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STRUCTURE AND DYNAMICS OF POLYMER CHAINS TETHERED AT THE SOLID-LIQUID INTERFACE

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ABSTRACT

The structure of polymer chains tethered at the solid-liquid interface, and their response to shear, is briefly reviewed. Experiments to date on static structure support both scaling and self-consistent field calculations. The forces between polymer-bearing surfaces undergoing shear can yield information on the dynamics of the tethered chains, and we may expect extension of this approach in the future.

INTRODUCTION

In this brief overview I discuss some recent developments in our understanding of the structure and dynamic behaviour of polymeric chains end-tethered at a solid liquid interface, as illustrated schematically in fig. 1.

A recent and very readable review by the organizers of this meeting[1] details several aspects of tethered chains, including structure and dynamics in related systems such as diblock copolymers, polymeric micelles, and branched polymers. Here we focus on the simpler situation shown in fig. 1, and in particular on the questions of the equilibrium structure of the tethered layer on the one hand, and its response to shear on the other. This latter property in particular is expected to be a function of the dynamics as well as the equilibrium properties of the confined chains.

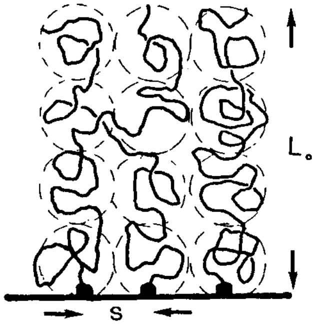

Fig. 1

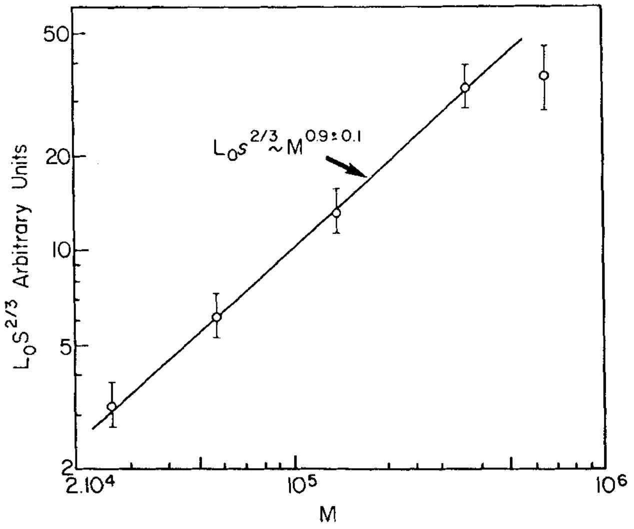

Fig. 2. Data taken from ref. 7 showing how the quantity $L_0 s^{2/3}$ varies with molecular weight M for a series of end-grafted polystyrene chains in toluene.

BRUSH THICKNESS AND SEGMENTAL DISTRIBUTION

The earliest treatment of the structure of tethered chains is due to S. Alexander[2,3], who recognized the essential point that densely grafted chains in a good-solvent medium will be stretched, normal to the end-anchoring substrate - the so-called 'brush' regime - in order to minimize their overall free energy. Alexander assumed a step function form of the segment density profile, and minimised the sum of the osmotic and elastic chain energies. Using scaling relationships known to be true for the semi-dilute regime of the chains in bulk solution, he obtained the equilibrium value L_0 of the layer thickness

$$L_0 = \text{constant. } N a^{5/3} s^{-2/3} \qquad (1)$$

where N is the number of monomers (each of size a) per chain, and s the mean interanchor spacing (fig. 1). As in all scaling treatments, the constant prefactor is undetermined to within order unity.

More recent calculations based on self-consistent mean-field (SCF) models developed independently by a number of workers[4,5], yielded the concentration profile without *a priori* assumptions. This calculated profile has a parabolic rather than a step-function shape, with a characteristic thickness L_0 which varies with N and s precisely as in equn. (1) (though with an explicitly calculated numerical prefactor). Direct experimental studies of how the thickness of polymer brushes - as in fig. 1 - varies with N and s have been carried out using a force-measurement technique[6,7], whereby two surfaces, each bearing such a brush are made to approach each other: the distance at which they start to repel (due to segmental interactions in the good-solvent medium) is taken as twice the brush thickness[3]. The experimental relationship derived is shown in fig. 2, for a system[7] where both L_0 and s are independently evaluated.

