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Roughening, deroughening, and nonuniversal scaling of the interface width in electrophoretic deposition of polymer chains

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Growth and roughness of the interface of deposited polymer chains driven by a field onto an impenetrable adsorbing surface are studied by computer simulations in $(2+1)$ dimensions. The evolution of the interface width W shows a crossover from short-time growth described by the exponent β_1 to a long-time growth with exponent $\beta_2 (> \beta_1)$. The saturated width increases, i.e., the interface roughens, with the molecular weight L_c , but the roughness exponent α (from $W_s \sim L^\alpha$) becomes negative in contrast to models for particle deposition; α depends on the chain length—a nonuniversal scaling with the substrate length L . Roughening and deroughening occur as the field E and the temperature T compete such that $W_s \approx (A + BT)E^{-1/2}$.

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As polymer chains are driven by a field toward a substrate, e.g., the pore boundary of a gel, in a DNA electrophoresis [1,2], it is not clear how the polymer interface width W evolves and scales with multiscaling fields such as molecular weight L_c (chain length), electric field E , and temperature T . Understanding of the driven polymer interface is also important in the design of composite materials via molecular deposition and evolution of their physical properties [3,4]. In coatings technology [5], knowledge of the density profile and roughness of the polymer layer on the adsorbing surface [4,6] is the key to characterizing surface properties [7]. In general, these studies are useful in understanding polymer characteristics at the interface [8] in mixtures or adhesion of dissimilar substances.

While considerable progress has emerged in the understanding of the growth of the interface width and its scaling in deposition of particles [9], very little is known about the interfacial dynamics in polymer deposition [7,10,11]. We find unexpected results for the growth of the driven polymer interface width, which exhibits unusual nonuniversal scaling with multiscaling variables (L_c, E, T) . In the following, we show that the interface width (i) decreases, i.e., deroughens, with increasing field strength and (ii) increases with increasing temperature and molecular weight, but the magnitude of the deroughening exponent is enhanced with a larger molecular weight. Reduction in surface roughness by the polymer chains in the deposition process may be related to drag reduction by polymers in fluid flow [12].

Using Monte Carlo simulations, we study the surface dynamics of polymer chains driven by a field toward an impenetrable adsorbing barrier in a $(2+1)$ -dimensional discrete lattice. We consider polymer chains, each of length L_c , which consist of $L_c + 1$ nodes connected consecutively by rigid unit bonds along the lattice using a self-avoiding-walk constraint. All lengths (chain, substrate) are measured in arbitrary units of the lattice constant. In polymer simulations [13], implementation of the local dynamics of polymer chain movement is very important in studying the physical properties on various time scales. Kink-jump dynamics is used ac-

ording to the Verdier-Stockmayer algorithm [14] to move chain nodes on a $L_x \times L \times L$ lattice with a large aspect ratio L_x/L . It should be pointed out that the kink-jump move provides a slow chain dynamics in contrast to the relatively faster dynamics used in a recent study [7] where a reptation move is implemented in combination with the kink-jump moves. Some of the microscopic details arising from the slow kink-jump moves are generally lost when reptation is implemented with the kink jump since the former dominates over the latter. The details of conformational and density evolution are, therefore, better taken into account due to small scale kink-jump dynamics for the model considered here. Chains are released at nearly a constant rate from a source end (near $x=1$) of the sample and are driven by an electric field toward an impenetrable adsorbing wall (in the yz plane) at $x=L_x$. In addition to excluded volume, nearest-neighbor polymer-polymer repulsive and polymer-wall attractive (adsorbing) interactions are implemented. The external field E couples with the change in energy, $\delta E = E dx$, for the displacement $dx=0$ or ± 1 of each node along the x direction. A randomly selected chain node is attempted to move according to the Metropolis algorithm [15]. N attempts to move randomly selected nodes are defined as one Monte Carlo step (MCS), where N is the number of occupied lattice sites. Even though the measure of time in units of MCS is arbitrary, it provides a way to analyze the growth and evolution of quantities such as interface width with the MCS time, i.e., $W \sim t^\beta$. However, it is observed that the interface width reaches steady state, i.e., saturates, and so the scaling of the saturated width W_s with the substrate length $W_s \sim L^\alpha$, where α is the roughness exponent, and with other parameters such as field and temperature (see below) is independent of the time unit. A snapshot of the system is shown in Fig. 1.

