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Molecular dynamics study of adsorption and spreading of a polymer chain onto a flat surface

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Abstract

We present results from a series of molecular dynamics simulations for adsorption and spreading of polymer chains onto a flat surface. We consider both homopolymer chains and "protein-like" copolymer chains in the simulations. For homopolymer chains, we have considered both good and poor solvent conditions, and for copolymer chains, we have considered several conformations of the non-adsorbing monomers. Our results indicate that when the adsorption strength is strong enough, a scaling description of the adsorption kinetics works well for homopolymers in both good and poor solvent conditions. When the adsorption strength is not strong enough, the chains adsorb partially, and one needs to consider effects of this partial adsorption in the scaling description. For each of the three primary structures of the copolymers considered in this study, the polymer chain does get adsorbed to the surface but the kinetics of the adsorption process depends on the specific structures of the copolymer chains. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Molecular dynamics simulations; Adsorption of Polymers; Spreading of Polymers

1. Introduction

Both theoretical and experimental studies of adsorption of polymer chains onto solid surfaces have received wide attention in the last decade. A detailed knowledge of conformations and cooperative motion of polymer chains near a solid surface is of interest to many diverse areas such as biochemistry, tribology and pharmaceutical research [1–3]. Along with analytical and experimental studies, recent numerical studies [4,5] have revealed a rich variety of structure and dynamical behavior of homopolymer chains in the adsorbed layer. Systems of random, heterogeneous chains have also received wide attention [6–20], partly because these chains may be tailored for specific applications, such as adhesion [21]. Further, such copolymer chains constitute a reasonably simplified model of protein molecules, because different coarse-grained groupings of A- and B-type chain beads can be seen as mimicking many different protein constituents [23], with a broad variety of *effective* interactions.

Recently, we have carried out extensive multi-chain Monte Carlo lattice simulations of adsorption of both homopolymers [4] and random copolymers [22] from a semi-dilute solution onto flat solid surfaces. We have studied in detail the growth, equilibrium structure, and dynamics of the adsorbed layers for both chemically pure and impure systems. However, Monte Carlo calculations may not be suitable for studying kinetics, as the stochastic moves used in such studies do not correspond to the real movements of monomers. As a first step toward a more realistic modeling of the kinetics of adsorption and spreading of polymer chains, we have carried out extensive Molecular Dynamics (MD) simulations in this paper. This type of simulation, however, is extremely demanding on computational resources for studying *kinetics* even in the simplified situation where no torsional potential is included in the model, as one needs to average over many initial configurations for obtaining statistically accurate data. For this reason, we have been limited to study adsorption and spreading of single polymer chains in this work. A recent paper [24] addresses the spreading kinetics of a single poly-(ethylene oxide) (PEO) chain on a graphite sheet by carrying out MD simulations for relatively short chains (chain length ≈30). Rather than starting from a chemically accurate description of the polymer chain, our simulations are designed to work for time- and length-scales intermediate between a chemically accurate atomistic description and a hydrodynamic description. It is possi-

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ble then to study long polymer chains in the simulation by spending a reasonable amount of computer time. This, in turn, allows us to extract useful information about the role played by solution condition and impurity conformation on the kinetics of spreading.

The rest of the paper is organized as follows: In Section 2, we describe the model and numerical techniques used in the MD simulation. In Section 3, we present results for adsorption and spreading of a single homopolymer chain in both good and poor solvent conditions. In this section, we also study adsorption of "protein-like" copolymers introduced by Khokhlov and Khalatur [25]. Finally, in Section 4 we conclude with a short summary and discussion of the results.

2. Model and numerical method

For long chains, a chemically accurate atomistic description of the adsorption process is beyond the reach of computational resources available to us. For this reason, we consider a suitably coarse-grained model which maintains the chain structure of the polymer molecules, and extract useful information about the role played by chain conformation and mobility of polymer chains on the adsorption process by carrying out MD simulations. The MD simulation method used in this work is similar to the one previously employed by Grest and co-workers [26] for studying polymer melts and polymer brushes. In this MD method, any pair of monomers interacts with each other via a Lennard-Jones (L-J) potential U_{LJ} given by:

$$U_{\mathrm{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r_{\mathrm{c}}}\right)^{12} + \left(\frac{\sigma}{r_{\mathrm{c}}}\right)^{6}\right]; \quad r \le r_{\mathrm{c}} \tag{1}$$

where r_{c} is the cut-off distance beyond which the L-J potential is set to be zero. The parameter ε is the L-J energy parameter, and σ the L-J length parameter. Note that the L-J potential is a purely repulsive potential if the cut-off distance r_{c} is $2^{1/6}\sigma$. This is an efficient way of modeling a good (athermal) solvent condition. When the cut-off is set at $r_{\mathrm{c}} = 2.5\sigma$, both good and poor solvent conditions can be achieved by changing the temperature of the system. The θ-temperature for this model has been calculated by several authors [27] and is given by $T_\theta \approx 3.0\varepsilon/k_{\mathrm{B}}$.

