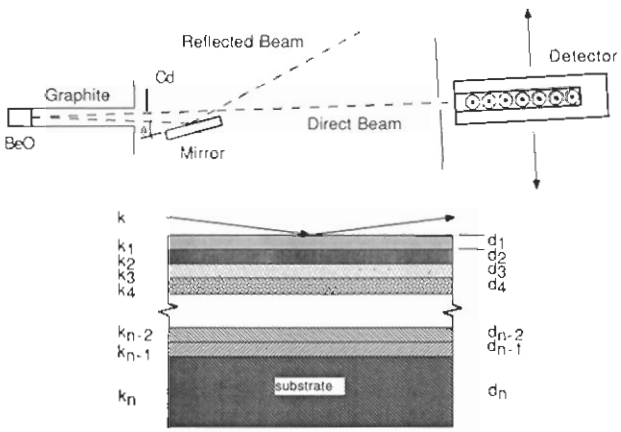

Figure 1. *On top: sketch of an early neutron reflectivity experiment, from "Pile Neutron Research" of D.J. Hughes, Addison-Wesley, 1953. The Fresnel reflectance is* $R=(k_0-k_t)/(k_0+k_t)$*, where* $k_0=2\pi\sin\theta/l$ *is the momentum perpendicular to the surface for neutrons of wavelength l.* k_t*, the momentum in the mirror, is instead* $k_t=(k_0^2-4pbN)^{1/2}$ *in term of the mean scattering amplitude of the mirror and its number density N. Below: in a modern experiment, the mirror is substituted by a sample with graded scattering amplitude.*

Neutron News has already given accounts of what neutron reflectivity is about (1). Neutron reflectivity was really invented to determine the scattering amplitude of materials, in the manner sketched in Figure 1. To obtain the value of the scattering amplitude of a material is enough to take just one measurement. But the reflectivity can be measured for one angle of incidence, at a full slate of different wavelengths, or if preferred with a monochromatic beam over a range of angles: in other words, the reflectivity can be measured over an extended region of neutron momenta. Quite an overkill to find just one number, which is overdetermined to death or, to speak more compassionately, measured with utmost precision. Things become tougher when a sequence of layers lies below the surface. Each layer boundary partially reflects the beam, and all reflected waves interfere (each with its own phase) toward the resulting reflectivity. Suppose that the scattering amplitudes of all the strata are known. Can their sequence and their thickness be reconstructed from reflectivity? To a straight question an ambiguous answer. After poring with patience and perseverance on the data a profile can always be spirited. But is it sensible? Is it real? Do you believe in it? The only thing on which the experts agree is that, *in principle*, that profile is not unique. But, as often is the case, if a problem cannot be solved with a frontal assault, there are ways to go around it.

Here is an example of one of the earliest problems that first took the fancy of researchers. Polymers with different chemical formula are usually incompatible. Since they do not stick to each other, what is their contact? Polymers are made largely of the same components: mostly hydrogen and carbon, sometimes with a dash of oxygen or a more exotic atom. To provide enough contrast in neutron optics, recourse is made to one of the oldest "tricks": one component is colored by isotopic substitution. The most popular and cheapest operation is to substitute light hydrogen with deuterium. The interface of a couple of poly-styrene (PS) and polymethyl-metacrylate (PMMA) layers was found to be

sharp indeed, less than three nanometers thick (2).

