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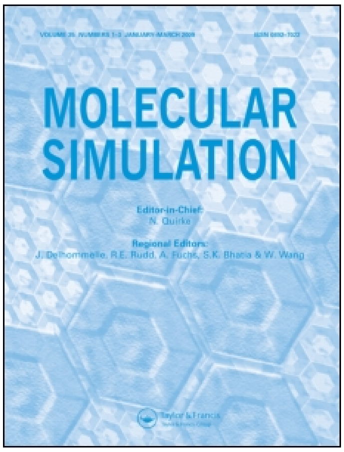

Molecular Simulation

Publication details, including instructions for authors and subscription information:
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Weixiong Li[a]; Anna C. Balazs[a]
[a] Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, PA

To cite this Article Li, Weixiong and Balazs, Anna C.(1994) 'Cluster Formation in Grafted Polymers with Interactive End-Groups', Molecular Simulation, 13: 4, 257 — 265

To link to this Article: DOI: 10.1080/08927029408021992

URL: http://dx.doi.org/10.1080/08927029408021992

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Molecular Simulation, 1994, Vol. 13, pp. 257-265
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CLUSTER FORMATION IN GRAFTED POLYMERS WITH INTERACTIVE END-GROUPS

WEIXIONG LI and ANNA C. BALAZS[1]

Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, PA 15261

(Received October 1993, accepted January 1994)

We performed a Monte Carlo simulation to model the behavior of grafted polymers that contain functional groups on the "free" ends of the chains. When the attraction between these end-groups is sufficiently strong to overcome the stretching energy of the chains, the end-groups aggregate and the system thereby undergoes a micro-phase separation. Our results indicate how to tailor the end-group interactions, the chain length and the grafting density in order to control the lateral properties of the grafted layer.

KEY WORDS: Grafted polymers, Monte Carlo simulation, micro-phase separation.

1 INTRODUCTION

Both the chemical and physical properties of a surface can be dramatically altered by attaching polymer chains onto the substrate. In particular, the adhesive and lubricating properties of the surface can be controlled by tailoring the characteristics of the adsorbed layer. In order to adsorb the polymers onto the substrate, functional groups are commonly added to one end of the chains. The strong attraction between the functional group and the substrate anchors a chain onto the surface. The other end of the chain is free to extend into the surrounding solvent. In this paper, we determine how the behavior of the polymer layer can be controlled by attaching a functional group onto the "free" end of the grafted chain. To carry out this investigation, we perform a Monte Carlo computer simulation based on a Hamiltonian for the end-groups that are attached to the tethered chains. As our findings show, the presence of these end-groups modifies the morphology of the layer and consequently, has significant implications for controlling the lateral properties of polymer/surface assemblies.

The overall properties of the polymer layer depend on the interplay among several variables, such as: the grafting density ρ, the polymer chain length N, and the energy parameters that characterize the monomer-monomer and the monomer-solvent interactions. Before describing our model, we first consider how these parameters govern the behavior of grafted homopolymers. This analysis will provide insight into the factors that also control the properties of the tethered, bifunctional chains. We first consider the effect of varying the grafting density. If the grafting density is sufficiently

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[1] To whom all correspondence should be addressed.

high, so that the graft spacing, d, is much smaller than the chain dimension (or, $d \ll R_g$, where R_g is the radius of gyration of the chain), there will be considerable contact between neighboring chains. Consequently, the polymers will be squeezed and stretched, and the "brush" height will scale linearly with the chain length, N. On the other hand, if the grafting density is low, so that $d \gg R_g$, the layer height is expected to scale according to the usual Flory exponent [1].

The nature of the solvent also affects the properties of the polymer layer. Recent evidence, from computer simulations [2, 3] and analytical calculations [4, 5], indicates that in the presence of a bad solvent, the polymer layer displays inhomogeneities in the lateral direction. In particular, as the solvent quality is decreased, contact between the monomers and solvent becomes energetically unfavorable. As a consequence, the chains clump together to form a "dimpled" surface. In this paper, we show that a similar "dimpling" phenomena is observed in the grafted polymers when strongly attractive end-groups are attached to the free ends of the chains.

