Dynamical Scaling Anomaly for a Two Dimensional Polymer Chain in Solution

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Extensive molecular dynamics simulations indicate that for time scales $t < \tau_g$, where $\tau_g \propto N^{3\nu}$, the dynamical scaling exponent $x = 2 + \nu_D/\nu$ for a polymer chain in solution is anomalous ($x = 2$) in two dimensions, contrary to the well known prediction ($x = 3$) of the Zimm model. A numerical solution of the 2D hydrodynamic Zimm model equations, which extends into the regime $t > \tau_g$, supports this value, suggesting a breakdown of dynamical scaling in 2D. [S0031-9007(97)03873-8]

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The properties of thin film polymers and polymer interfaces are of great interest for both practical and theoretical reasons. There is currently much research in areas such as reactions across the interface [1], sheer and slip properties of such interfaces [2], especially where diblock polymers are used to control adhesion [3], liquid crystals [4], and wetting [5]. These different systems share the property that most of the polymer dynamical behavior is occurring within a very thin layer with thickness less than the radius of gyration R_g. In this "Helfand-Tagami" regime [6], motion within the layer is thus essentially two dimensional (2D). Clearly, to predict the behavior of such systems one needs to understand 2D polymer dynamics. This area has generally been overlooked in the past, presumably because a purely 2D polymer system is experimentally difficult to access and because it was thought the dynamics would be well described by similar theory in 3D. The experimental difficulties, however, are now being overcome, with various methods available to create essentially 2D monolayers [7,8]. Gao and Rice [9] have proposed a method of evanescent light scattering to analyze such layers, this procedure being used by Lin and Rice [8] to study a diblock copolymer on an air/water interface. Since this technique involves light scattering, the polymer structure factor, both static and dynamic, is the essential quantity of interest.

The purpose of this Letter is to report on extensive molecular dynamics (MD) simulation studies for the 2D polymer in solution. An analysis of the structure factor data has revealed anomalous dynamical scaling behavior currently not predicted by theory. Subsequently, a closer scrutiny of the Zimm model predictions reveals a breakdown of the preaveraging approximation due to the logarithmic infinite range structure of the 2D Oseen tensor. Numerical studies of the Zimm equations upon introducing the 2D Oseen tensor yield results in accord with the MD simulations in the scaling regime. While this offers some insight into the observed anomaly, our results show that the scaling arguments in 2D are in need of a careful reexamination.

Dynamical scaling theory is now a well-established tool which has been applied to many areas [10–12]. For a 2D polymer whose dynamical structure factor $S(k,t)$ is given by

$$S(k,t) = \frac{1}{N}\sum_{ij}\langle J_0(k|\boldsymbol{R}_i(t) - \boldsymbol{R}_j(0)|)\rangle, \tag{1}$$

where N is the number of monomers, $\boldsymbol{R}_i$ their positions, $J_0(x)$ is the zeroth order Bessel function, and k is the scattering wave vector amplitude, dynamical scaling arguments [13] predict that $S(k,t)$ has the following functional form:

$$S(k,t) = NF(kR_g, tD_g/R_g^2), \tag{2}$$

where R_g is the radius of gyration of the chain and D_g the center of mass diffusion constant. In the scaling regime $kR_g \gg 1$, $S(k,t)$ should be independent of N since local chain motion is expected to be independent of the total chain length. If we assume that $R_g \propto N^{\nu}$ and $D_g \propto N^{-\nu_D}$, then $S(k,t)$ must have the form

$$S(k,t) = N(kR_g)^{-1/\nu}F(tD_gR_g^{-2}(kR_g)^x), \tag{3}$$

where

$$x = 2 + \frac{\nu_D}{\nu}. \tag{4}$$

Thus a plot of $k^{1/\nu}S(k,t)$ vs tk^x is expected to give one universal curve for all values of k in the scaling regime. The Zimm model [14] predicts that $\nu = \nu_D$, thus $x = 3$, while the Rouse model [15] predicts $\nu_D = 1$, $\nu = 1/2$, thus $x = 4$ assuming no excluded volume effect, while $x \approx 3.7$ in 3D and $x \approx 3.33$ in 2D with excluded volume [13]. Other than through the static critical exponent ν, the scaling argument used to derive these relations is independent of dimension and is expected to hold in both 2D and 3D.

