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HAL Id: jpa-00248279
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Submitted on 1 Jan 1996

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Dynamics of Polymer Chains Confined in Slit-Like Pores

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(Received 26 June 1995, accepted 11 October 1995)

PACS.83.10Nn – Polymer dynamics
PACS.02.70Lq – Monte Carlo and statistical methods
PACS.36.20Ey – Conformation (statistics and dynamics)

Abstract. — Monte Carlo simulations of an off-lattice bead spring model of polymer chains are presented, confining the chains between two repulsive parallel planes a distance $D$ apart. Varying the chain length $N$ from $N = 16$ to $N = 128$, we show that under good solvent conditions the chains behave like two-dimensional self-avoiding walks, their mean square gyration radius scales as $\langle R_g^2 \rangle \propto N^{2\nu}$ with $\nu = 3/4$. The density profile across the slit is independent of $N$ and maximal in the center of the slit. The dynamical properties of the chains are found to be in full agreement with the Rouse model with excluded volume in $d = 2$ dimensions, the relaxation times vary like $\tau \propto N^z$ with $z = 2\nu + 1 = 5/2$, the diffusion constant still being given by $D_N \propto 1/N$. The dynamical behavior of various mean square displacements is analyzed in detail.

1. Introduction

There has been much interest in polymers in constrained geometries (polymers at surfaces or interfaces [1–5], polymers confined in thin films (e.g. [5–13]) or in pores of cylindrical or slit-like cross-section [14–22]). This interest is due to applications in technology (lubrication, corrosion-protecting coatings, adhesives, etc.) and biology (proteins confined between cell membranes, etc.), but also due to the challenging theoretical problems from the point of view of statistical mechanics: the geometric constraints influence the chain structure significantly, and this in fact changes also the chain dynamics. This is the aspect in the focus of interest here.

In the present paper we consider the idealized situation of a very dilute polymer solution confined between parallel repulsive plates. While previous work [17] has already considered the crossover of the static configurations of such confined polymer chains from three-dimensional (swollen) coils (gyration radius square $\langle R_g^2 \rangle \propto N^{2\nu(d=3)}$ with $\nu(d = 3) \approx 0.59$) to two-dimensional self-avoiding walks ($\langle R_g^2 \rangle \propto N^{2\nu}$ with $\nu \approx 0.75$), but - unlike the case of chains confined in quasi-one dimensional pores [16, 20] - the dynamics has found less attention. Our study completes related work on the same model, where adsorption of chains at planar walls [23] or concentrated polymer solutions confined between walls [24] are studied. In the present work we want to investigate the dynamical behavior of chains in such quasi-two-dimensional geometry, and show that it is qualitatively identical to a strictly two-dimensional

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Rouse model [25,26] with excluded volume (where chain configurations are strictly limited to a plane). Note that we do not consider any hydrodynamic interactions mediated by the solvent here.

In Section 2 we now briefly recall the model and simulation technique [20,27], while Section 3 summarizes the static properties of the confined chains. The bulk of our results on dynamic properties is presented in Section 4, while Section 5 summarizes our conclusions, and places our results in context with related work.

2. Model and Simulation Technique

For the sake of simulation efficiency, we use a coarse-grained bead-spring model [20,23,27], where each effective bond is described by the finitely extensible nonlinear elastic (FENE) potential, where the bond length \( l \) can vary between \( l_{\text{min}} = 2l_0 - l_{\text{max}} \) and \( l_{\text{max}} \),

\[
U_{FENE} = -K(l_{\text{max}} - l_0)^2 l_n \{ 1 - (l/l_0)^2/(l_{\text{max}} - l_0)^2 \}.
\]  

We choose the parameters \( l_0, l_{\text{max}}, \) and the reduced spring constant \( K/k_B T \) as

\[
l_0 = 0.7, \quad l_{\text{max}} = 1, \quad K/k_B T = 20.
\]  