Further, two successive monomers in a chain are subject to a finite-extension anharmonic spring-potential $U_{\mathrm{chain}}(r)$ which is given by:

$$U_{\mathrm{chain}}(r) = -k \ln\left[1 - \left(\frac{r_{ij}}{R_0}\right)^2\right] \tag{2}$$

where k is an energy parameter, r_{ij} the distance between two successive monomers of the same chain, and R_0 a length parameter describing the range of extension between two successive monomers. In this paper, we use $k = 30$ and $R_0 = 1.5$ which make chain crossing practically impossible. For this choice of parameters the bond length (r_{b}) of the chain is about $r_{\mathrm{b}} = 0.97\sigma$.

To simulate a constant temperature ensemble, the monomers are coupled to a heat bath and the equations of motion for the monomers can be written as

$$m\ddot{\vec{r}}_i = -\vec{\nabla} U_i(r) - \Gamma \dot{\vec{r}}_i + \vec{W}_i(t) \tag{3}$$

where i is the index of the monomers, Γ the monomer friction coefficient, and $\vec{W}_i(t)$ the term describing the random force of the heat bath on the monomers. We consider $\vec{W}_i(t)$ to be a Gaussian white noise with zero mean value ($\langle \vec{W}_i(t) \rangle = 0$) and satisfying fluctuation-dissipation relation:

$$\langle \vec{W}_i(t) \cdot \vec{W}_{ij}(t') \rangle = 6k_{\mathrm{B}} T \Gamma \delta_{ij} \delta(t - t') \tag{4}$$

where T is the temperature of the heat bath. The equations of motion (Eq. (3)) have been integrated in this paper by using an accurate scheme developed by van Gunsteren and Berendsen [28]. In this scheme a bivariate distribution of Gaussian random numbers is used to integrate the stochastic forces. In our code of the molecular dynamics algorithm, a fast Gaussian random number generator [29] was implemented to make the integration quite efficient. This algorithm has previously been successfully used by us for an MD simulation of phase separation kinetics of polymer solutions [30], and dewetting kinetics of microscopically thin polymer films cast on a flat surface [31]. Throughout this paper, we use the following reduced units: ε as the unit of energy, $\varepsilon/k_{\mathrm{B}}$ as the unit of temperature, σ as the unit of length, and $\sigma(m/\varepsilon)^{1/2}$ as the unit of time. We use $\Gamma = 0.5$ as the friction coefficient and $\Delta t = 0.01$ as the time step of integration.

Since we are interested in the adsorption and the spreading process of polymer chains on a surface, we need to model interactions between monomers and the adsorbing surface. In practice, this interaction between an element of the surface and a monomer is quite complicated. In our model, we simply assume that the surface is structure-less, and that the interaction between a molecule of the continuum surface and a monomer is given by a Lennard-Jones potential. Then, monomers at various locations z interact with the surface at $z = 0$ by the following interaction potential:

$$U_{\mathrm{s}}(z) = \frac{2\pi}{3}\rho_{\mathrm{s}}\varepsilon_{\mathrm{s}}\left[\varepsilon_1\left(\frac{\sigma}{z}\right)^3 + \frac{2}{15}\left(\frac{\sigma}{z}\right)^9\right] \tag{5}$$

where ε_{s} is the energy parameter for the surface, ρ_{s} the particle density of the solid surface, and ε_1 a parameter which can be either -1 or zero, for monomers which are attracted or (purely) repelled by the surface, respectively. We choose $\rho_{\mathrm{s}} = 2$ and vary ε_{s} in this work. When the surface is adsorbing ($\varepsilon_1 = -1$), note that the minimum position of the surface potential is at $z = 0.858\sigma$. We consider the zone of $z \le 1.5$ as the adsorbed zone, that is, monomers which are within the zone $z \le 1.5$ are said to be adsorbed onto the surface.

