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GLOBAL AND LOCAL STRUCTURE IN TETHERED CHAINS

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ABSTRACT

The deformation of polymer chains when their ends are confined *e.g.* to a surface can be viewed at two levels. At the global level, one may treat the deformation of a chain as a single variable. This view accounts for fundamental ways in which tethered chains are distinctive, such as the large energy scale for bending, compressing and shearing the layer. This large energy scale has far-reaching consequences: it imposes strong equilibrium constraints locally along the length of each chain. In this way the tethered layer acquires complex nonlocal interactions among the chains. We discuss two ways in which this interaction manifests itself in distinctive responses to local perturbations. The distinctive response of composition gives rise to new modes of pattern-forming phase separation. The distinctive response of pressure makes possible the controllable partitioning of the chains into two populations.

INTRODUCTION

Figure 1 shows a simulated layer [1] of grafted polymer chains—a central subject of this meeting. Each chain has the self-avoiding-walk appearance that it would have in solution. But there is a clear difference, seen in the average chain dimensions indicated on the right side of the figure: the chains are distinctly elongated. If each chain is lengthened, the degree of elongation is observed to increase progressively [1]. The elongation of the chains represents significant stored free energy. In the picture it amounts to roughly a thermal energy kT per chain. If the chains are made longer, the stored energy per chain increases proportionately. This stored elastic energy implies a stress in the layer, similar to that found in a deformed gel. As in a gel, the stress and elongation must be described by statistical laws that are essentially independent of the chemical nature of the polymers used. But the grafted layer is different from a gel: here the chains are quite free to move—almost as much as in solution.

Our goal in this meeting is to explore what matter in this ambiguous tethered state can do. The famous double-diamond microdomain structure seen in block copolymers [2,3] is one example. The polymers in this material are each made of two immiscible chains. The two species thus phase separate with the junction points at the phase boundary. Each chain is thus tethered to the phase boundary, like those of Figure 1. The distinctive structure—not seen in other forms of matter—is that which minimizes the elastic energy of the elongated polymers, combined with the interfacial energy of the two species. The self-organization seen here takes a wide variety of forms in polymer [4] and surfactant [5] liquids. It is clear that the forms are controlled by simple principles of entropic elasticity and are largely independent of the chemical nature of the flexible chains. But our power to predict and control these structures is at a primitive stage [6].

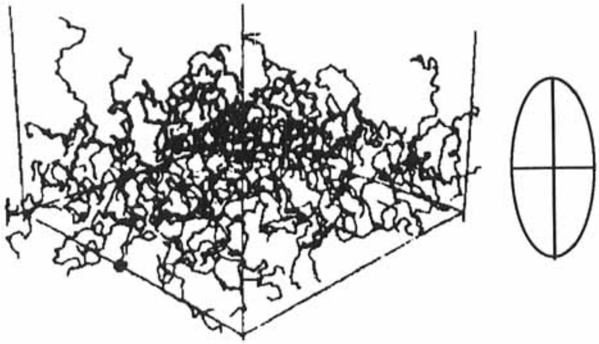

Figure 1 Configuration of a simulated layer of flexible grafted chains [1]. Chains are simulated as impenetrable balls joined by springs and equilibrated by dissipative molecular dynamics. The ellipse shows the root-mean-square chain dimensions in two directions.

Naturally the constraints and stress of the tethered state lead to distinctive mechanical properties. A well-known example is the dynamic shear modulus $G(\omega)$ of microphase-separated diblocks—*i.e.*, the ratio of stress to strain under a small oscillating shear [7]. When microphase separation (and tethering) occur, the low-frequency response departs from that characteristic of a liquid and assumes a mysterious fractional power-law dependence on frequency.

In this talk I want to explore the consequences of the tethering constraint in flexible-chain liquids like the polymers and surfactants mentioned above. I want to consider the ways in which tethered chains should give distinctive behavior to liquids. To complement other talks in this meeting, I'll emphasize structural and energetic properties. A great deal has been discovered about tethered chains in the last decade—much of it by participants in this meeting. This work has been treated in three excellent recent reviews [8,9,6]. But I want to convince you that despite this work we have only begun to explore the potential behavior of tethered-chain liquids.

