Glassy Relaxation at Polymer–Solid Interfaces

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ABSTRACT: We present a kinetic Ising model for the cooperative dynamics associated with the relaxation of adsorbed polymer chains. At low temperatures, the chain molecules are frozen in nonequilibrium conformations. Over a range of temperatures the dynamics of relaxation are found to be described by stretched exponential (KWW) functions. Average relaxation times exhibit a strongly non-Arrhenius temperature dependence.

The motivation to study the structure and dynamics of polymer chains near solid surfaces stems from both the challenging scientific questions that need to be addressed and the broad technological importance of synthesizing polymer–solid interfaces. These interfaces may broadly be classified into two classes: one, wherein the segment–surface interactions are strong and specific (e.g., polymer–metal interfaces), and, two, those characterized by weak dispersive segment–surface energetics (e.g., the polyethylene–graphite interface). Much is currently known about the structure of weakly interacting polymer–solid interfaces (e.g., refs 1 and 2), and an understanding of the nature of polymer–solid interfaces characterized by strong and specific interactions is just beginning to emerge (e.g., refs 3–8). One notable result for the latter systems is that the dynamics associated with creating the interface is crucial for determining the interfacial chain structure.[6] However, progress in understanding adsorbed chain dynamics has been modest.[9–11] In this paper, we provide a simple model that captures the key physical processes associated with interfacial chain relaxation. We make predictions regarding the kinetics of chain relaxation that should be testable via direct experimentation. We also make connection with the relevant experimental data that exist in the literature. The model is currently restricted to the low-coverage limit. However, as will be made clear, we do not expect the qualitative features of the observed dynamics to change at higher surface coverages. We begin by identifying a specific problem and developing our model in that context. The model can easily be generalized to encompass other situations, and results for various polymer architectures and chain lengths will be presented elsewhere.[12]

We first consider polymer–solid interfaces wherein specific functional groups of the organic polymer interact strongly with the surface. For example, the poly(methyl methacrylate) (PMMA)–aluminum system has been shown[5,7] to have two strongly interacting functional groups per segment. As a model for such a system, consider a linear chain with two pendant groups per segment that interact with the surface by binding to it with energies E_1 and E_2, respectively. Let E_1 be greater than E_2, and let both energy scales be significantly larger than the thermal energy, kT. Physically, it is clear that the segment–surface interaction energies in systems such as these are characterized by many orientation- and configuration-dependent minima that are often separated from each other by barriers that are greater than kT. Consider a segment that approaches the surface in an orientation and conformation wherein the group with binding energy E_2 attaches itself to the surface. This segment will now be adsorbed in a local minimum that is not the global minimum. On the basis of this and other reasons, Chakraborty et al.[6] have argued that the adsorption of chain molecules on surfaces characterized by strong and specific interactions is kinetically controlled. These authors have also provided results of molecular dynamics (MD) simulations for short chains which show that each realization of the adsorbed chain structure leads to a different nonequilibrium conformation. The collection of nonequilibrium interfacial chain conformations may be considered to be analogous to a bulk polymer glass. We note that the existence of glassy adsorbed polymer layers has been considered before by Kremer.[13] Kremer argued that, for temperatures below the bulk glass transition temperature, the enhanced density near the surface may lead to a glassy layer adjacent to the surface because there is an insufficient amount of solvent to plasticize the polymer. As has been pointed out above and by Chakraborty et al.,[6] the reason for the existence of nonequilibrium structures near polymer interfaces characterized by strong and specific interactions is that the nature of the interactions with the surface traps the chains in nonequilibrium conformations. The issue of concern here is not related to glassification due to lack of enough solvent, and no connection is to be made with the bulk glass transition temperature of the polymer.

The existence of nonequilibrium interfacial chain conformations raises the interesting question of how the interfacial chain structures relax toward equilibrium as a function of time and temperature (or segment–surface interaction energy scale). MD simulations cannot address these issues, because they cannot probe the relevant time scales associated with these relaxation processes. Previous MD[6] and experimental[10] studies show that the first step of adsorption from solution is fast and leads to a nonequilibrium chain conformation. The dynamics associated with the subsequent relaxation of the initial nonequilibrium conformation and its dependence on segment–surface interaction energies is the focus of this work.

