

# THE BEHAVIOUR OF MACROMOLECULES AT PHASE BOUNDARIES

A. SILBERBERG

*Polymer Department, Weizmann Institute of Science, Rehovot, Israel*

## ABSTRACT

Macromolecules can appear as new components at a pre-existing interface, produced by contact between phases composed of molecules of low molecular weight, or they themselves can be the components responsible for the phase separation. In either case an extensive interfacial zone of diffuse structure is built up. At a pre-existing interface strong energetic interactions are possible and a large measure of distortion of the macromolecule may be expected. On the other hand, where the interface occurs between a gel and a sol, or between two solutions of different macromolecular concentration or composition, small changes in configuration will occur. A number of cases arise but only some of these have been studied to any extent despite the importance of the results for biology and technology.

The pertinent literature is reviewed and some points of general significance are discussed, why macromolecules tend to adsorb so well even from dilute solutions, how we can interpret the thickness of the adsorbed layers, and whether there is adsorption in multilayers.

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## INTRODUCTION

When the high multiplicity of energetically equivalent conformations of macromolecules came to be appreciated, the random coil model was born<sup>1</sup>. This was to be so successful and mentally captivating, that we today have only hesitatingly come to terms with the fact that a large number of polymers spontaneously fold into single and unique configurations in solution<sup>2</sup>. The biopolymers amongst these, of course, possess a great deal of chemical specificity, but even homopolymers will voluntarily arrange themselves in helices, or produce unique folds when passing from solution to the crystal. The interaction energies which stand behind these effects, per segment, turn out, moreover, to be surprisingly small.

Perhaps one tends to forget that also the free energy increase, which results, per segment, from the freezing in of a single conformation, is very small, of the order of, but actually less, than  $kT$ . Individual conformation-holding interactions in a macromolecule do not, therefore, have to be strong, provided that they are abundant, which is automatically the case if compact structures result. This does not mean that strong interactions and covalent bonds do not play a big role in those cases where they exist. The point to note is that interactions, which by themselves are quite weak but are extensively distributed, can serve the purpose just as well.

## THE ISOLATED MACROMOLECULE AT AN INTERFACE

It is this point exactly which comes into play at interfaces and it is most important to realize how it functions in this context. A molecule of ordinary size will be adsorbed from solution at an interface, if the energetic exchange with the surface overcomes the increase in free energy which accompanies the removal of the molecule from solution. This is  $kT \ln X$  if the solution is ideal and of mole fraction  $X$ , and will exceed  $kT$  if  $X$  is larger than  $1/e$ . It follows that adsorption in cases of small interaction energies, i.e. of order  $kT$ , will occur only from concentrated solutions. A very strong bond must be formed with the interface to reduce this requirement significantly.

Such an exceptional situation arises in the case of polymers. Not that the individual contacts here are so rich in energy, but that their number is so large. If the degree of polymerization is  $P$  and all  $P$ , or most of the  $P$ , segments are in the surface, the resultant contact energy will be of order  $PkT$ . In principle, therefore, the critical concentration for adsorption could then drop to the order  $X = (1/e)^P$ , or effectively to zero.

This is in practice almost true. The high interaction energy of which we are talking, however, occurs only at the expense of considerable conformational distortion. Much of what is gained, therefore, must go towards the compensation of this effect. The free energy increase, when restricting a three-dimensional random coil to two dimensions in the surface, is of the order of  $kT$  per segment. Consequently, the interaction energy of the segment with the interface must exceed this critical amount if adsorption is to occur. Once, however, the energy of interaction is larger, the excess per molecule builds up extremely rapidly and adsorption increases enormously. Molecular weight must be sufficiently large, but once it is so the amount adsorbed ceases to depend on it to any marked extent.

The situation, however, is just somewhat more complex<sup>3</sup>. At the surface the contact with the existing interface produces two kinds of chain sections, surface hugging *trains*, and surface protruding *loops*. At the two ends, in addition, two freely dangling *tail* portions will arise. In the tails and loops, by definition, none of the segments makes contact with the interface; in the trains all of them do. There are thus three basic elements which build up an adsorbed linear macromolecule, trains, loops and tails. The rest becomes an exercise in statistical mechanics, and it is easy to deal with some simple cases exactly.

The trains can be treated as two-dimensional random coils, the tails and loops as particular cases of random walks undertaken in the presence of a barrier. These can be solved if the appropriate boundary conditions are selected and excluded volume effects are neglected. The case of the isolated adsorbed macromolecule, in particular, has been extensively treated<sup>3,4</sup>.

It turns out, however, that these results have only limited practical application.

