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Dynamics and scaling of polymers in a dilute solution: Analytical treatment in two and higher dimensions

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Dynamics and scaling of polymers in a dilute solution: Analytical treatment in two and higher dimensions

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We consider the dynamical scaling of a single polymer chain in good solvent. In the case of two-dimensional systems, Shannon and Choy [Phys. Rev. Lett. **79**, 1455 (1997)] have suggested that the dynamical scaling for a dilute polymer solution breaks down. Using scaling arguments and analytical calculations based on the Zimm model, we show that the dynamical scaling of a dilute two-dimensional polymer system holds when the relevant dynamical quantities are properly extracted from finite systems. Most important, the polymer diffusion coefficient in two dimensions scales logarithmically with system size, in excellent agreement with our extensive computer simulations. This scaling is the reason for the failure of the previous attempts to resolve the dynamical scaling of dilute two-dimensional polymer systems. In three and higher dimensions our analytic calculations are in agreement with previous results in the literature. © 2005 American Institute of Physics. [DOI: 10.1063/1.1855876]

I. INTRODUCTION

Polymers comprise one of the most important classes of technologically important molecules that play a central role in materials science.^{1,2} They are ubiquitous in living systems as exemplified by a variety of biopolymers such as DNA, proteins, and lipids,^{2,3} whose basic features can be described by polymer physics. Consequently, polymers offer us a genuinely interesting and cross-disciplinary research topic, in particular, both their structural and dynamical properties that dictate their function.

Of particular interest is the dynamics of polymers in two dimensions (2D). As an example, the diffusion of enzymes such as phospholipase A2 in the plane of a cell membrane is essentially a 2D process.⁴ In the same context, lipids and proteins embedded in cellular membranes diffuse in the plane of a membrane⁵⁻⁹ in a 2D fashion. The diffusion of DNA oligonucleotides confined to a biological interface¹⁰⁻¹⁴ is also two dimensional, not to mention technologically important thin films, where processes such as wetting and flow in confined geometries are examples¹⁵ of dynamic phenomena.

The above-mentioned applications highlight the importance of understanding the physical principles that govern the dynamics of polymer systems in 2D. In general this is a highly nontrivial problem, and developing well-grounded theoretical descriptions is nontrivial. One of the relatively rare exceptions is the Rouse model,^{16,17} which has been very successful in describing the dynamics of 2D dilute polymer systems in the absence of hydrodynamic interactions. By hydrodynamic interactions we mean the interactions mediated by the solvent in the presence of momentum conservation,

and since the Rouse model does not take them into account, it is a suitable approximation to “dry” systems such as polymer diffusion on a flat, inert surface without a solvent.^{18,19}

The biological and engineering applications we have mentioned illustrate the importance of including hydrodynamic interactions in the description of a variety of “wet” soft matter systems. The problem is that analytical studies of 2D polymer dynamics with full hydrodynamics have turned out to be a major challenge. This is well exemplified by recent attempts to clarify the dynamical scaling and related exponents of dilute polymer systems in 2D.²⁰⁻²² The results have been partly controversial, and it has even been suggested that the dynamical scaling is broken in 2D.²⁰ Our purpose is to address this question in detail, using both analytic and computational techniques, and demonstrate that dynamical scaling is obeyed when the relevant quantities are properly extracted from systems of finite size.²²

In the theory of dynamical scaling, the two key quantities to consider¹⁶ 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 functions of the degree of polymerization or number of monomer units N , they follow the scaling relations

$$R_g \sim N^\nu \quad (1)$$

and

$$D \sim N^{-\nu_D}, \quad (2)$$

with scaling exponents ν and ν_D . The center-of-mass diffusion coefficient is defined as

$$D = \frac{1}{d} \int dt \langle \mathbf{v}_{\text{c.m.}}(t) \cdot \mathbf{v}_{\text{c.m.}}(0) \rangle, \quad (3)$$

where $\mathbf{v}_{\text{c.m.}}(t)$ is the c.m. velocity of the polymer chain at time t and d is the dimensionality of the system. Another central quantity is the intermediate scattering function defined as

$$S(\mathbf{k}, t) = \frac{1}{N} \sum_{m,n} \langle \exp\{i\mathbf{k} \cdot [\mathbf{r}_m(t) - \mathbf{r}_n(0)]\} \rangle, \quad (4)$$

where \mathbf{k} is a wave vector and $\{\mathbf{r}_n\}$ are the positions of the monomers. This function should scale as¹⁶

$$S(k, t) = k^{-1/\nu} F(tk^x), \quad (5)$$

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

$$x = 2 + \frac{\nu_D}{\nu}. \quad (6)$$

This relation is valid for $k \in (2\pi/R_g, 2\pi/a)$, where a describes the size of a monomer. Note that Eqs. (5) and (6) can be considered as the cornerstones of the dynamical scaling of polymers, and they should hold true in all dimensions $d > 1$.