Consider a single chain of our model polymer to be adsorbed in some arbitrary nonequilibrium conformation. Each pendant sticker can now be considered to be either adsorbed or desorbed. Each sticker may thus be viewed to be a two-state system, with spin up (desorbed) or spin down (adsorbed). There is, therefore, an isomorphism between the adsorbed chain structure and a spin $^1/_2$ Ising model. The collection of $2N$ spins constitutes our model for an adsorbed chain of length N segments. The dynamics of adsorbed chain relaxation is described by the time evolution of the spin states. As such, our model belongs to the class of kinetic Ising models first discussed by

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Glauber[14] and heretofore employed as models for bulk glassy systems.[15] Our model is different from that used to describe spin glasses.

The temporal evolution of the spin system that constitutes our model for the adsorbed chain is described by a master equation with transition probabilities that satisfy detailed balance. A description of the relevant physical processes that determine the dynamical phenomena under consideration is contained in the rules that are invoked in constructing the transition probability matrix for spin flips in the master equation. We now turn to the formulation of these rules, which have been developed on the basis of purely physical considerations. Hence, we first carefully examine the physical situation that we are concerned with.

The relaxation of the adsorbed chain molecule involves adsorption–desorption events for the sticker groups (or spin flips). If the sticker groups (or spins) were independent, then the rate of, say, desorption of a given sticker would be (according to transition-state theory)

$$r_{\mathrm{des}} = k_0 \exp(-E_{\mathrm{well}}/kT)$$

where E_{well} is the binding energy for the sticker and k_0 is an intrinsic time scale or attempt frequency. However, for the system under consideration the individual stickers are not independent, and there are several impediments in the escape routes available for desorption and channels for adsorption. These impediments arise due to many reasons, such as chain connectivity, steric constraints imposed by neighboring segments, and rotational strain in the bonds connecting a given segment to adjacent ones. This implies that the rates of adsorption and desorption of a given sticker are strongly correlated with the state of the neighboring segments. The strong dependence of the individual spin flip rates on the local environment of spin states leads to a highly cooperative dynamics for adsorbed chain relaxation.

To account for the cooperativity that characterizes adsorbed chain relaxation, we may formally write the rate at which a spin flips up against the field imposed by the surface to be

$$W_{j,\mathrm{up}} = k_0 f(\text{local spin state}) \exp(-E_{j,\mathrm{well}}/kT)$$

where f is a constraint function that depends on the local spin state. The corresponding rate for a spin to flip down is determined by the condition of detailed balance. In this paper, we state the rules that we have invented to incorporate the effects of the various physical issues that determine f and outline the rationale that underlies the formulation of these rules. A detailed description of the same will be published elsewhere.[12]

The first physical issue concerns steric constraints imposed by neighboring segments that influence adsorption or desorption events of any given sticker. These constraints can be visualized easily. As an example, consider a sequence of three segments adsorbed on the surface with all six stickers adsorbed. In this case, the desorption of either sticker emanating from the central segment is hindered by the fact that its neighbors are pinned down. Since the stickers are connected along a contiguous chain, the desorption of such a sticker will take place only when a certain set of constraints imposed by the neighboring segments is released, allowing access to the desorption route available to the sticker in question.

The second issue relates to the rotational conformational state of a sequence of sorbed segments. Previous studies[7,16] have shown that a sequence of bound segments may exist in rotational conformations that are strained with respect to the bulk. Physically, this is so because in these systems favorable interactions between particular functional groups and the surface can stabilize rotational conformations for a sequence of bound segments that may be high-energy conformations for the free polymer. The rates of adsorption–desorption events that lead to relaxation of rotational strain will be enhanced.

The third physical issue that must be described by the constraint function reflects a manifestation of chain connectivity. The configurational entropy decreases when a segment that is part of a loop or a tail adsorbs. This leads to impediments in certain adsorption channels.

