End-Grafted Polymer Melt with Nematic Interaction

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ABSTRACT: We study the grafted polymer melt with an imposed local nematic interaction between monomers in the limit of small, fixed coverage and large molecular weight. The interaction couples the orientation of a single monomer to a self-consistently determined field describing the local nematic order parameter. For interaction strengths which avoid the nematic transition of an equivalent ungrafted molten droplet, we find that the pressure profile is reduced in magnitude and corrected by quartic terms in height. We also find that, under these conditions, the nematic ordering in the layer is proportional to the pressure in the layer. It is also the case that the free end density per unit height depends on the nematic interaction strength only through the pressure profile. The form the nematic transition takes in the brush is discussed, and the limit of very strong nematic ordering is described.

1. Introduction

Flexible-chain molecules attached to a surface at one end occur frequently in nature and technology.[1] Surfactant micelles and bilayers,[2] as seen in cell membranes and microemulsions, are a major example. In such a layer, surfactants are constrained to have their polar heads together in one plane, while their hydrocarbon tails extend into an adjacent layer. Often the tails are packed so closely that crystalline order occurs. But often the tails are less densely packed, and the local structure of the tail region is like that of a polymer melt. Nevertheless, the tails are sufficiently crowded together that they are obliged to stretch out substantially relative to their span in a melt. The elastic energy implied by this stretching is an important factor in the mechanical properties of surfactant layers.[2] Similar stretching occurs when higher molecular weight polymers are held at an interface by one end; this state occurs with amphiphilic polymers[3] and in polymer-stabilized colloids.[4]

The steric interactions of the chains are clearly important in determining their mutually stretched state. In large part this interaction may be expressed as a position-dependent pressure or monomer chemical potential. This pressure accounts for the work required to crowd an additional bit of polymer into a given position—work done to displace and stretch the surrounding chains. To understand this chemical potential in detail requires a knowledge of the local liquid structure of the polymer liquid.[5] But in many grafted layers this local structure is modified arbitrarily little by the chain stretching; thus, it becomes independent of position and does not effect the energy of mechanical deformation of the layers.

Another form of interaction has recently been shown important in the melt state of polymers.[7] It is a nematic interaction: the energy required to insert a bit of chain depends on its *orientation*. These effects can be treated formally by introducing local operators describing the orientation of the monomers on a chain as executed by Carton and Leibler.[6] The orientation of a group of monomers along a chain is determined by two local quantities: the chain tension and the average alignment of the neighboring monomers. This problem was first investigated by P.-G. de Gennes in the case of liquid crystalline elastomers, with the chain tension being applied externally by shearing an initially isotropic cross-linked network. Our calculation builds on these approaches.

Experimentally, one way to gauge the importance of the nematic interaction is to impose a slight overall nematic order in a given region except for one chain. This chain will then acquire some fraction of the surrounding nematic order because of the nematic interactions. If this fraction exceeded unity, the melt would be unstable against the growth of spontaneous nematic order. By probing the alignment of un-cross-linked guest chains in a stretched rubber, Ylitalo, Fuller, and Pearson showed[7] that this fraction can be of order 0.4 in polypropylene. It is expected to be even higher in polyethylene, the polymer homologue of a simple surfactant tail.

The strength of this nematic interaction raises the question of how nematic effects modify the structure of a grafted layer. Such layers are observed in the melt lamellar phase of diblock copolymers with a nemategenic block.[8] In this paper we explore this question. The grafted state in itself represents a subtle equilibrium between elastic and interaction energies coupled across the entire layer.[9,10] The addition of nematic interactions increases the potential for cooperative effects. We first show how self-consistent-field (SCF) methods developed for the grafted layer may be augmented to include nematic interactions. Here we consider the most tractable limit that shows nematic effects: the limit of very weak nematic alignment owing to grafting, but local nematic interactions approaching the threshold of spontaneous order. We then discuss the potential quantitative importance of nematic interactions in real grafted layers of various types.

Nematic interactions have been treated in earlier studies of grafted-chain layers. The lattice method of Scheutjens and Fleer implicity contains a degree of nematic interaction,[11] as do other numerical methods that use an explicit monomeric representation of the chains.[12,13] These treatments may well be more suitable than ours for including nematic effects in a realistic way—especially for surfactant layers. Our approach is aimed instead at isolating the effects of nematic interactions and educing features that are independent of the explicit chain structure.

In a grafted melt without nematic interactions, the mechanical pressure in the layer and the distribution of free ends are fixed rather simply by imposing monodispersity of the chains and incompressibility.[10] However, when nematic interactions are included, the chain trajectories depend on another field describing the average nematic ordering as a function of position in the layer. This average

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ordering depends in turn on the chain trajectories. Thus, the nematic ordering must be dealt with in a self-consistent manner.