Without hydrodynamic interactions and excluded volume effect, the values of the scaling exponents for polymer chains are well understood.¹⁶ In the dilute limit the simple Rouse model gives $\nu = 1/2$ and $\nu_D = 1$, and hence $x = 4$. When the excluded volume effect is taken into account, $\nu \approx 3/4$ and $\nu_D = 1$,^{16,23} where the latter holds for all polymer concentrations in 2D.¹⁸ As a result, $x \approx 10/3$. For dilute systems in 3D, the inclusion of excluded volume effects results in $\nu \approx 3/5$ and $\nu_D = 1$, and therefore $x \approx 11/3$.^{16,23}

When both the excluded volume effect and hydrodynamic interactions are taken into account, the situation becomes more complicated. While in 3D numerical simulations agree with the prediction of the Zimm equations that $\nu = \nu_D$, i.e., $x = 3$,^{24–29} in 2D the situation is much more subtle. Both theoretical^{16,17} and computational^{20–22} studies have confirmed that in good solvent conditions $\nu \approx 3/4$ in 2D. For the scaling exponent of the diffusion coefficient, Vianney and Koelman²¹ found through lattice-gas simulations that $\nu_D = 0.78 \pm 0.05$, yielding $x \approx 3$. The molecular dynamics (MD) simulation results for $S(k, t)$ by Shannon and Choy²⁰ gave $x = 2$, which implies that $\nu_D = 0$, if Eq. (6) holds. From their MD data for D versus N , however, Shannon and Choy concluded that $\nu_D > 0$, thus predicting $x > 2$, which contradicts the scaling law. They also solved the Zimm equations numerically in 2D and verified the result that $x = 2$, but found that now $\nu_D < 0$.²⁰ These results prompted the authors of Ref. 20 to suggest that dynamical scaling is *broken* for 2D polymers.

We have recently conducted²² large-scale simulations for the dynamics of a 2D polymer chain with full hydrodynamic interactions, aiming to resolve the issue. The use of a highly efficient mesoscopic simulation technique^{30,31} allowed us to carry out an extensive finite-size scaling study and show that the diffusion coefficient follows the form

$$D \sim \ln \frac{L}{R_g}, \quad (7)$$

where L is the linear size of the system. This result means that $\nu_D \approx 0$, implying that $x = 2$. Dynamical scaling is therefore satisfied.²² Equation (7) also suggests that the results of the previous studies were affected by strong finite-size effects, which were not properly accounted for.

Since the discussion in Ref. 22 focused on the results of computational studies, the theoretical basis of Eq. (7) has remained incomplete. Hence, our aim in the present study is to discuss the dynamical scaling of 2D polymers with full hydrodynamics from an analytical perspective. We first employ scaling arguments to gain insight into the scaling exponents at a rather general level. The scaling arguments suggest that Eq. (6) is valid. We then approach the issue from a more rigorous direction using the Zimm model as a starting point. Calculations in 2D show how a description of the form of Eq. (7) emerges, showing that D depends on system size in a logarithmic manner. Using the same theoretical framework, further analysis in three and higher dimensions leads to results consistent with previous results in the literature. Finally, for the sake of completeness, we briefly summarize the main results of our recent mesoscale simulations²² and discuss numerical evidence for the observed logarithmic scaling of D with N , which is in excellent agreement with the analytical predictions.

II. SCALING ARGUMENTS

In this section we discuss scaling arguments for the c.m. diffusion coefficient D . Consequently, these arguments should be considered as qualitative rather than rigorous, and are given as a motivation for the proper analytical treatment of hydrodynamics discussed in detail in Sec. III A. However, it turns out that in certain limits these scaling arguments do actually give the correct results for the scaling of the c.m. diffusion coefficient.