The consequences of tethering can be thought of in three broad classes. The first is tethering without the crowding and elongation seen in Figure 1. Even without crowding, tethered chains have certain distinctive properties, and I want to mention these. When chains are tethered at sufficient density, crowding and chain stretching results. The main resulting properties can be understood by considering this stretching globally, as a single degree of freedom common to all the chains in a given region. I want to mention how this global point of view works, and list some of the properties that result.

The focus of my talk, though, are those properties that require a more local analysis—*viz.* the equilibrium within each chain and between regions much smaller than the layer thickness. It is natural to express the distinctive properties in terms of response functions. These tell how a small perturbation at one point in the layer affects conditions at another. I'll discuss two kinds of response functions. The first and easiest to understand is the compositional response of a layer with two species of chains. Perturbing the composition at one point affects the composition elsewhere in a well-defined and distinctive way. When the two species are immiscible, this response property leads to a distinctive type of phase separation within the layer. A second type of response results when the total monomer density is perturbed at a given point. This naturally results in extra pressure in the region around the perturbation. The pressure response function can be formally related to the compositional response function. I will sketch its behavior in simple cases. An unusual pressure response occurs when the perturbation is larger than infinitesimal. Here a local perturbation of the monomer density can lead to a qualitative redistribution stress.

LOCAL AND GLOBAL EQUILIBRIUM

The properties discussed below depend on a few fundamental principles common to all flexible polymer liquids. A polymer melt is essentially incompressible. Thus each chain displaces a volume V proportional to the number of monomers in it. (In solution, where the polymers can be compressed, one must modify these principles in a straightforward way.) The natural length scale describing a polymer of volume V is its average end-to-end distance R. This R arises from the fact that flexible chains in the melt state are random walks: $R^2 = a^{-1}V$. The coefficient a is a microscopic length of order ten Angstroms for hydrocarbon chains. It depends on the local structure of the chains and the liquid, and is insensitive to global constraints like tethering. By contrast, the volume V can in principle be indefinitely large. For typical diblock copolymers V is of the order of 10^5 cubic Angstroms. Throughout this talk we shall consider the asymptotic behavior that results when V is arbitrarily large. Such a random walk chain evidently pervades a volume of order $R^3 \sim V^{3/2}$. This volume is asymptotically much larger than the volume V displaced by a chain; thus many chains share this volume. The chains interpenetrate strongly. A given small fraction of a long chain thus touches and interacts directly with indefinitely many others. The interactions are self-averaging. This justifies the use of the mean-field methods to be introduced below. Finally, these random-walk chains have a characteristic energy of deformation. The work to stretch a chain of unperturbed radius R is to a distance h is $\frac{3}{2}kT(\frac{h}{R})^2$. The chains behave elastically like ideal springs. The work required for a deformation of order unity is kT.

The gentlest way to tether the chains in a liquid like this is to join several ends together to form star polymers. Unless the number of arms is very large, this causes little deformation of the type seen in Figure 1. Still, there are dramatic consequences. If even three chains are joined a given chain can no longer move by slithering along its own length. This inhibits the motion of the star and slows mechanical relaxation qualitatively [10]. A subtle feature develops in the static structure as the number of arms increases, as well. It is called the correlation hole [11] effect: the density of nodes is slightly depleted around any given node, out to a distance of order R. These simple consequences of tethering are important to keep in mind, even in the strongly tethered cases considered below. For crowding may not be the essential feature responsible for anomalous properties like the dynamic modulus mentioned above.

The simplest case of tethered chains with crowding is a grafted-chain layer, with σ chains per unit area, like that shown in Figure 1. Here the chains stretch out to a height h which makes the best compromise between the intra-chain elastic stretching energy and the inter-chain excluded-volume repulsion. The overall scaling of this height, and the corresponding stored energy can be found by a simple global analysis [12,13]. In such systems with or without solvent the interaction (free) energy density Π depends on the height h only through the local volume fraction $\phi = \sigma V/h$. This energy is necessarily of the same order as the stretching energy density. This is the elastic energy per chain, h^2/V times the number of chains per unit volume σ/h. Combining these factors, one sees that the elastic energy is of order $\phi(h/V)^2$. To keep this stretching energy in balance with the interaction energy, it must remain a bounded multiple of ϕ as $V \to \infty$: h must increase in proportion with V. This must be true whether the interaction is that of a good solvent, bad solvent, or incompressible melt. These two forms of energy must stay in balance under deformation. Thus whether the layer is stretched by an external force or sheared, the scale of energy stored per unit volume is that of a uniform gel or rubber of the same density ϕ. In this qualitative, global sense the layer is elastically isotropic.

