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Electrophoretic Deposition of Polymer Chains on an Adsorbing Surface in $(2 + 1)$ Dimensions: Conformational Anisotropy and Nonuniversal Coverage

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Electrophoretic deposition of polymer chains flowing in a (2 + 1)-dimensional system is studied by computer simulations. Steady-state surface coverage (θ_j) is found to decay with the chain's length, i.e., $\theta_j \sim L_c^{-\alpha}$ with a nonuniversal exponent $\alpha \simeq 0.0-0.9$ depending on the magnitude of driving field and temperature. Conformational crossover occurs for chains from a surface or wall to an adjacent bulk region with different scaling exponents for their longitudinal and transverse spread. [S0031-9007(98)05906-7]

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In an electrophoretic deposition, polymer chains are driven by a field B, say, along an x direction, toward an impenetrable two-dimensional adsorbing wall, i.e., yz planar surface in our $(2 + 1)$-dimensional system. Questions that we would like to address are as follows: Is there a conformational crossover of the polymer chains from bulk to surface and how does conformation at the surface depend on the field (B)? Is there a power-law scaling for the equilibrium surface coverage with the chain length (L_c)? In regard to the former, the transverse and longitudinal conformational spreadings of directed polymer chains in a gel matrix [1] are related to interfacial growth phenomena [2–5]. About a decade ago, Kardar and Zhang [1] predicted that the transverse fluctuation (R_y) of the polymer chain scales with length (L_c) of the polymer chain,

$$R_y \sim L_c^{\nu_y}, \tag{1}$$

with a superuniversal exponent $\nu_y = 2/3$ [6,7] in all dimensions (d). This scaling, for an electrophoretic deposition model in $(1 + 1)$ dimensions, has been very recently revisited by computer simulations [8] in which it is pointed out that the scaling exponent depends on the magnitude of the driving field, nature of the barriers (impenetrable adsorbing surface), and possibly on temperature. In our computer simulation study in $(2 + 1)$ dimensions, here we observe a nonuniversal scaling of the conformational spreading, different from that in $(1 + 1)$ dimensions.

A second issue deals with the universal nature of the power-law dependence of the equilibrium coverage of surface by polymer and somewhat related to the jamming coverage in a random sequential absorption (RSA). Considerable interest has been devoted in recent years [9–19] to understanding the basic laws for the growth of the coverage in RSA of particles and objects of polydisperse shapes such as polymer chains. Very recently, a quality computer simulation study of the jamming coverage (θ_j) for the random sequential adsorption of polymer chains on a two-dimensional lattice [19] reveals a power-law scaling

$$\theta_j \sim L_c^{-\alpha}, \tag{2}$$

with $\alpha \simeq 0.1$. In our electrophoretic deposition of polymer chains here, we evaluate the stead-state (or equilibrium) coverage (θ_j) under the influence of a field (B) and find that the coverage exponent α depends on the magnitude of the field and is nonuniversal.

Studies of the conformation of the polymer chains in electrophoretic flow and growth of their density at the impenetrable surface or wall have enormous applications, i.e., in understanding and assessing the errors in DNA fingerprinting in gel electrophoresis [20–27], coating under pressure, designing composites, stability and interfacial sliding of polymers, and friction in lubrications [28–32]. The adsorption processes have yet related applications [33–38] in physical, chemical, and biological systems such as binding of ligands on polymer chains, chemisorption, and reaction of molecular species including globular protein on surfaces and interfaces. Thus, it is desirable to study the conformational and interfacial growth phenomena in model polymer systems and identify the unusual properties as they change from bulk to surface.

We consider a discrete lattice of size $L_x \times L_y \times L_z$ with comparatively large L_x; typically, $L_x = 300$, $L_y = L_z = 50$ is used for most of our data, but different lattice sizes are used to check for the severe finite size effects. Polymer chains [each of length L_c, for $L_c = 40$, 80, 120, 160, and 200, with $(L_c + 1)$ nodes connected by a constant bond of unit length] are released at a constant rate from near the source end (i.e., $x = 1$ to $x = 0.2 \times 300$) of the sample and deposited on an impenetrable wall (yz plane) at the opposite end ($x = L_x$) via reptation dynamics. The concentration of the chains in the lattice after a sufficiently long deposition time is rather low, varying from 1% for $L_c = 40$ chains to 5% for $L_c = 200$ chains. In addition to excluded volume, nearest-neighbor polymer-polymer repulsive and polymer-wall attractive (adsorbing) interactions are considered. The external field B is coupled with the chain node via interaction energy $-B\Delta X$, where ΔX is the displacement along the x direction. As before, the Metropolis algorithm is used to reptate the chains. An attempt to move the chains $N(= L_x \times L_y \times L_z)$ times is defined as unit Monte Carlo step (MCS).

