Statics and dynamics of the freely jointed polymer chain with Lennard-Jones interaction

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Using a dynamic Monte Carlo method we investigated the thermodynamics of static and time-dependent properties of the freely jointed polymer chain with Lennard-Jones type intramolecular forces. The Θ temperature is calculated to k_B θ/ε = 3.70 ± 0.01 (ε is the Lennard-Jones energy parameter). We give estimates for the equilibrium values of end-to-end distances, radii of gyration, and densities for chains consisting of up to N = 63 segments and for various temperatures. The detailed structure of the extended coil state (T > Θ) and the dense globular state (T < Θ) are demonstrated by their average internal distances and their structure functions. The results seem to confirm the predicted scaling laws. Especially we found that for T = Θ the mean size of the coil is ~ N^{1/3} but the detailed structure is different from a random walk shape. Although the specific heat exhibits a maximum below the Θ temperature, the finite size effects are too serious to confirm a relation to the collapse transition. The dynamics of our Monte Carlo method simulate the Rouse model. The density correlation function and the associated relaxation time are calculated. The results are consistent with dynamic scaling predictions. The segment correlation function exhibits the initial ~ t^{1/2} behavior and the diffusional behavior ~ t at large times.

I. INTRODUCTION

The effects of intramolecular forces on the thermodynamics and statistics of a single polymer chain in dilute solution have attracted considerable attention in the past.1-25 In particular, computer simulations have been used to generate on-lattice26-27 or off-lattice28 self-interacting walks simulating polymer configurations.

The intramolecular forces are usually assumed to be the van der Waals type consisting of hard core repulsion and longer-range attraction. At sufficiently high temperatures the repulsive forces dominate, leading to a swollen polymer coil. At the so-called θ temperature,1 a balance can be achieved between repulsive and attractive forces. It is commonly supposed that at the θ point the polymer has its random coil dimension. If at lower temperature the attraction becomes sufficiently large the polymer collapses to a globule whose density is close to that of a dry polymer.24

Although considerable progress has been made in recent years, the present state of our knowledge regarding the collapse transition and the globule phase is by no means as advanced as for the swollen state.25-27

In the work described here we used the Monte Carlo method to investigate the various thermodynamic states of a single polymer. Avoiding the geometrical restrictions of lattice polymers14-25 we considered the freely jointed chain first proposed by Kuhn.1,24 This model assumed a chain molecule as a linear succession of bonds of fixed length with uncorrelated orientations. A bond is understood to represent a segment of a real chain. Each segment consists of an average number1b of skeletal atoms. The average length of the segments that fixes our length scale should not depend on temperature and has to be chosen larger than the hard core distance of the intramolecular forces. This short-range repulsion takes into account the limited flexibility of the real polymer. The longer-range attraction between the bonds resulting from the mutual interaction of polymer and solvent is taken into account by a Lennard-Jones potential (Sec. II) whose depth measures the energy of polymer–polymer interaction relative to that of polymer–solvent interaction.

So far, investigations on the freely jointed polymer chain have been performed in the presence of pure hard core interactions only26-27 which supply information on the configurational properties at high temperatures.

The Monte Carlo technique used in the present work may be characterized as dynamic and has been applied recently to the freely jointed chain with excluded volume potential.27 Similar dynamic techniques have been performed on lattice polymers28-29 and Ising models.30 The dynamics produced by these Monte Carlo techniques27-30 simulate the so-called free-draining limit (Rouse model31-34) where all hydrodynamic effects coupling distant segments are neglected; this corresponds to an extreme case, which is probably not often realized in practice. Presumably, in the globule state when the density of segments is high enough, hydrodynamic effects can be neglected.

In Sec. II we describe the model and the Monte Carlo technique, and outline the means by which the quantities of interest may be estimated. The reliability of these estimates is discussed. In Sec. III the Monte Carlo results are presented in three subsections, concerning the calculation of the θ temperature, the static properties, and the dynamics.