It can be seen from fig. 2 that the theoretical prediction of equn. (1) is close to the experimental situation. Very recently, small angle neutron scattering studies[8] of polymers end-tethered on the pore surfaces of a porous silicon medium have been interpreted to yield a relationship between L_0, s and N which is again in good agreement with equation (1). It is fair to say that there is now a consensus that the mean thickness of a densely tethered ($s \ll R_F$, the swollen polymer size in a good solvent) polymer brush is in good quantitative agreement with the prediction (equn. (1)) of both the scaling approaches[2,3] (with the 'step-function' segmental concentration profile assumption) and the SCF calculations[4,5].

It is also possible to predict the detailed variation with surface separation of the forces between two surfaces bearing tethered polymer brushes. In this case too, the predictions of the scaling and SCF-approach are both in good agreement with the experimental data, as can be seen in fig. 3, to the extent that it is not possible to discriminate between them on the basis of the force-distance profiles.

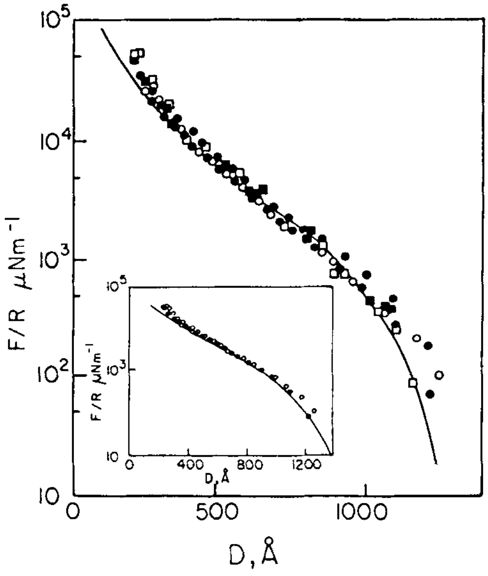

Fig. 3. Comparison of scaling[2,3] (main figure) and SCF calculations[5] (inset) with experimental force-distance profiles, for grafted polystyrene layers in toluene. (taken from reference 7. R is mean curvature of surfaces)

Direct experimental determination of the segmental density profile within the tethered layers (as opposed to their mean thickness) is more challenging. Neutron reflectrometry[9] (itself a somewhat indirect approach) may provide the best prospects for such a determination, but this has not yet been unambiguously done. Density profiles of 'brushes' generated in computer simulation studies[10] are closer to a parabola than to a step function with its sharp edges 'smoothed out', but it is by no means clear that real experiments will be able to resolve this. A further predicted difference between the Alexander and the SCF approach is in the distribution of free chain ends of the tethered brushes. The step-function assumes these will all be close to the outer edge of the brush, in contrast to the SCF calculations which predict a distribution of ends within the layer. Experiments employing fluorescent labels may provide a means for probing such a distribution.

TIME DEPENDENT PROPERTIES

Time-dependent properties of chains within the tethered layers may be considered at a number of levels. Kinetics of grafting to a surface from the surrounding amphiphile solution have been studied by a number of groups[11-13]: while the systems and probes used are different, the indications are that the limiting surface coverage is attained significantly more rapidly than for adsorbing chains (those where every point on the surface has a propensity to adhere to the substrate), for given polymer size and comparable final surface coverage. Qualitatively, this may be due to the fact that, for the case of adsorbed chains, those initially reaching the empty surface adopt a rather flat conformation, and the final extended conformation is attained only rather slowly as more chains adsorb. Grafted chains on the other hand stick essentially point-wise (at their tethering end), and subsequent rearrangement (e.g. stretching normal to the surfaces as more chains graft) requires no desorption of segments.

SHEAR OF POLYMER BRUSHES

A different time-dependent effect has to do with internal relaxations of grafted chains. Some analysis of the collective 'breathing modes' in brush layers has been done[3], but direct experiments are challenging and have yet to be carried out.

Surface force measurements are direct and suggest an attractive approach; however, when two polymer-bearing surfaces approach or separate normal to each other across a liquid medium the time-dependence of the forces between them provides little information on the dynamics of the chains themselves. This is because the forces measured are then dominated by hydrodynamic effects due to the flow of the liquid medium within the intersurface gap. These hydrodynamic effects will be modulated by the structure and overall amount of the polymer segments in the gap, but only marginally by their time-dependent properties[14]. On the other hand, the forces between two polymer-bearing surfaces moving parallel to each other may reflect more directly the relaxations of the chains. This is because, in the absence of net fluid flow into or out of the intersurface gap, such forces will depend on the time-dependent interactions (for example, disentanglement or chain stretching) of the chains themselves, and less on bulk hydrodynamic forces between the surfaces.