2 THE MODEL

Figure 1 shows a schematic diagram of the grafted layer. We assume that polymers are tethered at one end onto a flat, impenetrable surface. Furthermore, these grafting points form a two dimensional square lattice, with lattice spacing d. Thus $1/d^2$ is the grafting density of the adlayer. Functional groups are attached to the other ends of the polymers. These end-groups can interact with each other. We assume that the polymers behave like Gaussian chains. This condition can be achieved by immersing the system into the appropriate θ-solvent. The Greens function for a Gaussian chain confined to a box of size $L_x \times L_y \times L_z$ has been calculated [6, 7], and we will make use of this

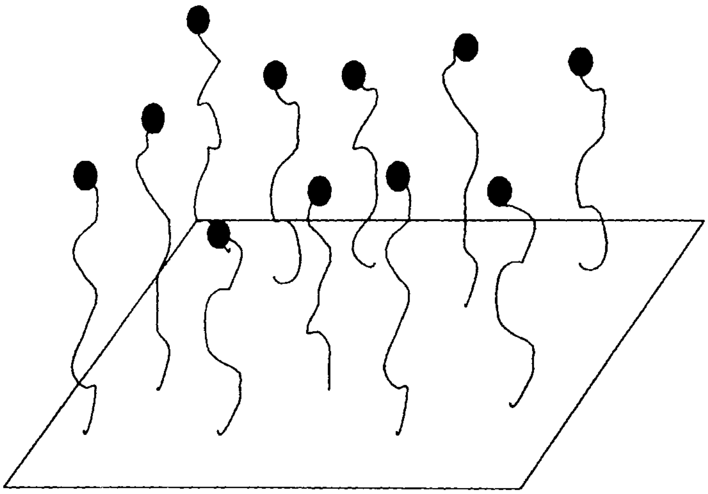

Figure 1 In our model, the polymer chains are anchored onto a flat surface by one end and mutually attractive end-groups are attached to the other end of the chains.

solution in our problem. Note that in our problem, there are no boundaries in the x–y directions, we therefore expect the x–y components of the Greens function to simply be Gaussian. For the z-component, the Edwards and Freed solution [6, 7] gives the following expression:

$$g_{EF}(z_1, z_2|N) = \frac{2}{L_z}\sum_{p=1}^{\infty} \sin\left(\frac{p\pi z_1}{L_z}\right)\sin\left(\frac{p\pi z_2}{L_z}\right)\exp\left(-\frac{p^2\pi^2 N}{6L_z^2}\right) \tag{1}$$

where z_1 and z_2 are the z-coordinates of the two end monomers, and N is the chain length. In our problem, we only have a hard wall at $z = 0$. Therefore, by letting $L_z \to \infty$ and replacing the summation with integration, we obtain

$$g_z(z_1, z_2|N) = \sqrt{\frac{3}{2\pi N}}\left\{\exp\left[-\frac{3}{8N}(z_1 - z_2)^2\right] - \exp\left[-\frac{3}{8N}(z_1 + z_2)^2\right]\right\}. \tag{2}$$

The total Greens function is then:

$$G(\vec{r}_1, \vec{r}_2|N) \propto \exp\left\{-\frac{3}{2N}[(x_1 - x_2)^2 + (y_1 - y_2)^2]\right\} \times \left\{\exp\left[-\frac{3}{8N}(z_1 - z_2)^2\right] - \exp\left[-\frac{3}{8N}(z_1 + z_2)^2\right]\right\} \tag{3}$$

where the $\vec{r}_i = (x_i, y_i, z_i)$ coordinates represent the positions of the two end monomers in the polymer.

The partition function for our model is:

$$\psi = \int \prod_{i=1}^{n} G(\vec{r}_i, \vec{r}_{0i}|N)\exp\left[-\frac{1}{2}\sum_{j \neq i} V_1(|\vec{r}_i - \vec{r}_j|)\right] d\vec{r}_i \tag{4}$$

where n is the total number of polymer chains, and $G(\vec{r}_i, \vec{r}_{0i}|N)$ is the Greens function of the ith Gaussian chain, which has two ends at $\vec{r}_i$ and $\vec{r}_{0i}$, respectively. In particular, $\vec{r}_i$ is the position of the "free" end and on the ith chain, and $\vec{r}_{0i} = (x_{0i}, y_{0i}, a)$ is the grafting point. The hard surface is located at $z = 0$, however, we assume that the grafting point is a small distance a above the hard surface in order to avoid G from vanishing. The potential $V_1(|\vec{r}_i - \vec{r}_j|)$ describes the interactions between the end-groups.