The scaling analysis is based on the Zimm theory,¹⁶ which states that in good solvent conditions the chain dynamics is governed by the overdamped hydrodynamic equations. Furthermore, the chain diffusion coefficient D is defined as a trace over the hydrodynamic tensor. This *Oseen tensor* is a solution for the overdamped hydrodynamic equations of motion for incompressible fluid, i.e., the Stoke's equation

$$\begin{cases} \nabla P + \eta \nabla^2 \mathbf{v} - \sum_{m=1}^N \mathbf{f}_m = 0 \\ \nabla \cdot \mathbf{v} = 0. \end{cases} \quad (8)$$

Here P is the pressure, \mathbf{v} the velocity of the fluid (surrounding the monomers), and η the kinematic viscosity of the fluid. Monomers are taken to be pointlike, and the force monomer m exerts on the surrounding fluid is taken to be $\mathbf{f}_m = -\mathbf{g}_m \delta(\mathbf{x} - \mathbf{x}_m)$. In order for this equation to be dimensionally valid, one can see that the dimension of the kinematic viscosity η must be $[\eta] = k_B T s / b^d$, where b is the unit of length characterizing the distance between monomers, s is the unit of time, and $k_B T$ sets the thermal energy scale. The

other relevant parameters are the degree of polymerization N and the linear size of the system L . Using dimensional analysis and scaling arguments, the most general form of the c.m. diffusion coefficient in d dimensions can be written as

$$D = \frac{k_B T}{\eta R_g^{(d-2)}} G(R_g/L), \quad (9)$$

where $R_g = bN^\nu$ and the scaling function G has to be calculated from the full hydrodynamic equations (8). It is often assumed that in the thermodynamic limit the scaling function becomes independent of L and N (or R_g). However, as will become clear in Sec. III, this claim holds only in those cases where the hydrodynamic equations have a solution in the limit $L \rightarrow \infty$.

From Eqs. (1), (2), and (9) it is clear that the exponent ν_D must be given by

$$\nu_D = \nu(d-2). \quad (10)$$

Substituting this result to Eq. (6) it immediately follows that the dynamical scaling exponent reads as

$$x = d. \quad (11)$$

This agrees with the numerical results of previous studies of polymer dynamics in 2D.^{20,22} The scaling relation Eq. (10) also predicts that in the 2D case we should find $\nu_D=0$, which is in agreement with the logarithmic form of the scaling function G found in our recent simulations.²²

To predict ν_D and x in 3D we need an additional piece of information: the value of the exponent ν . This exponent, with excluded volume interactions, can be extracted using simple Flory arguments:^{16,23}

$$\nu = \frac{3}{d+2}, \quad (12)$$

which holds for $1 \leq d < d_u \equiv 4$. Using Eqs. (6), (10), and (12), we obtain the well-known exponents predicted by the Zimm theory, i.e., $\nu_D = \nu$ and $x=3$.

The four-dimensional case differs from the 2D and 3D ones. Above the *static upper critical dimension* $d_u=4$, the excluded volume interaction is irrelevant, i.e., Eq. (12) no longer holds, and the radius of gyration scales as $R_g \propto N^{1/2}$.³² This means that as long as there are no long-range forces such as Coulomb interactions between the monomers, the chain behaves as an ideal Gaussian chain. If we use $\nu=1/2$ in 4D, we end up with the results predicted by the Rouse model, i.e., $\nu_D=1$ and $x=4$. Note that in the Rouse theory the hydrodynamic interaction is discarded. Thus, our scaling results can be taken as an indication that in 4D the hydrodynamics might behave in a different manner compared to lower dimensions. In Sec. III A we will see explicitly that the exponent ν_D saturates to its 4D value $\nu_D=1$, which means that in the sense of the Zimm theory the dimension four is also the *dynamical upper critical dimension*.