The Zimm model attempts to predict the dynamics of a single polymer chain in solution by including the effects of the hydrodynamic interaction. Writing this in the form of a Langevin equation for the nth monomer we have

$$\frac{\partial}{\partial t}\boldsymbol{R}_n = \sum_m \boldsymbol{H}_{nm}\left(-\frac{\partial U}{\partial \boldsymbol{R}_n} + \boldsymbol{f}_m(t)\right), \tag{5}$$

where U is the intermonomer potential, $\boldsymbol{H}_{nm}$ the hydrodynamic Oseen tensor, and $\boldsymbol{f}_m(t)$ a random Brownian noise force. It is assumed that $\boldsymbol{H}_{nn} = \boldsymbol{I}/\zeta$, where $\boldsymbol{I}$ is the unit tensor and ζ is the friction coefficient [13]. Since this model leads to a set of coupled differential equations, $\boldsymbol{H}_{nm}$ being a nonlinear function of $\boldsymbol{R}_n - \boldsymbol{R}_m$, it is not in general solvable. Zimm [14] introduced the preaveraging approximation, which simplifies the problem and allows quantities such as the diffusion constant and relaxation times to be calculated.

The most direct method, however, of verifying the predicted dynamical scaling behavior of a polymer chain in solution is to perform a MD simulation. This approach has been taken by numerous workers in the past [16,17] to study 3D systems. However, the few studies which have been concerned with 2D polymer chains have been lattice based, and have analyzed highly concentrated melts [18], or have used cellular automata methods [19]. The 2D dynamic structure factor has been overlooked. We have performed 2D MD simulations for a single polymer and a many particle fluid in a square cell with periodic boundary conditions, using the velocity form of the Verlet algorithm [20] to solve the equations of motion. Our program, running on a Connection Machine CM-5, allocates virtual processors to individual particles to calculate and store their positions and velocities, as well as to square subcells of size $2^{1/6}\sigma$, σ being the typical Leonard-Jones (LJ) length parameter, to determine particle collisions [21]. The particles interact via a truncated LJ potential [22]

$$U_{LJ}(r) = 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6} + \frac{1}{4}\right], \quad r \le 2^{1/6}\sigma \tag{6}$$

$$= 0, \qquad r \ge 2^{1/6}\sigma\,, \tag{7}$$

where ϵ is the LJ energy parameter. This provides a purely repulsive interaction, implying the presence of a good solvent and avoiding complications arising from a Θ transition. We use a reduced density of $\rho = 0.581\sigma^{-3}$ and temperature $k_BT = 1.2\epsilon$. A 40 link polymer chain is introduced into the system by including an attractive FENE [23] potential between the monomers given by

$$U_{Ch}(r) = -\frac{1}{2}\,aR_0^2 \ln(1 - r^2/R_0^2)\,, \tag{8}$$

where $a = 7\epsilon\sigma^{-2}$ and $R_0 = 2\sigma$. The monomer mass is set to $2m$, where m is the mass of the fluid particles, and used a time step of $\Delta t = 0.005\tau_{LJ}$, where $\tau_{LJ} = \sigma(m/\epsilon)^{1/2}$. The square box edge length was set at $L = 64 \times 2^{1/6}\sigma$. Up to 90 starting configurations were generated for the combined system of a 40 link chain and 2960 solvent particles, each of these running for approximately $350\tau_{LJ}$. This is less than the Zimm time $\tau_g \approx R_g^2/D_g$ although long enough to reach into the intermediate time regimes [24]. The initial $50\tau_{LJ}$ was discarded to allow time for hydrodynamic correlations to build up, the remaining data being used for the analysis of the dynamics. The average end-to-end distance R_N was found to be 14.5σ, so there are no polymer self-overlap effects.