The chains are treated as fully flexible, thus no potential for bond angles is included, while excluded volume interactions between the beads are represented by a Morse potential,

\[
U_M(r)/\varepsilon_M = \exp[-2\alpha(r - r_{\text{min}})] - 2 \exp[-\alpha(r - r_{\text{min}})],
\]  

with parameters [23]

\[
\varepsilon_M/k_B T = 1.0, \quad \alpha = 24, \quad r_{\text{min}} = 0.8.
\]  

As shown in previous work [27], the decay of this potential with distance \( r \) is so rapid that \( U_M(r) \approx 0 \) for \( r > 1 \) with negligible error; this allows the use of a link-cell algorithm with a cell linear dimension of unity and leads to a reasonably fast performance of our Monte Carlo program. Since the Theta temperature [28] where a single coil in dilute solution in the bulk behaves as ideal random walk occurs for \( T = 0.62 \) in our model [27], choosing units \( \varepsilon_M \equiv 1, \ k_B \equiv 1, \) our choice of temperature in equation (4) implies that we work in the good solvent regime.

Dynamics is introduced into the model by an algorithm where the attempted Monte Carlo update consists of randomly selecting a bead which one attempts to displace randomly by amounts \( \Delta x, \Delta y, \Delta z \) chosen uniformly from the intervals \(-0.5 \leq \Delta x, \Delta y, \Delta z \leq +0.5\). From the total change \( \Delta U \) of the potentials defined above, the transition probability \( W \) is calculated as usual [29],

\[
W = \min\{\exp[-\Delta U/(k_B T)], \quad 1\},
\]  

and this attempted move is accepted only if \( W \) exceeds a random number \( \eta \), uniformly distributed in the interval \( 0 \leq \eta < 1 \). The choice of parameters in the above potentials (Eqs. (1)-(4)) is such that chains cannot interact themselves in the course of their random motions: thus entanglement constraints are automatically taken care of. This algorithm yields a rather fast performance (about \( 5 \times 10^4 \) attempted updates of monomeric units per CPU second are performed on simple RISC workstations such as IBM RS 6000/370). As a time unit, we henceforth use Monte Carlo steps per bead (MCS), and study chains with chain lengths \( N = 16, 32, 64 \) and 128.
Fig. 1. — a) Log-log plot of the longitudinal part of the mean square gyration radius, \( \langle R^2_g \rangle \), versus chain length \( N \) for three choices of slit width \( D \). Straight lines indicate effective exponents \( 2\nu_{\text{eff}} \{ (R^2_g) \propto N^{2\nu_{\text{eff}}} \} \) as quoted in the figure. b) Log-log plot of the mean square gyration radius \( \langle R^2_g \rangle \) versus \( N \), for a chain in dilute solution in the bulk.

3. Static Properties of Chains Confined between Parallel Plates

As the distance \( D \) between the plates (measured in our unit of length, \( l_{\text{max}} = 1 \)) we use three values throughout, \( D = 1, 2 \) and \( 4 \), while the linear dimension \( L \) along the plates (where periodic boundary conditions are applied) is chosen as \( L = 32 \). This choice is large enough such that interactions between the “primary” chain and its periodic images are negligible, even for \( N = 128 \).

Figure 1a presents the parallel component of the gyration radius as a function of chain length \( N \). While for \( D = 1 \) and \( D = 2 \) we see a rather perfect agreement with the law applicable for self-avoiding walks in \( d = 2 \) dimensions,

\[
\langle R^2_g \rangle \propto N^{2\nu}, \quad \nu = 3/4, \quad d = 2, \tag{6}
\]

for \( D = 4 \) the effective exponent \( 2\nu_{\text{eff}} \) is already significantly smaller, indicating that crossover towards the behavior of three-dimensional chains has set in \( \{2\nu(d = 3) = 1.18 \text{[28]} \} \). It should be noted, however, that for the studied range of chain lengths in the three dimensional bulk (simulated by choosing a \( L \times L \times L \) geometry with \( L = 32 \) and periodic boundary conditions in all three spatial directions) do not show exactly the expected theoretical value, but a slightly enhanced value (Fig. 1b); thus the good agreement between the effective exponent for \( D = 1 \) and \( D = 2 \) and the theoretical value (Eq. (6)) may be a bit accidental.