The inclusion of nematic interaction alters the free energy for a single chain in the layer, coupling the orientation of monomers in the chain to a self-consistently determined field arising from the orientation of neighboring monomers. We shall see that the main effect of this coupling is to cause the chain elastic constant, the packing length a, to become a function of position in the layer. We exhibit the altered single-chain free energy and use the limit of strong global yet weak local stretching to make a connection between the chain trajectories and the classical mechanics of a particle with position-dependent mass. Imposing a constant monomer concentration and calculating the nematic order self-consistently, we exhibit a nonlocal, nonlinear integral equation determining the nematic field as a function of pressure. The interaction strength which marks the onset of a strongly nematic state is calculated in the Alexander model,[14,15] in which all free chain ends are constrained to reside at the extreme edge of the layer. For interaction strengths weaker than the nematic threshold, all fields can be calculated to second order in the grafting density, or coverage, of the brush. Below this threshold, small corrections to the noninteracting grafted brush appear. Just after the transition has occurred, the major effect is that the effective packing length for the chains is cut approximately in half. Far beyond the transition, when strong nematic order has been induced, the packing length becomes one-third of its noninteracting value and ceases to become a function of position in the layer; thus, the pressure profile for the layer again returns to that of the noninteracting case: a parabolic form.[10]

2. Alexander Model

We first consider the case of nematic interactions in the Alexander brush. In doing this, we derive the microscopic responses of a short sequence of monomers to a small chain tension and an arbitrary nematic field in the layer. This model was essentially studied by Jäning[16] (his case of infinitely rigid polymer chains). Our calculation here follows closely that of ref 17; additionally, a treatment of this model is also possible by way of a Landau free energy.[18] Here, we stress a mechanical view of monomers as rods in an orientation-dependent potential. We are primarily interested in the self-consistent form of the nematic responses in this problem.

The chains we consider are composed of N freely jointed links of rigid length a. Each chain has one end attached to a flat plane, at a coverage of σ grafted ends per unit area. The free end of each chain is constrained to lie at a height h above the grafting plane, through the application of an external tension, α. Furthermore, the rods are assumed to interact with each other via the classic Maier–Saupé interaction

$$U_{ij}^{\text{int}} = -t\delta(r_i - r_j)q_i^{\alpha\beta}q_j^{\alpha\beta} \tag{1}$$

where t is a dimensionless interaction parameter (when all energies are scaled by the temperature) and $q^{\alpha\beta}$ (sometimes denoted $S^{\alpha\beta}$) is the orientational tensor for the monomer under consideration

$$q_i^{\alpha\beta} = \frac{1}{2}(3u_i^{\alpha}u_i^{\beta} - \delta^{\alpha\beta}) \tag{2}$$

with u_i^{α} a unit vector oriented along the ith rod. The mean-field reduction of (1) is accomplished by assuming that $q_j^{\alpha\beta}$ is given by the average alignment in the system, $\overline{q^{\alpha\beta}}$. Therefore, we can write that

$$U_i^{\text{int}} = -\beta^{\alpha\beta}q_i^{\alpha\beta}, \quad \text{with } \beta^{\alpha\beta} = t\overline{q^{\alpha\beta}} \tag{3}$$

As a result of rotational symmetry perpendicular to the grafting plane, $\overline{q^{\alpha\beta}}$ is specified entirely by its 3–3 component, and we can write that

$$U_i^{\text{int}} = \beta q_i, \quad \text{with } q_i = P_2(u_i^z) \tag{4}$$

where P_2 is, of course, the second Legendre polynomial. At this point, our treatment of the nematic interaction is that of Maier and Saupé.

But, the rods also feel the influence of the tension α. The tension adds to the energy of a rod an elastic term

$$U_i^{\text{el}} = -\alpha u_i^z \tag{5}$$

In this model, all monomer links are subject to the same local conditions and are therefore statistically independent. Therefore, we are justified in recasting the problem of the Alexander brush in the form of determining the statistical mechanics of a collection of noninteracting rigid rods subject to the microscopic Hamiltonian

$$H_i = -\beta q_i - \alpha u_i^z \tag{6}$$

in accordance with the self-consistency in (3). All relevant quantities may now be calculated in the canonical ensemble.