After substituting equation (3) into equation (4), it is apparent that the partition function in equation (4) can be viewed as describing a system of particles (the end-groups) acting under the following Hamiltonian:

$$H(\{\vec{r}_i\}) = \sum_i V_0(\vec{r}_i, \vec{r}_{0i}) + \frac{1}{2}\sum_{i \neq j} V_1(|\vec{r}_i - \vec{r}_j|), \tag{5}$$

where

$$V_0(\vec{r}, \vec{r}_0) = -\log G(\vec{r}, \vec{r}_0|N) = \frac{3}{2N}[(x - x_0)^2 + (y - y_0)^2] - \log\left\{\exp\left[-\frac{3}{8N}(z - z_0)^2\right] - \exp\left[-\frac{3}{8N}(z + z_0)^2\right]\right\} \tag{6}$$

is the effective potential that acts on each end-group and arises from the fact that this unit is attached to the end of the chain. This potential is harmonic in the x–y directions, but not in the z-direction. In the limit $z_0 \ll \sqrt{N}$, we find that the minimum of V_0 is located at $(x_0, y_0, \sqrt{8N/3})$. Thus $\sqrt{8N/3}$ respresents the height of this Gaussian polymer layer in the absence of end group interactions. Finally, we emphasize that each end-group only "feels" its own value of V_0; interactions among the end-groups are described by the second term, V_1.

By reformulating our system in terms of the above Hamiltonian, we can model the system of tethered chains with reactive end-groups by a set of particles whose behavior is governed by the potentials in equation (5). Furthermore, we can develop a Monte Carlo (MC) simulation for these particles, where the potential V_0 reflects the presence of the grafted layer. The details and results of such a MC simulation are described below.

3 NUMERICAL RESULTS AND DISCUSSIONS

To carry out the MC simulation, we initially place 400 particles on a 200 × 200 square lattice. The spacing between these particles is 10 lattice sites. These particles model the functional groups at the end of 400 polymers. The initial configuration corresponds to all the end-groups being directly above their grafting points and lying in a uniform plane, which is $1.5\sqrt{N}$ units above the $z = 0$ plane, or the grafting surface.

The motion and subsequent location of the particles is determined via the Matropolis algorithm, in conjunction with the Hamiltonian in equation (5). The interaction between the end groups is mediated by V_1, a Lennard-Jones potential, which is given by:

$$V_1(\vec{r}) = \varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - 2\left(\frac{\sigma}{r}\right)^{6}\right] \tag{7}$$

where we fix $\sigma = 2.5$. To avoid numerical overflow, we treat the Lennard-Jones potential as a hard core when $r < 0.2\sigma$. We also make the truncation: $V_1(r) = 0$ when $r > 20\sigma$.

As the first step in simulation, a particle is picked at random. Next, three independent random numbers in the range of $[-\Delta, \Delta]$ are generated. These numbers represent the incremental change in particle's current x, y, z coordinates, respectively. The energy change, ΔE, associated with moving this particle to the new coordinates is calculated from equation (5). If the energy is lowered, the move is accepted. Otherwise, the move is only accepted with the probability $\exp(-\Delta E)$. In practice, test runs with different values of step size Δ were performed to ensure a reasonable acceptance ratio of MC moves (typically between 40% to 60%). This condition is satisfied for values of Δ between 0.3 and 0.8 (depending on the chain length).

Open boundary conditions are used in the simulation. Since the particles are attached to the polymers, which are tethered to the $z = 0$ plane, these groups cannot diffuse away. The particles are equilibrated for 12 million steps. The simulation is then run for an additional 12 million steps, during which we collect data.

Figure 2 shows the projection of the positions of the end-groups onto the x–y plane for a fixed value of $\varepsilon = 4$ and varying $N = 25, 50, 100$. At $N = 25$ (Fig. 2a), the end groups are roughly uniformly distributed in space. Most particles are isolated from the other particles in the system. Although some clusters can be observed, they are few in