## LAYERS OF MACROMOLECULES ADSORBED FROM SOLUTION<sup>5</sup>

Conditions where macromolecules occur in isolation on the surface are approached only at such dilutions in the bulk phase that the assessment

of the effects lies outside the range of sensitivity of most presently available techniques. Hence practical discussion of the adsorption phenomena will in general refer to surface accumulation of polymers where a layer of high polymer segment concentration is present at and near the interface. In these layers there is considerable interpenetration and overlap of the macromolecules. It is a fact, however, that such highly concentrated and polymer-rich layers are present in equilibrium with extremely dilute solutions. Why this should be so requires some further thought and explanation.

We consider first the case of phase separation in mixtures in bulk. These are known to occur when mixing is accompanied by a sufficiently large increase in internal energy. It is then energetically more advantageous for each molecule to be in an environment rich in its own kind than to be uniformly mixed. With macromolecular solutions, the contribution from the ideal mixing terms, as already pointed out, is small when compared with the  $P$ -fold energy of interaction of the polymer with its environment. Macromolecular solutions, consequently, become unstable at segment interaction energies much smaller than in the low molecular weight case. Most solutions of macromolecules in fact, even in so-called good solvents, are fairly close to instability. When a phase separation does occur, moreover, the two consolute phases, except extremely close to the critical point, are of very disparate concentration in the macromolecular component, the one extremely dilute, the other fairly concentrated<sup>6</sup>.

One may thus look upon the equilibrium established between a dilute polymer solution and a concentrated surface phase as an embryonic phase separation. The interaction with the interface produces that extra energetic advantage which encourages the creation of a concentrated polymer phase in cases where such a phase separation would not otherwise arise. Surface phases will, therefore, be all the more developed the closer the polymer solution, from which adsorption occurs, is to the point of instability, i.e. the poorer a solvent the medium represents.

It is clear, of course, that if each macromolecule in the concentrated surface phase has to establish contact with the interface, only a single layer, i.e. a monolayer of macromolecules, will constitute the embryonic phase separation. There is competition, therefore, for a place on the interface and the number of macromolecules adsorbed will depend on the ease with which solvent is expelled from the surface and on the number of contacts which each molecule can establish with the interface. Assuming that the coverage of the interface by polymer segments is high, the amount of polymer adsorbed will depend on what fraction of the polymer chain actually establishes contact. If a fraction  $\theta$  of the adsorption sites is covered by polymer segments and a fraction  $p$  of all polymer segments has contact with the interface there will be  $\theta/p$  polymer segments adhering to the interface per adsorption site. Since  $\theta$  is generally about 0.8 and  $p$  about 0.4 the equivalent of two completely filled (by polymer) layers are predicted and commonly found to be adsorbed<sup>5,7</sup>.

### THE THICKNESS OF THE ADSORBED LAYER

While  $p$  tells us how the polymer segments are distributed between trains,

loops and tails, it does not tell us how long, on the average, any of these structures are. If most of the non-adsorbed segments are in the tails, the thickness of the adsorbed layer will be dominated by the tails and will be a strong function of molecular weight. If on the other hand the loops dominate, then, theoretically, molecular weight dependence should vanish in the limit of very large molecular weight<sup>8</sup>.

### **ADSORPTION FROM EXTREMELY DILUTE SOLUTIONS IN THE FORM OF ISOLATED MACROMOLECULES**

We have embarked on a very carefully designed and precise investigation enabling us to study adsorption in that region<sup>9</sup>. The results obtained are beginning to provide us with interesting information about the nature of the conformation adopted. We have been able to follow for example, the predicted<sup>8</sup> change in conformation of the isolated adsorbed macromolecules as the molecular weight is raised. From conformations in which the tails dominate and where the thickness is a function of molecular weight we find the transition to molecular weights where the loops are determining and the thickness ceases to depend on chain length<sup>9</sup>.

### **ADSORPTION FROM MODERATELY DILUTE SOLUTIONS IN THE FORM OF A COMPLETE MONOLAYER**

In the region of about  $10^{-5}$  to  $10^{-4}$  g/ml polymer in the bulk phase a plateau in thickness and amount adsorbed is reached. The macromolecules are strongly interpenetrated on the surface and local concentration is high. The reasons for this plateau have already been discussed and the essentials of experimental behaviour are correctly predicted by theory<sup>7</sup>. Overthick layers with a strong molecular weight dependence are, however, found as well<sup>10</sup>. There are a number of possible explanations for these discrepancies.