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Profiles of polymer density and radius of gyrations are studied in detail. The simulation is carried out for a sufficiently long time (1000 MCS) to obtain stable profiles at the wall and around the bulk. Even though the chains are in constant motion driven by the field, their mobility becomes highly restricted at or near the wall due to steric hindrances as the polymer density increases. In a sufficiently long deposition (observation) time, the polymer densities at the wall ($x = 300$) and in the bulk (typically, $x = 220-295$) reach their stable value; the density in the region, $x < 220$, may not reach a stable value. While the polymer density is evaluated at each yz plane ($x = 1, 2, \ldots, L_x$), the profile of the radius of gyration is evaluated from the chains whose center of mass is binned in each three consecutive yz planes. Thus, the average radius of gyration of the chain at the wall is evaluated from the chains with their center of mass lying within $x = 297-300$. We use ten independent samples to evaluate the average quantities.

Figure 1 shows a snapshot of the polymer chains after a sufficiently long time of deposition. Although it is difficult to see each detail in three-dimensional snaps as vividly as in two dimensions, a close examination provides a rough idea of the conformation of the chains and their distribution. We see that the chains conform differently at the wall and in surrounding layers in the bulk. Further, the polymer density has approached its stable value at the wall and in the adjacent region of the bulk. Since the chains are deposited on the wall, the transverse (yz) layers from the wall end begin to reach their equilibrium density as expected. Note that the whole deposition process is far from equilibrium, but the evolution of polymer density at the wall and in surrounding layers has reached steady state.

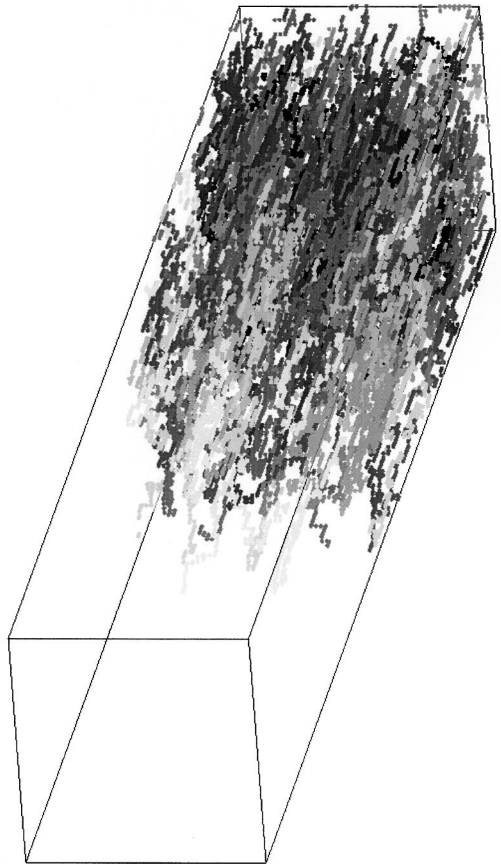

FIG. 1. Snapshot of chains on lattice, length $L_c = 160$, under field $B = 2.0$ at temperature $T = 1$. Chains are color coded (appearing as shades of gray) from a table of 20 colors according to time of release. Generally, the lighter the color (shade) the later the chain is released.

Figure 2 shows a typical density profile, i.e., the variation of the yz planar polymer density with x for different values of field. We find that the density at the wall is very high at low values of field ($B = 0.5$ and 2.0), in contrast to low value at high field ($B = 5.0, 10.0$). The wall absorbs the chains relatively easily at low B since the interaction between the polymer chains and the wall in attractive. At first glance, one would expect that the high field value would enhance the adsorption, in contrast to our observation. However, one may reconcile with the facts by the following reasonings: (i) the high magnitude of the field may reduce the entropy substantially (by elongating the chains in a brushlike configuration), and (ii) it may constrain the movement on the wall (by enhancing the degree of trapping in a relatively less mobile configuration, an effective quenching due to competition between the field and the wall barrier). At $B = 0.5$, the high density at the wall ($x = 300$) drops drastically in the neighboring layers ($X = 280-299$), followed by a linear density gradient in the bulk—a specific gradient material in this parameter space. On increasing the field to $B = 1.0$, onset of oscillations in the density profile sets in and becomes more prominent at $B = 2.0$ in nearly the same region of growth near the wall ($x = 150-300$). At the high field ($B = 5.0, 10.0$), on the other hand, the density on the wall drops down drastically, and only half of the oscillations in the density appears as one end of the density profile is pinned at the wall to a low value; within our simulation time we do see a signal of oscillation with perhaps a longer period than that at the lower field. These oscillations are the signature of layering formation during the growth of polymeric deposition. Further, we find that the oscillations (layering) vanish on increasing the temperature (i.e., $T = 10$).