Figure 2 shows a typical evolution of the polymer density profile. Because of a high degree of ramification, it is rather difficult to identify the surface; therefore, an accurate algorithm is needed with good statistics to evaluate the average height \bar{h} of the growing surface and its fluctuation, i.e., the interface width

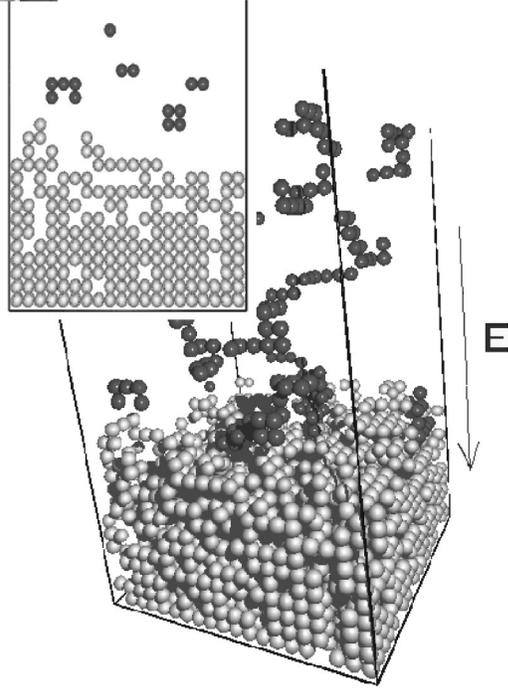


FIG. 1. Snapshot of a $40 \times 20 \times 20$ system with chains of length $L_c = 10$ at $E = 0.5$ and $T = 1$. The light beads (in bulk) are polymer nodes that are connected to the wall via a network of occupied nearest-neighbor sites. The charged polymer chains are driven from top to bottom (x direction) by a uniform electric field \mathbf{E} . The inset shows a two-dimensional slice in the xy plane. The height h_{ij} of the interface at each column is the distance from the substrate (bottom) to the highest light bead in that column.

$$W^2 = \frac{\sum_{ij} (h_{ij} - \bar{h})^2}{L^2}, \quad (1)$$

where

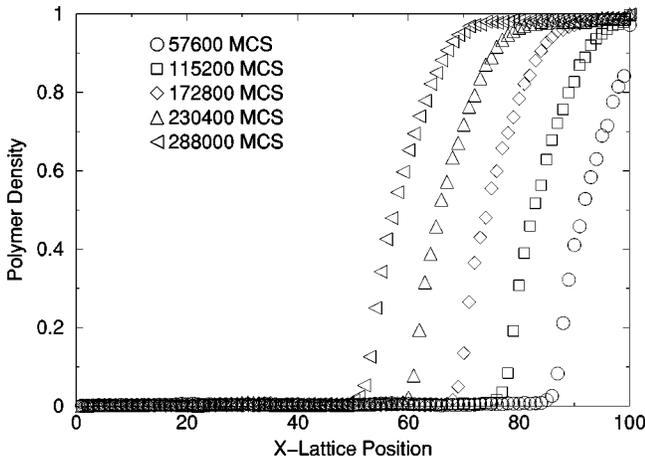


FIG. 2. Density profile of polymer coating on a $100 \times 30 \times 30$ lattice for polymer chains of length $L_c = 30$ at $T = 1$ and $E = 0.5$. Plots are shown for several different times in units of Monte Carlo time steps (MCS). The x lattice position is measured in units of the lattice constant, and polymer density is the fraction of occupied sites.