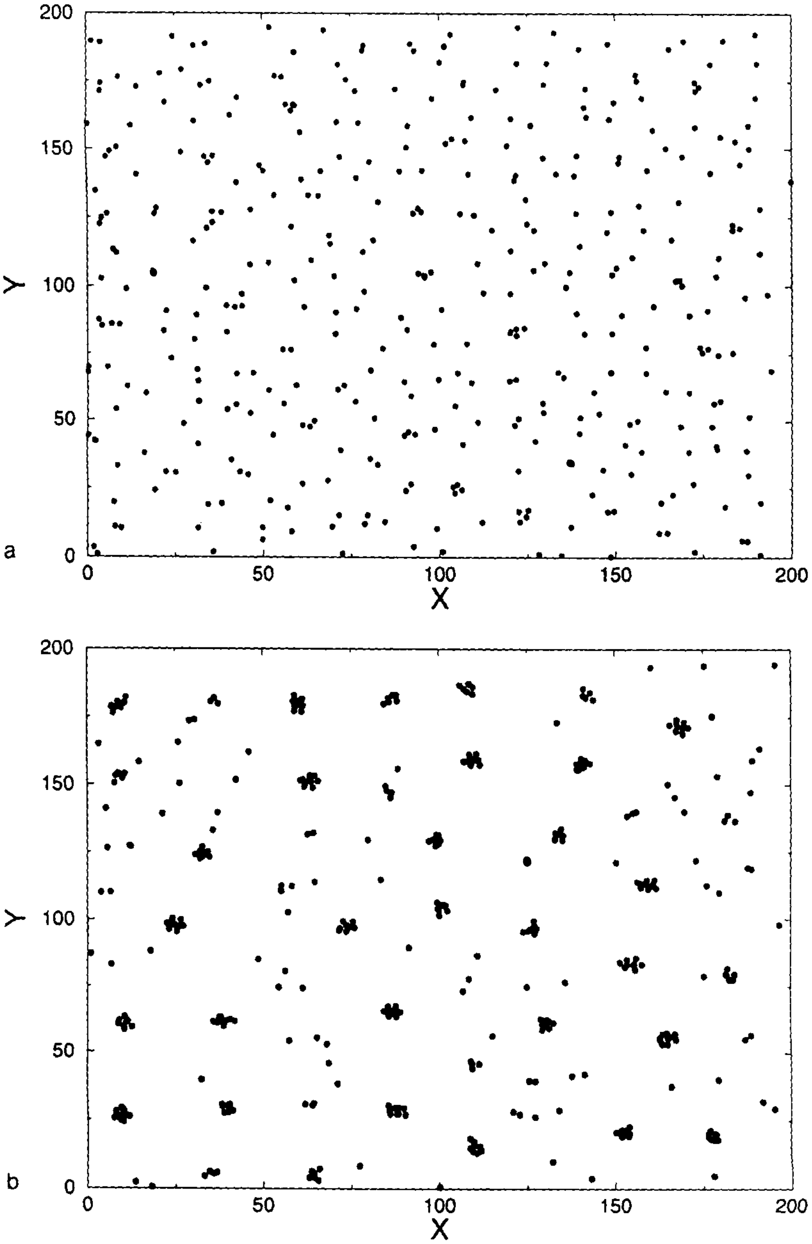

Figure 2 Projections of the x, y coordinates of the end-groups for the different chain lengths, N. **a** $N = 25$. Almost no clusters are formed. **b** $N = 50$. **c** $N = 100$.

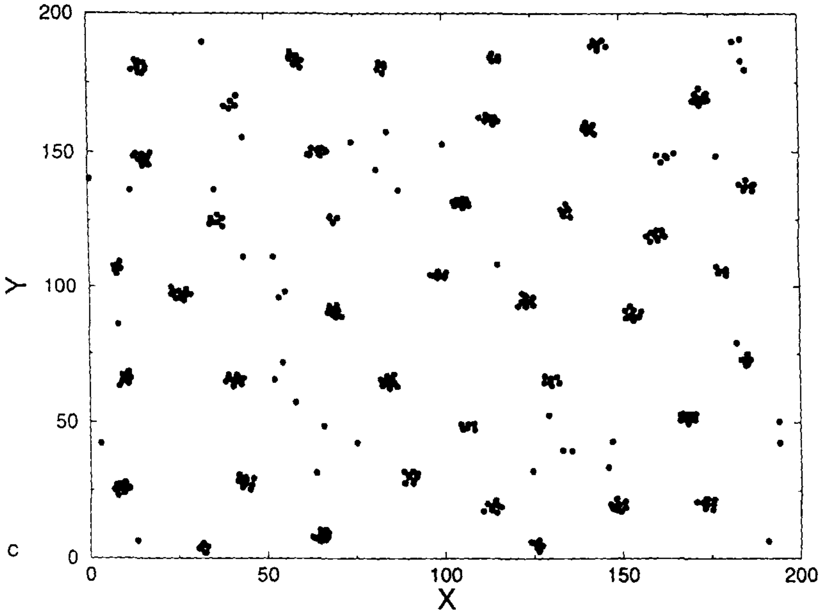

Figure 2 (*Continued*)

number and small in size, typically consisting of 2, 3 or 4 particles. As we increase the chain length, more particles aggregate to form clusters, the sizes of these clusters also become larger, and there are fewer isolated particles (Figs. 2b, 2c).