II. POLYMER MODEL AND MONTE CARLO TECHNIQUE

The freely jointed polymer chain consists of N + 1 beads of infinitesimal diameter indexed from 1 to N + 1, which are connected by N bonds of length l = 1 (Fig. 1). The angles between neighboring bonds are not restricted. The beads interact in pairs according to a Lennard-Jones potential

\[ \frac{k_B T}{\varepsilon} = 3.70 \pm 0.01 \]

where \( \varepsilon \) is the Lennard-Jones energy parameter.
The local potential acting on the $j$th bead at position $r_j$ or $r_j'$ is given by

$$E_j = \sum_{r_{(j)}} U_{ij}, \tag{7a}$$

$$E'_j = \sum_{r_{(j)}} U_{ij}, \tag{7b}$$

respectively. As a consequence of Eq. (6) the transition probability is determined only up to a parameter $\tau_s$ which determines the time scale of the dynamic processes. $\tau_s$ is the relaxation time of a single free bead interacting with the heat bath. For a detailed discussion of this scheme we refer to Ref. 30. Here we merely summarize the main points.

Following the usual procedure we use the transition probability

$$\tau_s W_j (r_j') = \begin{cases} \exp[\beta(E_j' - E_j)], & \text{if } E_j' - E_j < 0, \\ 1, & \text{otherwise}. \end{cases} \tag{8}$$

For $\tau_s W_j < 1$, one flips the $j$th bead if $\tau_s W_j$ exceeds a random number between 0 and 1. If $\tau_s W_j = 1$, the $j$th bead is also moved. In this manner a sequence of new configurations is generated. Since the system tends to equilibrium by construction, there is a correspondence between the time lapse and the number of configurations. So that the time unit does not depend on the chain length $N$, this unity is defined as a sequence in which, on the average, any bead has the possibility to move once.

The first summation corresponds to the total number of ways that the system can flip into the state $\{r_1, \ldots, r_{N+1}\}$, whereas the second summation corresponds to the total number of ways the system can flip out of the state $\{r_1, \ldots, r_{N+1}\}$. The predictions of Eq. (2) depend upon the choice for the transition probability $W$. A reasonable constraint is the requirement that $W$ has such a form that it is capable of bringing the stochastic polymer model to the same equilibrium as that of the corresponding static model.

In equilibrium the left-hand side of Eq. (2) is by definition equal to zero. This condition corresponds to the principle of detailed balance, which asserts that

$$W_j (r_j) P_0 (r_1, \ldots, r_j, \ldots, r_{N+1}) = W_j (r'_j) P_0 (r_1, \ldots, r_j, \ldots, r_{N+1}), \tag{3}$$

where $P_0 (r_1, \ldots, r_{N+1})$ denotes the probability of finding the polymer configuration $\{r_1, \ldots, r_{N+1}\}$ when the system is in equilibrium. Observing that

$$P_0 (r_1, \ldots, r_{N+1}) = e^{-\beta E}, \quad \beta = 1/k_B T, \tag{4}$$

$$E = \sum_{i=1}^N \sum_{r_{(i)}} U_{ij}, \tag{5}$$

Equation (3) leads to

$$W_j (r_j')/W_j (r_j) = e^{\beta E_j - \beta E'_j}. \tag{6}$$
\[ \rho_R (t) = \frac{(N+1)}{S_N^q (t)} , \quad \text{(12)} \]

the internal energy [Eqs. (1) and (5)]
\[ E(t) = \sum_{i=1}^{N} \sum_{j=N+1}^{N} U_{ij} (t) , \quad \text{(13)} \]

the structure function
\[ \langle S(k,t') \rangle (0) = \frac{1}{N+1} \sum_{i=1}^{N+1} \exp[i k \cdot r_i(t)] \left| \right|^2 \quad \text{(14)} \]

the segment-correlation function
\[ \langle G_{ij}(t') \rangle (t) = \left| r_i(t) - r_j(t+t') \right|^2 \quad \text{(15)} \]

or the corresponding dynamic structure function
\[ \langle S(k,t') \rangle (t) = \left| \frac{1}{N+1} \sum_{i=1}^{N+1} \sum_{j=N+1}^{N} \exp[i k \cdot (r_i(t) - r_j(t+t'))] \right|^2 \quad \text{(16)} \]