This global energy balance is sufficient to account for most of the fundamental properties of grafted layers. How the height h depends on the grafting density σ depends strongly on the nature of the energy $\Pi(\phi)$. The scaling has been worked out for melts [14], solvents [12,13,15], and polyelectrolytes [16]. Curving the layer to form *e.g.* a many-armed star polymer produces power-law density profiles [17,18]. Deforming the layer also requires work, expressed in the form of bending moduli, spontaneous curvatures [19,20] compressional energies [13] and shear moduli [21]. Often the chains are grafted by specific attraction of the end for the surface; then the chains may achieve a dynamic equilibrium with the solution in which chains continually attach and detach. The kinetics of these processes and their dependence on the solution properties are altered strongly by the crowding of the chains [22,23,24]. The interaction energy within the layer often acts to exclude any untethered chains outside. This influences *e.g.* entanglement of the grafted chains with the free chains [13]. Finally, the global balance of energies explains the main features of self-assembly in amphiphilic chains, such as surfactants, immiscible diblock polymers [14], and partly rigid copolymers [25]. We have seen above that for global purposes a grafted layer resembles a gel or rubber at the same density. Yet a grafted layer must be rather different from a rubber, in which chains are constrained by cross-links all along their length. Deformation of chains in a rubber occurs by direct tension through these cross-links and the entanglements they trap. But in a grafted layer, there are neither cross-links nor entanglements to cause the equilibrium stretching. Instead each chain is forced upward by the pressure of the chains around it, which are forced upward as well. Asking how these forces arise and what form they take leads us to consider *local* equilibrium within the layer. Otherwise put, we must understand the ensemble of chain configurations in this strongly interacting system. This ensemble has long been recognized as a subtle self-consistency problem, and elegant means have been devised to solve it numerically [26,27,28,29,30]. Our point of view here is to look for the simplifying features that appear when the chains are taken to be asymptotically long and strongly stretched, as was first done by Semenov [31].

To this end, let us consider a melt layer, and let us imagine our chains as consisting of N conventional "monomers", each displacing volume v. Without interaction each chain obeys the usual Gaussian random-walk statistics [11]. But as we have seen the interactions stretch each chain to an average height indefinitely greater than its unperturbed length R. We can readily see how this interaction influences a given monomer if we imagine putting an extra, detached, monomer into the layer at height z from outside. Putting in this extra monomer displaces a volume v and forces the overall height to increase slightly. Thus the surrounding chains must stretch slightly more to accommodate the new monomer; work must thus be done. This work is proportional to the volume displaced: it is a pressure $p(z)$.

This pressure strongly influences the statistics of a chain. We may see how the chains are deformed by considering the equilibrium position of some monomer i of a chain whose free end is at height z_0. This position z_i is that at which the average forces on the monomer balance. Since the chains are strongly stretched we expect the monomer to be usually close to this equilibrium position. There are three forces to consider. The pressure exerts a force $v\nabla p$. In addition the chain feels elastic forces from the preceding monomer $i-1$ and the subsequent one $i+1$ along the chain. We shall take our monomers large enough that each may be considered as a small polymer for this purpose. Then the elastic forces have the ideal-spring form discussed above: they are proportional to the displacements

$r_i - r_{i-1}$ and $r_{i+1} - r_i$. The balance of the three forces amounts to a condition of the form $-(r_i - r_{i-1}) + (r_{i+1} - r_i) = v\nabla p(r)$. Assuming that N is large and taking a continuum limit, this says $v\nabla p = d^2r/di^2$. This force-equilibrium condition has the same form as Newton's equation of motion for a particle in an external potential. [31,32].

This analogy may be filled out into the following picture. The path r_i of a chain from its free end r_0 to the grafting surface is the trajectory $r(t)$ that a Newtonian particle with potential energy $p(r)$ would follow if released from rest at r_0. This analogy contains the condition for equilibrium within each chain. It shows that a monomer at one point is influenced substantially by the pressure at distant points higher or lower within the layer.