The influence of steric constraints on the rates of adsorption or desorption of a given sticker is determined by the state of the two neighboring segments to the right and left of the sticker in question and the sticker emanating from the same segment as the one being examined. Consider an adsorbed sticker or a spin-down state. If the other sticker emanating from the same segment is also adsorbed, for the sticker under consideration to desorb, both stickers on at least one adjacent segment must be in the spin-up state. On the other hand, if the sticker emanating from the same segment is not adsorbed, than at least one sticker on the adjacent segments must be in the desorbed state. Let β be the function that reflects the steric constraint contribution to f. For the first scenario considered above

$$\beta = \{[q(q-1) + r(r-1)]/n_1\}$$

where q and r are the number of spins that are up on the segment to the left and to the right, respectively. n_1 is just a normalization factor. For the second scenario

$$\beta = [q + r]/n_2$$

where n_2 is another normalization factor. We note that this type of constraint is similar to that introduced by Fredrickson and Andersen[15] to model simple bulk glassy systems.

The contribution of rotational strain (γ) to the function, f, is obtained by discretizing the various degrees of rotational strain that may be present. Strained states exist if the stickers emanating from adjacent segments are off from purely trans or gauche states. In our spin model this translates to the following rule for determining γ: If there is exactly one up spin for a pair of adjacent segments, then the bond connecting the segments is rotationally strained. In such a situation spin flips that relax rotational strain are aided by a factor of $\gamma = \exp(E_{\mathrm{tor}}/kT)$. In other situations, $\gamma = 1$. We have taken E_{tor} to be the barrier height of a 3-fold symmetric modification of the torsion potential for butane. Note that to determine γ we must examine both bonds that link the sticker in question to its adjacent segments. This implies that γ, like β, is determined by the states of five neighboring spins.

Following previous efforts,[17] the entropic penalties associated with shortening loops and tails can be worked out from the expressions

$$S_{\mathrm{loop}} = k[(L-1)\ln z - (3/2)\ln L]$$

$$S_{\mathrm{tail}} = k[(L-1)\ln z - (1/2)\ln L]$$

where L is the length of the loop or the tail and z is the coordination number of the lattice. The function, δ, that reflects the contribution of entropic penalties to the transition probability for a spin flip is simply $\exp(\Delta S/k)$, where ΔS is the change in entropy associated with the event. Note that for this constraint function the length

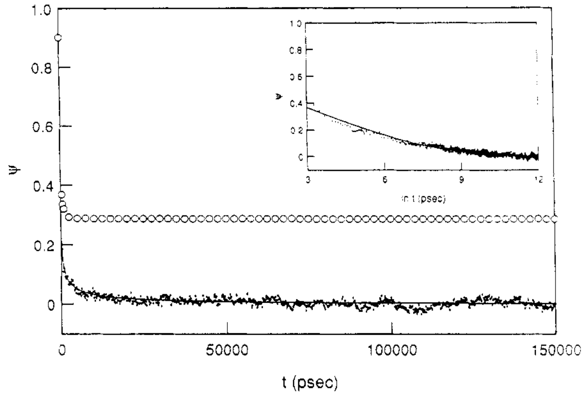

Figure 1. Temporal variation of ψ from Ising model for 500-segment chains for (○) $E_{\mathrm{weak}}/kT = 3.84$ and $M_{\mathrm{eq}} = -0.99$ and (···) $E_{\mathrm{weak}}/kT = 0.64$ and $M_{\mathrm{eq}} = -0.54$; (—) fit of KWW law. (Inset) fit of KWW law ($\beta = 0.2$) on an expanded logarithmic time scale for $E_{\mathrm{weak}}/kT = 0.64$.

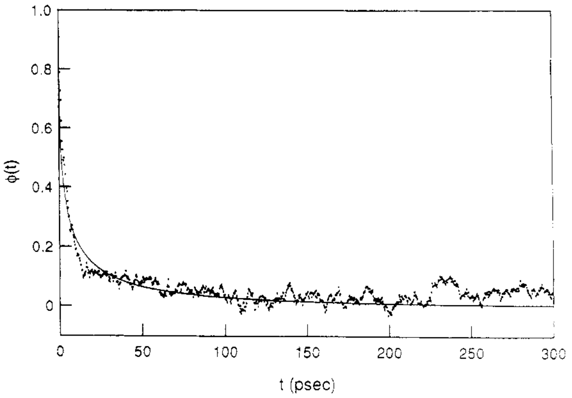

Figure 2. Temporal variation of $\phi = \langle \sigma(t)\sigma(0) \rangle - \langle \sigma \rangle^2$ (the one-spin correlation function) for $E_{\mathrm{weak}}/kT = 0.72$.

scale over which cooperative motions must occur is much longer than that for β and γ.