Figure 2a considers the density profile of the monomers as a function of the distance \( z \) across the slit. Since the profile is symmetric around the midpoint \( D/2 \), \( n(z) = n(D - z) \), only the left half of the profile is shown. We always choose a normalization \( \int_0^{D/2} dz \ n(z) = 1/256 \), since we apply along the \( z \)-direction a grid containing 256 points from \( z = 0 \) to \( z = D/2 \), in order to record the density histogram. One can see that for \( D = 1 \) there is relatively little variation in density, while for \( D = 4 \) the density near the repulsive wall \( \{n(z = 0)\} \) is smaller than the density in the center of the film \( \{n(z = D/2)\} \) by about one order of magnitude. Figures 2b, c show that these density profiles are completely independent of chain length. In
Fig. 2. — a) Monomer density profile $n(z)$ as a function of distance $z$ across the slit, for $D = 1, 2,$ and 4 as shown. Only the region $0 \leq z \leq D/2$ is shown in each case. All data refer to $N = 64$. (○) $D = 1$; (□) $D = 2$, (△) $D = 4$. b) Monomer density profile $n(z)$ versus $z$ for $D = 1$ and four values of $N$ as indicated. c) Same as b) but for $D = 4$. Full curve shows the result of a theory applicable to Gaussian chains and the boundary condition $n(z = 0) = 0$. 

\[ n(z) = \begin{cases} 
\text{data for } D = 1, 2, 4 \\
\text{theory for } D = 4 
\end{cases} \]
Figure 2c we include the theoretical profile for Gaussian chains that applies in the limit where one uses the boundary condition \( n(z = 0) = 0 \).

The lack of variation of \( n(z) \) with \( z \) for \( D = 1 \) again is an argument that for \( D = 1 \) the chain behaves as a two-dimensional object, while the strong variation with \( z \) for \( D = 4 \) indicates that in the latter case the third dimension cannot be ignored.

4. Mean Square Displacements and Relaxation Times of the Confined Chain

Following previous work on chains confined into tubes \([16, 20]\), we introduce mean square displacements of inner monomers \( g_1(t) \), mean square displacements \( g_2(t) \) of inner monomers measured in the center of mass system of each chain, and the center of mass displacement \( g_3(t) \), and distinguish longitudinal components (i.e. \( x, y \) coordinates parallel to the walls) and transverse ones (i.e. \( z \) components perpendicular to the walls). For the inner monomers, we always take an average over the four innermost monomers of each chain. These time-dependent displacements hence read

\[
g_{11}(t) = \frac{1}{4} \sum_{i=N/2-1}^{N/2+2} \left( [x_i(t) - x_i(0)]^2 + [y_i(t) - y_i(0)]^2 \right),
\]

\[
g_{1t}(t) = \frac{1}{4} \sum_{i=N/2-1}^{N/2+2} (z_i(t) - z_i(0))^2,
\]

\[
g_{21}(t) = \frac{1}{4} \sum_{i=N/2-1}^{N/2+2} \left( [x_i(t) - x_i(0) - X_{CM}(t) + X_{CM}(0)]^2 + [y_i(t) - y_i(0) - Y_{CM}(t) + Y_{CM}(0)]^2 \right),
\]

\[
g_{2t}(t) = \frac{1}{4} \sum_{i=N/2-1}^{N/2+2} (z_i(t) - z_i(0) - Z_{CM}(t) + Z_{CM}(0))^2,
\]

\[
g_{31}(t) = \langle [X_{CM}(t) - Y_{CM}(0)]^2 + [Y_{CM}(t) - Y_{CM}(0)]^2 \rangle,
\]

\[
g_{3t}(t) = \langle [Z_{CM}(t) - Z_{CM}(0)]^2 \rangle.
\]