Polymer density at the wall is defined as the surface coverage (θ_j). A variation of coverage with the chain length at $T = 1.0$ is presented in Fig. 3 for different values of field. First, we find that the coverage decays with the chain length with a power-law exponent, α [Eq. (2)] at certain values of field (B). We find $\alpha \simeq 0.0, 0.8, 0.9$ at $B = 0.5$, 2.0, and 10.0, respectively. It is important to point out that a power-law decay of the jamming coverage is also observed in a random sequential adsorption of chains in an athermal simulation [19] but with the exponent $\alpha \simeq 0.1$. Since the chains are relatively free to relax in our electrophoretic deposition, the growth of the coverage should be different from that in

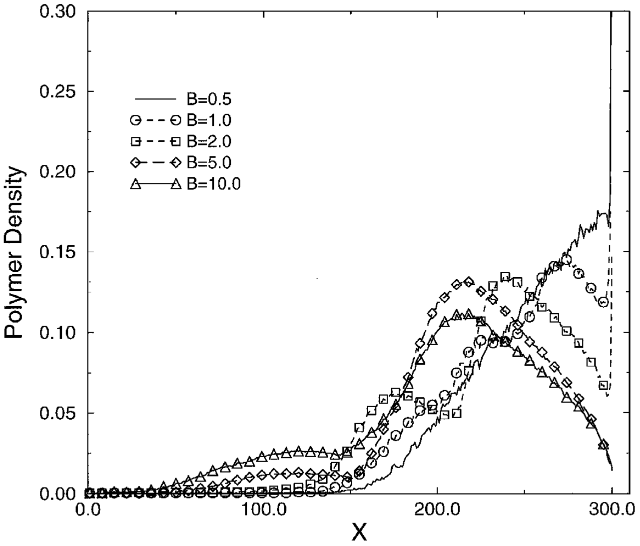

FIG. 2. Density profile ($L_c = 160, T = 1, B = 0.5, 1.0, 2.0, 5.0, 10.0$).

RSA. Nevertheless, we see that the coverage decays with the chain length with a power-law exponent (α) similar to that in RSA. Since the exponent α depends on the magnitude of the field and possibly on temperature, the scaling of coverage with the chain length is nonuniversal.

Next, let us now examine the conformation of the polymer chains. We evaluate the radius of gyration (R_g) of the chains along x at the wall ($x = 300$) and in the bulk ($x = 220-295$) and study its scaling with the chain length, i.e.,

$$R_g \sim L_c^{\nu} . \tag{3}$$

A typical variation of the radius of gyration with the chain length is presented in Fig. 4 on a log-log scale. The slope of the linear fit provides us with an estimate of the exponent ν. Deviations from a power-law scaling cannot be ruled out in a few of the data sets, which may be due to fluctuation in the data.

We have analyzed scaling of both longitudinal (R_{gx}) and transverse (R_{gyz}) components of the radius of gyration. Estimates of these exponents are presented in Table I. We see that at high temperature ($T = 5.0, 10.0$), the conformation of the chains is relatively isotropic in the bulk with the exponent $\nu_{\mathrm{bulk}} \simeq 0.6$ at $B = 0 - 2.0$. At the wall, on the other hand, it is highly anisotropic, with the longitudinal exponent $\nu_x \simeq 0.2$ and the transverse exponent $\nu_{yz} \simeq 0.65$. Thus, at high temperature, chains are compressed along the field direction on the wall. At low temperature $T = 1.0$, conformation of the chains are still relatively isotropic in the bulk, particularly at low $B(= 0.5)$. However, on increasing the field, they seem to expand in an effective rodlike configuration (see Table I). Conformation of the chains at the wall becomes a little more relaxed in the sense that the chains are spread out a little ($\nu_x \simeq 0.3$ at $B = 0.5$). At lower temperature $T = 0.1$, the chains in bulk are rodlike even at low $B = 0.5$. The chains at the wall are highly anisotropic with $\nu_x \simeq 1.0$, seemingly a conformational crossover with respect to temperature (see Table I). Thus, we see a remarkable conformational crossover from bulk to wall: (i) at high temperature ($T = 5.0, 10.0$), isotropic conformation in bulk to longitudinally compressed, i.e., an anisotropic conformation, at the wall. (ii) There is a conformational crossover in the bulk from a self-avoiding walk (SAW) to stretched-out (rodlike) conformation as a function of biased field. The crossover is sensitive to temperature, the lower the temperature the lower the field needed to stretch out the chains. These conformational crossover behaviors in our (2 + 1) system here are quite different from those in the (1 + 1) system [8].

In summary, the growth in polymer density profile exhibits spatial oscillation near the wall at large driving field.