In the real world, many applications can be found where it is desirable to bond together two polymers. Adhesion strongly depends on the interpenetration of molecules at the interface and the entanglements between molecules from different polymer phases. One way to provide adhesion is via chemical reaction or grafting, but this requires particular effort in selecting the winning combination of polymer components. In contrast, adhesion can be improved simply by adding to two layers (which, with the supreme indifference of a physicist when talking about chemical things, I call A and B) a small amount of the block copolymer A-B, obtained by chemically joining molecules of the A and B types. The block copolymers physically segregate to the interface and sew together A to B. Each of its blocks stretches into its respective homopolymer forming entanglements with polymer chains from both phases. Thus, there are three interfaces: A with A-B, A-B with B and the middle of A-B. The last interface was derived from reflectivity curve (Figure 2) for a system where the A components were deuterated. Its thickness is comparable to that of the interface of the bare A, B couple. The selective deuteration of the four components of the system gives rise to 16 different profiles of the scattering amplitude. Some of these are traced in Figure 3, and show that indeed the homopolymer/copolymer interfaces are broader than the A, B interface. Yet, even for the latter case, the interface is not infinitely sharp. It has been said that this is not due to diffusion but to the fact that the surface is not flat, because capillary waves (already observed at the interface of polymeric liquids (3)) have been frozen in.

The possibility of examining piecemeal molecules at the surface has been exploited by physicists that had the guts to enter into the realm of biology. Avidin is a protein which can be found in the white of birds eggs. It very readily couples with biotin (or vitamin H) and for this reason is routinely used by biologist for marking. Here is how the system works: a protein, a fatty acid or lipid, or even a selected piece of DNA can be covalently bonded to biotin and this is bound to avidin. Many biotin molecules can be coupled to one large molecule. If the biotinilation is performed under gentle conditions, its biological activity can be preserved. On the other hand, avidin can be covalently bonded on its own with a dye, thus literally painting our molecule. For the reflectivity experiment the planar geometry was obtained by biotinilizing a lipid, which has a strongly hydrophobic tail, and having avidin in a water solution (deuterated or not). One can see that even sparse density of biotin

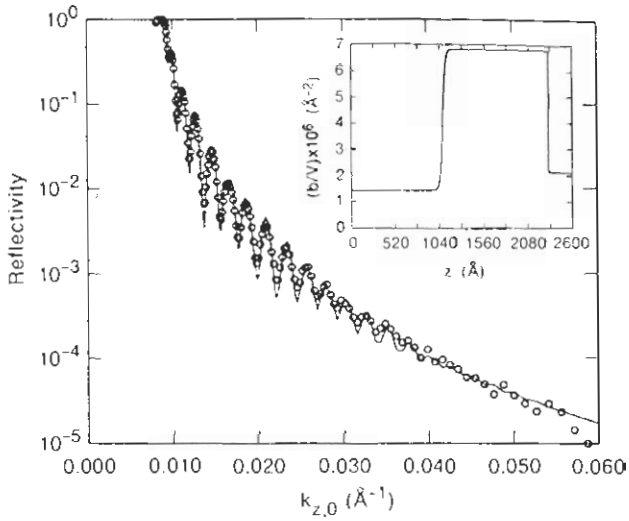

Figure 2. Neutron reflectivity profile for a PS/PMMA bilayer with a thin layer of PS-PMMA copolymer at the interface (PMMA is deuterated). T.P. Russell et al., Macromolecules **24**, *5721 (1991). In the insert, the scattering density profile (starting from the surface) fitted to the reflectivity. Since somebody said that all reflectivities look the same, this is the only experimental pattern I am going to show.*

(Figure 4) is sufficient to bind the lipid, which forms a monomolecular layer directly above the avidin layer. The two layers have strongly correlated thickness.

Selective deuteration becomes cumbersome when an excessive number of combinations is deemed necessary for an unambiguous answer. An alternative approach is that of complementing reflectivity with a depth profile in real space even with poor resolution, as it can be seen

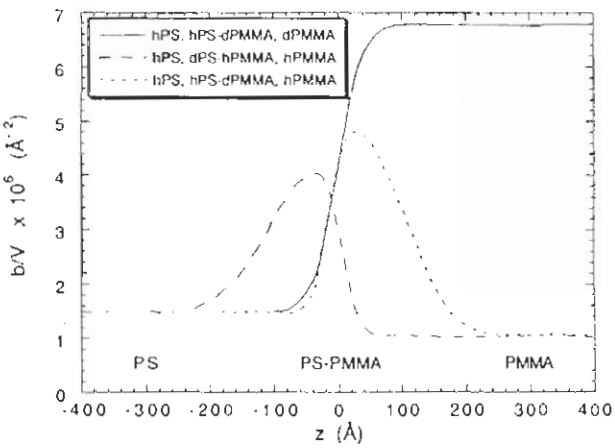

Figure 3. Some of the scattering density profiles obtained by selectively deuterating two homopolymer layers joined by a copolymer. The copolymer here is formed of two symmetric blocs.