Taking the $t = 0$ limit of Eq. (3), one predicts that in the large k limit the static structure factor $S(k)$ has the form $S(k) \propto k^{1/\nu}$. Figure 1 shows a log-log plot of $S(k)$ and $k\sigma$, the slope of the linear region being $1/\nu$. This allows one to estimate a value for ν and simultaneously to predict a range of k values for which dynamic scaling should hold. From the gradient we calculate $\nu \approx 0.70$, slightly less than the known exact exponent $\nu = 0.75$ [25]. From similar data for a 60 link chain, and by analyzing the dependence of the mean end-to-end distance R_N with N for several values of N, we calculate $\nu \approx 0.72$, indicating the exact value is being reached, but is influenced by finite size effects and slow relaxation. Figure 2 shows the resultant structure factor data plotted with a scaling exponent $x = 2$, a value not predicted by the Rouse or Zimm models. Also shown (inset) are the same data plotted with the Zimm exponent $x = 3$. Clearly, the data scale correctly only for the former exponent. Similar data were also checked for a 20, 30, and 60 link chain, sufficiently long considering the expected scaling is reproduced in 3D for shorter chains [17], and also for a reduced density of 0.38. These cases also scaled with the $x = 2$ exponent. If we assume the form of Eq. (4) is valid, then our result could imply that $\nu_D = 0$ for the chain diffusion constant. This, however, is not the case. For when we ran simulations for various chain lengths between $N = 15$ and $N = 100$ to determine ν_D (see Fig. 3), the data were indicative of $\nu_D > 0$, thus not in conflict with the expected diffusive behavior [19], although its exact value was difficult to establish due to similar difficulties encountered by previous studies [17]. In addition, one can easily show [22] that while the interaction of the chain with its images may alter the diffusion constant from that predicted by the Kirkwood theory [13,26], it should *not* effect the scaling exponent of

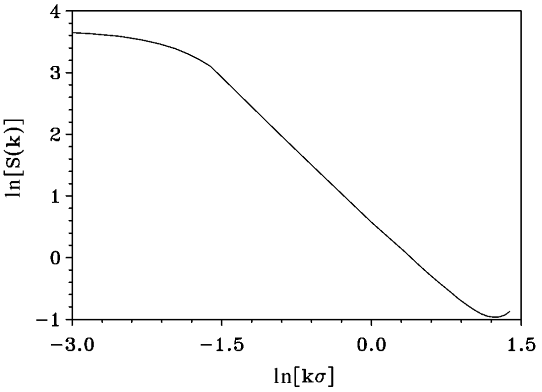

FIG. 1. Plot of $\ln[S(k)]$ vs $\ln[k\sigma]$, $0.05\sigma^{-1} \le k \le 4.0\sigma^{-1}$, for the 40 link chain 2D MD data. The linear section gradient equals $1/\nu$.

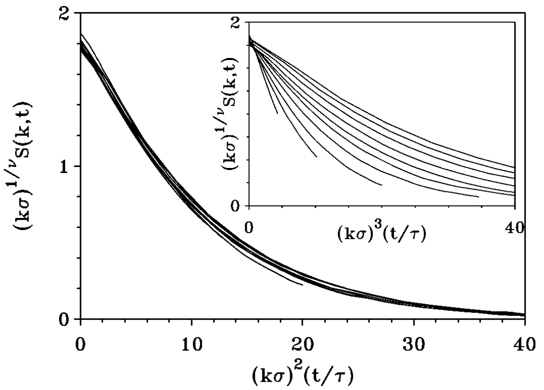

FIG. 2. Scaling plot of $(k\sigma)^{1/\nu}S(k,t)$ vs $(k\sigma)^2 t$, $0.6\sigma^{-1} \leq k \leq 2.4\sigma^{-1}$, for the 40 link chain 2D MD data. The inset is the same data plotted with the Zimm exponent $x = 3$. Analysis is performed over the same time period for different k, thus smaller k display shorter data lines.