Foremost among these is the ever-present uncertainty as to whether adsorption equilibrium was attained. Where this point was in fact checked, by desorption, equilibrium was often shown not to have been established. Desorption experiments are difficult to perform so that usually no checks are conducted at all. Proven cases of equilibrium are very few<sup>11</sup>. In our own investigation so far we have been able to confirm equilibrium only in one case and that in adsorption from extremely dilute solutions in a good solvent.

Doubts exist also about the uniformity of the adsorption characteristics, both of the surface of the adsorbent, and of the polymer. The non-smoothness of the adsorbent surface is another factor. Such artifacts would be extremely hard to assess since the commonly available methods for measuring adsorbed film thickness, which are either hydrodynamic (e.g. effective change in the diameter of a viscometer capillary)<sup>9, 12</sup>, or optical (e.g. ellipsometry)<sup>13</sup>, are insensitive to such detail.

### **MULTILAYER ADSORPTION**

It is possible, moreover, that such concentrated surface phases involve more than one monolayer of adsorbed polymers, and that additional macro-

## THE BEHAVIOUR OF MACROMOLECULES AT PHASE BOUNDARIES

molecules are attracted to the densely populated region created by the segments of the first layer. To the extent that successive layers of relatively undistorted macromolecules can make use of the propagated effect of the presence of the first, a truly macromolecular multilayer adsorption can be envisaged to arise<sup>14</sup>.

### MACROMOLECULES AT PREFORMED INTERFACES IN GENERAL

So far we have discussed the adsorption of macromolecules, from dilute solution, at a solid/liquid interface. It is clear, however, that the same arguments will apply to adsorption at the liquid/liquid and liquid/gas interface, or, in fact, at any preformed interface, i.e. at any interface which is primarily defined by the contact of two phases based on low molecular weight components. A number of cases of relevance to this type of interface are listed in *Table 1*. Essentially the same theoretical approach and model<sup>4,7</sup> can be applied to all these cases.

*Table 1.* Macromolecules at preformed interfaces

Examples		Examples	
Solid/Solid	Macromolecular adhesive films	Solid/Liquid	Protective and dispersive colloid action
	Paints and coatings		Flocculation
	Plastic embedding		Lubrication
	Sealing		Drag reduction
	Fillers		Melt-extruder wall
	Solid propellants		Biological interfaces: for example, the surface blood/endothelial lining
		Liquid/Liquid	Emulsions-stabilization
		Gas/Liquid	Foams Sprays

Some generalization can, moreover, be made from the analysis of the model. Certain of the effects are seen to be dominated by the energetic interactions with the surface. The fraction  $\theta$  of the surface covered by polymer segments, for example, is found to depend on energetics alone. Similarly the change in surface tension (liquid/gas interface) is dominated by surface energies. Moreover, as already pointed out above, a certain critical energy value (about  $0.7 kT$ ) must be exceeded, per segmental contact, otherwise no adsorption of the macromolecule on the surface will occur.

On the other hand, the fraction  $p$  of segments in the chain which make contact with the surface is determined, predominantly, by the solvent properties of the medium. So also are the sizes of the loops and tails which characterize the thickness of the monolayer. In other words, while the surface influences mainly the state of the layer of segments in immediate contact with it, the solvent medium will determine the structure of the diffuse layer of segments adjacent to the surface.

Our understanding of adsorption from solution has considerably aided our understanding both of protection and of flocculation by macromolecules<sup>18</sup>.

Adsorbed films may be the cause, moreover, of the far-reaching effects of low concentrations of macromolecules on the flow behaviour in pipes<sup>16</sup> and on the break-up of liquid jets into drops<sup>17</sup>. Perhaps the most important consequence is simply the growing realization that small amounts of macromolecular additions in solution produce concentrated surface phases and may have far-reaching effects. This leads to a proper understanding of existing phenomena and to new applications.

So far we have assumed that the macromolecules are being adsorbed from dilute solution. More concentrated solutions have not been studied in any detail<sup>18</sup> but some experimental investigations on the surface tension of polymer melts have been reported<sup>19</sup>. In keeping with what we have just concluded it is found that the surface tension in these cases can be computed from the parachor.

An extreme situation arises at the interface between amorphous polymer and a non-macromolecular solid. Such interfaces occur frequently<sup>20, 21</sup>, in adhesives, in paints and coatings, in filled plastics and resins, and in the contact of polymer melts with solid interfaces during flow and extrusion. Strangely enough not too much fundamental work<sup>21</sup> has been done in this area despite its importance and interest. The macromolecular distortions and interpenetrations at the interface must considerably influence the many practical applications of these situations.