Of course this same stretching of the chains produces the pressure p in the first place. The necessary balance of energies, considered at the level of individual chains, determines the form of the pressure profile. The stretching of each chain must be such as to minimize its elastic-plus-interaction energy $S(z_0)$ (the action of the corresponding classical particle). This action also controls the distribution of end positions: the relative probability that an end is at z_0 must be the Boltzmann weight $\exp[-S(z_0)/(kT)]$. The elastic part of the action S is indefinitely large relative to kT, and scales as z_0^2/V, as we have seen. But if chain ends are to be found at all heights z_0 within the layer, their Boltzmann weights, and thence their energies S must be equal to within about kT. The energy $S(z_0)$ must be virtually constant for all heights z_0: the large changes in the elastic term must be almost completely compensated by the interaction energy. This latter scales as V. We are led to the conclusion that $(p(z_0) - p(0))$ must scale with height like the elastic energy [33]: $p(z) \sim z^2/V^2 +$ constant. The pressure profile is parabolic. One may, by pursuing the Newtonian-mechanics analogy make this statement precise and infer the coefficient of z^2 [32]: it is $(-kT\pi^2a)/(8V^2)$. Remarkably, although this pressure arises from the interaction between chains, its form may be determined completely without reference to how the chains interact, except for an additive constant. The only material property that enters the z^2 coefficient is the elastic constant a. This p continues to have the same form in any kind of solvent, provided we maintain our interpretation of p as the work per unit chain volume required to insert a small section of chain at height z. (Thus p is essentially a chemical potential.) We see that the requirements of local equilibrium impose strong conditions throughout the layer. Even with the pressure profile determined, the chain statistics are not yet fixed. It remains to find the distribution of end positions z_0. This distribution may readily be found by imposing the constitutive properties of the melt or solution in question. For a melt, the local volume fraction must be unity everywhere; for a "marginal" solvent, it must be proportional to the local p, etc. In either case, the relative number of monomers at each height z is fixed. It is a straightforward process to determine how the chain ends must be placed to produce the proper number of monomers at each height [34]. One finds as assumed that ends are distributed throughout the layer, with a simple functional form that differs according to the nature of the solvent. The end density falls to zero at a specific height h.

Having sketched the conditions for local equilibrium, we can see that the "coupling" within a grafted layer has a level of complexity not found in simpler condensed-matter systems. We may see these complex couplings by considering a region inside the layer much smaller than the height, yet much larger than the chemical repeat unit. Thus a large number of chains pass through this local region. Our question is how much can such a region be influenced by distant regions of the layer. One form of influence is via the tensions of the chains passing through the region. We have seen that these chains end at heights ranging from that of the region in question up to the maximal height h. This means that the region has a distribution of tensions $P(T)$. It turns out that in a melt layer this distribution has the functional form of a cosine; the most likely tension is zero. It is clear that this distribution of tensions is controlled by distant regions of order h away. Moreover, the distribution can be altered in detail by changing conditions far away. Thus *e.g.* the cosine distribution may be altered to approach a delta function by curving the layer [35]. This example suggests that in a grafted layer a local region is influenced in some detail by distant regions. Influence from distant regions is common in condensed matter. Thus in an ordered material like a magnet the local order parameter or magnetic field is controlled by faraway boundary conditions. The same is true of the local velocity in a flowing fluid. In these systems a small set of quantities is determined by distant conditions. In the grafted layer, by contrast, an entire distribution of quantities—an indefinitely large set of numbers—is determined by distant [36] conditions. The complex coupling of our grafted layer resembles that found in exotic condensed matter systems, like weakly localized electronic systems.