III. HYDRODYNAMICS

A. General solution of Stoke's equation

In this section we solve the Stoke's equation (8) and show that the solution exists in infinite systems only for 2

$< d \leq 4$. To this end, we consider a d -dimensional cube of linear size $2L$ centered at the origin. We use periodic boundary conditions and expand the solution using independent Fourier modes $\psi(\mathbf{x}) = \exp(i\mathbf{q} \cdot \mathbf{x})$, where \mathbf{x} is the position of an infinitesimal fluid element and $\mathbf{q} = \mathbf{n}\pi/L$, where $\mathbf{n} = (n_1, n_2, \dots, n_d)$ consists of positive integers. The orthogonality of the Fourier modes makes the solution convenient. We further must assume no-slip boundary conditions between the solvent and the monomers, i.e., the velocity of monomer n in position \mathbf{x}_n is the same as the velocity of the fluid at that position, $\mathbf{v}_n = \mathbf{v}(\mathbf{x}_n)$. After some algebra, we arrive at a relationship for the velocity of the n th monomer and the force acting on it

$$\begin{aligned} \mathbf{v}_n &= \sum_m \left(\frac{1}{(2L)^d \eta} \sum_{\mathbf{q}}' \frac{e^{i\mathbf{q} \cdot (\mathbf{x}_n - \mathbf{x}_m)}}{q^2} \{\mathbf{I} - \hat{\mathbf{q}}\hat{\mathbf{q}}\} \cdot \mathbf{g}_m \right) \\ &= \sum_m \mathbf{H}(\mathbf{x}_n - \mathbf{x}_m) \cdot \mathbf{g}_m = \sum_m \mathbf{H}_{nm} \cdot \mathbf{g}_m, \end{aligned} \quad (13)$$

where $\hat{\mathbf{q}}$ is a unit vector in the direction of \mathbf{q} . The prime in the summation signifies that the $\mathbf{q}=0$ mode is excluded. The latter two equations define a new tensor $\mathbf{H}_{nm} = \mathbf{H}(\mathbf{x}_n - \mathbf{x}_m)$. This tensor turns out to be the well-known Oseen tensor, see, e.g., Ref. 16.

In converting the summation over discrete wave vectors into a continuum integral, it is easy to see that the integral converges only for $2 < d \leq 4$. For $d \leq 2$ there is a divergence caused by the longest wavelengths, while for $d > 4$ the origin of the divergence is the upper bound in the integral. In the case of $d \leq 2$, we therefore must consider a finite system and exclude the region $|\mathbf{q}| < \pi/L$. Furthermore, we also have to omit the wave vectors $|\mathbf{q}| > \pi/R_g$ to keep the Oseen tensor finite in dimensions $d > 4$. This upper cutoff means that we are discarding information about the internal modes of the polymer chain. However, as long as we are only interested in the c.m. diffusion coefficient, it is enough to consider only the large length-scale properties. With these cutoffs

$$\mathbf{H}(\mathbf{x} - \mathbf{x}') \rightarrow \frac{1}{\eta(2\pi)^d} \int_{|\mathbf{q}| \geq \pi/L}^{|\mathbf{q}| \leq \pi/R_g} d^d \mathbf{q} \frac{e^{-i\mathbf{q} \cdot (\mathbf{x} - \mathbf{x}')}}{q^2} \times \{\mathbf{I} - \hat{\mathbf{q}}\hat{\mathbf{q}}\}. \quad (14)$$

In 3D the Oseen tensor defined in Eq. (14) is identical to the well-known result (without the cutoffs).¹⁶

If we use periodic boundary conditions, the Oseen tensor is translationally invariant, and depends only on the distance $\mathbf{r} = \mathbf{x}_n - \mathbf{x}_m$. The tensor can therefore be written in terms of the identity tensor and the unit vector $\hat{\mathbf{r}}$ parallel to \mathbf{r} according to

$$\mathbf{H}(\mathbf{r}) = A(\mathbf{r})\mathbf{I} + B(\mathbf{r})\hat{\mathbf{r}}\hat{\mathbf{r}}. \quad (15)$$

The coefficients A and B can be extracted from

$$dA(\mathbf{r}) + B(\mathbf{r}) = \frac{1}{(2\pi)^d \eta} \int' d^d \mathbf{q} \frac{d-1}{q^2} e^{-i\mathbf{q} \cdot \mathbf{r}} \quad (16)$$

$$A(\mathbf{r}) + B(\mathbf{r}) = \frac{1}{(2\pi)^d \eta} \times \int' d^d \mathbf{q} \frac{[1 - (\hat{\mathbf{q}} \cdot \hat{\mathbf{r}})^2]}{q^2} e^{-i\mathbf{q} \cdot \mathbf{r}}, \quad (17)$$

where the prime means the integral to be restricted to $\pi/L \leq |\mathbf{q}| \leq \pi/R_g$.