The formation of the clusters results from an interplay among various variables, such as the chain length N, the graft spacing d, and the strength of Lennard-Jones potential ε. We can, however, gain insight into the conditions under which cluster formation will occur by considering the energetic scales that characterize the system. The stretching energy arising from the association of neighboring end-groups is on the order of d^2/N [see equation (6)], while the energy scale of the Lennard-Jones potential is ε. A criterion for cluster formation is that the attractive energy, ε, must overcome the stretching energy, i.e.,

$$\varepsilon \gg \frac{d^2}{N} \quad \text{or} \quad \frac{N\varepsilon}{d^2} \gg 1. \tag{8}$$

For $\varepsilon = 4$ and $d = 10$, this condition is not satisfied when $N = 25$, however, it is fulfilled with $N = 50$ or 100. Thus the results shown in Figure 2 are consistent with the prediction given by equation (8).

Obviously, the size of the clusters will always remain finite for finite length chains. In this manner, the formation of aggregates is similar to micro-phase separation. Furthermore, we expect cluster sizes will increase as the chain length N increases. Along the same lines as the arguments that lead to equation (8), we can obtain an expression for the average cluster size. Consider a cluster that contains an end group from a chain grafted a distance pd away from the center of the cluster. This distance represents the furthest grafting point for a chain that is involved in the cluster. Then, as an approximate estimate, p^2 represents the number of particles in the cluster. In order for this chain to participate in the cluster, the stretching energy should again be compensated by the Lennard-Jones attractions among the end groups. Thus we have

$$\frac{p^2 d^2}{N} \sim \varepsilon. \tag{9}$$

We then have the cluster size n_c:

$$n_c \sim \frac{N\varepsilon}{d^2}. \tag{10}$$

Clearly, in the infinite N limit, we will have an infinite size cluster, thus a true macro-phase formation. It should be pointed out that equations (8) and (10) are purely based on energetic considerations, since we neglected the entropy loss associated with aggregation. The results from the simulation, however, indicate that the general trend predicted by equation (8) will still be observed when entropic factors are taken into account.

Figure 3 shows the density profiles of the end-groups (normalized by the number of chains in the simulation) along the z-direction. In these simulations, we fix the chain

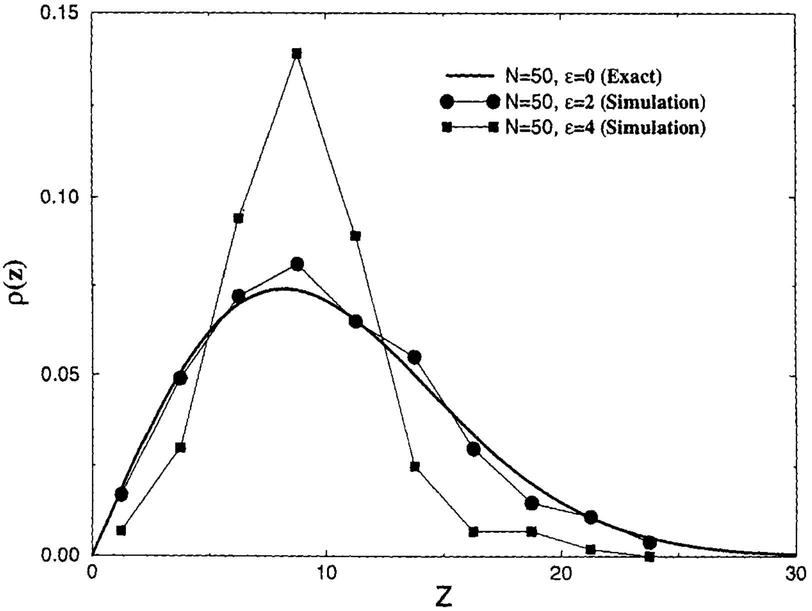

Figure 3 Density profiles of the end-groups as a function of z, with $N = 50$, and $\varepsilon = 0, 2, 4$. Note that in the case where $\varepsilon = 0$, there is no attraction between the end-groups. The term "exact" is applied to this example (see figure legend) since the density profiles can be obtained analytically from equation 2. The higher values of ε refer to the intensity of the attraction between the end-groups in the simulation.

length at $N = 50$ and vary the interaction strength ε. For $\varepsilon = 0$, the density profile is exactly solvable and is given by equation (2). For $\varepsilon = 2$ ($N\varepsilon/d^2 = 1$), we predict that clustering does not occur, and, in fact, we see that the density profile is close to that of the $\varepsilon = 0$ case. When $\varepsilon = 4$, we find that the density profile develops a sharp peak around $z = 9$. This peak signifies that clusters have formed, since the end-groups now lie at roughly the same height.