SPATIAL RESPONSE TO LOCAL PERTURBATIONS

One way to investigate what this complexity can do is to explore the linear response properties of our grafted-chain system. The basic types of response are those found in any polymer liquid. A fundamental response property in any dense polymer liquid is the compositional response. To define it we imagine a blend of two species of chain—say black and white—which are identical except for labeling. At any point there is a local volume fraction of black monomers, ϕ_B and a volume fraction of white monomers ϕ_W, which are equal on average. The difference $\phi_B - \phi_W$ at a point tells how far that point has departed from the average composition. Now we imagine a local external energy perturbation ΔE proportional to $\phi_B - \phi_W$ at a point r. This perturbation attracts white monomers and repels black ones; accordingly, in the region around the perturbed point r there is a slight excess of white monomers over black ones; the amount of excess is evidently proportional to the strength of the perturbation. The compositional response function $C_c(r, r')$ is defined as $\langle \phi_W - \phi_B \rangle (r')$ caused by the perturbation ΔE at r (up to a constant factor proportional to the strength of the perturbation).

Evidently the reason for this nonlocal response is that any monomer attracted to r belongs to a chain that occupies many other points r'. Indeed, $C_c(r, r')$ is simply the probability that the monomer at r belongs to the same chain as the one at r', in the absence of the perturbation. This is a well-known manifestation of the relationship between linear response and spatial correlations in an equilibrium system [37]. The range of $|r - r'|$ over which C_c is appreciable is evidently the average size R of the polymers.

This same approach may be used to find the compositional response of a grafted layer [38] of black and white chains. Again, one may show that the response $C_c(r, r')$ is related to the probability that a given chain passes through both points. From this fact, we may readily infer the general shape of the response function. Its vertical range is the entire height h of the layer, since a typical chain extends a vertical distance of this order. Its lateral range is the width of the region that a chain typically explores. Since there are no external forces like $p(z)$ in this direction, the chains are simple random walks in the lateral directions. Accordingly, the lateral range of the response function is of the order of the unperturbed size R. The response of composition is quite anisotropic and quite different from that of ungrafted chains. Using the Newtonian-mechanics methods of the last section, we can evidently treat these single-chain configurations quantitatively, and thus compute $C_c(r, r')$ explicitly. The result is shown on the left side of Figure 2.

Aside from its fundamental interest, the compositional response controls phase separation of two species in a grafted layer, just as it does in a simple blend [11] or a melt of diblocks [39]. If the species are partly immiscible, any random perturbation in the composition itself serves as a ΔE to drive further changes in composition. For large enough immiscibility, the induced response is larger than the initial perturbation, leading to a runaway increase in the fluctuation. This runaway first appears when there is a compositional pattern $\phi(r) \equiv \phi_B(r) - \phi_W(r)$ satisfying

$$\phi(r) = \frac{\Lambda}{2} \int_{r'} C_c(r, r') \phi(r'). \qquad (1)$$

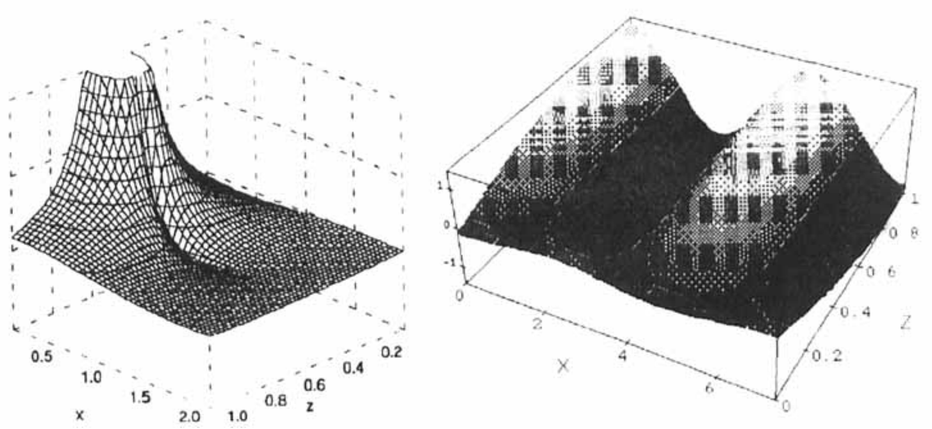

Figure 2 left: Compositional correlation function $C_c(r, r')$ for grafted chains in the melt state, after Ref. 38. The point r is taken at $h/2$, *i.e.*, in the middle of the grafted layer. The function has a similar shape for other choices of r. Horizontal scale x is in units of ungrafted chain rms end-to-end distance; the chains are grafted at $z = 0$. The "notch" for $z \simeq z'$ arises because any segment of the stretched chain connecting points of equal height is necessarily much shorter than V, and accordingly has a natural lateral dimension much smaller than R. right: Incipient phase separation pattern $[\phi_B - \phi_W](x, z)$ for a symmetric mixture of grafted black and white chains as inferred from C_c using Eq. (1) [41].