Generally, the c.m. diffusion coefficient of any system obeying Stokesian hydrodynamics can be written as a trace over all the degrees of freedom of the Oseen tensor. In the case of a polymer chain, the trace is over the monomers and over all possible configurations the chain can assume, and reads¹⁶

$$D = \frac{k_B T}{dN^2} \sum_{nm} \text{Tr}(\mathbf{H}(\mathbf{x}_n - \mathbf{x}_m)). \quad (18)$$

The calculation of the chain diffusion coefficient requires averaging the Oseen tensor of Eq. (14) over the whole distribution function of the polymer, which is generally very complicated to do analytically. The approximation commonly adapted here is the so-called preaveraging approximation: the average of the Oseen tensor over all configurations is replaced by its average¹⁶ over a Gaussian chain. For a Gaussian (ideal) chain, i.e., a chain in the absence of excluded volume interactions, the distribution of the distance $\mathbf{x}_n - \mathbf{x}_m$ between any two monomers n and m becomes

$$\Phi(\mathbf{x}_n - \mathbf{x}_m, |n - m|) = \left(\frac{d}{2\pi|n - m|b^2} \right)^{d/2} \times \exp \left[\frac{-d}{2b^2|n - m|} (\mathbf{x}_n - \mathbf{x}_m)^2 \right], \quad (19)$$

where b is the bond length.

When excluded volume interactions are accounted for, the distribution function can only be calculated approximately. For the end-to-end distance, it can be done on the mean-field level.³² This analysis shows that the distribution function is highly peaked around $R \propto N^\nu b$, and is almost Gaussian around the maximum. In the case of the monomer-monomer distribution function, the analytical calculation is even more involved, and gives very little insight into the situation. However, if one is merely interested in the large length-scale properties, it is reasonable to use a trial distribution function which correctly reproduces the properties of excluded volume chains at large length scales, e. g., the radius of gyration and the end-to-end distance. This means that we assume every chain segment to behave as the excluded volume chain itself. The simplest way to include the excluded volume interaction approximately is to assume that the distribution between monomers is still Gaussian, but with a variance given by $|n - m|^{2\nu} b^2 / d$, where the exponent ν is given by Eq. (12). Clearly, this function satisfies the requirements set above, i.e., gives the correct large length-scale properties. Averaging over this modified Gaussian distribution gives the following result:

$$\langle \mathbf{H}_{nm} \rangle = \frac{1}{\eta(2L)^d} \sum_{\mathbf{q}}' \frac{e^{-\mathbf{q}^2 [b^2 |n - m|^{2\nu} / 2d]}}{q^2} \{\mathbf{I} - \hat{\mathbf{q}} \hat{\mathbf{q}}\}. \quad (20)$$

From Eq. (20) one can see that the upper bound for the summation over wave vectors has become unimportant, and we can extend it to infinity. This is a consequence of the form of the Gaussian distribution. In the continuum limit the general result for the preaveraged Oseen tensor can be written as

$$\begin{aligned} \langle \mathbf{H}_{nm} \rangle &= \frac{\mathbf{I}}{\eta b^{(d-2)}} \frac{C(d)}{2} |n - m|^{2\nu(1-d/2)} \\ &\times \Gamma \left[\frac{d}{2} - 1, (\pi/L)^2 \left(\frac{b^2 |n - m|^{2\nu}}{2d} \right) \right] \\ &\equiv \mathbf{I} h(|n - m|), \end{aligned} \quad (21)$$

where the dimension dependent prefactor $C(d)$ is given by

$$C(d) = \frac{(d-1)}{(2\pi)^{d/2} \Gamma(d/2)} d^{(d/2-1)}. \quad (22)$$

From Eqs. (18) and (21) it follows that the chain c.m. diffusion coefficient can be written as

$$D = \frac{k_B T}{N^2} \sum_{nm} h(|n - m|) \simeq \frac{k_B T}{N^2} \int_0^N dn \int_0^N dm h(|n - m|). \quad (23)$$

