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# Dynamics and scaling of two-dimensional polymers in a dilute solution

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The breakdown of dynamical scaling for a dilute polymer solution in two dimensions has been suggested by Shannon and Choy [Phys. Rev. Lett. **79**, 1455 (1997)]. However, we show here through extensive computer simulations that dynamical scaling holds when the relevant dynamical quantities are properly extracted from finite systems. To verify dynamical scaling, we present results based on mesoscopic simulations in two dimensions for a polymer chain in a good solvent with full hydrodynamic interactions. We also present analytical arguments for the size dependence of the diffusion coefficient and find excellent agreement with the present large-scale simulations.

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The dynamics of polymer chains has attracted attention for decades already. In three dimensions, polymer dynamics exhibits rich and complex behavior which depends on the solvent conditions and polymer concentration [1,2]. The two-dimensional case, however, has attracted much less attention. Recently, it has been realized that it has important applications in the field of colloids and biomolecules. Examples include the 2D diffusion of DNA oligonucleotides confined to interfaces [3] and the lateral diffusion of lipids and proteins along biological interfaces [4] such as cell membranes. Further, the dynamics of polymers in two dimensions is of major importance in thin films thinner the size of the polymer. Wetting, surface adhesion, and flow in confined geometries are examples [5] of such problems.

An important feature of essentially all the 2D diffusion processes in soft matter is that they take place in a solvated environment, which implies that the role of the *hydrodynamic interaction* (HI) cannot be disregarded. It originates from interactions mediated by the solvent in the presence of momentum conservation. In three dimensions the effects of hydrodynamics are well understood: it is well known that the dynamics of polymers in dilute solution is well described by the Zimm model [2]. In two dimensions, however, the situation is more subtle as will be discussed below.

The dynamics of polymer chains is described by the theory of dynamical scaling [2]. The two key quantities are the radius of gyration $R_g$ and the center-of-mass (c.m.) diffusion coefficient $D$ of the chain. In the dilute limit, as a function of the degree of polymerization $N$, they follow the scaling relations $R_g \sim N^{\nu}$ and $D \sim N^{-\nu_D}$, with scaling exponents $\nu$ and $\nu_D$, respectively. Another central quantity is the intermediate scattering function defined as

$$S(\vec{k},t) = (1/N) \sum_{m,n} \langle \exp\{ i\vec{k} \cdot [\vec{r}_m(t) - \vec{r}_n(0)]\} \rangle, \tag{1}$$

where $\vec{k}$ is a wave vector, and $\{\vec{r}_n\}$'s are the positions of the monomers. This function should scale as [2]

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

where $x$ is the *dynamical scaling exponent* related to the other exponents through the relation

$$x = 2 + \nu_D / \nu. \tag{3}$$

This is valid for $k \in (2\pi/R_g, 2\pi/a)$, where $a$ is the size of a monomer. Equations (2) and (3) are the cornerstones of dynamical scaling of polymers.

In the purely dissipative case, the values of the scaling exponents for polymer chains are well understood [2]. In the dilute limit the simple Rouse model gives $\nu = 1/2$ and $\nu_D = 1$. When proper volume exclusion is taken into account, $\nu = 3/4$ in two dimensions and $\approx 3/5$ in three dimensions, while $\nu_D = 1$ still holds for dilute 3D systems and for *all* polymer concentrations in two dimensions [6].

However, when the HI is taken into account, the situation becomes different. While in 3D theory and numerical simulations agree with the prediction of the Zimm equations that $\nu = \nu_D$ (i.e., $x = 3$) [7,8], in two dimensions the situation is less clear. It has been established both theoretically [1,2] and computationally [9,10] that in good solvent conditions $\nu = 3/4$ still holds in two dimensions. The situation with $\nu_D$ is more subtle. Using lattice-gas simulations Vianney and Koelman [10] found $\nu_D = 0.78 \pm 0.05$. The molecular dynamics (MD) simulations of $S(k,t)$ by Shannon and Choy [9], in turn, gave $x = 2$ which implies that $\nu_D = 0$, if Eq. (3) holds. However, from their MD data for $D$ vs $N$ they concluded that $\nu_D > 0$ thus contradicting the scaling law. They also solved the Zimm equations numerically in two dimensions and verified the result that $x = 2$, but found that now $\nu_D < 0$ [9]. These results prompted the authors of Ref. [9] to suggest that dynamical scaling is *broken* for 2D polymers. Essentially, the very basis of polymer dynamics is being questioned.