Figure 3 Sketch of a grafted layer with a small region of perturbed density $\Delta\phi$. Curved black lines suggest pressure response Δp.

Here Λ is roughly speaking the work required to insert a unit volume of black chain into a melt of white chains, in units of kT. As soon as Λ exceeds this threshold, the system begins to phase separate with a position-dependent amplitude proportional to $\phi(r)$. The phase separation pattern for a symmetrical grafted blend in melt conditions is shown on the right side of Figure 2. The intriguing thing about this phase separation is its controllability. Changes in the stretched configurations of the chains necessarily alter the phase separation pattern. We can hope to create a wide variety of patterns, by adding solvent, by altering the architecture of the chains, and by departing from the symmetric conditions shown here. A pattern of special interest is simple stratification, with the white chains above and the black below, or vice versa. Since either of these choices is equally stable, this gives the possibility of switching the layer into either of two inequivalent states [40] with different transport or wetting properties.

Another type of response is even more fundamental than the compositional response discussed here. This is the elastic response, which describes how a force exerted at one place in the layer is propagated elsewhere. A fundamental elastic response is the response of pressure at r' when the density is perturbed at r. To realize this perturbation, we could blow up a tiny balloon at r and hold it there, as illustrated in Figure 3. Physically, we might graft an extra chain with a bulky end group to the surface beneath r. Under melt conditions, the perturbation cannot change the total density anywhere; thus the monomer density must have a small dip where the additional matter was inserted and must be unchanged elsewhere. In general this causes the pressure to change near the perturbation.

In an ordinary melt, this pressure response $C_p(r, r')$ is normally not of interest, because it is so small. It may be readily calculated from the compositional response function $C_c(r, r')$. We saw above that C_c is the response of the monomer density $\Delta\phi$ to a small change of pressure Δp elsewhere, taking the chains to be independently moving in the pressure field $p(r)$:

$$\Delta\phi(r) = \int_{r'} C_c(r', r)\Delta p(r').$$

But the chains in our melt layer are not independent; $p(r)$ must always be shaped so that $\phi(r)$ has the imposed form. In the present case, this is the unperturbed ϕ of unity, plus a delta-function perturbation at r_0:

$$\delta(r - r_0) = \int_{r'} C_c(r', r)\Delta p(r'). \tag{2}$$

This Δp is the response we seek. It is evidently the inverse of $C_c(r', r)$ considered as a linear operator.

This inverse is simple to perform for the melt case by expressing the perturbations as plane waves. Then the compositional response to a plane wave of wavevector q is simply the single-chain scattering function [11] $S_0(q)$. The pressure response to a plane wave is evidently $1/S_0(q)$. The integrated pressure response is $1/S(0) \sim 1/N$, where N is the chainlength. (This integrated pressure is the work needed to add the external object; this is of order 1/N per monomer [11].) The tiny perturbed pressure extends to a range of the order of the polymer size.