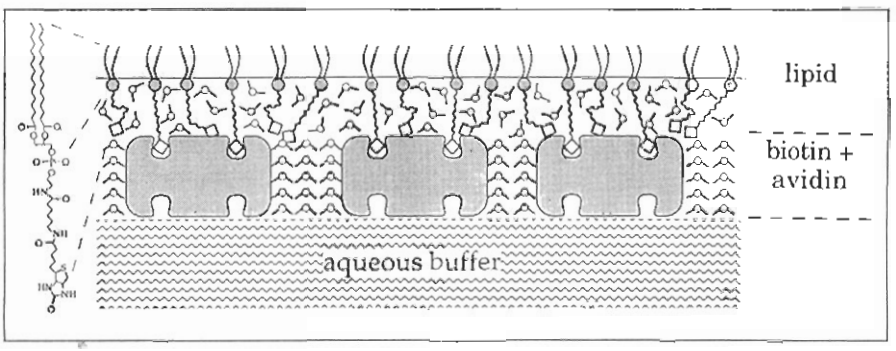

Figure 4. Molecular interpretation of the scattering density profile obtained for a lipid/biotin/avidin layer on water. Courtesy of D. Vaknin et al., Biophys. J. **60**, *1545 (1991). The molecular structure of the lipid is shown on the side: note its characteristic hydrophobic tail.*

backpedaling to polymers. A dramatic phase separation takes place in a polymer blend when one of the components is chemically different, even if the difference is limited to just a few of the tens of thousands of atoms that form each molecule. The segregation may take place at the surface or, more commonly, at the substrate, with an excess profile that depends heavily on the grafting density. At low values of the surface excess, each chain is essentially independent of its neighbors: it is shaped like a mushroom with the size of the radius of gyration of the grafted polymer. As the interfacial density becomes larger, the anchored chains start to repel each other: the chains are stretched to form a brush (Figure 5). The segregation from a blend of polystyrenes of a polystyrene terminated with a short butadiene segment is shown in Figure 6. The profile obtained by forward recoil spectroscopy and neutron reflection show the same excess of deuterated polymer at the silicon substrate (not surprisingly, because polybutadiene shows strong adhesion with various glass surfaces). The difference of resolution of the two techniques is obvious. Only the profile refined from neutron reflection permits a detailed comparison with theory, verifying that over the range of concentrations sampled the brushes are moderately stretched out. However, such profile was chosen among the model profiles that had an excess at the silicon surface.

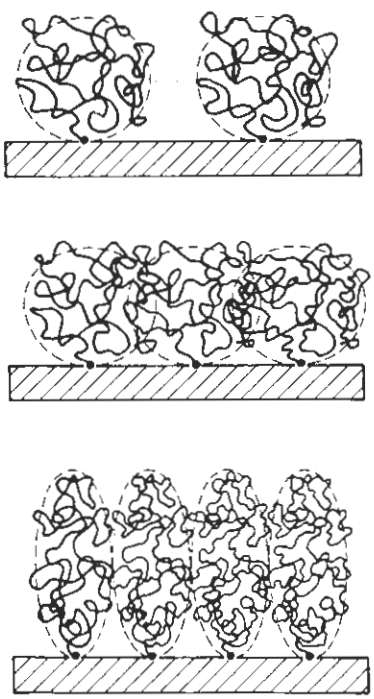

Figure 5. Configuration of polymers (in solutions and in melts) with the end grafted on a surface. The concentration of the grafts increases from top to bottom, causing a gradual stretching of the molecule.