Following our recent investigations where we have demonstrated that in our dynamic simulation method the nonergodicity is in practice not a serious problem, one may define time averages as
\[ \langle A \rangle = \frac{1}{t_m-t_n} \int_{t_n}^{t_m} A(t) \, dt , \quad \text{(17)} \]

which should provide a reliable estimate for the canonical ensemble average of the model system. \( A(t) \) may be one of the defined quantities, Eqs. (9)–(16). The integration should be performed on equilibrium states of \( A(t) \) and over an interval \( t_m - t_n \) which is much larger than correlation times of the order \( -N^2 \):
\[ t_m - t_n \gg N^2 . \quad \text{(18)} \]

For a detailed discussion of this problem we refer to Ref. 30.

From the fluctuations of the internal energy \( \langle E \rangle \) [Eq. (13)] we may estimate the specific heat
\[ \frac{C}{k_B} = \left( \frac{1}{k_B T} \right)^2 \left( \int_{t_m}^{t_n} dt \, \langle E(t) - \langle E \rangle \rangle^2 \right) \quad \text{(19)} \]

similarly the density-correlation function
\[ \phi_{\rho \rho}(t) = \frac{t_m-t_n}{t_m-t_n} \left( \int_{t_n}^{t_m} dt' \langle \rho(t') - \langle \rho \rangle \rangle \langle \rho(t+t') - \langle \rho \rangle \rangle \right) \times \left( \int_{t_n}^{t_m} dt' \langle \rho(t') - \langle \rho \rangle \rangle^2 \right) \quad \text{(20)} \]

and the associated equilibrium relaxation time
\[ \tau_{\rho \rho} = \int_{0}^{t_m-t_n} dt \, \phi_{\rho \rho}(t) , \quad \text{(21)} \]

which characterize the decay of density fluctuations in thermal equilibrium states. In addition to this relaxation time we may also introduce the nonequilibrium relaxation time which characterize the approach to thermal equilibrium. Suppose at time \( t = 0 \) a sudden change in temperature \( \Delta T \) is performed; then we describe the relaxation of density by the function
\[ \phi_{\rho \rho}^{\Delta T}(t) = \left( \frac{\rho(t) - \rho(t)}{\langle \rho(0) - \langle \rho \rangle \rangle} \right) , \quad \text{(22)} \]

and the associated relaxation time is
\[ \tau_{\rho \rho}^{\Delta T} = \int_{0}^{t_m} dt \, \phi_{\rho \rho}^{\Delta T}(t) . \quad \text{(23)} \]

So far we have explained how we estimate the quantity of interest using the Monte Carlo method and have given the appropriate definitions. In our recent work we asserted the accuracy of our Monte Carlo method as applied to static quantities. From the good agreement with predicted results, we conclude that our Monte Carlo technique provides reliable estimates for dynamic quantities also. Of course, also detailed statistical tests have been performed with the present data to ensure their accuracy.

## III. RESULTS AND DISCUSSION

### A. The \( \theta \) temperature

Here we present the calculation of the \( \theta \) temperature for the freely jointed polymer chain with the Lennard-Jones interaction defined by Eq. (1). This interaction consists of a hard core repulsion and a longer-range attraction. At some intermediate temperature a balance can be achieved between repulsive and attractive forces. Traditionally, in polymer physics this temperature is called the \( \theta \) temperature (for a fluid this is the Boyle temperature) and has two definitions:

(i) The point at which an isolated polymer molecule behaves as a random coil, e.g., the endpoint separation diverges according to
\[ \lim_{N \to \infty} \left( \frac{R_N^2}{N} \right) = \text{const.} \quad \text{(24)} \]

for an infinite long polymer. Commonly this definition is replaced by a similar one where the endpoint separation at the \( \theta \) point is supposed to be exactly that of a random coil \( \langle R_N^2 \rangle = f N \) which occurs if intramolecular forces are completely neglected. In Sec. III.B we present Monte Carlo results that supply evidence against this assumption: there seems to be a difference between the absence and the average compensation of competing forces.