In this paper, our objective is to determine the validity of dynamical scaling for 2D polymers. To this end, we extract the exponents $\nu$, $\nu_D$, and $x$ through extensive mesoscopic simulations of a 2D polymer in a good solvent with the full HI included. To complement this, we briefly describe analytic arguments which show that when finite-size effects are taken into account, the scaling of $D$ with respect to $N$ is truly logarithmic, leading to $\nu_D = 0$ and thus to $x = 2$. Our numerical results verify both that $x=2$ and the predicted logarithmic scaling of $D$. Thus we conclude that dynamical scaling *is* obeyed in two dimensions.

To overcome the significant difficulties in simulating polymers with full HIs, we employ a novel mesoscopic simulation method introduced by Malevanets and Kapral (MK) [11,12]. It is essentially a hybrid molecular dynamics scheme, where the polymer chain is treated microscopically while the solvent obeys coarse-grained dynamics. In practice this idea is implemented by choosing the monomer-monomer and monomer-solvent interactions as in MD simulations, while the conservative interactions between the solvent particles are absent. This description preserves the hydrodynamic modes through so-called collision rules, and allows for a major speedup compared to other techniques such as MD.

To describe the dynamics of the coarse-grained solvent, time is partitioned into segments $\tau$ and the simulation box is divided into collision volumes or cells. The effective interactions between the solvent molecules take place at each $\tau$: this is called a collision. In a collision the velocities of the solvent particles are transformed according to $\vec{v}_i(t+\tau)=\vec{V}+\vec{\omega}\cdot[\vec{v}_i(t)-\vec{V}]$. Here $\vec{v}_i$ is the velocity of the particle $i$, $\vec{V}$ is the average velocity of all the particles in the cell the particle $i$ belongs to, and $\vec{\omega}$ is a random rotation matrix chosen for that particular cell. It can be shown [11] that this multiparticle collision dynamics conserves the momentum and energy in each collision volume, and thus gives a correct description of the hydrodynamics of the velocity field.

Our model system consists of a polymer chain with $N$ monomers immersed in a 2D coarse-grained solvent. The mass of a solvent particle is set to $m$, and the monomer mass is $2m$. The monomer-monomer and monomer-solvent interactions are described by a truncated Lennard-Jones (LJ) potential:

$$U_{LJ}(r)=\begin{cases}4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]+\epsilon, & r\leqslant 2^{1/6}\sigma\\ 0, & r>2^{1/6}\sigma.\end{cases} \quad (4)$$

Here $\sigma$ and $\epsilon$ together with $m$ define the LJ unit system, where the unit of time is defined as $\tau_{LJ}=\sigma\sqrt{m/\epsilon}$. In addition to the LJ potential, there is an attractive finite extensible nonlinear elastic potential between the nearest-neighbor monomers:

$$U_C(r)=-(aR_0^2/2)\ln(1-r^2/R_0^2), \quad (5)$$

where $a=7\epsilon\sigma^{-2}$ and $R_0=2\sigma$.

The solvent density was set to $\rho=0.581\sigma^{-2}$, and the temperature was $k_BT=1.2\epsilon$, yielding good solvent conditions. The equations of motion were integrated using the velocity Verlet algorithm with a time step $\delta t=0.005\tau_{LJ}$. The choice of the parameters that determine the collision dynamics fixes the properties of the coarse-grained solvent, e.g., its viscosity. Here we set the collision time to $\tau=\tau_{LJ}$ and the linear size of the cell to $l_c=2\sigma$. The random rotation angles were chosen from a uniform distribution in $[0,2\pi)$. The size of the polymer chain $N$ varies from 20 to 150 monomers, and the linear system size $L$ ranges from $40\sigma$ up to $420\sigma$. Periodic boundary conditions were employed for all system sizes. The c.m. diffusion coefficient $D$ was determined using the memory expansion method of Ref. [13]. As shown explicitly in Ref. [13], the memory expansion gives a result fully consistent with the mean square displacement analysis, but is numerically more efficient.