All the talk up to now has been on films well settled in a state of equilibrium. How about taking a movie of an unstable system? This ambition, I am afraid, will be satisfied by the new generation of neutron sources. In the meantime a cheap, and possibly unreliable, shortcut has been used. Take the case in which a system evolves only above a certain temperature. The idea is to warm up, check the timing, freeze, take a snapshot, warm it up again...still in this way some cute experiments were run.

Although the diffusion of polymer chains in the liquid state can be described over long distances by classical diffusion laws, chain entanglements make a description of the short-range behavior more complex. In the standard reptation model, the polymer chains are considered to move in a curvilinear manner along their own contours, exhibiting snake-like motion through the entangled sea of surrounding molecules. Reptation of

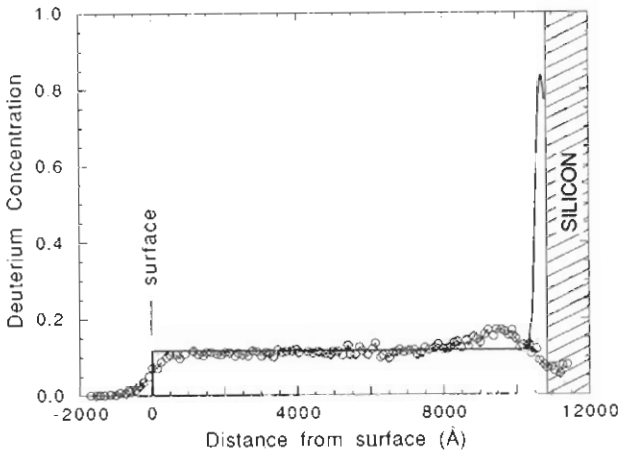

Figure 6. *Profile of the deuterium concentration of a blend of end-functionalized polystyrene (deuterated) and polystyrene. The open circles represent measurements of forward recoil spectrometry. The variation of the signal at the edges is indicative of the resolution. The continuous line has been obtained by fitting neutron reflectivity data. Derived from R.A.L., Jones et al.,* Macromolecules **25**, *2359 (1992).*

molecules has been observed across the interface between two layers of polystyrene which were partially deuterated. Here is the idea. Each of the two layers consists of polystyrene chains where 50 percent of the protons on the chains are substituted with deuterium. However, one layer consists of polystyrene deuterium-labeled at the ends (DHD) while for the second layer the labeling is reversed (HDH). No contrast exists between the two layers: gray on gray (Figure 7). By warming above the glass-transition temperature, the polymer chains start to interdiffuse across the interface. If the motion of the polymer were the same for each portion of the molecule, the concentration of deuterium across the interface would remain constant. However, if the molecule were to move by its ends, a concentration ripple would appear across the interface. See the sketch in Figure 7, together with a concentration profile given by simulating the reptation model–a profile unabashedly identical to that derived from neutron reflection.

Adequate understanding of organic materials can be reached only by mapping their phase diagram, and its microscopic underpinning consisting of the type and degree of structural order at each temperature or composition. True, these are bulk properties, but are modified in films with thickness comparable to the periodicity of the ordered regions. Such films *diffract* a neutron beam sent at grazing incidence: well defined diffraction spots or diffraction rods are expected to appear in some direction outside of the reflected beam. Of course, any type of disorder gives rise to scattering, of the more diffuse kind, at grazing incidence (only a structure that is exactly laminar gives rise to a pure reflected beam). Disorder may occur in many ways. The system of terraces at the surface of a copolymer film illustrated in Figure 8 is just an example.