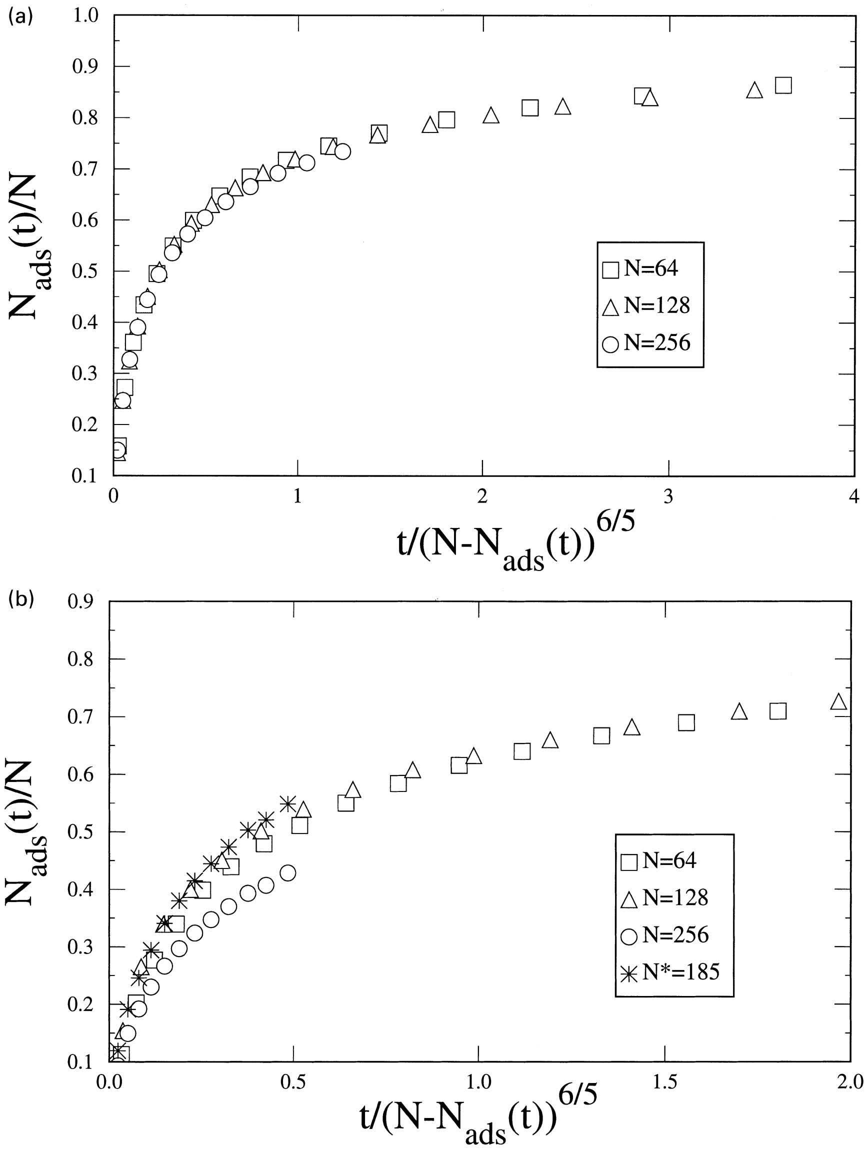

Fig. 1. Scaling plot for the rescaled number of adsorbed monomers N_{ads} versus rescaled time t in a good solvent condition: (a) Here $\varepsilon_s = 2$ and complete adsorption is achieved for all chain lengths considered; (b) Here $\varepsilon_s = 1$ and complete adsorption is achieved for $N = 64$ and 128 but not for $N = 256$. To incorporate effects of this incomplete adsorption, we estimate (see text) that the normalization factor $N_{ads}(t)$ for $N = 256$ is $N^* = 185$. This improves scaling.

Before we study the spreading of a polymer chain onto a surface, we have prepared an initial configuration of this chain in a free space at a certain temperature T. For this purpose, we first use a pearl-necklace model [32] of the chain with a fixed bond length of 0.97σ and use a Monte Carlo method [32] to equilibrate the chain at a temperature T. By changing the temperature and the cut-off distance, both good and poor solvent conditions can be modeled. The final configuration after this equilibration process is used as the input for further equilibration via the molecular dynamics method. After a well-equilibrated configuration is obtained, the chain is then artificially 'brought' near the surface so that the initial position of the monomer closest to the surface is just beyond $z = 1.5$ from the surface. At this time the surface interaction is turned on and the time is set to be $t = 0$.

During the adsorption process, we measure several physical quantities as a function of time. These quantities include the number $N_{ads}(t)$ of the adsorbed monomers, the x–y component of the radius of gyration of these adsorbed monomers (R_{xy}), and the average distance $\langle z(t) \rangle$ from the surface to the polymer chain. The number of adsorbed monomers (as a function of time) describes how adsorbing the surface is while R_{xy} is a measure of the spreading behavior of the adsorbed chain. The average distance describes how the monomers approach toward the surface and is a measure of how fast the polymer chain is adsorbed by the surface.