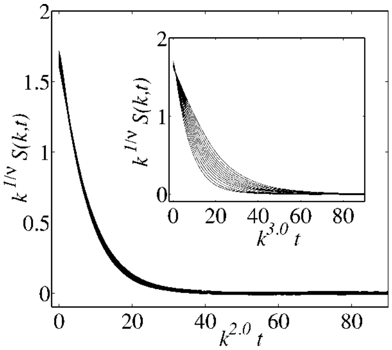

FIG. 1. Scaling of $S(k,t)$ for $N\in\{30,40,60,80,120,150\}$ for systems where the ratio $L/R_g>10$ has been kept constant and for a polymer chain with $N=40$ for different $L\in\{40,80,120,60,200\}$. All the 120 curves corresponding to different $k\in[1.0,2.4]$, $N$, and $L$ coalesce. The inset shows a scaling plot of $S(k,t)$ for a polymer with $N=40$ in a simulation box with $L=120$ with an exponent $x=3$.

First, we checked the scaling of $R_g$ with $N\in[20,150]$ [14] and found that $\nu$=0.75±0.02, in excellent agreement with theory. Next, we computed the intermediate scattering function $S(k,t)$ which is depicted in Fig. 1. Our data show the best collapse with $x=2.0\pm0.1$. We find that *all the datasets* corresponding to different $N$ and $L$ coalesce when $LR_g^{-1}\gg 1$, as they should. This confirms the MD results of Shannon and Choy [9], and shows that the 3D Zimm result $x=3$ is invalid in two dimensions.

Next, we address the crucial question of the value of the exponent $\nu_D$. In the 3D case [8], the finite-size dependence of $D$ is $D\sim 1/L$. Hence, in principle it is easy to determine $D$ for a fixed chain length $N$ by running a series of simulations for different values of $L$, and then extrapolating to $L\rightarrow\infty$. By repeating this procedure for several values of $N$, the exponent $\nu_D$ can be determined.

However, in the 2D case the finite-size effects are much more subtle due to the infinite range of the HI. We have calculated $D$ analytically for a 2D polymer in a finite system of size $L$ using the approaches presented in Refs. [8,9,15]. Here we shall assume that a finite $D$ exists in the limit $t\rightarrow\infty$ (see the discussion below) and follow Ref. [15] starting from Eq. (3.6):

$$D=\frac{k_BT}{N^2\eta A}\sum_{q\in[2\pi/L,q_0]} q^{-2}S(q)\lim_{k\rightarrow 0}k^{-2}\sum_{\lambda=1}^{2}(\vec{k}\cdot\hat{\epsilon}^{\lambda})^2, \quad (6)$$

where $A$ is the area, $\eta$ the solvent viscosity, $S(q)$ the static structure factor, $q_0$ a cutoff implying that intermediate wave vectors are considered, and $\hat{\epsilon}^{\lambda}$ a member of an orthonormal set with $\hat{\epsilon}^2=\vec{q}/q$. Using the well-known result for long