The formulation of our simple model is now complete. The rate of spin flips is given by $W_{j,\mathrm{up}}$ with $f = \beta\gamma\delta$. We start the computation by randomly choosing 10% of the stickers to adsorb on the surface in some nonequilibrium conformation. The master equation is then numerically solved on a $2 \times N$ lattice to obtain the evolution of the spin states as the system progresses toward equilibrium. The final results for any given case are obtained by averaging over several (at least five) realizations of the initial nonequilibrium conformation.

Since our rules determining the rates of spin flips have been obtained by physical induction rather than rigorous deduction, it is important that we first test the validity of our model. We do so by comparison with results of MD simulations for octamers of our model chain molecule. The sticker–surface interactions are characterized by parabolic wells, and the solvent molecules are explicitly represented. The backbone atoms and solvent molecules interact with the wall via truncated and shifted Lennard-Jones potentials. In all cases that we have simulated, the well for the strong sticker's interaction with the surface is twice as deep as that for the weaker sticker. The MD results for various values of the energy scale for sticker–surface interactions were compared with the results of our kinetic Ising model. Details of the comparison will be presented elsewhere.[12] Herein we state that the final states attained by both methods are equivalent. Furthermore, on a coarse grained time scale, upon using a value for k_0 that is 6 times larger than that obtained from the curvature of the parabolic wells used in the MD simulations, we find that the frequency of adsorption–desorption events also compares very well. With the validity of our model thus established, we now present results for the dynamics of adsorbed chain relaxation for long chains over time scales that are not accessible using MD simulations.

We focus first on how the number of sorbed stickers evolves with time. Of course, the number of sorbed stickers is directly and trivially related to the average magnetization in our Ising model by noting that a desorbed sticker corresponds to spin up ($\sigma = +1$) and an adsorbed state corresponds to spin down ($\sigma = -1$). The quantity that we will be concerned with is $\psi = [(M - M_{\mathrm{eq}})/(1 - M_{\mathrm{eq}})]$, where M is the average number of sorbed stickers at any given time $[M(t) = \langle \sigma(t) \rangle]$ and M_{eq} is the value of the same quantity at equilibrium (for a given temperature). In Figure 1, circles represent the results of Ising model simulations for ψ as a function of time for the weak stickers of a polymer chain that is 500 segments long. The sticker–surface interaction energies for this case (circles) are such that $E_{\mathrm{weak}}/kT = 3.84$ and $E_{\mathrm{strong}}/kT = 7.68$. At the low temperatures under consideration, it is clear that the chain gets trapped in a nonequilibrium state and thereafter remains "frozen". We have shown results of calculations only up to 150 ns. However, it is clear that, at this temperature, the adsorbed chain will remain in a nonequilibrium frozen state over experimental time scales. This state may be considered to be analogous to a bulk polymer glass only in the sense that the adsorbed chain is trapped in a nonequilibrium state due to the nature of the segment–surface interactions; no connection is to be made with the glass transition temperature for the bulk polymer.

In Figure 1, dots represent the results of Ising model simulations for ψ as a function of time at a higher temperature ($E_{\mathrm{weak}}/kT = 0.64$ and $E_{\mathrm{strong}}/kT = 1.28$). In this case, the system is seen to be slowly evolving toward equilibrium. Furthermore, the kinetics of relaxation cannot be described by one time constant. In fact, the line drawn through the data in the main plot represents a fit of the data to the Kohlrausch–Williams–Watts (KWW) expression.[18] We note that for the various cases that we have studied a single exponential does not fit the data. The inset in Figure 1 demonstrates more clearly that a stretched exponential function, $\exp[-(t/\tau)^{\beta}]$, fits the data well (with $\beta = 0.20$) over five decades in time. We find that, as the temperature below which relaxation to equilibrium does not occur (in reasonable time scales) is approached, over a range of temperatures, the temporal evolution of the magnetization is described by KWW expressions (with β ranging from 0.2 to 0.5).

Other dynamical quantities are also found to obey the KWW law. Figure 2 demonstrates that the time evolution of the one-spin time correlation function, ϕ, which describes a much more local phenomenon that $\psi(t)$, is also well represented by the KWW functional form (with $\beta = 0.53$).