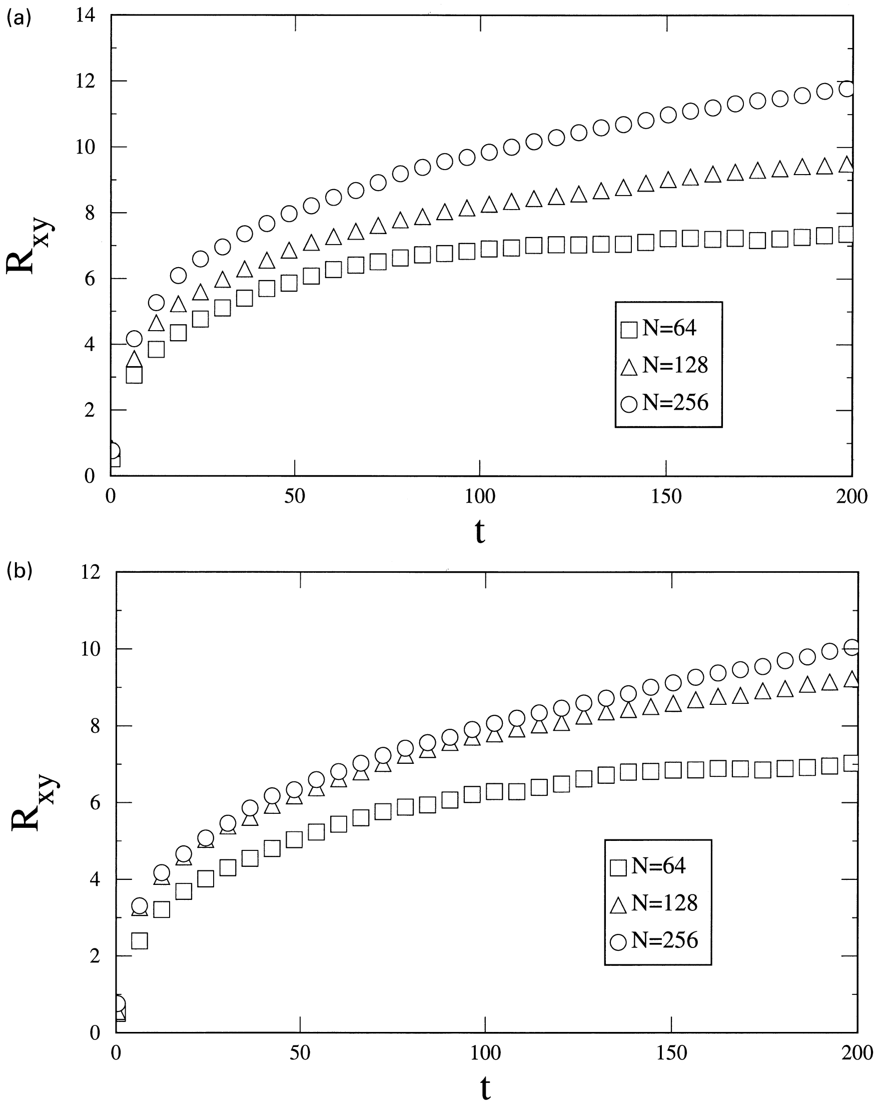

Fig. 2. The x–y component of the radius of gyration of the adsorbed monomers (R_{xy}) plotted against time t for chains in a good solvent condition: (a) Here $\varepsilon_s = 2$ and complete adsorption is achieved for all chain lengths considered; (b) Here $\varepsilon_s = 1$ and complete adsorption is achieved for $N = 64$ and 128 but not for $N = 256$.

3. Results

In this section we present results for adsorption and spreading of both homopolymer and copolymer chains onto a flat surface. For homopolymer chains we consider both good solvent and poor solvent conditions. Several different chain lengths ($N = 64$, 128, and 256) are considered in this work, along with several different strengths of the surface interaction ($\varepsilon_s = 2$ and $\varepsilon_s = 1$). All physical quantities analyzed in this section have been averaged over 200 different initial configurations of the polymer chains in each case.

3.1. Adsorption and spreading of homopolymers in good solvent condition

As mentioned earlier, the good solvent condition can be modeled by considering the cut-off for the L-J interaction to be $r_c = 2^{1/6}\sigma$. In this case there is no attractive interaction between the monomers, and this is an efficient way of simulating good (athermal) solvent condition. In the simulation we have kept $T = 2$.

In Fig. 1(a), we show a *scaling plot* for the (rescaled) number of adsorbed monomers, $N_{\mathrm{ads}}(t)$, on the surface against (rescaled) time t for various chain lengths N. For different values for the chain length N, the number of adsorbed monomers $N_{\mathrm{ads}}(t)$ is normalized in this plot by dividing $N_{\mathrm{ads}}(t)$ by N. The time rescaling is done in the following way. We assume that the monomer adsorption rate is a constant at $z = 1.5$ where the monomers become adsorbed by the surface. The non-adsorbed part of the chain, in contrast, still has an unperturbed, bulk-like shape with a radius of gyration $R_g(t)$ which scales as $R_g(t) \sim N_{\mathrm{non}}(t)^{\nu}$, where $N_{\mathrm{non}}(t)$ is the number of monomers not adsorbed by

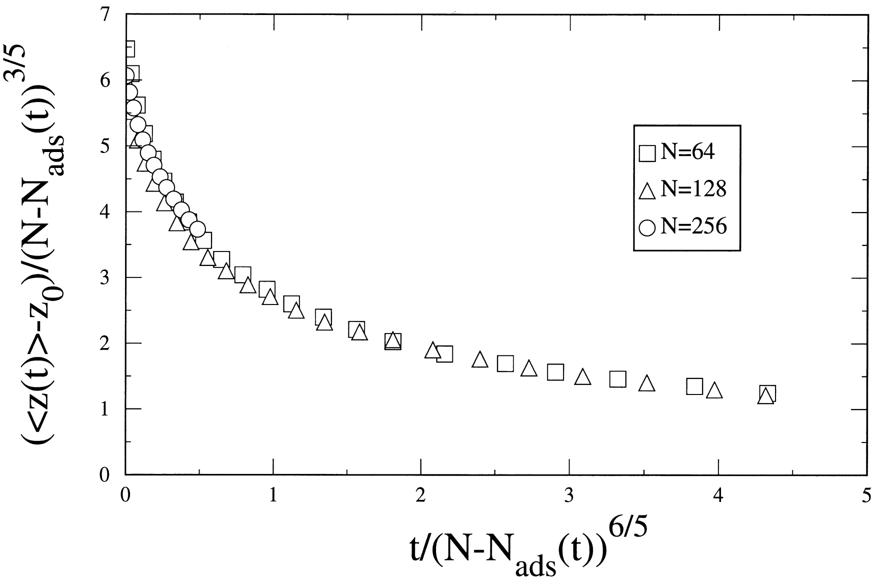

Fig. 3. Scaling plot for the rescaled average distance of a chain from the surface ($\langle z\rangle$) vs. rescaled time t in a good solvent condition. Here $z_0 = 0.6$.