In the limit of small coverage, $h \ll Na$, and the chains are weakly stretched. This corresponds to small chain tensions, and we therefore expand (6) to lowest nontrivial order in α in calculating all quantities. We introduce the usual single-rod distribution function, $f \equiv e^{\mathrm{H}}$, and the usual partition function as the f-weighted sum over orientations: $Z = \int f$. We can then calculate the average nematic order and the average normal extension of the rods as

$$\bar{q} = \frac{\partial \ln Z}{\partial \beta} = L(\beta) + \frac{\alpha^2}{3}\frac{\mathrm{d}L}{\mathrm{d}\beta} + O(\alpha^4)$$

and

$$\overline{u^z} = \frac{\partial \ln Z}{\partial \alpha} = \alpha\frac{1 + 2L(\beta)}{3} + O(\alpha^3) \tag{7}$$

The function $L(\beta)$ for freely jointed chains is shown in Figure 1; $L(\beta)$ is analogous to the Langevin function appearing in calculating dipole response. $L(\beta)$ gives the ungrafted nematic response of a rod coupled through (6) to a nematic field β. All model dependence in this discussion is contained in this function.

The field β, however, is supposed to have arisen self-consistently from (3). Thus, we find self-consistent solutions for $\beta(t)$ only when

$$\frac{\beta}{t} = L(\beta) + \frac{\alpha^2}{3}\frac{\mathrm{d}L}{\mathrm{d}\beta} \tag{8}$$

is satisfied. We note that with $\alpha = 0$, $\beta = 0$ for $0 < t < t^*(\alpha{=}0) \sim 4.5$, at which point there is a discontinuous jump in $\bar{q} = \beta/t$ to approximately a third of its saturation value. Thus, with no chain tension, i.e., the case of an ungrafted droplet, the model exhibits a first-order nematic transition. With α small, $\bar{q}$ no longer vanishes for $t < t^*(\alpha)$ but is of order α^2. Also, the imposition of a tension is sufficient to move t^* downward by order α^2. Thus, we anticipate the possibility of a stretch-induced nematic transition. The stretch is most conveniently controlled by adjusting the coverage, σ.

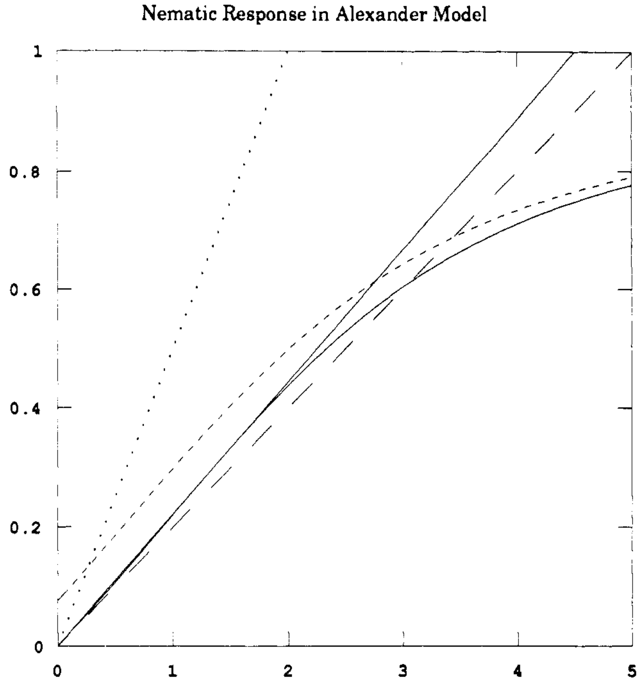

Figure 1. Solid curve indicating $L(\beta)$ for $0 < \beta < 5$. The long-dashed line has $t = 5.0$ and marks the onset of linear instability of the droplet to forming spontaneous nematic order. The solid line has $t = t^* = 4.5$ and marks the value of coupling at which the nematic transition occurs. The dotted line has $t = 2.0$, approximately that of polypropylene. The short-dashed curve represents the nematic response when a large ($\alpha = 1$) tension is applied. With $\alpha = 0$ and $t = t^*$, we see that $\beta^* = 1.44$ and that $L(\beta^*) = 0.32$. This choice of tension is well above that which removes the nematic transition.

When the tension becomes too large, the discontinuous jump in $\bar{q}$ at t^* disappears. In our model, this occurs when $\alpha = 0.37$. With this tension and β given by its self-consistent value with zero stretch, (7) implies that $\overline{u^z} = 0.16$. In other words, when the tension is sufficient to cause the height of the brush to exceed 16% of its fully extended height, the jump no longer occurs, and the self-consistent nematic response is continuous.

When we move to the SCF calculation below, we will need to be able to translate the responses given in (7) to the continuum language, where we specify the volume, V, of our polymer chains, and parametrize monomer segments along a chain by chain volume. Thus, we envision a short sequence of n monomers of small volume $\Delta v = nv$ subjected to a small tension and a nematic field such that the average extension of the short chain along the field direction is Δz. Then we can calculate

$$\overline{u^z} = \frac{\Delta z}{na}\frac{nv}{\Delta v} = \frac{\Delta z}{\Delta v}\frac{v}{a} = \frac{\mathrm{d}z}{\mathrm{d}v}\frac{1}{\sigma_{\mathrm{sat}}} \tag{9}$$

where at the saturation coverage, σ_{sat}, all chains are fully stretched. Small chain tension is only possible for $\sigma \ll \sigma_{\mathrm{sat}}$.