This integral does not have a closed form solution, but we can simplify it by noting that $bN^\nu \ll L$. Consequently, the argument of the incomplete gamma function can be expanded at the limit of small argument. For $d > 2$ the function is analytical and we may write

$$\begin{aligned} \Gamma[d/2 - 1, \mathcal{A}^2 |m - n|^{2\nu}] &= \Gamma[d/2 - 1] - [\mathcal{A}^2 (m - n)^{2\nu}]^{d/2-1} \\ &+ O([\mathcal{A}^2 (m - n)^{2\nu}]^{d/2}), \end{aligned} \quad (24)$$

where we have defined the expansion parameter as $\mathcal{A}^2 = (b\pi/L)^2 / (2d) \ll 1$. Integrating over the monomer coordinates gives to lowest order in \mathcal{A}

$$\begin{aligned} D &= \frac{k_B T}{\eta b^{d-2}} C(d) \left\{ \frac{\Gamma[d/2 - 1]}{2 + \nu(d-2)[\nu(d-2) - 3]} \right. \\ &\times \left[N^{-\nu(d-2)} + \frac{\nu(d-2) - 2}{N} \right] - \frac{1}{2} \mathcal{A}^{d-2} \left. \right\}. \end{aligned} \quad (25)$$

Taking the thermodynamic limit $L \rightarrow \infty$ gives

$$D \propto \frac{k_B T}{\eta b^{d-2}} \times \begin{cases} N^{-\nu(d-2)} & \text{for } d < d_{cr} \\ N^{-1} & \text{for } d > d_{cr}, \end{cases} \quad (26)$$

where the dynamical upper critical dimension d_{cr} is determined by

$$\nu(d_{cr} - 2) = 3 \frac{d_{cr} - 2}{d_{cr} + 2} \equiv 1. \quad (27)$$

Equation (27) shows that the dynamical upper critical dimension here is given by $d_{cr} = 4 \equiv d_u$, and is thus the same as in the static case. We can see that the leading term for $d > 4$ is $1/N$, whereas for $2 < d < 4$ it is $N^{-\nu(d-2)}$. In the case of d

$=4$, $\nu=1/2$, diffusion coefficient given by Eq. (25) diverges. However, starting directly from Eq. (23) it follows that in 4D

$$D = \frac{k_B T}{2\pi^2 \eta b^2} \left[-\frac{1}{N} + \frac{\ln N}{N} \right], \quad (28)$$

which explicitly demonstrates the appearance of a logarithmic correction term to scaling, as expected.³³

From our results in Eqs. (25) and (28) we can conclude that the behavior of chain diffusion changes as a function of dimension, as was already anticipated by using the simple scaling arguments discussed in Sec. II. In particular, for $d > 4$ the leading term is $1/N$. This means that in and above four dimensions polymer diffusion can be described in terms of the Rouse model which assumes the diffusion tensor of a Gaussian chain to have the simple diagonal form¹⁶

$$\mathbf{H}_{nm} = \frac{k_B T}{\zeta} \delta_{nm}. \quad (29)$$

From this it immediately follows that the diffusion coefficient is given by

$$D = \frac{k_B T}{\zeta} \frac{1}{N}, \quad (30)$$

which agrees with our analytic solution of Eq. (25) above $d=4$.

B. 2D and 3D cases

It is particularly interesting to consider the case of $d=2$, which plays the role of a *lower critical dimension* here. We will also present results for $d=3$, in order to compare the finite-size corrections to D with those in the literature.^{29,34} In order to calculate D , we expand Eq. (16) to lowest order in r/L and discard the upper bound, obtaining

$$\mathbf{H}(\mathbf{r}) = \begin{cases} \frac{1}{8\pi\eta r} [\mathbf{I}(1 - \frac{8r}{3L}) + \hat{\mathbf{r}}\hat{\mathbf{r}}] & \text{for } d=3 \\ \frac{1}{4\pi\eta} [\mathbf{I} \ln(\frac{L}{r}) + \hat{\mathbf{r}}\hat{\mathbf{r}} + \text{const.}] & \text{for } d=2. \end{cases} \quad (31)$$

The Oseen tensor for the 2D case resembles the result of Shannon and Choy,²⁰ except for the logarithmic dependence on the system size L . This dependence is important because the kinetic energy density of the fluid, defined by

$$f_k = \lim_{L \rightarrow \infty} \frac{\int d\mathbf{x} \frac{1}{2} \rho(\mathbf{x}) \mathbf{v}(\mathbf{x})^2}{L^d}, \quad (32)$$

remains finite only when the system size dependence is properly included. If one uses the well-known definition of the thermodynamic limit through the free energy density of the fluid, it means that the thermodynamic limit for the solution of Eq. (31) is well defined.³⁵ The solution obtained by Shannon and Choy²⁰ gives a (logarithmically) diverging kinetic energy density and is therefore unphysical. We note that for $d=3$ the size independent part of the Oseen tensor of Eq. (31) is equal to the Zimm result.¹⁶ Here we can, in addition, calculate explicitly the leading finite size correction.