Figure 3 gives a typical example, presenting data for our longest chains \((N = 128)\). One can see that \( g_{3t}(t) \) reaches a very small saturation value always, at rather short times. Thus the center of mass of the chain is very well localized in the plane \( z = D/2 \) in the center of the slit. The longitudinal component, on the other hand, yields a simple diffusive law

\[
g_{3t}(t) = 4D_N t
\]

Due to the almost perfect localization of the chain center of mass in the plane \( z = D/2 \), the distinction between \( g_{1t}(t) \) and \( g_{2t}(t) \) is almost negligible. The longitudinal displacements \( g_{11}(t), g_{21}(t) \) coincide for small times, while for large times \( g_{11}(t) \) coincides with \( g_{31}(t) \), and \( g_{21}(t) \) reaches a finite saturation value. In the regime where \( g_{11}(t) \) is still distinctly smaller than \( \langle R_0^2 \rangle \), we verify the anomalous diffusion expected for the Rouse model in the presence of excluded volume \([16]\),

\[
g_{11}(t) \propto t^{1/(1+1/2\nu)} = t^{0.6}
\]

Qualitatively, the data of Figure 3 (and related ones for the other chain lengths that are not shown here) hence do not bear any unexpected surprises. For a more quantitative analysis, it
Fig. 3. — Mean square displacements $g_{11}(t)$, $g_{11}(t)$, $g_{21}(t)$, $g_{31}(t)$ and $g_{31}(t)$ plotted vs. time $t$, for $N = 128$ and three choices of $D$: $D = 1$ (a), $D = 2$ (b) and $D = 4$ (c). Dotted horizontal lines show the corresponding observations of $\langle R^2_{g1} \rangle$ (lower curve) and $\langle R^2_{g3} \rangle$ (upper curve). Straight lines on these log-log plot denote power laws, as indicated.
is convenient to define relaxation times from “crossing criteria” [20,30],

\[ g_{21}(\tau_3) = g_{31}(\tau_3), \]  

(15)

and

\[ g_3(\tau_{23}) = \frac{2}{3} \langle R_g^2 \rangle. \]  

(16)

Notice that it would seem slightly more natural to choose a factor unity in equation (16) rather than 2/3, but the latter choice allows to save a significant fraction of the computer time that otherwise would be necessary, because the accuracy of \( g_{31}(t) \) deteriorates significantly when \( t \) becomes of the same order as the total “observation time” of the simulation. Figures 4a, b now demonstrate the central result of the present work, namely

\[ \tau_3 \propto \tau_{23} \propto N^{2\nu+1} = N^{2.5} \]  

(17)

It is seen that the times are only weakly dependent on \( D \) - since the chains are rather well localized near the plane \( z = D/2 \), the thickness of the slit has only a minor effect on the prefactor of the time. Consistent with this interpretation, the diffusion constant \( D_N \) scales as (Fig. 5)

\[ D_N \propto 1/N \]  

(18)

and again the prefactor depends on the slit thickness \( D \) only rather weakly.

Discussion

In this work, we have considered the statics and dynamics of chains confined between two parallel plates a distance \( D \) apart, which is chosen comparable to the length \( l_0 \) of the effective
Fig. 4. — Log-log plot of $\tau_3$ versus $N$ (a) and of $\tau_{23}$ versus $N$ (b). Straight lines show effective exponents $z_{\text{eff}}$ in the relation $\tau \propto N^{z_{\text{eff}}}$, for the choices of $D$ as indicated. Within accuracy of the data (statistical errors of $\tau_3$, $\tau_{23}$ are comparable to the size of the symbols) these data confirm $z_{\text{eff}} = 2\nu + 1 = 2.5$.

bonds (in the chosen units, we use $t_0 = 0.7$, while choices $D = 1$, 2 and 4 were considered). We have assumed that the chains are in dilute solution under good solvent condition, and the walls have purely excluded volume interaction with the beads of the chain (i.e., positions $z < 0$ or $z > D$ for the beads were forbidden, while a bead in the interval $0 < z < D$ does not feel the walls). For such small distances $D$, it is reasonable to assume that three-dimensional hydrodynamic flows cannot occur in the narrow slit, and hence hydrodynamic forces (which otherwise dominate chain motions in dilute solution [25]) have been ignored altogether.
Fig. 5. — Log-log plot of the chain diffusivity $D_N$ versus chain length $N$, for the three choices of slit width $D$ as indicated, straight lines indicate equation (18).