We next calculate the layer thickness, h, as a function of the chain length. The layer thickness is calculated as the average height of the end-groups, which is measured in our simulation at every 1000 Monte Carlo sweeps. Figure 4 shows the thickness versus the chain length N. The top curve is the average height of the chains when there is no interaction among the end-groups, i.e., $h = \sqrt{8N/3}$. The bottom curve is a plot of our simulation results. We see that attractions among the end-groups decrease the layer thickness. In order to form clusters, several chains are stretched along the lateral direction; this effectively reduces the height of the chains. Within numerical accuracy, the scaling behavior for large N is, however, quite close to $\sqrt{N}$.

4 CONCLUSIONS

In conclusion, by reducing the original problem to the effective Hamiltonian in equation (5), we show through our Monte Carlo simulations that when the attractions

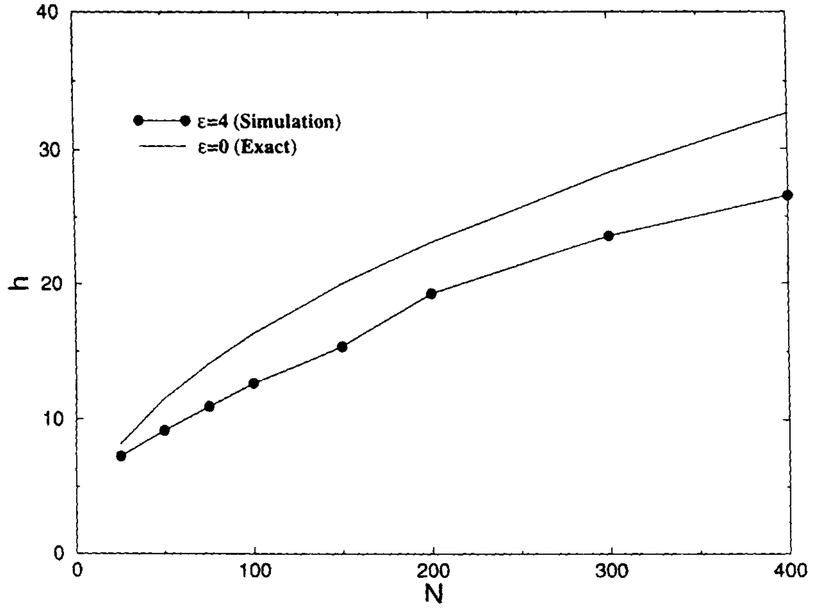

Figure 4 Layer height versus chain length. The top curve corresponds to the case where there are no interactions between the end groups ($h = (8N/3)^{1/2}$), while the bottom curve represents the results from the simulation.

among the end-groups are sufficiently strong, clusters will form in the grafted layer. The clusters are finite in size, thus resembling micro-phase formations. Only in the infinite chain length limit will the formation of clusters be a true macro-phase transition.

There are, however, many interesting questions that remain to be answered. In particular, what is the effect of excluded volume interactions? Preliminary results from MC simulations of grafted, self-avoiding chains indicate that cluster formation will again occur for strong end-group attractions [8]. Furthermore, what is the exact nature of this cluster formation: is it continuous or discontinuous? Do cluster sizes obey our estimate in equation (10)? And finally, do these end-group clusters form certain periodic patterns? We expect that a more analytic approach may answer some or all of these questions.

Finally, we note that the presence of these clusters can have important implications on the properties of the adlayer. In particular, there are significant advantages to having the majority of the end-groups lie at roughly uniform heights (as seen in Fig. 4). Specifically, this property can enhance the adhesive, lubricating or wetting properties of the surface. Thus, our results can provide guidelines for fabricating coatings or films with these enhanced characteristics.

Acknowledgements

A.C.B. gratefully acknowledges financial support from the Office of Naval Research, through Grant N00014-91-J-1363, the National Science Foundation, through Grant DMR-9107102, and the University of Pittsburgh Materials Research Center under AFOSR Grant 91-0441. The authors thank Prof. David Jasnow, Drs. Ari Shinozaki and Dilip Gersappe for helpful discussions.

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