the surface at a time t (i.e. $N_{\mathrm{non}}(t) = N - N_{\mathrm{ads}}(t)$), and for a good-solvent case, $v = 3/5$. Under these assumptions, the number of adsorbed monomers in a certain time is proportional to the surface area of the spherical volume of the non-adsorbed part of the chain, and time t should be rescaled as: $t/R_{\mathrm{g}}(t)^2$, or, equivalently, t/N_{non}^{2v}, i.e. $t/(N - N_{\mathrm{ads}}(t))^{6/5}$. As shown in Fig. 1(a) this scaling description works well for $\varepsilon_{\mathrm{s}} = 2$ and for all chain lengths considered in this study.

The situation is more complicated for a weaker adsorption strength, $\varepsilon_{\mathrm{s}} = 1$. A scaling plot similar to Fig. 1(a) is shown in Fig. 1(b). We can see that the curves for $N = 64$ and 128 do fall on top of each other, but the curve for $N = 256$ shows strong deviation from this scaling behavior at late times. We suspect that this deviation at late times is due to an incomplete adsorption of large chains when the surface interaction is not strong enough. If the chain does not become totally adsorbed onto the surface, the normalization factor for $N_{\mathrm{ads}}(t)$ should be replaced in the scaling description by N^* (instead of the chain length N), where N^* is the maximum number of monomers that can be adsorbed onto a surface for a particular choice of the parameters such as N and ε_{s}. We will now try to estimate this N^* from free-energy considerations.

The free-energy of an ‘excluded volume’ chain in three-dimension is given by [33]:

$$F_{3\mathrm{d}}/k_{\mathrm{B}}T = \frac{3R^2}{2Nb^2} + \frac{1}{2}v_{3\mathrm{d}}\bar{c}^2V_{\mathrm{d}} \tag{6}$$

where R is the Flory radius of the polymer, b the bond length of the polymer chains, $v_{3\mathrm{d}}$ is the excluded volume parameter in three-dimensions, $\bar{c}$ the average density of the polymer coil, and V_{d} is the volume of the coil of a polymer. Minimizing $F_{3\mathrm{d}}$, one finds:

$$R = \left(\frac{3v_{3\mathrm{d}}b^2}{8\pi}\right)^{1/5} N^{3/5} \tag{7}$$

and the corresponding free-energy

$$F_{3\mathrm{d}}/k_{\mathrm{B}}T = \frac{5}{2b^2}\left(\frac{3v_{3\mathrm{d}}b^2}{8\pi}\right)^{2/5} N^{1/5}. \tag{8}$$

A corresponding expression in two-dimensions read as:

$$F_{2\mathrm{d}}/k_{\mathrm{B}}T = \frac{2}{b^2}\left(\frac{v_{2\mathrm{d}}b^2}{2\pi}\right)^{1/2} N^{1/2} = \left(\frac{2v_{2\mathrm{d}}}{\pi b^2}\right)^{1/2} N^{1/2}. \tag{9}$$

Thus, the free energy of a polymer in three-dimensions is proportional to $N^{1/5}$ but in two-dimensions it is proportional to $N^{1/2}$. The pre-factors in the free-energy expressions can be computed by using a standard excluded volume formula:

$$v = \int \mathrm{d}\vec{r}\left[1 - \exp\left(-\frac{u(r)}{k_{\mathrm{B}}T}\right)\right]. \tag{10}$$

For the L-J potential with a cut-off distance $r_{\mathrm{c}} = 2^{1/6}\sigma$, we estimate that $v_{3\mathrm{d}} = 0.325$, and $v_{2\mathrm{d}} = 0.102$. Then $F_{3\mathrm{d}}/k_{\mathrm{B}}T \approx 0.71N^{1/5}$, and $F_{2\mathrm{d}}/k_{\mathrm{B}}T \approx 0.26N^{1/2}$. The loss of entropy for an adsorbed polymer must be compensated by the gain in surface energy, and for the purpose of estimation, one can write

$$0.26N^{*1/2} + \langle V_{\mathrm{s}}\rangle/k_{\mathrm{B}}T = 0.71N^{1/5} \tag{11}$$

where $\langle V_{\mathrm{s}}\rangle$ is the average value of the surface potential and can be estimated by integrating $V_{\mathrm{s}}(z)$ from z_{cut} to $z_{\max}$. We take z_{cut} to be such that $V_{\mathrm{s}}(z_{\mathrm{cut}}) = 0$ near the surface, and $z_{\max} = 1.5$, the maximum distance from the surface where a monomer is considered to be adsorbed. For $\varepsilon_{\mathrm{s}} = 2$ and $T = 2$, we estimate

