Confinement and compression of an oligomer brush

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Self-assembled monolayers and oligomer brushes confined between two parallel plates show compressional forces that are nonmonotonic as a function of plate separation. In a realistic model of short alkanethiols, based on the rotationally isomeric state model with parameters from *ab initio* calculations, the authors show that nonmonotonic forces arise from the elimination of longer conformers as the distance between the plates is reduced. This nonmonotonicity is a size effect that disappears when the length of the polymer molecule is sufficiently increased. An analytical model is developed that allows experimentalists to extract energy-averaged brush height distributions from compressional force curves. © 2010 American Vacuum Society. [DOI: 10.1116/1.3455152]

I. INTRODUCTION

Self-assembled monolayers (SAMs) of polymers have been the subject of intense research for decades,¹ due in large part to their industrial and medical applications as antifouling paints and protein resistant coatings.²⁻⁷ Early works by Alexander⁸ and de Gennes⁹ elucidate the scaling behavior of SAMs at different grafting densities. Moderately dense SAMs are further illuminated by the Milner-Witten-Cates theory,¹⁰ which can be derived using a self-consistent field approach,^{11,12} and are appropriate when the detailed tertiary structure of the polymer brush can be neglected. Recent efforts have focused on treating SAMs and polymer brushes in greater detail;¹³⁻¹⁸ however, most of these theoretical works deal with long chains, for which microscopic details of the structure of the polymer are less relevant and simple models such as the wormlike chain model suffice. Such microscopic details become important for short chains, which are the subject of this article.

Here we theoretically investigate the structural and dynamical responses of polymer brushes to confinement, with the intention to explain recent experiments showing nonmonotonic compressional forces of alkanethiol monolayers.¹⁹ Experimentally, oligomer molecules are end grafted to a surface: a second surface (which may also be covered with a SAM or oligomer brush) is then brought in contact with the first, and the resulting compressional force is measured as a function of the separation via the surface force apparatus^{20,21} (AFM).^{19,22,23} or atomic force microscope

Simple behavior of compressed SAMs can be understood using scaling arguments,⁸ creation of *gauche* defects,²⁴ geometrical models (cooperative tilting),²⁵ or cubic lattice models.²⁶ However, these models neglect polymer-specific characteristics that can result in unexpected behavior. For example, attractive electrostatic forces in polyelectrolyte brushes lead to a first order phase transition (collapse) unparalleled in neutral SAMs.²⁷ Polymer-specific characteristics can be included using single-chain mean-field theory, where

We begin this article by giving some details on the RIS model and the method used to calculate the free energies as a function of plate separation including volume exclusion fully. We show Helmholtz and internal free energies, force extension curves, entropy changes, and monomer distributions. The final discussion will elaborate on our finding that conformer exclusion as a function of decreasing plate separation is the physical origin for nonmonotonic forces. Here we also present a simple model that allows the experimentalist to extract the energy-averaged height distribution from the force curves.

II. THEORETICAL MODEL

We describe a single polymer molecule by a three-state RIS model. Such models have a number of parameters such as self-energies of the three states (*trans*, gauche +, gauche -), interaction energies between nearest neighbors along the chain and geometric parameters such as bond lengths, bond angles, and dihedral angles; all these parameters can be determined from first principles quantum mechanical calculations, valid for polymers of arbitrary length.³¹ For alkane molecules, we use the parameters determined by coupled cluster theory calculations, ³² as given in Table I.

single molecule statistics are treated exactly within a given model, and intermolecular interactions are included approximately using a mean-field approach.^{28–30} Alternatively, the statistics and interactions of *multiple* molecules can be treated exactly.³⁰ This is the rationale behind our approach: We represent alkanethiols between 10 and 16 monomers long using the rotationally isomeric state (RIS) model. Polymer brushes at various grafting densities are then modeled with a unit cell containing four polymer molecules and periodic boundary conditions, with excluded volume interactions included as hard core repulsions. At this level of detail, we find that nonmonotonic compressional forces can arise from the elimination of longer conformers as grafting plates approach one another. The nonmonotonicity is a size effect that disappears as the length of the polymer molecule increases.

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TABLE I. Self-energies and interactions in meV for the RIS model of alkanes, together with bond length, bond, and dihedral angles.

