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Interface Relaxation in Electrophoretic Deposition of Polymer Chains: Effects of Segmental Dynamics, Molecular Weight, and Field

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Interface relaxation in electrophoretic deposition of polymer chains: Effects of segmental dynamics, molecular weight, and field

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Using different segmental dynamics and relaxation, characteristics of the interface growth is examined in an electrophoretic deposition of polymer chains on a three (2+1)-dimensional discrete lattice with a Monte Carlo simulation. Incorporation of faster modes such as crankshaft and reptation movements along with the relatively slow kink-jump dynamics seems crucial in relaxing the interface width. As the continuously released polymer chains are driven (via segmental movements) and deposited, the interface width W grows with the number of time steps t, $W \propto t^{\beta}$, ($\beta \sim 0.4$–0.8), which is followed by its saturation to a steady-state value W_s. Stopping the release of additional chains after saturation while continuing the segmental movements relaxes the saturated width to an equilibrium value ($W_s \rightarrow W_r$). Scaling of the relaxed interface width W_r with the driving field E, $W_r \propto E^{-1/2}$ remains similar to that of the steady-state W_s width. In contrast to monotonic increase of the steady-state width W_s, the relaxed interface width W_r is found to decay (possibly as a stretched exponential) with the molecular weight.

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I. INTRODUCTION

The deposition process [1,2] is one of the common methods used for growing and designing composites, polymeric materials, interfaces, and surface coating [3]. As the polymer chains are driven toward an impenetrable substrate/wall, the polymer density at the substrate grows and the interface develops [4–6]. A number of parameters (e.g., temperature, pressure/field, and molecular weight of polymer) and processes (e.g., rate of polymer release, segmental dynamics, relaxation, etc.) affect the growth of the polymer density and its interface. Recently, we examined the growth of the interface, its scaling, and roughness in an electrophoretic deposition model on a discrete lattice using kink-jump segmental dynamics [4] and by including reptation [5,6]. We have observed many interesting scaling behaviors of the interface width in these continuous deposition processes where the polymer chains are released at a constant rate throughout the computer simulation.

As the polymer chains deposit, the polymer density spreads from the substrate toward the source of the polymer chains, and the interface width grows. Even in such a continuous deposition process, the interface width W reaches a steady-state (saturated) value (W_s) after an appropriate growth period. The steady-state width W_s exhibits interesting scaling with temperature, field, and molecular weight leading to roughening and deroughening [4–6].

In this paper we examine the characteristics of the density profile and the interface width as we relax the system (which includes the polymer bulk and interface). Recently, relaxations of polymer surfaces haave been studied qualitatively [7,8]. Characteristic surface relaxation times τ for some polymer materials have been measured by experiment [9–11]. One approach to achieve such a relaxation in simulations is to stop injecting new polymer chains after an appropriate amount of polymer chains are in the system but continue to allow segmental motion of the chains. Temperature T, field E, and molecular weight L_c play important roles in relaxing the interface width; here we restrict the analysis to the effects of field and molecular weight. We also probe the relaxation by examining the effects of incorporating the faster modes of movements such as crankshaft and reptation along with the relatively slow kink-jump segmental dynamics [12]. In the next section we briefly describe the model followed by results and discussion, and finally, a summary/conclusion.

II. MODEL

We briefly describe the model to point out the differences between the simulation procedure adopted here for segmental dynamics and relaxation and our previous studies [4–6]. We consider a discrete lattice of size $L_x \times L \times L$ with a large aspect ratio L_x/L. Typically, $L_x = 100$–200, $L = 40$, 60. Polymer chains each of length L_c, generated as the trail of a random walk of L_c steps along the lattice with excluded volume constraints, are released from the $x=1$ end of the sample. The lengths used here (L, L_x, L_c) are in units of the lattice constants. An external field E drives the chains from the source near $x=1$ toward the substrate (impenetrable wall) at $x=L_x$. The field couples with the change in energy, $E\Delta x$, where Δx is the displacement of the chain node along x direction. In addition to excluded volume, there is a nearest-neighbor polymer-polymer repulsive and polymer-wall attractive interaction. Chains are released at a constant rate and moved with the Metropolis algorithm [13] using segmental dynamics such as kink-jump, crankshaft [14], or slithering snake (reptation) or some combination [12]. Attempts to move each chain node once is defined as one Monte Carlo step (MCS). The simulation is performed for a relatively large number of time steps and for a sufficient number of independent samples to obtain a reliable estimate of averaged physical quantities.

