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Monte Carlo Renormalization Group Calculations for Polymers

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A simple method based on Wilson's renormalization group ideas is applied to calculate the dynamical critical exponent z for polymer chains in different dynamical regimes. It is shown that the Doi–Edwards reptating chain does not belong to the same dynamical universality class as the Rouse chain. The earlier results based on $\epsilon(4 - d$, $d \sim$ space dimensionality) expansion for chains with excluded volume effect are recovered without any ϵ expansion. When combined with the Monte Carlo techniques, this method results in a simple scheme for calculating the static and dynamic exponents for a polymer chain with a prescribed dynamics. Numerical results suggest that the slithering snake model of Wall and Mandel for the dynamics is in a different dynamic universality class than the Rouse chain.

KEY WORDS: Monte Carlo; renormalization group; dynamical exponent; polymer entanglements.

1. INTRODUCTION

The theoretical description of the transport properties of polymers in good solutions has attracted considerable attention in the past.(1) At infinite dilution the problem reduces to that of a single polymer chain in a good solvent. In this (Zimm) limit there is an interplay between the excluded volume and the hydrodynamic interactions. As the polymer concentration increases both the excluded volume and the hydrodynamic interactions get progressively screened. When these interactions are completely screened, the dynamics of the polymer is due to the connectivity of the chain only. This case is called the Rouse dynamics. When the polymer concentration is increased further, one is in the entanglement regime where the chain is assumed to possess reptationlike dynamics.(2–4)

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There are several treatments in the polymer literature to describe the dynamical aspects of polymer chains in solutions using the dynamical critical exponent, z. This exponent is defined according to the dynamic scaling hypothesis: if lengths are scaled by a factor of b then time scales by a factor of b^z. Once the significance of z is established in the context of polymer dynamics, then the various theoretical techniques to calculate z for systems undergoing critical phenomena can be employed for polymer problems. This has indeed been carried out by the earlier researchers(5–8) for the single-chain problem. For the case of a single chain in good solution, the characteristic time τ of the relaxation modes depends on the contour length of the chain (L) as $\tau \sim L^{z\nu}$, where ν is the end-to-end distance (R) exponent, $R \sim L^{\nu}$. Originally, de Gennes(5) conjectured that $z = d$ (the dimensionality of space) for the non-free-draining limit whether or not excluded volume forces are present. In the free-draining limit with fully developed excluded volume forces (not realizable in practice) de Gennes predicted that $z = 2 + 1/\nu$.

In order to confirm the phenomenological predictions of de Gennes, Jasnow and Moore(6) performed a dynamical renormalization group calculation to calculate z using an ϵ $(= 4 - d)$ expansion. Their value of z (calculated up to first order in ϵ) agreed with de Gennes' prediction for the free-draining case, although there was no agreement for the non-free-draining limit. A similar renormalization group calculation was carried out by Al-Noaimi *et al.*,(7) whose results correct up to first order in ϵ agreed with de Gennes' predictions for both free-draining and non-free-draining limits. Recently Oono and Freed(8) developed a chain configuration space renormalization group method for a self-avoiding chain with unaveraged hydrodynamic interactions. Using a particular coarse-graining procedure, they presented calculations of z to order ϵ. With their procedure for coarse graining, Oono and Freed also obtained the value of z for all orders of ϵ and the results agreed with the predictions of de Gennes for both non-free-draining and free-draining limit. All these theoretical treatments involve explicit coarse-graining (blocking) schemes and are technically complex.

We describe a simple scheme for calculating z for a polymer chain in any dynamical regime without any explicit coarse-graining procedure or ϵ expansion.

2. METHOD

Consider a polymer chain with contour length L_1, whose end-to-end distance is denoted by $R(L_1)$. We now construct a renormalization group (blocking) transformation so that all lengths in the problem are reduced by a scale factor b. Therefore the end-to-end distance of the blocked chain is $R(L_1)/b$. Wilson's renormalization group method(9) to calculate the static exponent ν (in polymer context) is basically to compare the end-to-end distance of an unblocked chain with that of the blocked chain and to find the corresponding contour lengths when the end-to-end distances are equal for an arbitrary choice of b. Our aim is thus to find two values of L, L_1 and L_2, such that $R(L_1)/b = R(L_2)$ where $R(L_2)$ denotes the end-to-end distance of an unblocked chain of contour length L_2. Since the exponent ν is defined by the relation $R \sim L^{\nu}$, it follows that $\nu = \ln b / \ln(L_1/L_2)$. Clearly this procedure is identical to scaling. However, if one considers a more complicated situation with additional variables in the system (e.g., with dynamics), the simple identification of the above method with scaling does not hold and it becomes necessary to keep track of the renormalization of all the variables.