In grazing incidence geometry neutrons can be scattered away from the reflected beam either in the reflection plane (above or below the reflected beam) or out of the reflection plane. As usual in scattering, the smaller is the size of the object that scatters, the larger the scattering angle. An object too small compared with the neutron wavelength scatters equally at all angles, and its size remains undetermined. An object too large scatters at an angle too small to be distinguished from the undeflected beam. Now, in the grazing incidence geometry, objects as large as ten thousand times the wavelength cause visible scattering in the reflection plane. For instance, with an angle of incidence of one degree, and neutron wavelengths that are just a fraction of a nanometer, objects as big as several microns can be

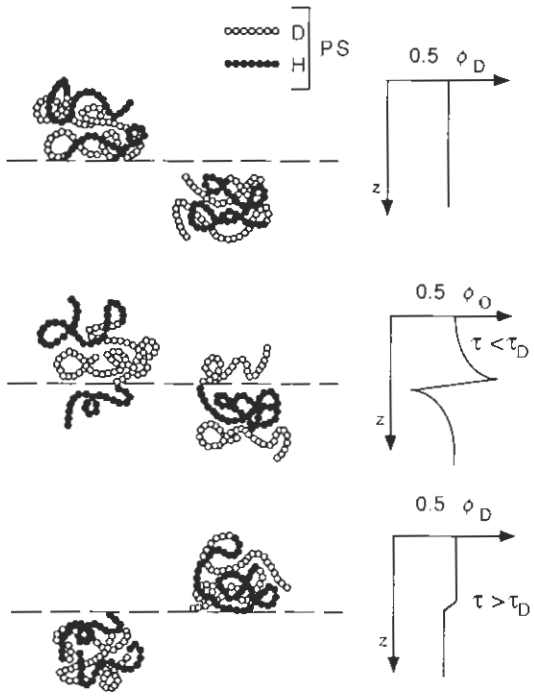

Figure 7. *Interdiffusion of two layers of polystyrene according to the reptation model. During the initial stage, a ripple is created in the deuterium concentration at the interface, which subsides at times greater than the reptation time t_D. The experiments (G. Agrawal et al.,* Macromolecules **27**, *4407 (1994)) confirm this behavior.*

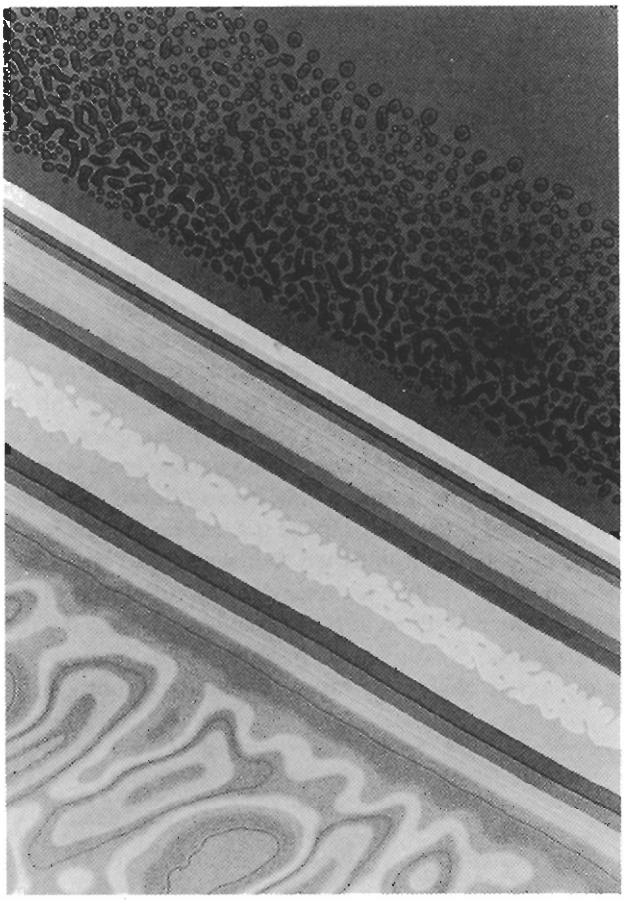

Figure 8. Microscopic image of the surface of a block copolymer. Each terrace gives the height of one copolymer layer, which is of the order of a few tens of nanometer (G. Coulon et al., J. Phys. France **51**, *2801 (1990).*