In particular, we can use (7) and (9) to eliminate the chain tension at a particular point in favor of the chain "velocity", $\mathrm{d}z/\mathrm{d}v$:

$$\alpha = \frac{3}{1 + 2L(\beta)}\frac{1}{\sigma_{\mathrm{sat}}}\frac{\mathrm{d}z}{\mathrm{d}v} \tag{10}$$

This will be a useful result in our discussion of the single-chain free energy in the SCF theory developed below.

3. SCF Theory: Single-Chain Free Energy

We envision a melt of monodisperse polymer chains, each with total volume V and one free end constrained to lie on a flat planar surface. Again, the coverage σ is the number of tethered ends per unit area at the grafting plane, and the overall height of the layer is fixed by $\sigma = h/V$.

We consider a single chain in this environment and parametrize the monomers on the chain by the partial volume along the chain at which they appear. The chain is made of small segments of volume Δv which have a small extension perpendicular to the grafting surface of length Δz. We can build up an identical chain by bringing short chains one by one into the layer to the appropriate height, putting them into contact with the local nematic field, β, and finally by imposing whatever tension is appropriate to supply the strain Δz, thus connecting them into a large chain. The free energy of the chain is thus the sum of the free energy costs to perform this operation for each segment on the chain, or

$$F_1 = \int_0^V \mathrm{d}v\, [p(z) + g(\alpha,\beta)] \tag{11}$$

where the pressure, p, is the free energy cost to bring a packet of monomers to height z, and $g(\alpha,\beta) = a\sigma_{\mathrm{sat}}^2 F(\alpha,\beta)$. $F(\alpha,\beta)$ is simply given by the free energy per rod from the Alexander model of section 3:

$$F(\alpha,\beta) = \ln Z(\alpha,\beta) \tag{12}$$

When expanding (12) for small α, it is important to note that the order α^0 term in $g(\alpha,\beta)$ depends on the parameter v only through an undetermined field, $\beta(z)$, just as does the pressure. Therefore, it is possible to combine these two terms into a single unknown function of position which we will simply refer to as the pressure from now on. With this consideration, the free energy takes the form

$$F_1 = \int_0^V \mathrm{d}v \left[p + \frac{1}{2}\left(\frac{a}{1 + 2L(\beta)}\right)\left|\frac{\mathrm{d}z}{\mathrm{d}v}\right|^2\right] \tag{13}$$

where the constant a is fixed to be the packing length by considering the $\beta = 0$ limit and trading the tension α for the chain velocity $\mathrm{d}z/\mathrm{d}v$ according to (10). This expression is correct to lowest order in $\mathrm{d}z/\mathrm{d}v$, but the higher orders which contribute to (13) are unimportant as long as $\sigma \ll \sigma_{\mathrm{sat}}$. The excluded terms remain small even when the nematic field is turned on. When all terms in the velocity are included in (13), the finite extensibility of the chains determines the brush configuration for extremely large tensions.[19,20] So, the single chain functional differs in form from the nonnematic case in the appearance of a position-dependent elastic constant, which we define so that

$$F_1 = \int_0^V \mathrm{d}v \left[p + \frac{1}{2}m(z(v))\left|\frac{\mathrm{d}z}{\mathrm{d}v}\right|^2\right] \tag{14}$$

With V large so that the end-to end distance of the typical chain is much greater than its gyration radius, the ensemble of available chain trajectories, $z(v)$, will fluctuate narrowly about those which minimize (14). Extremizing (14) leads to the classical mechanics of a particle moving in the potential $-p(z)$ with a position-dependent mass, $m(z)$. We can therefore state the analogy of the law of conservation of energy for a chain with its free end at a height z_0. As $\alpha \sim \mathrm{d}z/\mathrm{d}v$, mechanical equilibrium at the free end requires that $\mathrm{d}z/\mathrm{d}v|_{z_0} = 0$, we arrive at

$$\frac{\mathrm{d}z}{\mathrm{d}v} = \sqrt{\frac{2(p(z) - p(z_0))}{m(z)}} \tag{15}$$

Once we calculate $m(z)$ self-consistently, we can integrate (15) to find the chain trajectories, $z(v)$.

4. Constraints

With the single-chain "energy" conservation (15), we impose on the chains the further restrictions of constant density and self-consistency in order to determine β as a function of pressure. Once this is accomplished, monodispersity can be invoked in order to determine the pressure vs height profile in the layer.