The method for the calculation of the dynamical critical exponent z is similar to that in the static case except that we now consider the time-dependent correlation function, $\langle [\mathbf{R}(L,t) - \mathbf{R}(0,0]^2\rangle$ for a chain with contour length L, where $\mathbf{R}(0,0)$ is the position vector of one end of the chain at some conveniently chosen reference time zero, $\mathbf{R}(L,t)$ is the position vector of the end of the chain at time t, and $\langle [\mathbf{R}(L,0) - \mathbf{R}(0,0)]^2\rangle = R^2(L)$. According to the dynamic scaling hypothesis, if length is scaled by a factor of b, then time scales by a factor of b^z. If a chain of contour length L_1 is blocked such that all lengths in the problem have been reduced by a factor of b, then we expect from dynamic scaling that the original time scale, t_1, is reduced to t_1/b^z. Our method of finding z has two steps. The first is to find L_2 and L_1 so that $R(L_2)$ is equal to $R(L_1)/b$ for an arbitrary choice of b. The second is to compare the time dependencies of $\langle [\mathbf{R}(L_1,t) - \mathbf{R}(0,0)]^2\rangle$ and $\langle [\mathbf{R}(L_2,t) - \mathbf{R}(0,0)]^2\rangle$ and to find the times such that the time-dependent correlation functions match. In other words we search for two times t_1 and t_2 such that

$$\frac{\left\langle \left[\mathbf{R}(L_2,t_2) - \mathbf{R}(0,0)\right]^2\right\rangle}{\left\langle R^2(L_2)\right\rangle} = \frac{\left\langle \left[\mathbf{R}(L_1,t_1\,;b) - \mathbf{R}(0,0;b)\right]^2\right\rangle}{\left\langle R^2(L_1\,;b)\right\rangle} \tag{1}$$

where $\langle R^2(L_1,b)\rangle = R^2(L_1)/b^2$. The numerator on the right-hand side of Eq. (1) is the value of the correlation function $\langle [R(L_1,t_1) - R(0,0)]^2\rangle$ after performing the above-mentioned blocking once. We can then determine z since $t_2 = t_1/b^z$. This method is illustrated below for several model dynamics of polymer chains.

3. ROUSE–ZIMM DYNAMICS

Consider a chain with full excluded volume and hydrodynamic interactions between its monomers. Combining the fluctuation–dissipation theorem and the Langevin equation describing such a chain, the time-dependent correlation function is given by[10]

$$\left\langle [\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2 \right\rangle = \int_{-\infty}^{\infty} \frac{dq}{\pi} \frac{l_1(q)}{q^2} \left\{ 1 - \cos[q(s-s')] \times \exp\left[- \frac{3k_B T D(q) q^2 |t-t'|}{l_1(q)} \right] \right\}$$

$$l_1(q) = B(\nu) q^{1-2\nu}$$

$$B(\nu) = \frac{\pi \nu A(\nu)}{\Gamma(1-2\nu)\cos(\pi\nu)} \tag{2}$$

$$A(\nu) = 0.677(wl)^{1-\nu}$$

where $\mathbf{R}(s,t)$ is the position vector of the chain at arc length s and time t, $D(q)$ is the mode-dependent diffusion constant, l is the Kuhn step length, w is the strength of the excluded volume interaction,[11] $k_B T$ is the Boltzmann constant multiplied by the temperature, and Γ is the gamma function.

3.1. Non-Free-Draining Limit

In this limit, the hydrodynamic interaction between the various beads of the chain dominates over the frictional force arising from various beads rubbing against the solvent. Now $D(q)$ is given by

$$D(q) = C(\nu) q^{\nu - 1}$$

$$C(\nu) = \frac{\Gamma(1-\nu)\cos[(1-\nu)\pi/2]}{\eta_0 [6\pi^3 A(\nu)]^{1/2}} \tag{3}$$

where η_0 is the solvent viscosity. Substitution of Eq. (3) into Eq. (2) yields for the normalized time correlation function for the end-to-end distance vector

$$\frac{\left\langle [\mathbf{R}(L,t) - \mathbf{R}(0,0)]^2 \right\rangle}{\left\langle R^2(L) \right\rangle} = \frac{2\nu L^{-2\nu}}{\Gamma(1-2\nu)\cos(\nu\pi)} \int_0^{\infty} dq\, q^{-(1+2\nu)} \times \left\{ 1 - \cos(qL) \exp\left[- \frac{3k_B T C(\nu)}{B(\nu)} q^{3\nu} t \right] \right\} \tag{4}$$