In our earlier studies [4–6], polymer chains are released throughout the simulation. In this study, chains are released with a constant rate for a sufficiently long time (typically

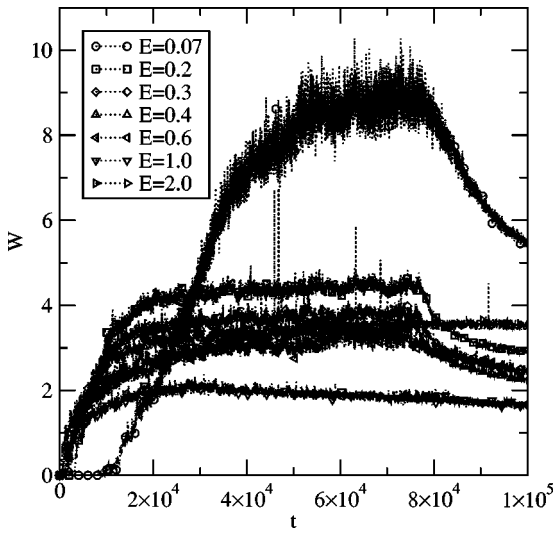

FIG. 1. W (in units of the lattice constant) vs time steps t (MCS) with K segmental dynamics for different fields with 10–20 independent samples.

about three-fourths of the entire simulation time) before stopping the release of new chains into the system. The simulation is then continued to allow chains (already released into the system) to deposit and relax. As discussed below, the relaxation makes a significant difference in characteristics of the interface.

III. RESULTS

Figures 1 and 2 show the variation of the interface width with the number of time steps for kink-jump (K) (Fig. 1) and kink-jump and crankshaft (KC) (Fig. 2) segmental dynamics for different driving fields. Data with both segmental movements are generated by (i) depositing chains for about three-fourths of the entire simulation steps as mentioned above and

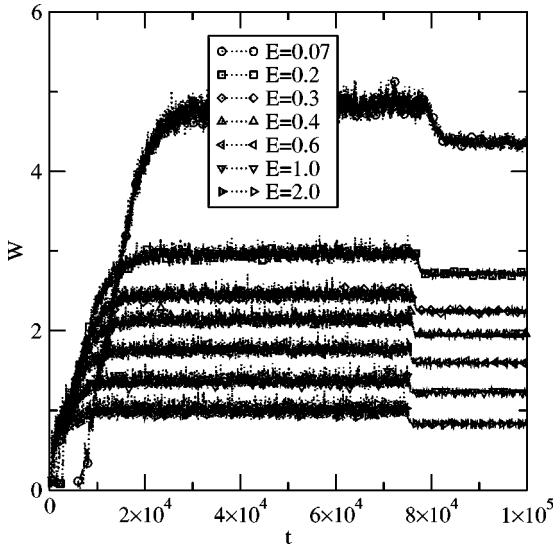

FIG. 2. W (in units of the lattice constant) vs time steps t (MCS) with KC segmental dynamics for different fields with 10–20 independent samples.