We can ensure a constant monomer volume fraction by building the layer from the outer surface inward by adjusting the concentration of free ends as needed. Letting the partial coverage $\sigma(z)$ stand for the number of chains passing through the height z per unit area parallel to the grafting surface (so that $\sigma(0) = \sigma$), we have that

$$\phi(z) = \int_z^h \mathrm{d}z_0 \frac{\mathrm{d}\sigma_0}{\mathrm{d}z_0} \phi(z;z_0) \tag{16}$$

$\phi(z)$ is the monomer volume fraction at the height z, which we now set equal to unity to express the lack of any solvent molecules, and $\phi(z;z_0)$ is the monomer density along a single chain at the height z given that the chain's free end is located at the height z_0. The expression $\mathrm{d}\sigma/\mathrm{d}z\ \Delta z$ gives the number of free ends in the interval $(z, z + \Delta z)$.

With our classical mechanics analogy, we identify $\phi(z;z_0)$ with the amount of time that the particle spends in the vicinity of z; in other words, this quantity is given by the inverse chain velocity, $\mathrm{d}\upsilon/\mathrm{d}z$.[10] Inserting this into (16) and changing the variable of integration from position to pressure, we have

$$1 = \int_0^p \mathrm{d}p_0 \frac{\mathrm{d}\sigma_0}{\mathrm{d}p_0} \frac{\mathrm{d}\upsilon}{\mathrm{d}z} \tag{17}$$

as the correct expression. Further, using (15) to eliminate $\mathrm{d}\upsilon/\mathrm{d}z$, we arrive at

$$1 = \int_0^p \mathrm{d}p_0 \left[\frac{\mathrm{d}\sigma_0}{\mathrm{d}p_0}\sqrt{\frac{m_0}{2}}\right]\frac{1}{\sqrt{p - p_0}} \tag{18}$$

Equations of the form (18) can be inverted directly,[21] but it is clear that (18) determines the combination in brackets uniquely, and further

$$1 = \int_0^p \mathrm{d}p_0 \left[\frac{1}{\pi}\frac{1}{\sqrt{p_0}}\right]\frac{1}{\sqrt{p - p_0}} \tag{19}$$

can be checked directly. Therefore, we conclude that when free ends are distributed per interval in pressure by

$$\frac{\mathrm{d}\sigma}{\mathrm{d}p} = \frac{1}{\pi}\sqrt{\frac{2}{m(p)\,p}} \tag{20}$$

the constant density condition is satisfied. Once the unknown function $m(p)$ is determined, (20) fixes the partial coverage as a function of pressure.

The new constraint in this problem expresses the self-consistency of the nematic order. The mass is an explicit function of β, for the time being an unknown function of position. However, we wish to think of β as arising from the average alignment of the monomers at that position. In other words

$$\beta(z) = t\langle q\rangle(z) \tag{21}$$

where $\langle q\rangle$ is the average nematic alignment of the monomers in the neighborhood of z. To calculate $\langle q\rangle(p)$, we can again think of building up the layer from the tip inward according to (20) while keeping track of the q of each monomer at the inspection site, p. More precisely, we have that

$$\langle q\rangle = \int_0^p \mathrm{d}p_0 \frac{\mathrm{d}\sigma_0}{\mathrm{d}p_0} q\left(\frac{\mathrm{d}z}{\mathrm{d}\upsilon},\beta\right) \phi(p;p_0) \tag{22}$$

where $q(\mathrm{d}z/\mathrm{d}\upsilon,\beta)$ is the nematic alignment of a short segment of monomers under the influence of the field β and the strain $\mathrm{d}z/\mathrm{d}\upsilon$. This response can be borrowed from (7):

$$q\left(\frac{\mathrm{d}z}{\mathrm{d}\upsilon},\beta\right) = L(\beta) + \frac{3}{{\sigma_{\mathrm{sat}}}^2}\frac{\mathrm{d}L}{\mathrm{d}\beta}\frac{1}{(1 + 2L)^2}\left|\frac{\mathrm{d}z}{\mathrm{d}\upsilon}\right|^2 \tag{23}$$

were the chain tension has again been replaced with the chain strain via (10). Using the form of $\phi(p;p_0)$ above and (23), the self-consistency equation can be written in full glory as

$$\beta(p) = t\int_0^p \mathrm{d}p_0 \frac{\mathrm{d}\sigma_0}{\mathrm{d}p_0}\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\left[L(\beta) + \frac{3}{{\sigma_{\mathrm{sat}}}^2}\frac{\mathrm{d}L}{\mathrm{d}\beta}\frac{1}{(1 + 2L)^2}\left|\frac{\mathrm{d}z}{\mathrm{d}\upsilon}\right|^2\right] \tag{24}$$