Ever since Kohlrausch[18] it has been known that the dynamics of strongly interacting materials (e.g., glass-forming liquids) can often be described by stretched exponential functions rather than the standard Debye form. Our model predicts that, over a range of temperatures, the relaxation of adsorbed chain molecules as they evolve toward equilibrium is also thus described. The physical reasons for this merit discussion. Palmer et al.[19] have shown that a class of models wherein the degrees of freedom may be considered to be hierarchically constrained leads to relaxation behavior governed by KWW expressions. Hierarchical constraints imply that the degrees of freedom constitute a series of levels; for a degree of freedom in a given level to change state (or relax), some degrees of freedom in a lower level must adopt a certain prescribed

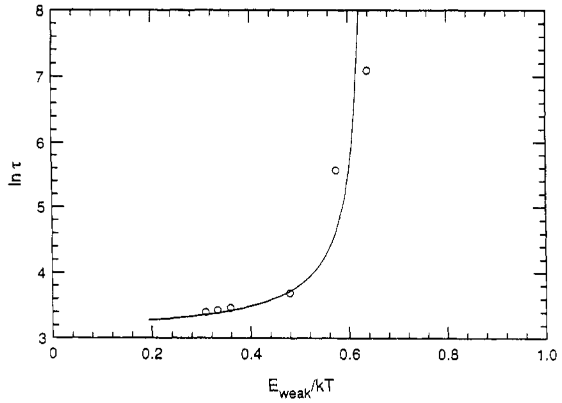

Figure 3. Temperature dependence of average relaxation time. (○) Ising model; (—) fit of Vogel–Fulcher law.

state. Our model for adsorbed chain dynamics belongs to this dynamical universality class. In our model, the spin being examined may be considered to constitute the highest level, and the spin states of the neighboring segments form the lower level degrees of freedom. For the spin being examined to change state, the neighboring spins must be in certain states to alleviate the various physical constraints to adsorption or desorption that we have discussed. For adsorbed chains, our model provides the microscopic physical reasons that naturally lead to hierarchically constrained dynamics.

The relaxation behavior that we observe (Figures 1 and 2) is analogous to that observed for glass-forming liquids. Further evidence for this is provided by examining the variation of an average relaxation time with temperature. We define an average nonlinear relaxation time, τ_{av}, as the area under $\psi(t)$. In Figure 3, we plot τ_{av} for the relaxation of the weak stickers as a function of temperature in the form of an Arrhenius plot. For temperatures below $E/2k$, we find that the relaxation time diverges. In other words, the system is not expected to relax to equilibrium in experimental time scales (see Figure 1). A temperature somewhat above $E/2k$ may be viewed to be analogous to a "glass transition" temperature. As Figure 3 shows, at high temperatures the variation of the relaxation time with temperature is of the Arrhenius form, while as the glass transition temperature is approached there is a sharp increase in slope and curvature. This non-Arrhenius temperature dependence (that may be fit to a Vogel–Fulcher function) is also characteristic of many glass-forming liquids.

The dynamics of adsorbed chains that we find to be characterized by frozen, nonequilibrium structures at low temperatures, stretched exponential relaxation at higher temperatures, and non-Arrhenius temperature dependence of average relaxation times is similar to that observed for the so-called fragile liquids described by Angell et al.[20]

Recently, Frantz and Granick[10] have performed insightful experiments that shed light on the dynamics of adsorbed chains. These authors concluded that the equilibration time for the adsorbed chains is very long and that the dynamics probably cannot be described by one time constant. Their experiments were performed under conditions wherein our model predicts slow glassy relaxation. More recently, Johnson and Granick[21] have experimentally found that the relaxation of adsorbed PMMA layers is characterized by stretched exponential kinetics and the relaxation times exhibit a strongly non-Arrhenius temperature dependence. This is consistent with the results reported in this work, wherein we find trapped nonequilibrium states at the interface. We note that Granick and co-workers[10,21] found the time scales for relaxation to be longer than what we have predicted. We believe that this is so because for multiple-chain systems the interchain interactions would constrain the dynamics even further, and the phenomena that we have reported here regarding glassy relaxation should be more pronounced.

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