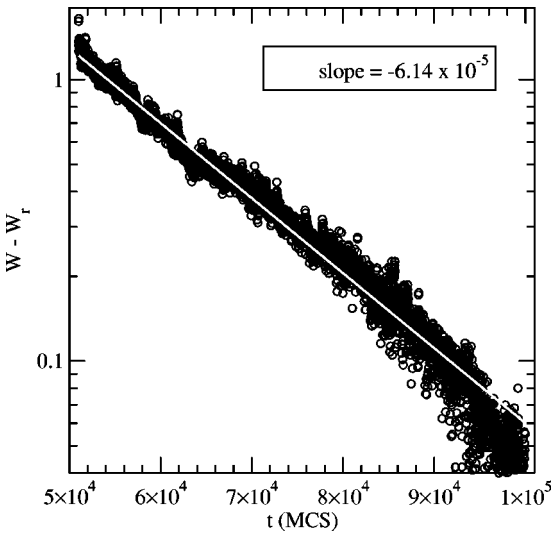

FIG. 3. Decay of W (in units of the lattice constant) at $E=0.4$, $T=1$ with K segmental dynamics on a semilog plot. The range of the Y axis ($W-W_r$) lies between 0.4 and 1.8 and has units of the lattice constant. The slope of the fit is provided in the legend. Statistics are the same as for Fig. 1.

(ii) relaxing chains already in the system (polymer bulk and the interface width) for the last one-fourth of the time steps without adding new chains. We see a rapid growth of the interface width W initially (time step $t \leqslant 10^3$) particularly at higher fields before reaching a steady state value (W_s). At the time step, $t=7.5\times10^4$, when the injection of new chains stops, the interface width decays rapidly and attains a constant relaxed value (W_r). At low fields ($E=0.07$), it takes longer for the interface to both grow and decay.

Although the general features of growth and decay of the interface width with K and KC movements appear similar, there are clear differences in the relaxation. Obviously, it is faster for the chains and the interface width to relax with the KC dynamics than with the K move alone. At low field ($E=0.07$), the interface width is not completely relaxed (approach a constant value) with K dynamics by the end of the simulation run. In fact, a complete relaxation even at higher values of field ($E \geqslant 0.6$) within the time of simulation with the K dynamics is questionable. Figure 3 shows the decay of the interface width from steady-state to equilibrium with the K dynamics during the relaxation period. One can identify an exponential decay

$$W - W_r \sim e^{-(t-t_0/\tau)},$$

where t_0 is the time for stopping the release of chains, and τ is the characteristic relaxation time for the interface (determined by the slope).

Initial interface growth $W \propto t^{\beta}$, ($\beta \sim 0.3$–1) has been studied in detail [4,5] and values of the growth exponent β are nearly the same with both K and KC dynamics. It is clear, though, that the relaxation of the interface width is much faster with the KC dynamics. However, it is because of the

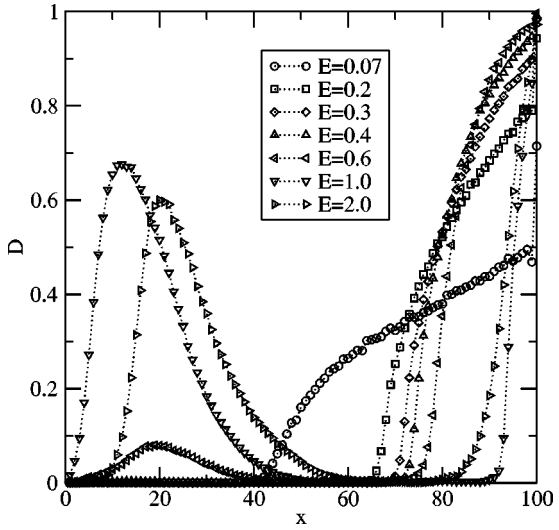

FIG. 4. Polymer density D (fraction of occupied sites) vs x (in units of the lattice constant) with the K dynamics for different fields.

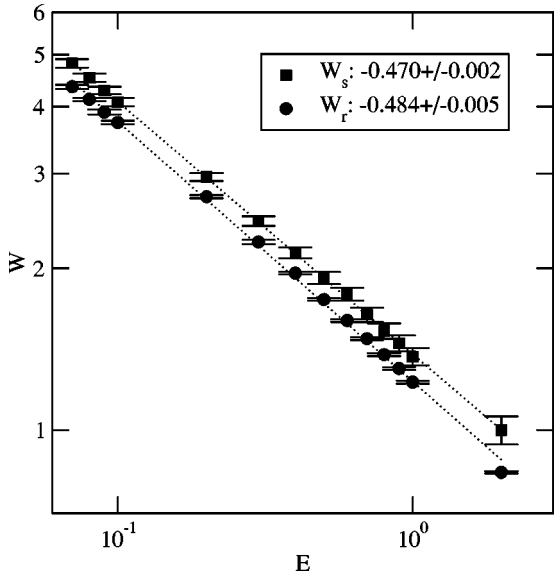

FIG. 5. Interface width (W_s and W_r in units of the lattice constant) vs field E (in arbitrary units) with KC segmental dynamics. Statistics are the same as for Fig. 1.