Now, the term in brackets depends on p_0 only through the $|\mathrm{d}z/\mathrm{d}\upsilon|^2$ expression. Thus the first, $L(\beta)$, term can be computed easily; the integral left behind is simply that of (17) which is equal to unity by the constant density constraint. The self-consistency is then expressed by

$$\beta(p) = tL(\beta) + \frac{3t}{{\sigma_{\mathrm{sat}}}^2}\frac{\mathrm{d}L}{\mathrm{d}\beta}\frac{1}{(1 + 2L)^2}\int_0^p \mathrm{d}p_0 \frac{\mathrm{d}\sigma_0}{\mathrm{d}p_0}\frac{\mathrm{d}z}{\mathrm{d}\upsilon} \tag{25}$$

With the help of (20) and (15), the final form this condition takes is

$$\beta(p) = tL(\beta) + \frac{6t}{\pi{\sigma_{\mathrm{sat}}}^2}\frac{\mathrm{d}L}{\mathrm{d}\beta}\frac{1}{(1 + 2L)^2}\frac{1}{\sqrt{m}}\int_0^p \mathrm{d}p_0 \sqrt{\frac{p - p_0}{m_0 p_0}} \tag{26}$$

As the mass is defined to be a definite function of β and the form of $L(\beta)$ is known numerically, (26) specifies the pressure variation of β. The term m_0 appearing in the integrand of the second term in (26) is the value of the mass at pressure p_0; thus, finding the solution of this equation is formidable.

However, the second term in (26) is of the order $(\sigma/\sigma_{\mathrm{sat}})^2$, as the integral expression will scale like p and $p \sim a\sigma^2$. With $\sigma \ll \sigma_{\mathrm{sat}}$, we see that β is determined primarily by the self-consistency expression for the Alexander model with zero stretch and is modified from this result in a pressure-dependent manner by a term of order $(\sigma/\sigma_{\mathrm{sat}})^2$. Therefore, if t is kept below its transition value, then β itself will be of order $(\sigma/\sigma_{\mathrm{sat}})^2$, as $\beta = 0$ is the self-consistent result from the Alexander model in this range of t.

Thus, the limit of small β is relevant, and the dependence of this calculation on the form of $L(\beta)$ given for freely jointed rods is limited only to the requirement that $L \sim \beta$ as $\beta \to 0$. This limit of linear response should display a high degree of universality, adequately describing most nematagenic liquids. In this limit, we find vast and glorious simplifications:

$$L(\beta) = \beta/5$$

$$\mathrm{d}L/\mathrm{d}\beta = 1/5$$

$$m(\beta) = a\left(1 - \frac{2}{5}\beta\right) \tag{27}$$

With these expressions, we can solve (26) for $\beta(p)$ exactly:

$$\beta(p) = \frac{3t}{5-t}\left(\frac{p}{a\sigma_{\mathrm{sat}}^2}\right) \tag{28}$$

This result should be valid up until the nematic transition in the layer occurs at $t \simeq 4.5$.

With β determined self-consistently by (28), we can easily find $m(p)$ and then integrate (20) to find the partial coverage

$$\sigma(p) = \sqrt{\frac{8}{a\pi^2}}\sqrt{p}\left(1 + \frac{1}{5}\frac{t}{5-t}\frac{p}{a\sigma_{\mathrm{sat}}^2}\right) \tag{29}$$

so that the pressure at the bottom of the layer, P (for which $\sigma(P) = h/V$), is given by

$$P = \frac{a\sigma^2\pi^2}{8}\left[1 - \frac{\pi^2}{20}\frac{t}{5-t}\left(\frac{\sigma}{\sigma_{\mathrm{sat}}}\right)^2\right] \tag{30}$$

The effect of the nematic interaction is to reduce the maximum pressure occurring in the noninteracting brush according to (30).

In order to describe the variation of the pressure in height, we impose monodispersity on our chains. If each chain is to have a volume V, we can build up this volume piece by piece:

$$V = \int_0^V \mathrm{d}v = \int_0^{z_0}\mathrm{d}z\,\frac{\mathrm{d}v}{\mathrm{d}z} = \int_{p_0}^{P}\mathrm{d}p\,\frac{\mathrm{d}z}{\mathrm{d}p}\frac{\mathrm{d}v}{\mathrm{d}z} \tag{31}$$