(ii) The point at which the second virial coefficient of the polymer solution vanishes. Analogously to the virial expansion of real gases this condition leads to the relation
\[ \lim_{N \to \infty} \left( \frac{1}{N^3} \sum_{i=1}^{N} \sum_{j=N+1}^{N} \left[ 1 - \exp \left( - \frac{U_{ij}}{k_B T} \right) \right] \right) \bigg|_{\tau = \theta} = 0 . \quad \text{(25)} \]

The brackets \( \langle \ldots \rangle \) denote the average over all chain configurations in the absence of the potential \( U_{ij} \) (i.e., under restricted random walks). This has been performed by simple sampling Monte Carlo techniques. The average has been taken over up to \( 10^7 \) configurations; of course, detailed tests have been performed with the data to ensure their accuracy. Equation (25) has been solved for various systems up to \( N = 1000 \) (Fig. 2). The temperature at which Eq. (25) holds for finite \( N \) has been called the Boyle temperature \( T_B(N) \) of the polymer chain with
\[ \lim_{N \to \infty} T_B(N) = \theta . \quad \text{(26)} \]

The Boyle temperature is approximately a linear function of \( 1/N \) (Fig. 2),
\[ T_B(N)/\theta \approx 3.4/N + 1 , \quad \text{(27)} \]
FIG. 2. Calculated Boyle temperature [Eq. (25)] for various chain lengths $N$. The extrapolation of the full line to $N \to \infty$ gives the $\theta$ temperature $k_B \theta/\epsilon = 3.70 \pm 0.01$.

where the $\theta$ temperature is extrapolated to the value $k_B \theta/\epsilon = 3.70 \pm 0.01$.

B. Static properties

In Figs. 3–6 the Monte Carlo results for various static quantities of interest are presented.

In Fig. 3 we plotted the $N$ dependence of end-to-end distances, radii of gyration, and density defined by Eqs. (10)–(12). End-to-end distance and radius of gyration have been normalized by their unperturbed values where intramolecular forces are ignored:

$$
\langle R^2 \rangle_0 = l^2 N,
$$

$$
\langle S^2 \rangle_0 = \sigma^2 (\frac{3}{2}N)(N+2)/(N+1),
$$

Since one expects a power law divergence in the presence of interaction and $N \to \infty$ (Refs. 7a and 6),

$$
\langle R^2 \rangle \propto N^{2
\nu},
$$

$$
\langle S^2 \rangle \propto N^{2\nu},
$$

$$
\rho \propto N^{\frac{\nu}{2}},
$$

with $\nu = 0.59$ for $T > \theta$, $\nu = 0.5$ at $T = \theta$ and $\nu = \frac{1}{2}$ for $T < \theta$, it is appealing to plot the quantities in a log-log plot. Although only systems up to $N = 63$ have been investigated the results seem to confirm the predicted asymptotic power laws. It is important to note that at the $\theta$ point, $k_B T/\epsilon = 3.7$, the quantities (29a)–(29c) exhibit the random coil behavior $\sim N$ and $N^{\nu/2}$, respectively: this supports the equivalence of the two definitions of the $\theta$ temperature [Eqs. (24) and (25)]. Moreover, since at

FIG. 3. Temperature dependence and chain length dependence of mean square end-to-end distance $\langle R^2 \rangle$, mean square radius of gyration $\langle S^2 \rangle$, and mean density $\rho$. The broken lines indicate the expected behavior for larger $N$.