slow relaxation of the interface width with the K dynamics that we are able to comment on the exponential decay of the interface width here.

Since the relaxations of chains and the interface are so different between the K and KC dynamics, the major question remains, which dynamics is appropriate? In our opinion, it depends on the situation. If one looks for the well-behaved relaxed or steady-state properties such as the interface width, KC dynamics would be preferable over the K movement of chains. Nevertheless, it is important to understand the details of results arising from different dynamics. Let us look at the density profile of polymer with the K motion presented in Fig. 4. We immediately note the difference in density profile at low ($E<0.6$) and high ($E\geqslant 0.6$) fields. At low field, the polymer density remains low ($\rightarrow 0$) from the source end (the region for releasing new chains) and increases monotonically toward the substrate. On the other hand, at high field there is a large density toward the source end indicating a build-up (accumulation) of polymer chains before they reach the bulk region growing from the substrate. Such a clogging restricts the deposition of polymer chains and the growth becomes independent of the rate of polymer release (i.e., dynamics-limited deposition). Clogging occurs due to slow motion of chains with the K dynamics alone. Thus, care must be exercised in analyzing the interface growth, decay, and its scaling to field at low and high fields where deposition rates differ substantially.

With the KC dynamics, there is no clogging at these values of field ($E\leqslant 2.0$) and the interface width relaxes very well within our simulation time. Variation of the relaxed interface width W_r with the field is presented in Fig. 5. We see that the interface width (W_r) decays with the field with a power law $W_r \propto E^{-1/2}$. Note that the nature of decay of the relaxed interface width W_r with the field remains similar to that of the saturated width W_s in steady state. Such a decaying trend of the interface width with the field is also observed with the K alone in the low-field regime ($E<0.6$). We have also studied the dependence of the interface width (W_r) on the molecular weight L_c and find a monotonic decrease as shown in Fig. 6. Note the contrast, while the relaxed width W_r decays with the molecular weight, the saturated steady-state width W_s increases. In the steady-state growth, polymer chains are continuously deposited. As a result the incoming chains at the surface are not relaxed. The contribution of unrelaxed chains at the growing surface to the interface width is dominant over the relaxed chains, since the conformation of incoming chains are relatively stretched out along the direction of the field.

We have also examined the effect of incorporating the slithering-snake (reptation) motion to kink-jump and crank-

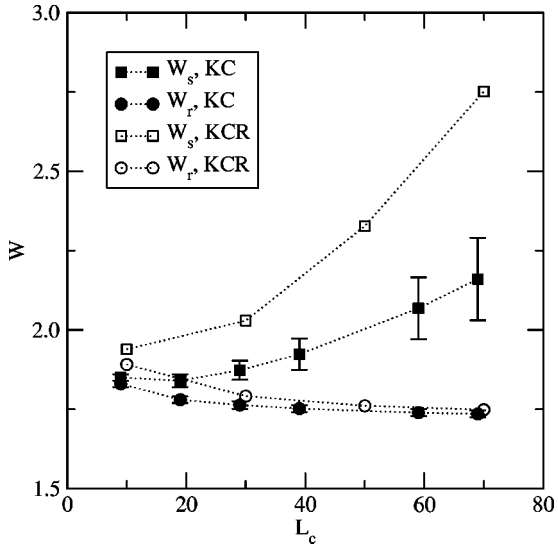

FIG. 6. Interface width (W_s and W_r) vs L_c with KC and KCR segmental dynamics. W_s, W_r, and L_c are in units of the lattice constant. Statistics are the same as for Fig. 1.