Eq. (4). We also performed a 3D MD simulation with our program, using a 40 link chain in 4960 solvent particles, and found our data scaled with $x = 3$, in agreement with the Zimm model and previous simulation [22].

To explore the anomalous scaling behavior of the 2D MD data, we have to reexamine the theory of a 2D polymer in a fluid. It appears that the unusual form of the hydrodynamic (Oseen) tensor $\boldsymbol{H}_{nm}$ in 2D has been overlooked in the past. It can be shown [27] that this is given by

$$\boldsymbol{H}_{nm} = \frac{1}{4\pi\eta}\left[-\boldsymbol{I}\ln(|\boldsymbol{R}_n - \boldsymbol{R}_m|) + \hat{\boldsymbol{r}}_{nm}\hat{\boldsymbol{r}}_{nm}\right], \tag{9}$$

where η is the viscosity and $\hat{\boldsymbol{r}}_{nm}$ is a unit vector from monomer m to n. The distance independence of the last term leads to an infinite range hydrodynamic interaction unique to 2D. The simplest way to predict the effective diffusion from such an interaction is to use the preaveraging approximation [14] where we take the average of $\boldsymbol{H}_{nm}$ over a Gaussian distribution in the Θ condition. Assuming that $\langle\hat{\boldsymbol{r}}_{nm}\hat{\boldsymbol{r}}_{nm}\rangle = \boldsymbol{I}/2$ one can easily show that

$$\begin{aligned}\langle\boldsymbol{H}_{nm}\rangle_{\mathrm{eq}} &= \frac{\boldsymbol{I}}{8\pi\eta} - \frac{\boldsymbol{I}[\ln(|n - m|b^2) - \gamma]}{8\pi\eta} \\ &\equiv h(|n - m|)\boldsymbol{I}\,. \end{aligned} \tag{10}$$

where b is the mean distance between monomers and γ is the Euler constant. The diffusion constant D_g can thus be calculated [13]

$$D_g = \frac{k_B T}{N^2}\int_0^N\int_0^N h(|n - m|)\,dn\,dm \tag{11}$$

$$= k_B T\,\frac{5 + 2\gamma - 2\ln(b^2 N)}{16\pi\eta}, \tag{12}$$

showing a logarithmic dependence on N. This is clearly only valid for N less than some critical value as $D_g \geq 0$, indicating the limitations of this approach. Thus Eq. (12) is not the true form for the diffusion of a real 2D polymer in solution because of the approximations implied by the preaveraging approach and since the diffusion coefficient calculated using Eq. (11) gives only the leading long wavelength diffusive mode. However, it does show the pathological nature of the 2D hydrodynamic interaction, and thus one may expect dynamical anomalies in 2D that are not present in 3D.

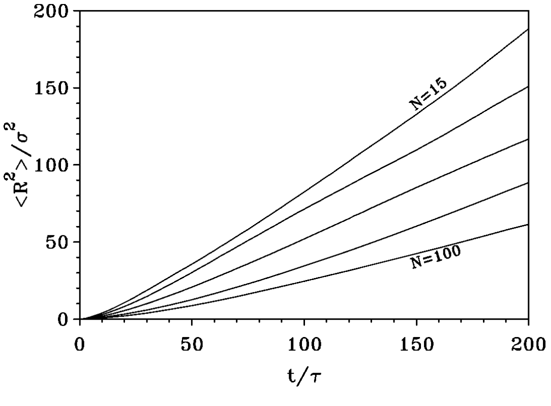

FIG. 3. Chain center of mass diffusion for 2D MD data for chain lengths $N = 15, 20, 30, 60$, and 100.