In the grafted layer, we expect a much larger pressure response. Here the work to add a monomer is the pressure times its volume. As we have seen, this pressure is independent of the chainlength and does not go to zero. To determine this response from the inverse condition Eq. (2), some delicacy is needed. To see this, we note that when the balloon is inserted, the height of the layer above it must rise: an unoccupied region becomes occupied. Rather than dealing with this displaced boundary explicitly, it is easier to retain the original top boundary and account for the matter that must pass through it by an additional density perturbation. Then we may express the desired C_p in terms of the compositional response C_c of the layer with the height held fixed (*i.e.*, a layer with a rigid lid at height h). We may find the amount of matter that must pass through this lid by the condition that $\Delta p(h) = 0$. The resulting operator $\mathbf{C_p}$ differs from $\mathbf{C_c^{-1}}$ by a simple projection operator [42]. We may readily guess the global behavior of the pressure response using energy-balance ideas mentioned in the last section. We recall that the global elastic behavior of the grafted layer should be like that of a rubber or gel bonded to the surface. If a tiny balloon were blown up in such a rubber layer, it would create a bulge at the top. This bulge must have a width the order of h, since the size of the balloon cannot be relevant, and h is the only other length scale. Thus the pressure response in our grafted layer must have a range of order h, even though the response function C_c that determines it has a much smaller range of the order of the ideal chainlength R. To see how the response depends on z', we may consider a perturbed density in the form of a thin, uniform layer inserted at height z. We've seen above that the density profile is controlled by the distribution of free-end positions $\{z_0\}$. The requisite slight depletion in the density at z may be achieved by removing ends from the vicinity. This by itself would also result in too few monomers below z; accordingly, extra ends must be supplied there. But all this moving of ends has little impact on the pressure profile. Before the perturbation we argued above that the pressure profile must be parabolic. Our reasoning did not depend on the density profile, but only on the equilibrium among chains ending at different heights. This equilibrium still holds in the presence of our perturbation. Accordingly, the profile remains parabolic. It simply shifts upward slightly, so that it vanishes at a slightly greater h. In this regard, our layer does not respond at all like a rubber, but rather like a simple liquid: the response is uniform throughout the layer.

This simple response relies on the perturbation being *weak*. If it is made too strong, something remarkable happens. Above we removed the needed monomers at z by removing chain ends there. But most of the monomers at z belong to chains that end above z. Thus, if we ask for too many monomers to be removed at z, we can easily deplete *all* the ends there. What happens if we must remove more monomers than this? The layer now responds in a new way. Once all the ends have been removed from the vicinity of z, the chain of reasoning leading to the parabolic pressure is broken. There is now an "depletion layer" with no ends near z. The energy $S(z)$ for a chain ending there is no longer the same as energies elsewhere (it must be larger). The pressure must still be parabolic from the surface up to the depletion layer, but in this layer it can break away from the parabolic shape. By dropping off faster with height than the parabola, the pressure profile can stretch out the chains at z to produce the required reduction in monomers. Beyond the depletion layer free ends are needed once again. The pressure must again be such that $S(z_0)$ above the zone is equal to that below; this determines its form for all heights above the depletion zone.

The depletion zone divides the chains into two populations—one set confined below the zone, and the other obliged to traverse it. The zone inhibits the otherwise free exchange of chain ends throughout the layer. This free passage may be turned on or off if one can perturb the density at one height by a small amount (how small depends on the width of the perturbed region and the shape of the perturbed density). The depletion zone mechanism thus offers a potential way to control transport across the grafted layer. This phenomenon illustrates the nonintuitive behavior that the cooperative stretching of tethered chains can show. In some ways it resembles the controlled transport possible in doped semiconductors, where the local carrier density is controlled by electrostatic equilibrium over relatively long distances. We do not yet have quantitative understanding of the depletion phenomenon in the case sketched here. But we do in a simpler case, *viz.* that of a convex grafting surface. In such a surface, like the outside of a cylinder, the chains must converge as they propagate inward from their free ends. Near the surface, there is an inevitable excess of monomers if the potential is parabolic. To remedy this the system must abandon the parabolic profile and create a depletion zone near the surface, as first anticipated by Semenov [31]. The equilibrium profiles of pressure and end density for such curved layers may be found by solving well-behaved integral equations [43]. In the case of a cylinder in melt conditions, the profiles can be found exactly [43]. One finds, *e.g.* that the depletion zone grows with the curvature and finally achieves a thickness of $2/\pi$ of the layer height, when the grafting cylinder is much smaller than the layer thickness.

CONCLUSION

In this talk I've tried to show that the cooperative stretching of chains densely tethered to a surface gives rise to qualitatively new behavior. Within the layer both local composition and local pressure respond to perturbations in ways not seen in other polymer fluids. As further types of response are explored, there is every reason to expect more new phenomena, not implicit in the response functions treated here. One hint of these possibilities is the abrupt apparent thickening in grafted layers under flow reported by Jacob Klein at this meeting. Another is the "igloo" profile that results from free-end attraction to a second surface, reported by Jean-François Joanny. These new behaviors hold out the hope that grafted layers can create controllable structure and transport properties in unanticipated ways.

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