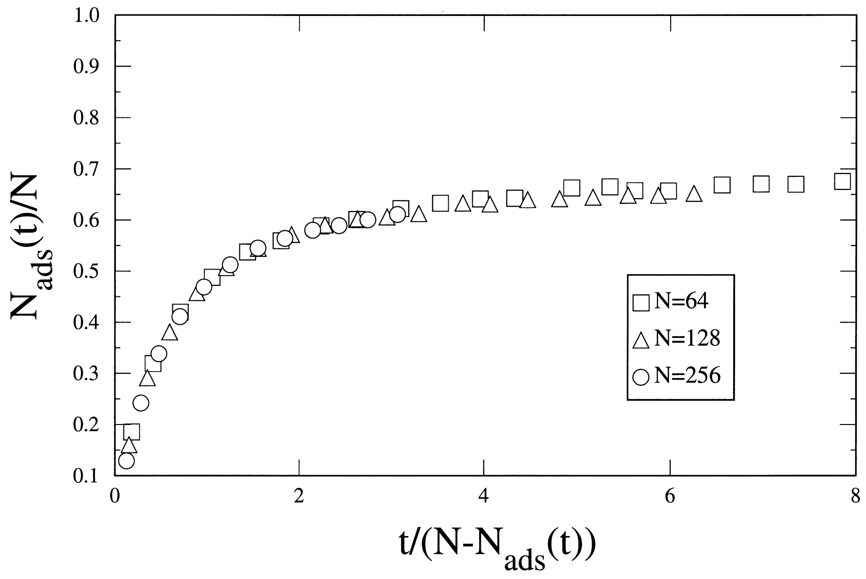

Fig. 4. Scaling plot for the rescaled number of adsorbed monomers N_{ads} versus rescaled time t in a poor solvent condition. Here $\varepsilon_s = 1$ and complete adsorption is achieved for all chain lengths considered.

N^* to be larger than N for all values considered in this work, and the chains are expected to be completely adsorbed. For $\varepsilon_s = 1$ and $T = 2$, chains with $N = 64$ and 128 are also completely adsorbed, but for $N = 256$, $N^* \approx 185$ and we expect that this chain will only be partially adsorbed by the surface. When we use $N^* = 185$ instead of $N = 256$ in the scaling plot of Fig. 1(b), scaling improves and all three curves now fall on top of each other.

In Fig. 2(a) and (b) we plot the x–y component of radius of gyration of adsorbed monomers, R_{xy}, versus time for polymers with different polymerization $N = 64$, 128 and 256. In Fig. 2(a) the strength of the surface interaction $\varepsilon_s = 2$, while $\varepsilon_s = 1$ in Fig. 2(b). From the figures, we can see that at t = 0 R_{xy} is zero as no monomer is adsorbed at this time. Subsequently, R_{xy} increases with time indicating that adsorption and spreading of the chain is taking place. When complete adsorption takes place (Fig. 2(a)), $R_{xy}(t)$ scales with $N^{\nu_{2d}}$ at late times, but for incomplete adsorption (Fig. 2(b)) such scaling does not hold. This is clear from Fig. 2(b) where the curve for $N = 256$ (which does not completely adsorb when $\varepsilon_s = 1$) is much closer to the curve for $N = 128$ for $R_{xy}(t)$ to scale with $N^{\nu_{2d}}$.

In Fig. 3 we show a scaling plot for the average distance $\langle z(t)\rangle$ from the surface to the polymer chain, versus t. In this case, the time rescaling should follow the same argument presented for Fig. 1(a) and (b). The scaling for $\langle z(t)\rangle$ can be worked out considering that there is an adsorbing zone for $z < z_0$, and that the average distance for monomers outside the adsorbing zone should be proportional to the radius of gyration of the coil of the non-adsorbed monomers. Since this radius of gyration is proportional to N_{non}^{ν}, the corresponding scaling for $z(t)$ is $(\langle z(t)\rangle - z_0)/N_{non}^{3/5}$. As can be seen in Fig. 3 this scaling works reasonably well for the N-values considered in this study.

3.2. Adsorption and spreading of homopolymers in poor solvent condition

We modeled a poor solvent condition by considering the cut-off for the L-J interaction to be $r_c = 2.5\sigma$. In this case there is an attractive interaction between the monomers, and for this value of r_c, the θ-temperature is known ($T_\theta \approx 3$). We have chosen a temperature of $T = 2$ for our simulations, which is below T_θ. The strength of the surface interaction is kept at $\varepsilon_s = 1$ throughout, as complete adsorption is seen with this value of ε_s for all chain lengths considered here.

In Fig. 4, we show a scaling plot for the number of adsorbed monomers, N_{ads}, against time t. Similar to the good solvent case discussed previously, we rescale the vertical axis by N as complete adsorption is seen for all values of chain lengths considered here. Again, following our analysis for the good solvent case, time is rescaled by $t/(N - N_{ads})^{2\nu}$, where we have considered $\nu = 1/2$ in this case. As shown in Fig. 4 such a scaling works quite well for the number of adsorbed monomers.