E_t	E_g	V _{tt}	V_{tg}	V_{gg}	$V_{gg'}$	b (Å)	ϕ (deg)	θ (deg)
0	23.4	0	0	-11.3	67.7	1.52	68	0 ± 70

To calculate the canonical partition function, we divide the grafting surface into repetitive unit cells chosen large enough to accommodate four polymers on equidistant grafting sites. Although the polymer brush will have the periodicity of the unit cell, choosing the latter large enough to accommodate several polymers gives some freedom on the small scale. The calculation proceeds in six steps.

- (1) We attach the thiol monomer of the first polymer on a grafting site at a fixed bond angle $\theta_0 = 20^\circ$ with respect to the surface normal and with arbitrary azimuthal angle ϕ_0 .
- We randomly choose the next monomer to be either t, g₊, or g₋ and store the corresponding self-energy.
- (3) We choose the next monomer randomly, and add its selfenergy and its interaction energy with the previous monomer.
- (4) At each step, we check for volume exclusion to all earlier monomers based on the van der Waals radius, also checking overlap to neighboring unit cells via the periodicity requirement. If overlap occurs the conformer is rejected, and a new calculation is started. Volume exclusion also includes a check that the polymer stays within the space allowed by the confining plate.
- (5) For a run in which all monomers are surviving, we form the corresponding Boltzmann factor and store it.
- (6) These five steps are repeated for the other polymers in the unit cell and their Boltzmann weights are added together resulting in the canonical partition function for the unit cell.

Biased configurational sampling can also be used in order to increase numerical efficiency,^{33,34} although this is not necessary for short chains and is thus not done in the present study. To get good statistics, we repeat these calculations often enough to obtain a large number of unit cell configurations, typically 10⁵. The result is a statistically averaged canonical partition function Z(T, h, N), where T, h, and N are the temperature, the plate separation, and the number of monomers in each oligomer, respectively. From the partition function, we get the Helmholtz free energy F(T,h,N) = $-k_BT \ln Z$ and by differentiation with respect to the plate separation, the force $f = -\partial F / \partial h$ exerted on the confinement plate by the compressed SAM. The partition function Z can also be connected with the potential E: $Z=\Sigma \exp(-\beta E)$ and with the thermodynamic internal energy $U=\Sigma E \exp(-\beta E)$, where the sums run over all states of the system.

III. RESULTS AND DISCUSSION

We begin with the simple case where alkanethiols of ten monomers are grafted on the bottom plate at such low density that no overlap is possible with its neighbors, i.e., at a Fig. 1, we show the monomer distribution as a function of the height above the grafting surface. As long as the top plate is further away than the longest, i.e., all-trans conformer, the pressure on the top plate is zero and all conformers contribute according to their Boltzmann weight. As the top plate is lowered the longest, energetically favorable conformers are successively excluded. Pressure builds up because the excluded conformers have the fewest gauche configurations and are thus energetically more favorable. Shorter and energetically less favorable conformers, i.e., those with gauche defects, play a larger role in the formation of the monomer density, changing the overall appearance of the monomer density. Note that the highly peaked structure of the distributions in Fig. 1 is not an artifact of the calculations. For short chains, peaks are visible in the density of states even if exact statistics are used.³⁵ Of course, one would expect somewhat smoother distributions in a model permitting continuous variations in bond length b, dihedral angle ϕ , or bond angle θ . On the other hand, it is important to note that nonmonotonous distributions result from maxima in the density of states around favorable configurations (conformers) and not from the discreteness of a particular model.³⁶

spacing larger than the end-to-end length of the polymer. In

In Fig. 2, we show the dependence of the Helmholtz free energy F on the separation or height h of the two plates and its derivative, the pressure, also shown is the height distribution of the brush.³⁷ As the top plate pushes past a group of conformers of roughly equal length and energy, there is a leveling off of the energy (barely visible in the energy but clearly in the derivative) resulting in a drop of the pressure. As another group of conformers gets eliminated from the density of states, another drop occurs in the pressure. This is clearly demonstrated in Fig. 2. We have also calculated the



FIG. 1. (Color online) Monomer distribution of an alkanethiol brush under compression for three plate separations. Oligomers are composed of ten monomers each and are grafted on a square lattice with a lattice constant of 20 Å and periodic boundary conditions. Here the temperature is T=300 K; other parameters are as in Table I.