We now apply the method presented in Section 2 to Eq. (4). Let us choose L_1 and L_2 so that the static correlation lengths match, $R(L_1)/b = R(L_2)$ where $b = (L_1/L_2)^{\nu}$. It therefore follows from Eqs. (1) and (4) that we search for t_1 and t_2 satisfying the equation

$$L_1^{-2\nu}\int_0^\infty dq\, q^{-(1+2\nu)}\left\{1-\cos(qL_1)\exp\left[-\frac{3k_BTC(\nu)}{B(\nu)}q^{3\nu}t_1\right]\right\}$$

$$= L_2^{-2\nu}\int_0^\infty dq\, q^{-(1+2\nu)}\left\{1-\cos(qL_2)\exp\left[-\frac{3k_BTC(\nu)}{B(\nu)}q^{3\nu}t_2\right]\right\} \quad (5)$$

where $L_2 = L_1 b^{-1/\nu}$. Substitution of the dynamic scaling criterion, $t_2 = t_1/b^z$ in Eq. (5) yields

$$\int_0^\infty dq\, q^{-(1+2\nu)}\left\{1-\cos(qL_1)\exp\left[-\frac{3k_BTC(\nu)}{B(\nu)}q^{3\nu}t_1\right]\right\}$$

$$= b^2\int_0^\infty dq\, q^{-(1+2\nu)}\left\{1-\cos\left(\frac{qL_1}{b^{1/\nu}}\right)\exp\left[-\frac{3k_BTC(\nu)}{B(\nu)}\frac{q^{3\nu}t_1}{b^z}\right]\right\}$$

$$= b^{2(1-z/3)}\int_0^\infty dx\, x^{-(1+2\nu)}$$

$$\times\left\{1-\cos\left[\frac{xL_1}{b^{(1/\nu)(1-z/3)}}\right]\exp\left[-\frac{3k_BTC(\nu)}{B(\nu)}x^{3\nu}t_1\right]\right\} \quad (6)$$

The right-hand side of Eq. (6) is equal to the left side only if $z = 3$. Note that the value of z in the non-free-draining limit is independent of the exponent ν, i.e., $z = 3$ for both good and theta solutions.

3.2. Free-Draining Limit

In the free-draining (Rouse) limit both the hydrodynamic and excluded volume interactions are completely screened out so that

$$D(q) = \frac{l}{\zeta}, \quad \nu = \frac{1}{2}, \quad l_1(q) = l \quad (7)$$

where ζ is the bead friction coefficient. Substituting Eq. (7) into Eq. (2) gives

$$\frac{\langle[\mathbf{R}(L,t)-\mathbf{R}(0,0)]^2\rangle}{\langle R^2(L)\rangle} = \frac{2}{\pi L}\int_0^\infty \frac{dq}{q^2}\left[1-\cos(qL)\exp\left(-\frac{3k_BTq^2t}{\zeta}\right)\right] \quad (8)$$

Choosing L_1 and L_2 so that the static correlation lengths match, $R(L_1)/b = R(L_2)$ $[b = (L_1/L_2)^{1/2}]$, the dynamical exponent z is obtained from the equality

$$\begin{aligned}
&\int_0^\infty \frac{dq}{q^2}\left[1 - \cos(qL_1)\exp\left(-\frac{3k_BT}{\zeta}q^2t_1\right)\right] \\
&\quad = b^2\int_0^\infty \frac{dq}{q^2}\left[1 - \cos\left(\frac{qL_1}{b^2}\right)\exp\left(-\frac{3k_BTq^2t_1}{\zeta b^z}\right)\right] \\
&\quad = b^{(2-z/2)}\int_0^\infty \frac{dq}{q^2}\left[1 - \cos\left(\frac{qL_1}{b^{2-z/2}}\right)\exp\left(-\frac{3k_BTq^2t_1}{\zeta}\right)\right] \qquad (9)
\end{aligned}$$

The equality in Eq. (9) is valid only if $z = 4$.