3.3. Adsorption and spreading of "protein-like" copolymers

In this section, we present results for the adsorption and spreading of copolymers on a surface. In particular we consider a model for "protein-like" AB copolymers introduced by Khokhlov and Khalatur [25]. In this simplified model for globular proteins, hydrophilic or charged amino acid residues are considered to be A-type monomers, and hydrophobic residues are considered to be B-type. In a globular protein, hydrophilic A monomers are mainly located on the surface of the globule, while hydrophobic B monomers form the core. To model this conformation of globular proteins, Khokhlov and Khalatur first construct a

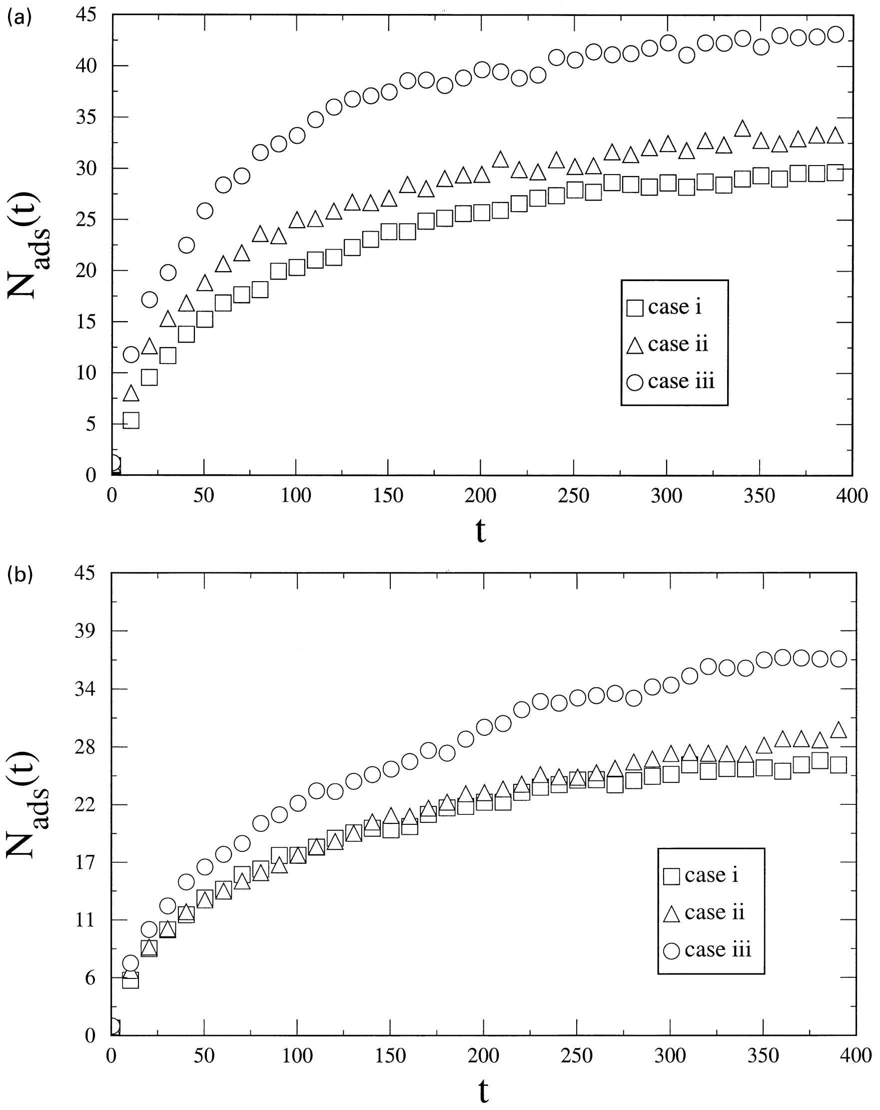

Fig. 5. (a) Number of adsorbed monomers ($N_{ads}(t)$) vs. time t for "protein-like" copolymers of three different primary structures denoted by case (i), case (ii) and case (iii) (see text). Here, $N = 128$ and $\varepsilon_s = 2$. No further re-equilibration of the copolymer chains is performed after the coloration process. (b) Same as in (a), except that a re-equilibration of the copolymer chains is performed here after the coloration process and before exposing them to the surface.

homopolymer in a poor solvent condition in their numerical study. Then, they 'color' the monomers on the surface of this compact homopolymer to be A-type, and the monomers in the core are considered to be B-type.

We follow this general prescription of Khokhlov and Khalatur to construct the "protein-like" copolymers. First, we start from an equilibrated conformation of a homopolymer at a temperature below T_θ. This is the same initial condition used in the previous section for homopolymers in a poor solvent condition. Now, we consider three different 'coloring' procedures. First, we locate the center of mass of the equilibrated chain, compute the chain radius of gyration R_G and define a distance $R_{1/2}$ such that it divides the polymer coil into a core and a shell which have equal volume. We have considered three "primary structures" of the copolymer chains. In case (i), all A-type monomers occupy the shell, the outer-half volume of the original chain, and the monomers inside the core are of B-type. In case (ii), 75% of A-type monomers are in the outer-half volume of the chain and the rest of A-type monomers are in the inner-half. Consequently, in case (ii), the outer-half comprises 25% of B-type monomers and the rest, 75%, of B-type monomers are in the inner-half. Finally, in case (iii), the primary structure of the copolymer is random, so that both A- and B-type monomers are uniformly, randomly distributed along the chain.