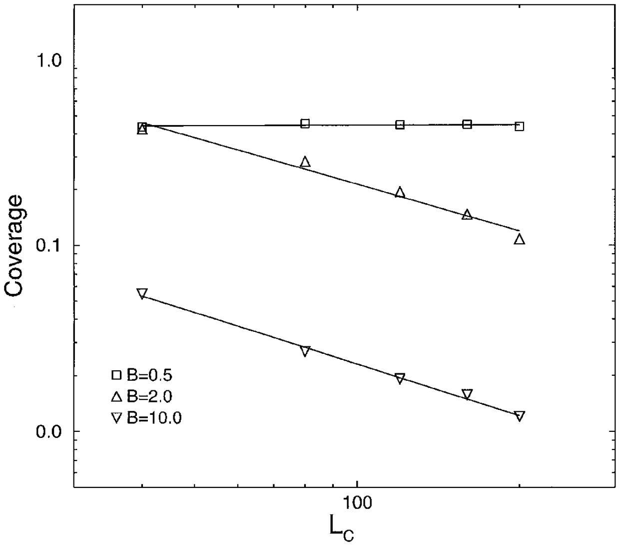

FIG. 3. Coverage versus L_c; $B = 0.5, 2.0, 10.0$.

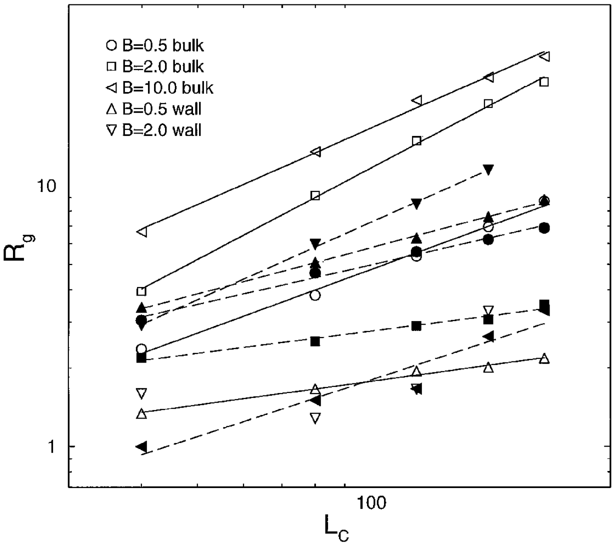

FIG. 4. R_g versus L_c on a log-log scale for chains at $T = 1.0$, showing x (open symbols) and yz (filled symbols) components.

TABLE I. Estimates of ν, ν_x, ν_{yz} at wall and in the bulk. The error bar $\Delta\nu$ in evaluating the exponents varies. $\Delta\nu \sim 0.04-0.10$ for the chains in the bulk. There are considerably larger error bars (as large as $\sim$0.15 for the chains at the wall due to poor statistics; many data points do not fit the power-law dependence indicated by (–). The value of exponents slightly larger than 1 are truncated to 1.

Temperature	Field	Bulk			Wall		
T	B	ν	ν_x	ν_{yz}	ν	ν_x	ν_{yz}
10.0	0.5	0.56	0.56	0.56	0.57	0.22	0.61
10.0	2.0	0.54	0.58	0.51	0.64	0.19	0.68
10.0	10.0	0.84	1.00	0.40	0.62	0.19	0.69
5.0	0.5	0.55	0.56	0.55	0.57	0.22	0.61
5.0	2.0	0.58	0.66	0.53	0.54	0.23	0.58
5.0	10.0	1.00	1.00	0.29	–	–	–
1.0	0.5	0.65	0.81	0.50	0.56	0.30	0.59
1.0	2.0	1.00	1.00	0.28	0.91	–	0.99
1.0	10.0	0.97	0.98	0.72	–	–	–
0.5	0.5	0.91	1.00	0.28	0.67	–	0.70
0.5	2.0	0.94	0.95	0.51	083	0.48	0.85
0.5	10.0	1.00	1.00	0.73	–	–	–
0.1	0.5	1.00	1.00	0.76	0.62	0.99	0.62
0.1	2.0	0.98	0.98	0.62	–	–	–
0.1	10.0	1.00	1.00	0.59	–	–	–

The steady-state coverage of the wall depends on the driving field, temperature, and chain length. In certain regimes of parameter space, we find that coverage decays with the chain length with a nonuniversal power-law exponent different from these found in random sequential adsorption of polymer chains on a surface. The conformation of chains shows interesting anisotropic crossover behaviors from bulk (isotropic at high T and SAW-to-extended conformation at low T) to surface (ansiotropic compressed conformation with different scaling exponents for the longitudinal and transverse components of R_g).

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