To avoid the approximations associated with the preaveraging approach, we have used the more direct method of solving the Zimm model equations numerically to observe the dynamics of the polymer chain. This approach has the advantage over MD that boundary conditions are eliminated, and thus diffusive behavior is not affected by self interactions due to long range hydrodynamic effects, and that the long time scale chain dynamics are reproduced immediately. We solved Eq. (5) for a 40 link chain using the 2D hydrodynamic tensor of Eq. (9). We kept the same LJ repulsive potential as before, while introducing an attractive harmonic potential $U = (k_B T/b^2)x^2$ between nearest neighbor monomers required by detailed balance [13]. We used a friction constant of $\zeta = 10/\tau_{LJ}$, a viscosity $\eta = m\zeta/2\pi$ [28], and a time step $\Delta t = 0.001\tau_{LJ}$, collecting data over several thousand τ_{LJ} so that $t > \tau_g$. From the log-log plot of the resultant static structure factor data we estimated a static exponent $\nu = 0.84$, which is higher than the expected 2D hard sphere value. This is an artifact of the long range hydrodynamic forces in Eq. (5) which lead to an additional net repulsive force between monomers. The resultant dynamical scaling data, see Fig. 4, clearly show the same scaling behavior as the MD data. This agreement is most significant as it shows that the scaling behavior is governed by the form of the hydrodynamic interaction for both cases, and that the MD data are not a result of incorrect diffusive behavior caused by the use of periodic boundary conditions. It also suggests the result $x = 2$ is valid over all time regimes. For comparison, we also solved Eq. (5) for a 40 link 3D polymer chain using the well known form of the 3D Oseen

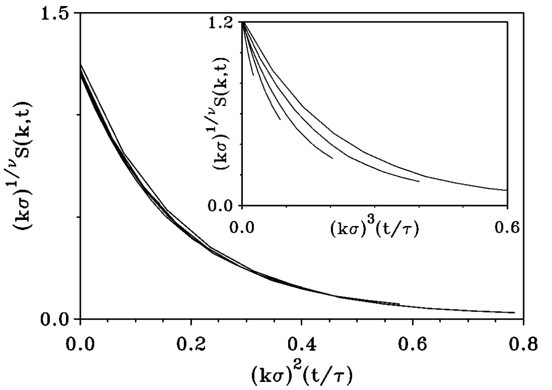

FIG. 4. Scaling plot of $(k\sigma)^{1/\nu}S(k,t)$ vs $(k\sigma)^2 t$, $0.2\sigma^{-1} \leq k < 1.4\sigma^{-1}$, for the 2D 40 link chain numerical Zimm model data. The inset is the same data plotted with the Zimm exponent $x = 3$, as in Fig. 2.

tensor [13]. These data scaled with the expected $x = 3$ Zimm model exponent. To check the form of Eq. (12), the diffusion constant was calculated for a variety of 2D chain lengths. Surprisingly, we found that D_g *increased* with N, a behavior not predicted by the preaveraging approach. This is in contrast to the MD results where D_g was found to monotonically decrease with N. To reduce the effect of the strong hydrodynamic interaction, the viscosity was increased to approximately three times its original value, which incidentally regains $\nu = 0.75$. The diffusion was then found to decrease with N up to $N \approx 10$, but beyond this chain length the diffusion increased. We again checked the scaling behavior of a 40 link chain, and it was in agreement with previous data, scaling with the anomalous $x = 2$ exponent. However, the 15 link chain data scaled with an exponent close to $x = 3$, in agreement with the Zimm prediction. This indicates a crossover in the scaling behavior with increasing chain length and viscosity from the normal Zimm-like diffusive behavior to the anomalous behavior. The 2D Zimm model thus shows a long chain scaling behavior which agrees with, and could help to explain, the scaling of our MD data. However, since our MD data did not display a scaling crossover or an increasing diffusion coefficient with chain length, a purely diffusion based explanation of the $x = 2$ scaling exponent seems inadequate, thus the entire scaling argument in 2D, which leads to Eq. (4), is brought into question.

In summary, we have performed MD simulations for a 2D polymer chain in solution and found that the dynamic structure factor scales with an anomalous exponent $x = 2$, in the regime $t < \tau_g$. A numerical solution of the 2D hydrodynamic Zimm model equations also gives this exponent for data extending into the regime $t > \tau_g$, suggesting $x = 2$ is valid over all time scales. Although the Zimm model equations may offer some insight into this result, a reexamination of the scaling argument in 2D is called for to fully understand and explain the anomalous exponent.

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