After the coloring procedure is over, we carry out two sets of simulations. In the first set, we bring the chain near the surface without further re-equilibration after coloring, and study the spreading behavior of the chain on the surface. In the second set of calculations, re-equilibration of the copolymers are carried out before the polymer chains are brought close to the surface. This way, one hopes to disentangle the effect of interaction with the surface from the new intrachain energies produced by the coloration. The interactions between similar monomers are considered to be given by an L-J interaction with a cut-off $r_c = 2.5\sigma$, so that both attractive and short-range repulsive interactions are present. In contrast, for unlike monomers the interaction is considered to be purely repulsive and the cut-off is considered to be $r_c = 2^{1/6}\sigma$. Finally, we assume that the interaction between the A-type monomers and the surface is purely repulsive ($\varepsilon_1 = 0$ in Eq. (5)) while the interaction between the B-type monomers and the surface is attractive ($\varepsilon_1 = -1$ in Eq. (5)). In all of these cases we have considered $\varepsilon_s = 2$. For this choice of parameters, in case (i) the outer-half consists of A-type monomers which are repelled by the surface, while the inner-half is made out of B-type monomers which are favored by the surface. In case (ii), the outer-half is made out of mostly A-monomers (75%) which are repelled by the surface, while in case (iii) both A- and B-type monomers are distributed randomly over the whole chain.

In Fig. 5(a), data for the number of adsorbed monomers of the copolymers, N_{ads}, is plotted versus time t, for three different primary structures of the copolymers mentioned above. In this case no further re-equilibration was done after coloration of the copolymers. We have used a chain length of $N = 128$ for all of these three cases. For each of the three primary structures considered in this study, the polymer chain does get adsorbed to the surface but the number of adsorbed monomers at a time t is different in these three situations as the influence of the repulsive monomers are different in each case because of the specific structures of the copolymer. Although all the repulsive monomers are in the outer-half of the chain in case (i), adsorption does take place and the chain spreads eventually, albeit slowly on the surface. This is because at the temperature considered in the simulation, the initial shape of the chain is not a compact globule and some fluctuations in the shape are present. This allows for a few of the strongly-adsorbing B-type monomers to be close to the adsorbing surface. Since the adsorption energy is quite large in the simulation ($\varepsilon_s = 2$), these few monomers pin the chain to the surface and further adsorption take place as the chain opens up and more favorable contacts take place. For case (ii), some initial favorable contacts between the B-type monomers and the adsorbing surface are already present and the chain adsorbs onto the surface a bit more efficiently than in case (i). In contrast, the adsorption kinetics is fast in case (iii), as half of the favorable contact sites is at the outer-half of the coil.

When re-equilibration of the copolymer chains are performed after coloration, the spreading kinetics is qualitatively similar to the results above. These results are shown in Fig. 5(b). Here, a slow adsorption is seen in case (i) similar to what is observed in Fig. 5(a). For case (ii) after re-equilibration, a larger number of A-type monomers are found on the outside shell of the chain than what one starts out with, due to a favorable interaction between A-type monomers. This results in a slower adsorption of the chain than seen in the case (ii) of Fig. 5(a), and very little difference in adsorption kinetics exists now when compared to the case (i) of Fig. 5(b). A similar effect is seen for case (iii) as well. In this case also, a larger number of A-type monomers are found on the outside shell of the chain after re-equilibration than what one starts out with. This results in a slower adsorption when compared with the case (iii) of Fig. 5(a).

4. Summary and conclusions

In this paper we have carried out molecular dynamics simulations of adsorption and spreading of both homopolymer and copolymer chains onto flat surfaces. For homopolymer chains, we have considered both good and poor solvent conditions, and for copolymer chains, we have considered several conformations of the non-adsorbing monomers. Our results indicate that when the adsorption strength is strong enough, a scaling description of the adsorption kinetics works well for homopolymers in both good and poor solvent conditions. When the adsorption strength is not strong enough, the chains adsorb partially, and one needs to consider effects of this partial adsorption in the scaling description.

We finally point out that the conformational complexity of adsorbed homopolymers is directly related to the chains' varied dynamical properties. Usually, an adsorbed layer is formed by placing the adsorbing surface in contact with a bulk solution of polymer chains. Therefore, one must bear in mind that the equilibrium state is characterized by a continual traffic of chains being exchanged with the bulk solution, and that this exchange plays an integral part in determining the structure of the equilibrium layer. Therefore, to achieve a more accurate picture it is necessary to adopt a method of investigation which incorporates chain dynamics explicitly. Thus, to compare with experimental situations one needs to consider simulations with a multi-chain system. This study should be considered only a first step toward that goal.

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