Of particular interest also is the fact that such surface phases and layers may have important biological functions, controlling the flow of blood, the permeation of tissue and membranes, the contact of cells and the topochemistry of biological reactions<sup>22</sup>.

## INTERFACES FORMED BY THE MACROMOLECULES THEMSELVES

In systems involving macromolecules another type of interface arises when two phases distinguished from each other only by a difference in the concentration of the macromolecular components are in contact (see *Table 2*).

*Table 2.* Interfaces formed by the macromolecules themselves

Examples		Examples	
Bulk polymer/ Bulk polymer	Bonding of amorphous to amorphous, crystalline to amorphous polymer solids Block copolymers	Gel/Gel	Biological interfaces : tissue/tissue tissue/cell membrane membrane/membrane
Gel/Solution	Gel chromatography Biological interfaces : tissue/plasma membrane/cytoplasm	Solution/ Solution	Emulsions of polymer phases

Such a case occurs, for example, when a macromolecular solution undergoes a phase separation and a more dilute and a more concentrated phase separate.

Since the solvent medium is continuous through the interface, the energetics of the interface are determined essentially by a difference in the number of polymer-polymer contacts.

Treatments of this problem so far<sup>23-25</sup> have assumed that no major conformational disturbance results and that the thickness of the interface is determined essentially by the mean dimensions of the undistorted macromolecule in solution. This is reasonable enough near the critical point of phase separation where the two consolute phases are close to each other in composition, but is definitely questionable when the two phases are very disparate in concentration.

Of particular interest is the interface which is formed when two chemically different macromolecular species, dissolved in the same solvent, cause a phase separation<sup>23, 25</sup>. The two phases are of roughly the same low overall concentration, and only the relative composition is different. The conditions here are almost ideal in the sense that no macromolecular distortions in the interface are to be anticipated. The thickness of the interfacial transition zone is hence a direct measure of macromolecular dimensions.

It is most instructive to regard these systems as if they were composed of macromolecules alone, the solvent in which the coils move and overlap acting only as the medium, or ether. One can visualize a transition going from a very dilute polymer system (a polymer gas) to a case where the coils just touch (a polymer liquid), to a situation where no solvent is present at all and there is complete interpenetration (a polymer solid). (Mixtures of macromolecules without solvent tend to separate completely into the pure species.) The interfaces between such phases can thus be looked upon as the interface polymer gas/polymer liquid, polymer liquid/polymer liquid, and polymer liquid/polymer solid respectively. It presents a number of interesting problems connected with the conformational adjustments of the two molecular species in contact with each other in each of these cases<sup>23</sup>.

Another special interface of this kind arises at the zone of contact between a gel (or a swollen rubber) and the solvent or swelling medium. While the network which constitutes the gel, or rubber, is three-dimensionally complete in the interior, the surface involves a collection of chains which are attached to the body of the network by one of their ends only. The transition zone, the interface gel/sol, is thus determined by these loose ends<sup>26</sup>.

An analysis of this problem particularly when taken in connection with transverse or normal flow is of importance for gel chromatography and for membrane solubility. It has many points of application to biology; the circulation/tissue interface, which controls and determines filtration flow, is a particular case in point.

## CONCLUSIONS AND SUMMARY

The extent of our presently available theoretical understanding has been outlined. Much more useful work will have to be done to improve the models and to extend the approach to some of the more complex situations discussed. Important questions which so far have not received sufficient attention are competitive adsorption, specific adsorption (on non-uniform adsorbent

of non-uniform polymers), multilayer adsorption and excluded volume effects and interpenetration. Equally important are non-equilibrium effects such as the kinetics of adsorption and conformational transition, hydrodynamic boundary layer effects and structural changes induced in the surface layer conformation by flow.

It must be admitted, however, that experimental rather than theoretical inadequacies are at present limiting the rate of progress in the field. Theoretical developments which serve only to introduce further parameters are not particularly useful when we are unable to get the information required.

It has turned out to be extremely difficult to establish the properties of macromolecular interfaces and not many techniques have been developed. The assessment of the hydrodynamic effects of the surface layer is one<sup>12</sup>, ellipsometry is another<sup>13</sup> and radio-isotope labelling is a third<sup>27</sup>. We ourselves have developed a high precision viscometric technique<sup>9</sup>, are building an ellipsometer system and are also exploring other methods for obtaining this information.

Perhaps more can be learned by studying macromolecular surface film applications directly. Many phenomena of great practical impact are being controlled by these layers. Their detailed study will, hopefully, provide us with hints as to the kind of further experiment that might be performed and the kind of theoretical model that should be examined.

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## THE BEHAVIOUR OF MACROMOLECULES AT PHASE BOUNDARIES

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