Under these conditions, we have obtained straightforward two-dimensional behavior both for the chain linear dimensions ($\langle R^2_{gl} \rangle \propto N^{2\nu}$ with $\nu = 3/4$, i.e. $\langle R^2_{gl} \rangle \propto N^{3/2}$) and the relaxation times ($\tau_3 \propto \tau_{23} \propto N^Z$ with $Z = 2\nu + 1 = 5/2$), although the chain is not strictly confined to the plane $z = D/2$, as the monomer density profiles in $z$ direction show (Fig. 2). This fluctuation of the local monomer position in the transverse direction obviously does not couple to longitudinal motions (parallel to the plates) in any significant way.

Of course, these results are fully compatible with a scaling [14,19,28] point of view. We can consider the chain as a two-dimensional self-avoiding walk of blobs, with a blob diameter $D$. Each blob contains $g$ monomers, with $g$ given by the requirement that $D \propto l_0 g^{v(d=3)}$, since on the scale $D$ the chain is still three-dimensional. Consequently one predicts [14]

$$\langle R^2_{gl} \rangle^{1/2} \propto D(N/g)^\nu \propto l_0^{\nu/v(d=3)} D^{1-\nu/v(d=3)} N^\nu$$

The range of $D$ values studied here is too small to prove the predicted scaling of $\langle R^2_{gl} \rangle$ with $D$, however. Similar relations can be anticipated for mean-square displacements and relaxation times: for times $t < \tau_D$ the mean-square displacements of inner monomers are essentially isotropic

$$g_{11}(t) \approx g_{1t}(t) \propto l_0^2 (Wt)^{1/((1+1/2\nu(d=3))}, \quad t < \tau_D,$$

where $W$ is the rate for monomeric reorientations, and

$$W \tau_D = (D/l_0)^{2+1/\nu(d=3)}$$

While $g_{1t}$ for $t > \tau_D$ saturates at a constant value of order $D^2$, the longitudinal displacement then follows a behavior of the type of the two-dimensional law, equation (14),

$$g_{11}(t) \approx D^2(t/\tau_D)^{1/(1+1/2\nu)}, \quad t < \tau_{23}$$

The relaxation time $\tau_{23}$ is then readily estimated, using equations (16) and the fact that $g_{11}(t = \tau_{23})$ and $g_{31}(t = \tau_{23})$ are of the same order

$$\tau_{23} = \tau_D N^{2\nu+1}(l_0/D)^{(2\nu+1)/v(d=3)} = W^{-1} N^{2\nu+1}(l_0/D)^{2[v/\nu(d=3)-1]}$$
These scaling relations would imply a diffusion constant $D_N$ (estimated from $4D_N \tau_{23} = (R_0^2/V)$) strictly independent of $D$, namely

$$D_N \propto \frac{Wl_0^2}{N}. \quad (24)$$

The numerical data do show a weak dependence of $D_N$ on the slit width $D$, however.

In real systems (where hydrodynamic interactions are present for large $D$) one must consider a crossover towards the Zimm-model [19,25] for large $D$ rather than the Rouse-model as done here, of course. However, the present results are a useful reference case for simulation studies of polymers confined in thin films, where one wishes to understand also the effects of both larger polymer concentrations (where individual coils overlap strongly) and attractive forces acting on the monomers at the walls. Such extensions will be described elsewhere [23,24].

Acknowledgments

This research has been supported by the Deutsche Forschungsgemeinschaft (DFG) under grant No. 435-BUL-113/45 and by the Bulgarian Ministry for Science and Education under Grant No. X-301/93. We are grateful to I. Gerroff and W. Paul for fruitful interactions in the early stages of this project.

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