To obtain D , we expand the incomplete gamma function in Eq. (21) in the limit $bN^\nu \ll L$, arriving at

$$h(|n-m|) = \frac{1}{4\pi\eta} \left[\ln\left(\frac{L}{b|n-m|^\nu}\right) - \frac{1}{2}(\gamma + \ln \pi^2/4) + \frac{\pi^2 b^2 |n-m|^{2\nu}}{4L^2} \right] + O\left[\left(\frac{b^2 |n-m|^{2\nu}}{L^2}\right)^2\right], \quad (33)$$

where γ is the Euler constant. Finally, we calculate the trace over monomer indices according to Eq. (18), and to leading order in b/L obtain

$$D = \begin{cases} \frac{k_B T}{\eta R_g} \left[\frac{8}{3(6\pi^3)^{1/2}} - \frac{2}{9\pi} \frac{R_g}{L} \right] & \text{for } d=3, \\ \frac{k_B T}{4\pi\eta} \left[\ln\left(\frac{L}{R_g}\right) + \text{const.} \right] & \text{for } d=2, \end{cases} \quad (34)$$

where we have used the result $R_g = bN^\nu$.

In $d=3$ our result is equal to the previous results obtained for the Zimm model,¹⁶ with a finite-size correction term in agreement with previous studies in the literature.^{29,34} Most important, in 2D we find that the logarithmic dependence on system size appearing in the Oseen tensor appears in D as well. Thus, although our result is similar to the one obtained by Shannon and Choy,²⁰ the logarithmic system size dependence has an important physical significance here. First, it prevents D from having negative values. This is because the system size always has to be larger than the size of the polymer characterized by the radius of gyration R_g . Second, the thermodynamic limit is well defined for the solution of Eq. (31), because it gives a finite kinetic energy density even in the limit $L \rightarrow \infty$. Finally, when values of D are obtained from numerical simulations as a function of L , it is crucial to know how D depends on L .²² This will be discussed in the following section in more detail.

IV. SIMULATION RESULTS IN 2D

To numerically study the scaling of D without approximations, we extracted the exponents ν , ν_D , and x through extensive mesoscopic simulations of a 2D polymer in a good solvent with full hydrodynamic interactions included.²² To overcome the significant difficulties in simulating polymers in an explicit solvent, we employed a novel mesoscopic simulation method introduced by Malevanets and Kapral.^{30,31} This simulation method is explained in detail in our earlier paper.²² From our data we determined the effective c.m. diffusion coefficient D for each $N \in [20, 80]$ for different values of L . For instance, for $N=30$ we considered the cases $L \in \{60, 90, 120, 150, 180, 210, 240\}$, where the unit of length is given by the Lennard-Jones parameter σ (and the unit of time by τ_{LJ}).²² For every N , we examined the behavior of D as a function of $\ln(L/R_g)$ and found that the behavior is indeed linear. To estimate the exponent ν_D in terms of the effective diffusion coefficients, we chose cutoff values $L_{\text{cut}} \in \{10^2, 10^3, 10^4, 10^5, 10^6\}$, and extrapolated a value $D(L_{\text{cut}}/R_g)$ for each chain size and cutoff. If the data complied with Eq. (34), we should, when plotting $D(R_g/L_{\text{cut}})$