3.3. Self-Avoiding Rouse Chain

This model (with no hydrodynamic interaction) has been extensively studied in the literature, although this limit cannot be realized experimentally. The time correlation function for this model is

$$\begin{aligned}
&\frac{\langle \mathbf{R}(L,t)\cdot\mathbf{R}(L,0)\rangle}{\langle R^2(L)\rangle} \\
&\quad = \frac{(2\nu - 1)L^{-2\nu}}{\Gamma(1-2\nu)\cos(\pi\nu)}\int_0^\infty \frac{dq}{q^{1+2\nu}}\left\{1 - \cos(qL)\exp\left[-Dq^{1+2\nu}t\right]\right\} \qquad (10)
\end{aligned}$$

where D is the effective diffusion constant. Let us choose L_0 and L_1 so that the static matching exists, $R(L_0)/b = R(L_1)$ where $b = (L_0/L_2)^\nu$. It therefore follows upon substitution of the dynamic scaling criterion, $t_1 = t_0/b^z$, that z is given by the equality

$$\begin{aligned}
&\int_0^\infty \frac{dq}{q^{(1+2\nu)}}\left[1 - \cos(qL_0)\exp(-Dq^{1+2\nu}t_0)\right] \\
&\quad = b^{[2-z+z/(1+2\nu)]}\int_0^\infty \frac{dq}{q^{1+2\nu}} \\
&\qquad \times\left\{1 - \cos\left[\frac{qL_0}{b^{[1/\nu - z/(1+2\nu)]}}\right]\exp\left[-Dq^{1+2\nu}t_0\right]\right. \qquad (11)
\end{aligned}$$

Therefore, $z = 2 + 1/\nu$.

4. DOI–EDWARDS DYNAMICS

The time correlation function for the end-to-end distance of the Doi–Edwards primitive chain is given by[4]

$$\frac{\left\langle \left[\mathbf{R}(L,t)-\mathbf{R}(0,0)\right]^2\right\rangle}{\left\langle R^2(L)\right\rangle}$$
$$=1+\frac{2Dt}{L^2}+\sum_{p=1}^{\infty}\frac{4}{p^2\pi^2}\cos(\pi p)\left[1-\exp\left(-\frac{D\pi^2p^2t}{L^2}\right)\right] \qquad (12)$$

where D is the curvilinear diffusion constant. Choosing L_1 and L_2 such that $L_2 = L_1/b^2$ and using $t_2 = t_1/b^z$ we get $z = 4$ from

$$\frac{2D_0t_1}{L_1^3}+\sum_{p=1}^{\infty}\frac{4\cos(\pi p)}{p^2\pi^2}\left[1-\exp\left(-\frac{D_0\pi^2p^2t_1}{L_1^3}\right)\right]$$
$$=\frac{2D_0t_1b^{6-z}}{L_1^3}+\sum_{p=1}^{\infty}\frac{4\cos(\pi p)}{p^2\pi^2}\left[1-\exp\left(-\frac{D_0\pi^2p^2t_1b^{6-z}}{L_1^3}\right)\right] \qquad (13)$$

where we have used the molecular weight dependence of D as $D \equiv D_0/L$.

5. WALL–MANDEL MODEL[12]

Banavar and Muthukumar[13] have recently considered z for the dynamics generated by the "slithering snake" model of Wall and Mandel. They have studied the statistics of chains of 64 and 32 steps by generating ten million configurations in both three and two dimensions. To ensure statistically independent sampling, every thirtieth configuration was used for calculating averages. The values of ν and z obtained by the above method are given in Tables I and II respectively. The value of z seems to have a systematic dependence on time t_1 thus necessitating the study of time correlation functions at sufficiently long times.

The values of z for different dynamical regimes for $d = 3$ are summarized in Table III. In conclusion Doi–Edwards dynamics belongs to the

Table I.

d	N	R^2	ν
3	64	156.33 ± 1.49	
	32	68.26 ± 0.48	0.598 ± 0.012
2	64	400.93 ± 4.51	
	32	143.44 ± 1.00	0.742 ± 0.014

Table II.

	t_2	t_1	z
$d=3$	30	109.7	3.13
	60	226.3	3.20
	120	459.9	3.24
	180	695.7	3.26
	240	938.8	3.29
	330	1313.5	3.33
	457	1821.3	3.34
	720	2927.1	3.38
	∞		~3.42
$d=2$	30	122.81	2.74
	90	377.26	2.79
	240	1020.75	2.81
	330	1404.63	2.82
	450	1932.99	2.83
	600	2589.47	2.84
	810	3513.46	2.85
	∞		~2.87

Table III.

Dynamics	z
Zimm: chain connectivity with hydrodynamic interaction in either theta or good solution	3
Rouse with excluded volume effect but not hydrodynamic interaction	$2 + 1/\nu$
Wall–Mandel model	3.4
Rouse: no hydrodynamic and excluded volume effects	4
Doi–Edwards: reptation of primitive chain	6

same dynamical universality class as that of Rouse dynamics while Wall–Mandel dynamics does not.

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