Again, we eliminate $\mathrm{d}v/\mathrm{d}z$ through (15), so that

$$V = \int_{p_0}^{P}\mathrm{d}p\,\frac{\mathrm{d}z}{\mathrm{d}p}\sqrt{\frac{m}{2}}\sqrt{\frac{1}{p-p_0}} \tag{32}$$

and recognize in analogy to the derivation of (20) that

$$\frac{\mathrm{d}z}{\mathrm{d}p} = \frac{V}{\pi}\sqrt{\frac{2}{m}}\sqrt{\frac{1}{P-p}} \tag{33}$$

valid at all heights z at which free ends reside. No "dead zones" appear in the nematically interacting brush for exactly the same reasons as in the nonnematic brush.[10] Therefore, we can use the known form of $m(p)$ to integrate (33) and calculate the pressure profile in the layer: we find that

$$p(z) = \frac{a\sigma^2\pi^2}{8}\left(1 - \frac{z^2}{h^2}\right)\left[1 - \frac{\pi^2}{20}\frac{t}{5-t}\left(1 - \frac{z^2}{h^2}\right)\right] \tag{34}$$

Again, we see that the pressure is reduced relative to the noninteracting case, making the brush looser than it would otherwise be and introducing quartic corrections in the height. The nematic interactions have their largest influence at the wall where the stretching of the chains is largest and vanish at the tip where all chains are unstretched.

It is interesting to note that (33) and (20) can be combined to give a mass-independent description of the free end density per unit height.

$$\frac{\mathrm{d}\sigma}{\mathrm{d}z} = \frac{\mathrm{d}\sigma}{\mathrm{d}p}\frac{\mathrm{d}p}{\mathrm{d}z} = \frac{1}{V}\sqrt{\frac{P-p}{p}} \tag{35}$$

This equation should hold for all t.

5. Nematic Transition and Beyond

The nematic transition may be induced by stretch if we adjust t to be within $o((\sigma/\sigma_{\mathrm{sat}})^2)$ of the ungrafted transition interaction strength. Further, the spatial variation of β should be given by the solution to (26) when L is no longer limited to linear response. At the transition in the Alexander model, the self-consistent value of β has $L(\beta) \sim 0.33$. Therefore, in calculating the mass, we find that $m^* \sim a/2$, since $m = a/[1 + 2L(\beta)]$. However, we have not yet determined the spatial variation of the mass at the transition. Certainly, once the transition has taken place, a linearization about the zero-coverage solution should make (26) again reducible by elementary means.[22] As t becomes very large, so that $\beta \rightarrow \infty$ and $L(\beta) \rightarrow 1$, we can exhibit the exact solution of the problem by noting that under such circumstances the mass would become nearly constant in the layer and approach a value of $a/3$. In particular, the pressure in the large t limit is simply reduced by a factor of 3 compared to the $t = 0$ result.

6. Discussion

Having shown how nematic effects may be treated formally, it is important to estimate how large the predicted effects might be in real polymer systems. Happily, there is experimental information about the main parameter of our theory, namely, the strength of the nematic interaction. The chief effect of this interaction is that if some nematic alignment is imposed on the molecules in a region, an added test molecule introduced into the region will inherit some fraction of this alignment. The fraction, called the "alignment ratio", is larger if the nematic interaction is stronger; if it reaches unity and if the test molecule is the same as the others, spontaneous nematic order must occur. Indeed, if this fraction reaches 0.9 and the chains are adequately described by a freely-jointed rod model, then a first-order nematic transition will occur in the bulk. Thus, if the bulk is not in an explicitly nematic state, it should be impossible to measure this fraction to be greater than 0.9.

If we denote the imposed alignment by Q, then, in the language of section 3, this region is characterized by a potential $\beta = tQ$. This potential in turn induces an alignment $q = L(\beta) = \beta/5 + O(\beta^2)$, so that for weak ordering $q = tQ/5$, or $q/Q = t/5$. With $t = t^*$, this fraction should be valued at $t^*/5$, or 0.9. We note that this ratio is independent of the normalization of q and Q, provided they are the same. It does, however, depend on what molecular axis is used to define q and Q.

Ylitalo et al.[7] were able to measure Q and q using a local optical probe of various cross-linked rubbers containing traces of dissolved polymer of the same type. Their probe detects nematic alignment of one particular bond in the monomer unit. Remarkably, they found that using this measure of alignment q/Q was large—0.4 for polypropylene and 0.45 for an ethylene–propylene copolymer. Translated into our language, this means that $t \simeq 2$ for these species. It is of great interest to know the corresponding t for polyethylene, the polymeric homologue of a surfactant tail, but this has not yet been measured. But in view of the shape of a polyethylene chain, it is plausible that its t parameter is at least as large as that of the molecules studied. This is because polyethylene lacks the methyl side branches of polypropylene, and these ought to interfere with alignment.