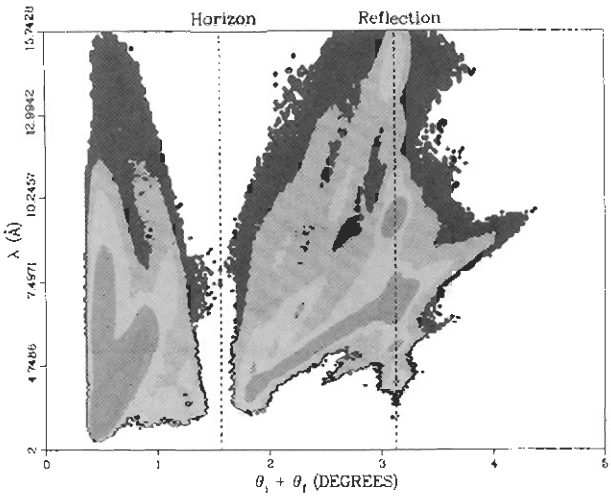

Figure 9. Intensity of the neutrons scattered from a stack of lamellae of PS-PMMA copolymers parallel to the film surface. A strong perturbation was introduced into the layering by adding 10 percent of pure PMMA , because the homopolymer is tucked in the PMMA portion of the copolymer. The abscissa gives the angle of scattering $\theta_i+\theta_f$ ($\theta_i=1.58°$ is the angle of incidence) and the ordinate is the neutron wavelength. Hot colors indicate the regions of highest intensity. Well visible is the reflection line at $\theta_i=\theta_f$. The angle $\theta_f=0$ is the surface horizon. Above it are the neutrons scattered back in free space, below it are the neutrons refracted into the substrate and exiting from its edge. G.P. Felcher et al., Phys. Rev. B, *September 1, 1994.*

seen. Perhaps this does not sound impressive enough. Drawing a parallel, it is as if King Kong, perched upon the top of the Empire state Building, were to cast a giant shadow down to the 'burbs of Chicago (4).

Even now, with the present neutron fluxes, scattering patterns are detected with increasing frequency–but for systems with gross disorder. Shown in Figure 9 is the contour plot of the intensities scattered from a film made of a pile of copolymer lamellae parallel to the surface; the laminar order has been disturbed by adding a dash of homopolymer. The picture was taken with a white (non-monochromatic) neutron beam. As in a Laue camera, here the whole scattering spectrum is recorded, for a broad range of wavelengths and for a fairly extended range of scattering angles in the reflection plane. What can be learned from it? Ahem, no satisfactory operation has been devised yet to transform to the real space the scattering pattern. Actually, up to now only the reverse has been attempted. For a few model (and well documented) structures, the scattering pattern has been calculated and successfully compared with grazing incidence experiments. Which is clever, except that nothing new is learned. Can something more be learned from such a gorgeous scattering pattern with the distinguishing features of a butterfly?

Acknowledgments and disclaimers

Thanks to Gerry Lander for pressing me to write this note, to the friends who supplied me with artwork and the Department of Energy that let me work on it while on contract W-31-109-ENG-38. Absolutely no claim is made that the views portrayed here are fair and unbiased. No mention has been made of the exploits of a chosen crew of neutron spin jugglers–their story is another tale.

References

1. R.K. Thomas, *Neutron News*, Vol. 2, No. 1, p. 23 (1991); J. Penfold, E. Staples and L. Thompson, *Neutron News*, Vol. 5, No. 2, p.25 (1994).
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3. L.T. Lee, D. Langevin and B. Farnoux, *Phys. Rev. Lett.* **67**, 2678 (1991).
4. If the earth were flat.