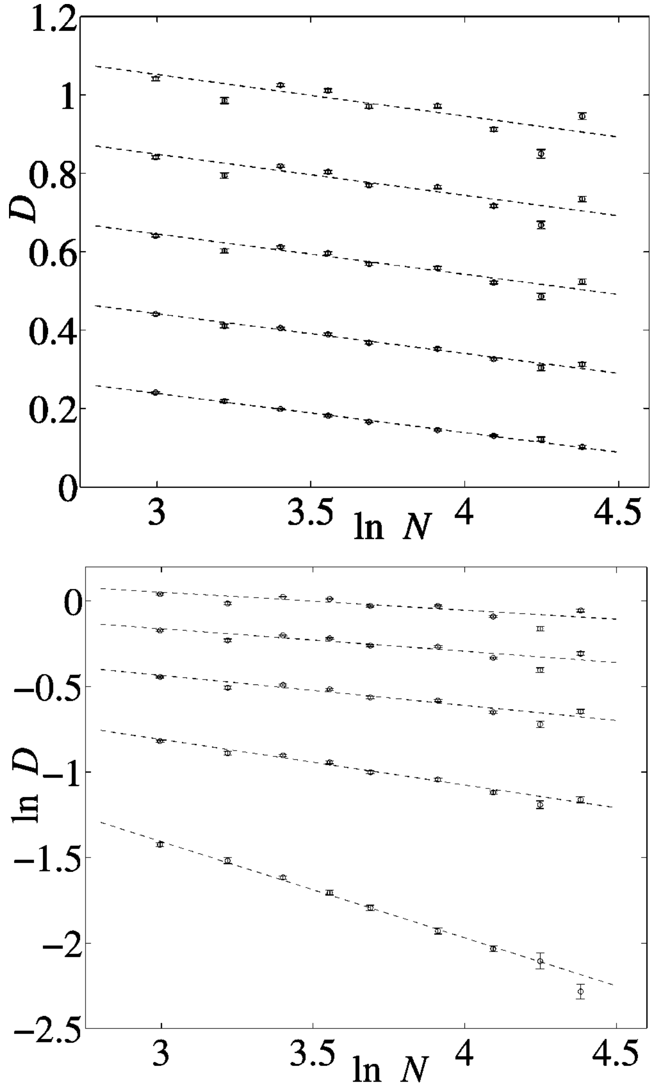

FIG. 2. The dependence of $D$ on $N$ for different cutoffs $L_{cut}$. The lines correspond to $L_{cut}\in\{10^2,10^3,10^4,10^5,10^6\}$ from bottom to top.

Gaussian chains that $S(q)=2N^2u^{-4}[\exp(-u^2)-1+u^2]$ [2], where $u=(R_gq)^2$, this can be written as

$$D=\frac{k_BT}{\eta\pi}\int_{2\pi R_g/L}^{q_0R_g}dy[\exp(-y^2)-1+y^2]y^{-5}. \tag{7}$$

Evaluating the integral and assuming that $q_0R_g\gg1$, we arrive at [16]

$$D=\frac{k_BT}{2\eta\pi}\{-\ln(R_g/L)+\text{const}+O((R_g/L)^2)\}. \tag{8}$$

This shows that extracting $\nu_D$ in the "traditional" sense in the thermodynamic limit $L\to\infty$ is no longer possible.

To numerically study the scaling of $D$ without any approximations, we determined $D$ for each $N\in[20,80]$ with different values of $L$. For instance, for $N=30$ we considered the cases $L\in\{60,90,120,150,180,210,240\}$. For every $N$, we examined the behavior of $D$ as a function of $\ln(1/L)$, and found that the behavior indeed is linear. To estimate the exponent $\nu_D$ in terms of effective diffusion coefficients, we chose cutoff values $L_{cut}\in\{10^2,10^3,10^4,10^5,10^6\}$, and extrapolated a value $D(N,L_{cut})$ for each chain size and cutoff. If the data comply with Eq. (8), we should, when plotting $D(N,L_{cut})$ vs $\ln N$, obtain a set of equally spaced straight lines. Each line corresponds to a certain cutoff, and the lines should all have the same slope $A$. As can be seen in Fig. 2, this indeed holds within the statistical uncertainties of our data. Moreover, a quantitative comparison with Eq. (8) yields a prediction $D=0.2\sigma^2\tau_{LJ}^{-1}\ln(R_g/L)$. Our numerical data suggest that $D=0.1\sigma^2\tau_{LJ}^{-1}\ln(N/L)$, in excellent agreement with our mean-field type of analytic approximation. Most importantly, Fig. 2 confirms the prediction of logarithmic scaling of $D$ with $N$, which means that $\nu_D=0$. To quantify this, we can extract the exponent $\nu_D$ from $\ln D(N,L_{cut})$ vs $\ln N$: for large values of $L$, we should have $\ln D\sim-\nu_D\ln N$. The results in Fig. 2 show that $\nu_D$ decreases steadily with $L$ as it should. For the largest $L_{cut}$ studied here, we find $\nu_D\approx0.05\pm0.05$.