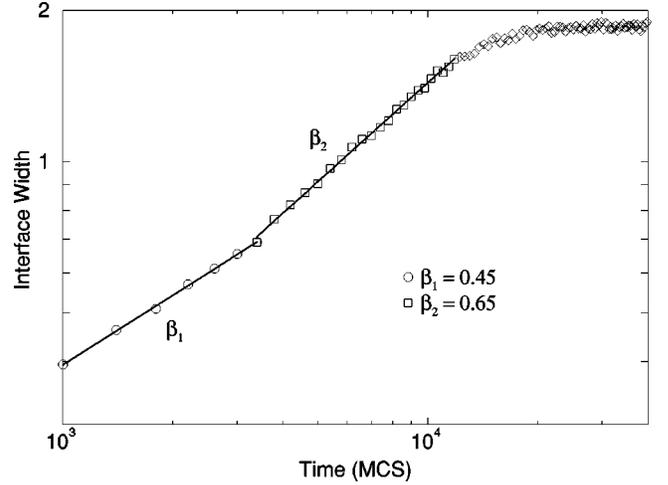


FIG. 3. Growth of the interface width W (in units of the lattice constant) with time on a log-log scale for $L = 30$ and $L_c = 5$ at $E = 0.5$ and $T = 1$.

$$\bar{h} = \frac{\sum_{ij} h_{ij}}{L^2}, \quad (2)$$

and h_{ij} is the surface height at location (i, j) on the wall/substrate. We identify the polymer surface coating as the locus of polymer nodes where each polymer node is connected to the adsorbing wall with a nearest-neighbor network of nodes as in cluster identification in standard percolation [17].

Evolution of a typical interface width is presented in Fig. 3. We note that the interface width initially grows comparatively slowly in the short-time regime ($t \leq t_1$) followed by a faster-growth regime ($t_1 \leq t \leq t_2$) before reaching saturation in the longtime regime ($t \gg t_2$). We examine the growth of the interface width in these regimes as power laws, i.e., $W \sim t^{\beta_1}$ in $t \leq t_1$ and $W \sim t^{\beta_2}$ in $t_1 \leq t \leq t_2$. Estimates of these growth exponents for various values of chain length and field are presented in Tables I and II, respectively. We find that $\beta_1 \leq \beta_2$ and the growth exponents have the values $\beta_1 \approx 0.50 \pm 0.10$ and $\beta_2 \approx 0.66 \pm 0.10$ for $E = 0.5$ and $T = 1$ and are nearly independent of chain length. The higher values of the growth exponent β_2 seem consistent with the experimen-

TABLE I. Growth exponents β_1 (initial) and β_2 (before saturation) with substrate length $L = 30$ at $E = 0.5, T = 1$ for different chain lengths.

Chain length L_c	β_1	β_2
2	0.46 ± 0.01	0.64 ± 0.01
3	0.51 ± 0.01	0.60 ± 0.02
4	0.44 ± 0.01	0.63 ± 0.01
5	0.45 ± 0.01	0.65 ± 0.01
9	0.41 ± 0.03	0.69 ± 0.01
11	0.43 ± 0.05	0.69 ± 0.02
14	0.56 ± 0.05	0.72 ± 0.03
19	0.41 ± 0.07	0.50 ± 0.03
25	0.41 ± 0.04	0.57 ± 0.03

TABLE II. Growth exponents β_1 and β_2 at with $L=30$ and $L_c=25$ at $T=1$ for different field strengths.

Field E	β_1	β_2
0.08	1.05 ± 0.07	1.08 ± 0.04
0.09	0.88 ± 0.05	1.05 ± 0.07
0.10	0.97 ± 0.10	1.13 ± 0.04
0.20	0.72 ± 0.08	0.76 ± 0.06
0.30	0.49 ± 0.04	0.62 ± 0.05
0.40	0.36 ± 0.03	0.55 ± 0.06
0.50	0.41 ± 0.04	0.57 ± 0.03
0.60	0.40 ± 0.04	0.47 ± 0.04
0.70	0.30 ± 0.05	0.48 ± 0.14

tal measurements of the surface roughness of plasma polymer films [10]. We note that the magnitude of the growth exponents in both initial and intermediate growth regimes (i.e., $0-t_1, t_1-t_2$) depend on the strength of the field, and therefore, the growth exponents are nonuniversal.