Very recently experiments which probe such dynamic features have been carried out[15] by measuring the forces between two mica sheets bearing grafted polymers in a good solvent as they shear past each other at relative velocities v. The geometry is illustrated in fig. 4. As the brush-bearing surfaces move past each other, the changes $\Delta F_{\perp}$ in the normal force $F_{\perp}$ between them are monitored, by observing the bending of a spring supporting the lower surface. The results are rather counter-intuitive: at low relative velocities v there is no detectable change in the normal forces between the surfaces (i.e. $\Delta F_{\perp} = 0$), but as v increases beyond a certain critical value, the repulsion between the surfaces increases sharply. One might guess that fluid flow past the brush-like layers would 'stroke' them down - i.e. creating a thinner layer and reducing $F_{\perp}$ rather than what is actually observed.

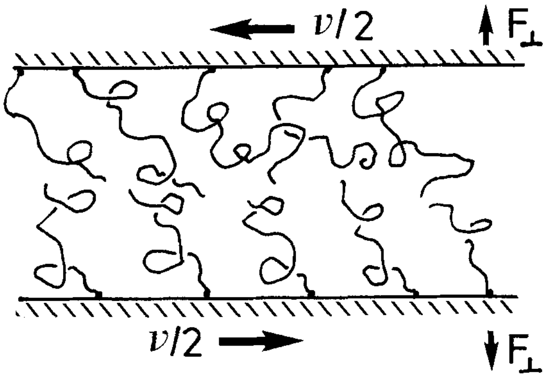

Fig. 4

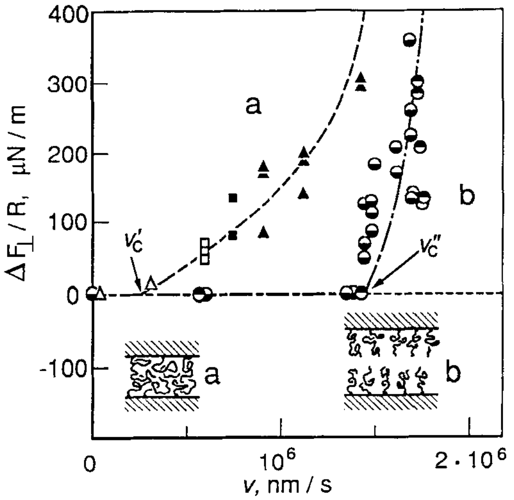

Fig. 5: Changes $\Delta F_\perp$ in the force between two surfaces (of mean curvature R) bearing grafted polystyrene (M = 141,000) layers undregoing shear, as a function of the relative shear velocity v. (taken from reference 15).

Results are shown in fig. 5 for two values of D, including one where the surfaces are initially separated by pure solvent ($F_\perp = 0$). The increase in D in this latter case suggests the grafted layers in the good solvent thicken when fluid flows past them sufficiently rapidly. There are two features to comment on here: the origin of the increase in $\Delta F_\perp$ at sufficiently high v is probably due to chain stretching[16,17]. This stretching of the chains is thought to result in a reduction in 'blob' size, and a consequent decrease of screening between the excluded-volume segmental interactions on each chain. This in turn leads to an increase in the local osmotic pressure within each stretched brush layer: there are more repulsive segment-segment interactions in the stretched brushes (smaller blobs) relative to the unstretched ones (larger blobs). The sudden onset in $\Delta F_\perp$ reflects the velocity above which the effective shear rate exceeds some molecular relaxation rate of the tethered chains, since it is then that the chains are stretched by the fluid flow[15]. This gives us an indication of the characteristic times involved, which are of order 10^{-3}s - though it is difficult to say without further study what part of the tethered chains this characteristic time is to be associated with. Experiments to probe these relaxations are currently in progress.

CONCLUSIONS

Both scaling approaches and self-consistent field calculations appear to describe well the static structure of grafted polymers in a good solvent as revealed by experiments. The internal dynamics of the chains within such layers are only recently beginning to be explored; our understanding of these features is likely to advance considerably in coming years.

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