FIG. 2. (Color online) Energies, height distributions, and pressure curve for a decanethiol brush on a square lattice with a lattice constant of 15 Å. Height distributions are given for two temperatures, 250 K (red) and 300 K (blue), with other parameters as in Table I.

internal energy U so that we can compute the entropy TS = F - U without having to take the numerically difficult derivative with respect to T. As expected, the entropy decreases as the top plate is lowered simply because the number of available conformers decreases. Both lowering the temperature and increasing grafting densities sharpen the nonmonotonic pressure features, see Fig. 3. A second brush grafted onto the top plate also enhances the nonmonotonic pressure features, as shown in Fig. 4.

The physical mechanism behind the nonmonotonic pressure features is the elimination of groups of conformers that no longer fit into the space between the plates. Harrison's argument,²⁴ that upon compression energetically costly *gauche* defects are inserted into the polymer brush, can thus be understood as follows. All those conformers of the polymer that are not eliminated by volume exclusion contribute to the brush; at large plate separation, the all-*trans* conformer is not the only one because at room temperature entropy demands that conformers with *gauche* defects contribute. As the top plate is lowered, more conformers are excluded with



FIG. 3. (Color online) Pressure curves for a decanethiol brush at a grafting spacing of 9 Å, given for two temperatures, 250 K (red) and 300 K (blue), with other parameters as in Table I.



FIG. 4. Hexadecane thiol brushes grafted on both bottom and top plates at a grafting density with 20 Å spacing. Shown are monomer distributions for two plate separations, the height distribution and the compressional pressure curve. Parameters are T=300 K and as in Table I.

the result that the shorter conformers with more *gauche* defects contribute with higher weights. Conformers with more *gauche* defects are not introduced but those without them are eliminated by confinement.

This picture can be condensed into a simple model: we assume that the polymer brush has a number of groups of conformers with separated height distributions depicted as their density of states D(h) in Fig. 5. The resulting canonical partition function is then given by

$$Z(h,T) = \exp[-F(h)/k_BT] = \int_0^h dh' D(h')$$
$$\times \exp[-E(h')/k_BT], \qquad (1)$$

where E(h') is the energy of the conformer of height h'.



Height Above Surface [arb.]

FIG. 5. (Color online) The simple model based on Eq. (1), connecting the height distribution D(h) with the free energy $Z(h,T) = \exp[-F(h)/k_BT]$ and the compressional pressure or force. The dashed lines are the Maxwell construction to obtain the stable equation of state.

Because we know from earlier work that statistically relevant conformers have energies within k_BT , we can ignore the Boltzmann factor. Choosing the density of states contributions as simple functions, such as exponentials or Gaussians, the integration can be done analytically with the result shown in the same panel as the density of states [Eq. (1)]. Given the partition function, we compute the compressional force as

$$f(h) = -\frac{\partial}{\partial h} \left[-k_B T \ln(Z(h)) \right] = k_B T \frac{D(h)}{Z(h)} \exp[-E(h)/k_B T],$$
(2)

as depicted in the lower panel of Fig. 5. As anticipated, the force drops when each group of conformers is eliminated by the confining upper plate, until the force diverges for small heights.³⁸

Regions of negative slope in the force curve are thermodynamically unstable, as the isothermal compressibility would be negative, as is well known from the isotherms of fluids, such as the van der Waals loop. To obtain the thermodynamically stable isotherm, one applies the Maxwell construction as indicated in the lower panel of Fig. 5. Thus, if the plate separation is changed slowly, then one expects to see regions of constant forces; this seems to have been the case in experiments on poly(ethylene glycol).²⁰

The simple model just discussed suggests that one should turn the argument around: take an experimental curve of compression force versus plate separation, f(h), and integrate it to get the Helmholtz free energy (up to an unknown function of temperature),

$$F(h,T) = -\int_{0}^{h} f(h')dh' + \phi(T)$$
(3)

from which we get the partition function Z(h). Thus, starting from the force versus height curve, we can extract the energy-averaged conformer distribution,

$$D(h)\exp\left[-E(h)/k_BT\right] = \frac{1}{k_BT}f(h)\exp\left[\frac{1}{k_BT}\int_0^h f(h')dh'\right].$$
(4)

Applied to the model force curve depicted in Fig. 2, we get, as expected, a conformer height distribution that is the envelope of the microscopic distribution that we originally started from, see the red curve in Fig. 2.