Variation of the asymptotic or saturated width W_s with L_c , E , and T is examined in detail. In the dynamic scaling analysis of fluctuating surfaces [16], one usually looks at the finite-size scaling of the saturated width with the substrate

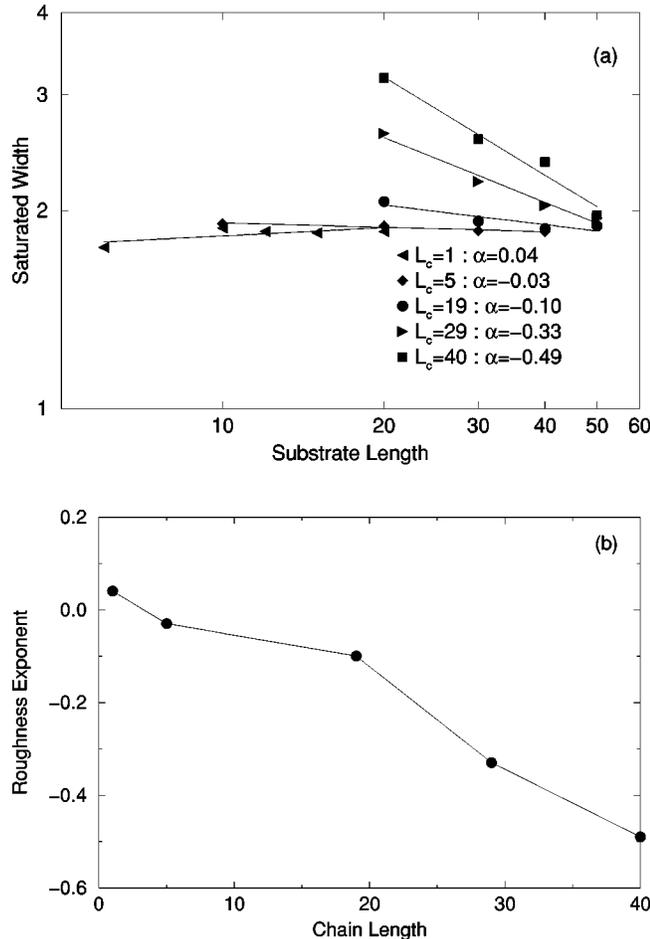


FIG. 4. (a) Saturated width versus substrate length (in units of the lattice constant) on a log-log scale for $L_c=1, 5, 19, 29, 40$ at $T=1$ and $E=0.5$. (b) Variation of the roughness exponent with the chain length (in units of the lattice constant).