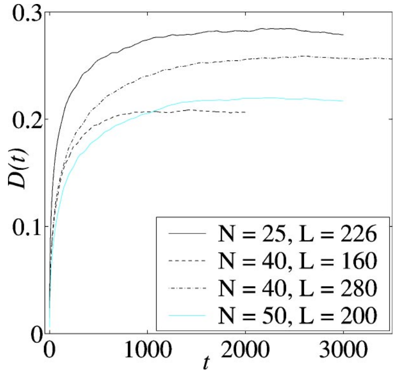

FIG. 3. The convergence of $D(t)$ vs time for systems with different $N$ and $L$. The diffusion coefficients have been computed using the memory expansion method [13]. The convergence has also been checked using the conventional mean squared distance vs time analysis. We have explicitly ensured that the mean squared distance depends linearly on time in the regime where the memory expansion seems to have converged; i.e., $\langle[\vec{r}(t)-\vec{r}(0)]^2\rangle\sim t^1$ for the time-dependent c.m. position of the polymer.

The analysis above reveals the reason for the suggested breakdown of scaling in Refs. [9,10]. While the result $x=2$ is correct, as verified here, the results in the previous studies for $\nu_D$ are incorrect because the exponent has been extracted without proper consideration of the finite-size effects [17]. Thus, we can conclude that dynamical scaling holds for 2D polymers with $x=2$, $\nu=3/4$, and $\nu_D=0$. Intuitively, this should be the case: in 2D and 3D dilute polymer solutions, HIs are expected to display so-called nondraining behavior [1,10], i.e., solvent particles within the polymer coil will remain inside the coil. From the solvent point of view, the polymer coil is an inpenetrable obstacle. In three dimensions, nondraining behavior means that the diffusion coefficient of a polymer scales with its size as any spherical object, i.e., it will be inversely proportional to the size of the polymer ($R_g$). Analogously, in two dimensions the c.m. diffusion coefficient of a polymer chain should behave like that of a circular disk, i.e., depend logarithmically on its size $R_g$ and on the system size $L$.

Finally, we wish to discuss the issue of long-time tails in 2D diffusion. In the presence of the HI it has been shown that the velocity autocorrelation function $\phi(t) \equiv \langle \vec{v}_i(t+t') \cdot \vec{v}_i(t') \rangle \sim t^{-1}$ [18], or $\phi(t) \sim [t\sqrt{\ln(t)}]^{-1}$ [19], which means that rigorously speaking, *D* is not well defined in two dimensions. This would seem to invalidate the present scaling arguments. However, there are several ways to resolve this problem. A standard method is to view the diffusion coefficients in two dimensions as time-dependent quantities $D(t)$ [19], from which one can define effective values of $D \equiv D(t_f)$ at some finite time $t_f$. In the present case, the issue of long-time tails is settled by recognizing that in dynamical scaling, the absolute values of the diffusion coefficients are irrelevant: only the behavior of *D* as a function of the chain or system size matters. Hence, we can use such effective values provided that they have been determined in a consistent way. To this end, we have determined *D*'s over a time interval where the coefficients have converged within numerical error. More precisely, assuming $D \sim \ell_D^2 / t_D$, where $\ell_D$ is the distance over which the chain diffuses during the time interval $t_D$, the diffusion coefficients have been measured at a point where the chain has diffused a scaled distance $\ell_D / R_g = 2–4$. The convergence of $D(t)$ on these time scales is demonstrated in Fig. 3 for systems with different values of *N* and *L*.

In conclusion, we have applied the MK method to a dilute 2D polymer solution. The method itself has proved to be an efficient tool for studies of macromolecular systems, especially in the dilute limit where the computational cost is mainly due to the explicit solvent. The technique has enabled us—at a moderate computational cost—to study system sizes that have not been previously amenable to simulations. This approach together with careful consideration of finite-size effects has allowed us to solve the controversy regarding the dynamical scaling of dilute polymer solutions in two dimensions with full HIs. We have found, in contrast to previous studies [9,10], that the exponent relation $x = 2 + \nu_D / \nu$ is valid within numerical error. This justifies the scaling hypothesis, and shows that the anomalous exponent $x = 2$ found in previous studies is due to the logarithmic scaling of *D* with *N*.

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[16] This result should be contrasted to the infinite system size result of Eq. (12) in Ref. [9] which also gives logarithmic dependence on *N*, but becomes negative with increasing *N*, which is unphysical.

[17] One can also write a general finite-size scaling form for $S(k,t)$ following Ref. [2] to include the *L* dependence of *D*. This leads to $x = 2$ in the present case, as proved by the collapse of all data in Fig. 1.

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