We also applied this procedure to the experimental data of Oncins *et al.*¹⁹ for decanethiol at a grafting density with a spacing of 5.5 Å. Our calculated height distribution is shown in Fig. 6. Using Eq. (4), we obtain a height distribution from the experiment that is in remarkable agreement with the theoretical prediction. As for the force curve, several points must be emphasized: (1) Our calculations produce the force per polymer. For a comparison with the experiment, we have followed the arguments of Oncins *et al.* with an uncertainty of roughly a factor of 2. (2) In the experiment, the force is already nonzero for separations beyond the maximum height of decanethiols. Because the experiments were performed in 0.1M KOH, the Si₃N₄ AFM tip is charged. Although the



FIG. 6. (Color online) Lower panel: Compressional force for decanethiol, experiment (Ref. 19) (red) is compared to theory (blue). Upper panel: Calculated height distribution in blue and extracted from the experiment in the lower panel using Eq. (4). Both experiment and theory are performed with grafting densities of one polymer per 30 Å². In the experiment, this corresponds to a noncompact $(\sqrt{3} \times \sqrt{3})$ R30° lattice with 30% vacancies (Ref. 19); in the theory this is approximated using a square lattice with a lattice constant of 5.5 Å.

SAM has (neutral) methyl terminal groups, it is possible that electrostatic interactions between the AFM tip and the thiolated gold substrate are responsible for small noncontact forces.³⁹ (3) Looking at the closest separations, our model calculation predicts that the compressional force should grow beyond bounds for separations less than 10 Å because there are no shorter conformers available in the SAM at that grafting density, as both the theoretical density of states and also the one extracted from experiment suggest. One might argue that a "nonflat"AFM tip will push the polymer brush out of the way, leading to the observed forces below a separation of 10 Å.

The calculations presented in this article do not include bond stretching or bending, which are important at high forces. For this reason, we do not use the present methods to describe compact SAMs; the present study is concerned with polymer brushes and noncompact monolayers, such as the experimental system in Fig. 6. Conversely, models such as cooperative tilting²⁵ are most appropriate for the description of single compact monolayers, and not of noncompact layers or islands.¹⁹ It will be interesting to see if both compact and noncompact SAMs can be understood consistently, within a single model that includes sufficient molecular freedom in both limits.

To summarize the main points of this article: Employing a realistic model for alkanethiols to calculate the compressional force/pressure curve for a SAM or oligomer brush, we have shown that nonmonotonic features arise from the elimination of conformers as the top plate is lowered. By simplifying the physics, we arrive at an analytical procedure that allows the experimentalist to extract the height or monomer distribution of the polymer brush from compressional force curves. The nonmonotonic dependence of the force/pressure on the plate separation is a size effect: as the length of the polymer molecule gets larger, the monomer and height distributions become smoother and the force increases monotonically for long enough molecules. In the calculations presented here, we have not included solvation effects. One might argue that although the presence of water changes the energies and end-to-end lengths of conformers,⁴⁰ the resistance from the polymer brush is still dominant, as solvation molecules can be squeezed out of the brush.

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- ³⁶For example, peaks in the density of states are still visible in situations where many states are accessible, such that distributions appear otherwise smooth, see Ref. 35.
- ³⁷In the energy versus height plot of the conformers, there are lines or bands of equal energy. Their origin is simple: introducing a gauche state in an all-trans conformer costs 23 meV according to Table I, independent of where along the chain it is introduced, but resulting in different heights. The next band has two gauche states and the next after that has a gauche defect $(ttg^{-}g^{+}tt)$, etc.
- ³⁸If the density is a series of delta-functions $D(h) = \sum a_i \delta(h-h_i)$, as it would be if only a small number of distinct conformers contribute to the brush,
- we get steps in the free energy and spikes on the force/pressure curve.
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