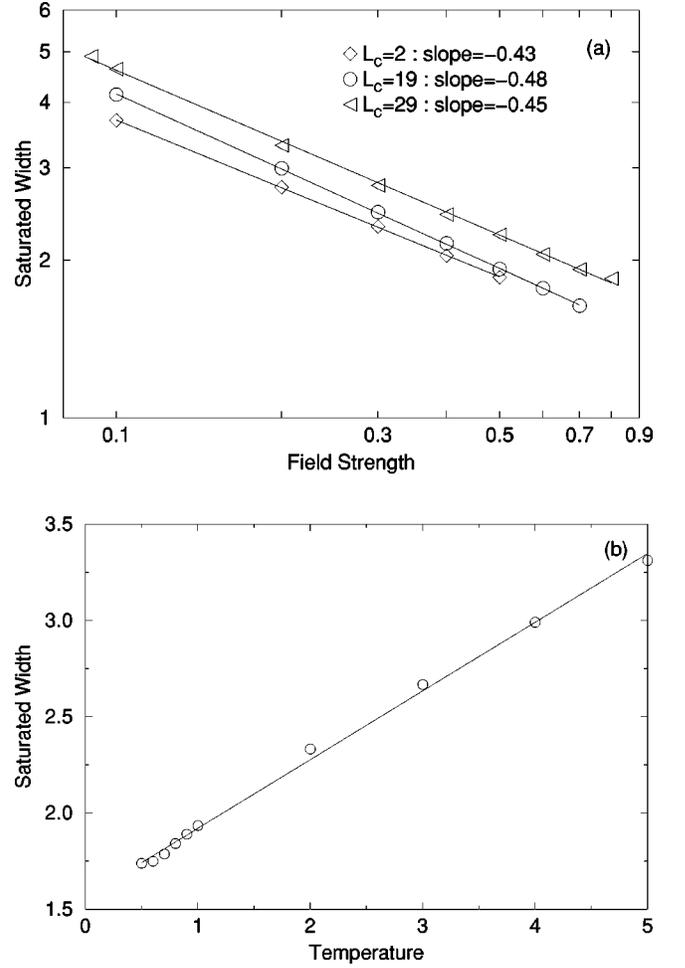


FIG. 5. Variation of saturated width (a) with field strength on a log-log scale for $L=30$, $L_c=2, 19, 29$, and $T=1$, and (b) with temperature for $L_c=19$, and $E=0.5$. Field and temperature are in arbitrary units.

length L to evaluate the roughness exponent α (i.e., $W_s \sim L^\alpha$). Single-parameter scaling of the asymptotic width with the substrate length L has been verified in detail via extensive particle simulations [9]. In our simulations (see Fig. 4), the saturated interface width is insensitive to the substrate length L with $\alpha \approx 0$ for short chain lengths ($L_c=1-5$). With the longer chain lengths ($L_c \geq 10$), on the other hand, α becomes negative, i.e., W_s decreases with L with a negative value of the roughness exponent α . To our knowledge, the dependence of the roughness exponent on the molecular weight has not been reported by computer simulation before, and the negative value of the exponent with higher molecular weight is a finding we report here. This implies that the roughness reduces upon increasing the substrate length as the polymer chains access more space to relax entropically. The (negative) magnitude of α increases with the chain length. (See the variation of α with the chain length in Fig. 4.) It is important to point out that the phenomena of deroughening with the substrate length L observed here is opposite to most roughening studies with particle deposition [9] and experiments on plasma polymer film [10]. At a fixed substrate size, we find that the saturated width increases monotonically with the molecular weight L_c .

We have also examined the variation of the saturated

width with the field strength and temperature (see Fig. 5). We find that $W_s \sim E^{-1/2}$ at the temperature $T=1$. Note that the saturation width increases linearly with temperature unlike the plasma polymer experiment [10] where the interface width seems to decrease with the temperature. In particle deposition models [9], one would expect a decrease in the interface width with the temperature as the particles diffuse to reduce the roughness. In our polymer system, on the other hand, each polymer chain is uniformly charged so the monomer-monomer repulsion causes the chains to take on an extended conformation. Upon contact with the deposited surface, the field tends to cause the extended chains to lie in the yz plane leading to a small interface width. At higher temperatures, however, the chains take on a more compact random-coil conformation that yields a larger interface width. There are various characteristic lengths involved in interfacial polymer dynamics, e.g., the height-height correla-

tion length ξ_h , radius of gyration of chains R_g , and density-density correlation length ξ_d , which are all interdependent. Effects of external parameters (E, T) on these lengths at the interface are difficult to evaluate. It is, therefore, rather difficult to propose a multiparameter scaling for the interfacial dynamics at this stage. However, it is clear that the interface width depends on the field and the temperature described by our empirical law $W_s \approx (A + BT)E^{-1/2}$, where A and B are constants. The observation that $W_s \sim L^{|\alpha|}$ with increasing magnitude of $|\alpha|$ with the chain length suggests that the deroughening exponent ($-\alpha$) is nonuniversal.

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