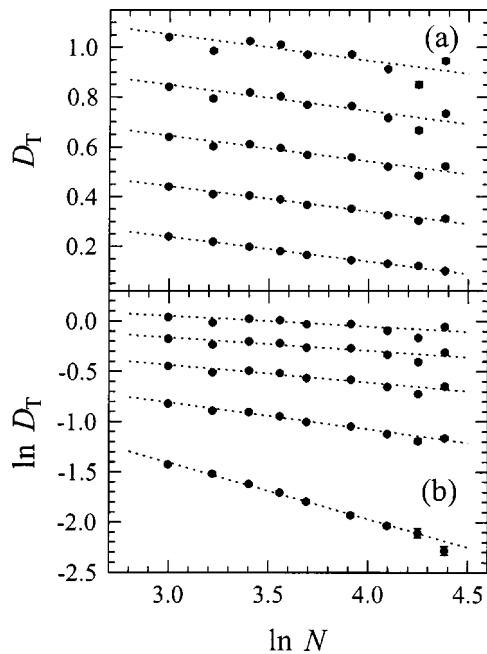


FIG. 1. The dependence of D on N for different cutoffs L_{cut} . The lines correspond to $L_{\text{cut}} \in \{10^2, 10^3, 10^4, 10^5, 10^6\}$ from bottom to top. (a) The diffusion coefficient presented vs $\ln N$. (b) The same data but now $\ln D$ given as a function of $\ln N$. Adapted from Ref. 22.

versus $\ln N$, obtain a set of equally spaced straight lines. Each line would correspond to a certain cutoff, and the lines should all have the same slope A .

Figure 1 shows that this indeed holds within the statistical uncertainties of our data. Moreover, a quantitative comparison with Eq. (34) yields a prediction $D = 0.1\sigma^2\tau_{\text{LJ}}^{-1} \ln(L/R_g)$. Our numerical data also suggest that $D = 0.1\sigma^2\tau_{\text{LJ}}^{-1} \ln(L/R_g)$, in excellent agreement with our analytical result for Zimm model. Most important, Fig. 1 confirms the prediction of logarithmic scaling of D with N , which means that $\nu_D = 0$. To quantify this, we can extract the exponent ν_D from $\ln D(L_{\text{cut}}/R_g)$ versus $\ln N$: for large values of L , we should have $\ln D \sim -\nu_D \ln N$. The results in Fig. 1 show that ν_D decreases steadily with L as it should. For the largest L_{cut} studied here, we find $\nu_D \approx 0.05 \pm 0.05$.

The analysis above reveals the reason for the suggested breakdown of scaling.^{20,21} While the result $x=2$ is correct, as verified here, the results in the previous studies for ν_D are incorrect because the exponent has been extracted without proper consideration of the finite-size effects.³⁶ Thus, we can conclude that dynamical scaling holds for 2D polymers with $x=2$, $\nu=3/4$, and $\nu_D=0$. These are clearly in full agreement with our scaling arguments given in Sec. II, and with the results presented in Sec. III B

V. DISCUSSION

In conclusion, we have studied polymer dynamics in general dimensions using the Zimm model as a starting point. In this model the hydrodynamic interactions are assumed to be governed by the Stokes equation. Using simple scaling arguments for hydrodynamic equations, we have found that the chain diffusion scaling exponent ν_D is given by $\nu_D = \nu(d-2)$. From this equation it follows that the dy-

namical scaling exponent is given by $x=d$. This means that, in particular, in the 2D case ν_D is effectively zero, which explains the anomalous numerical results of the previous studies.^{20,21} To further support this, we have approached the issue more rigorously and calculated analytically the chain diffusion coefficient in general dimensions, and especially the scaling function related to this quantity. Our results reveal that the scaling relation Eq. (10) for ν_D holds also for $1 \leq d \leq 4$. For dimensions higher than 4, we recover the mean-field results given by the Rouse theory, which neglects hydrodynamic interactions. Thus, the Rouse theory becomes valid for $d \rightarrow 4$, which is also the upper critical dimension for static scaling in polymer physics.³² On the other hand, the physically relevant 2D and 3D cases are governed by the Zimm model, and thus the hydrodynamic interactions are relevant for real polymers. In particular, for $d=2$ our analytic results show that D depends logarithmically on the quantity L/R_g . The logarithmic term in L is physically important since it guarantees the positiveness of the diffusion coefficient for all relevant values of N and L . It is also important because it guarantees the well-defined thermodynamic limit for the velocity field through a finite bulk free energy density. These theoretical results together with extensive numerical simulations considering finite-size effects have allowed us to solve the controversy regarding the dynamical scaling of dilute polymer solutions in 2D with full hydrodynamic interactions.

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- ³⁶One can also write a general finite-size scaling form for $S(k, t)$ following Ref. 16 to include the L dependence of D . To the leading term in R_g/L this gives $x=d$, as given by Eq. (11).