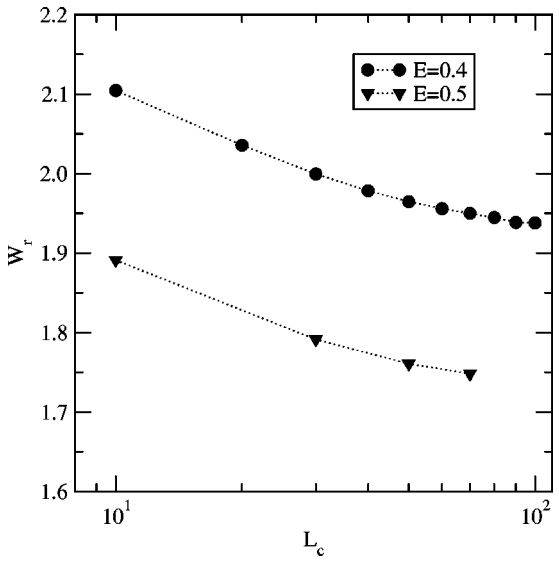

FIG. 7. Interface width (W_r) vs L_c with KCR segmental dynamics at $E=0.4$, 0.5, and $T=1$. W_r and L_c are in units of the lattice constant. Statistics are the same as for Fig. 1.

shaft dynamics (KCR). The relaxation of the interface width is relatively faster with the KCR than with KC and K segmental movements. However, the qualitative nature of the variation of the relaxed interface width W_r with the molecular weight L_c is similar to that with KC dynamics (see Fig. 6) with somewhat higher magnitude of the widths. It is worth pointing out the difference in the interface widths with KC and KCR segmental dynamics. While the difference in the steady-state width W_s increases with the molecular weight, the difference in relaxed interface width W_r decreases. At high molecular weights, it is rather difficult to distinguish the relaxed interface widths. The larger difference in steady-state and relaxed interface width ($W_s - W_r$) between KC and KCR dynamics suggests that the magnitude of W_s is dominated by the elongation of polymer chains (along the field direction) which is larger with the KCR semental motion. Figure 7 shows the variation of the relaxed interface width W_r with the molecular weight for two different fields with the KCR segmental dynamics. We see that the qualitative nature of the variation remain similar at these fields. Decay of the interface width (W_r) with the molecular weight appears to be stretched exponential. With the KCR dynamics, we have also observed a power-law decay of the interface width (W_r) with the field similar to Fig. 5 with the KC dynamics. As expected, the interface width is relatively well relaxed with the KC dynamics, and adding reptation enhances the relaxtion further.

IV. CONCLUSION

A computer simulation study was presented to investigate the effect of segmental dynamics on the growth and decay (relaxation) of the interface width for an electrophoretic deposition model for polymer chains. The results for the dependence of the relaxed interface width (W_r) on the molecular weight are quite different from that of the steady-state interface width (W_s) reported in previous studies [4,5] where polymer chains were continuously deposited throughout the simulation. In contrast to an increase of the steady-state width W_s, the relaxed width W_r decays with the molecular weight. The power-law decay of the relaxed width with the field ($W_r \propto E^{-1/2}$) remains the same as that of the steady-state width (W_s).

The relaxation of the width after stopping the addition of more polymer chains to the system depends on the segmental dynamics. For example, with the kink-jump dynamics alone, it is very difficult to reach relaxed interface width within a reasonable simulation time at low fields ($E \leqslant 0.07$). On the other hand, clogging occurs around the entrance area of polymer injection at high fields ($E \geqslant 0.6$), which reduces the rate of polymer deposition on the substrate. Thus, the scaling of the interface width at high fields should be different from those at low to moderate field values. Inclusion of crankshaft motion leads to faster growth and interface relaxation at all field values we studied. Adding large scale segmental dynamics (reptation) enhances the interface relaxation and reduces the magnitude of the relaxed interface width. The scaling of the interface width with the field and molecular weight is qualitative similar.

ACKNOWLEDGMENTS

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