Despite this large nematic tendency, the net effects for typical grafted polymers are small. This is because σ is generally small relative to σ_{sat} for such systems. For example, in the recent scattering study by Auroy et al.,[23] $\sigma/\sigma_{\mathrm{sat}}$ was roughly 1%. As the correction factor depends on the square of this coverage ratio, the effects in this case are tiny (of the order 10^{-5}). In order to get deviations on the order of 1% with $t \simeq 2$, it is clear that $\sigma/\sigma_{\mathrm{sat}} \simeq 20\%$. Unless the overall stretching of the chains is very strong, as is the case in surfactant layers, the sizes of the nematic effects are likely to be quite small.

In surfactant layers the grafting density is typically much larger; in many cases the hydrocarbon tails attain a fully-extended all-trans configuration. Our interest here is the disordered "liquidlike" state seen at lower grafting densities.[24] A typical grafting density for such a state is 0.04 chains/Å^2. We may estimate σ_{sat} by taking a height $h_{\max}$ of all-trans chains extended perpendicular to the surface; this yields $\sigma_{\text{sat}} = 0.09$ grafted chains/Å^2. Here the nematic interaction parameter t should be at least as great as in the polymers studied in ref 7: $t \geq 2$. Thus, using (30), we expect nematic effects to decrease the pressure by roughly 7% in such layers.

7. Conclusion

From this work it is clear that nematic interactions can alter the stress in a grafted polymer layer and that this alteration can be treated by extending the "Newtonian mechanics" approach. In such a treatment, the nematic interactions manifest themselves through a position-dependent mass. For grafting densities typical of high polymers, we have shown that even large nematic interactions (short of spontaneous nematic order in an equivalent ungrafted system) cannot alter the layer appreciably. But, for grafting densities typical of surfactants, the nematic interactions have significant effects. For these short chains close to full extension our theory cannot hope to give accurate quantitative predictions. But it can serve as a good semiquantitative guide as illustrated in the Discussion.

Even for small coverages, the effects of the stretching are likely to be dramatic if a nematic transition in the layer can be induced. For this analysis to be quantitatively valid, we must be able to tune the t interaction parameter finely. In this case, an exact solution of (26) should describe this important case well.

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References and Notes

(1) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1991**, *100*, 1.
(2) *Physics of Amphiphilic Layers*; Langevin, D., Meunier, J., Eds.; Springer: Berlin, 1987.
(3) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
(4) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic: London, 1983.
(5) Schweizer, K. S.; Curro, J. G. *Phys. Rev. Lett.* **1988**, *60*, 809.
(6) Carton, J.-P.; Leibler, L. *J. Phys. (Paris)* **1990**, *51*, 1638.
(7) Ylitalo, C.; Fuller, G.; Pearson, D. *Rheol. Acta* **1990**, *29*, 543.
(8) Adams, J.; Gronski, W. *Macromol. Chem., Rapid Commun.* **1989**, *79* (8), 687.
(9) Semenov, A. N. *Zh. Eksp. Teor. Phys.* (in Russian) **1985**, *88*, 1242; (Engl. *Transl.*) *Soc. Phys. JETP* **1985**, *61*, 733.
(10) Milner, S. T.; Witten, T. A.; Cates, M. E. *Europhys. Lett.* **1988**, *5*, 413. Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.
(11) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619.
(12) Ben-Shaul, A.; Szleifer, I.; Gelbart, W. M. *J. Chem. Phys.* **1985**, *83*, 3597.
(13) Viovy, J. L.; Gelbart, W. M.; Ben-Shaul, A. *J. Chem. Phys.* **1987**, *87*, 4114.
(14) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983.
(15) de Gennes, P.-G. *J. Phys. (Paris)* **1976**, *37*, 1443. de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.
(16) Jäning, F. *J. Chem. Phys.* **1979**, *70*, 3279.
(17) Warner, M.; Wang, X. J. *Macromolecules* **1991**, *24*, 4932.
(18) Halperin, A. *J. Chem. Phys.* **1986**, *85*, 1081.
(19) Shim, D. F. K.; Cates, M. E. *J. Phys. (Paris)* **1989**, *50*, 3535.
(20) Lai, P.-Y.; Halperin, A. *Macromolecules* **1991**, *24*, 4981.
(21) Milner, S. T.; Wang, Z.-G.; Witten, T. A. *Macromolecules* **1989**, *22*, 489.
(22) The linearization of (26) is possible for all t except those which are slightly greater than t^*, as $(\beta - \beta^*) \sim (t - t^*)^{-1/2} f(p/P)$ for $t > t^*$. Thus, only a small band about t^* is inaccessible to this linearization.
(23) Auroy, P.; Auvray, L.; Leger, L. *Phys. Rev. Lett.* **1991**, *66*, 719.
(24) Gaines, G. L., Jr. *Insoluble Monolayers at Gas–Liquid Interfaces*; Interscience: New York, 1965.