FIG. 4. (a) Structure function $S(k)$ vs $q$, where $q = k \cdot N^{\nu}$ and $\nu = 0.59$ for temperature $k_B T/\epsilon = 5$. The symbols represent the results of different values of $N$ (see right-hand notations). The structure function in the intermediate $q$ range is indicated by the line $S(k) = \text{const.} \cdot q^{-1/2}$. (b) Structure function $S(k)$ vs $q = k \cdot N^{\nu/2}$ at the $\theta$ temperature $k_B \theta/\epsilon = 3.7$. For notations compare (a). The line $S(k) = 12q^{-2}$ indicates the structure function in the intermediate $q$ range for the Gaussian case. (c) Structure function $k^2 S(k)$ vs $k$ at and below the $\theta$ temperature for two different chain lengths $N$ denoted below the curves.
finite size effects concerning \( \langle R^2 \rangle \) and \( \langle S^2 \rangle \) seem to be negligible for \( N \geq 30 \) (compare Fig. 3), the coil does not exhibit its random coil dimension (28) at the \( \theta \) point, but

\[
\frac{\langle R^2 \rangle}{\langle R^2 \rangle_0} \bigg|_{\theta = \theta_0} = \frac{\langle S^2 \rangle}{\langle S^2 \rangle_0} = 1.7.
\]

A similar effect has been observed in lattice polymers,19 i.e., self-avoiding walks in which attractive forces between nearest-neighbor segments had been included, where ratios [Eq. (30)] of \( \approx 1.13 \) for simple cubic lattice and \( \approx 1.2 \) for face-centered-cubic lattice has been obtained. Before continuing the discussion of the low-temperature behavior we want to establish our results for \( T \geq \theta \) by presenting the calculations of the structure function \( S(k) \) [Figs. 4(a) and 4(b)]. \( S(k) \) is defined by Eq. (14) with the small moment expansions47

\[
S(k) = 1 - \frac{1}{2} \langle S^2 \rangle_k^3 + O(k^4) \quad (k < \langle S^2 \rangle_{1/2}^{-1/2}),
\]

(31)

and the large moment behavior

\[
S(k) - 1/N \quad (k > \langle S^2 \rangle_{1/2}^{-1/2}).
\]

(32)

In the case of vanishing intramolecular forces it is well known37,37 that

\[
S_0(k) = 12/k^2 N \quad \langle \langle S^2 \rangle_{1/2}^{-1/2} < k < \langle t^2 \rangle,
\]

(33)

and if interactions are present, one expects a power law30

\[
S(k) \propto k^{-1/\nu} N^{-1} \quad \langle \langle S^2 \rangle_{1/2}^{-1/2} < k < \langle t^2 \rangle,
\]

(34)

where \( \nu = 0.59 \). The results presented in Figs. 4(a) and 4(b) exhibit the expected behavior according to Eqs. (31)–(34). The remarkable insensitivity to the number of bonds indicates that even a chain length of \( N = 7 \) is near the asymptotic limiting behavior already as long as distances larger than \( I \) are probed. It is also important to note that the deviation from the ideal coil dimension stated above [Eq. (30)] is obvious [Fig. 4(b)]; in Fig. 4(b) we have drawn the line corresponding to the ideal coil shape given by Eq. (33) for comparison. Similar to Eq. (30) the ratio of unperturbed and perturbed structure functions (33) and (34), respectively, yields the same order of magnitude

\[
\frac{S(k)}{S_0(k)} \bigg|_{\theta = \theta_0} = 2.4 \quad \langle \langle S^2 \rangle_{1/2}^{-1/2} < k < \langle t^2 \rangle.
\]

(35)
When the temperature below the $\theta$ point is decreased, a crossover due to finite size effects between the coil state ($T > \theta$) and the globule state ($T < \theta$) is observed (Fig. 3): the coil dimension shrinks continuously with decreasing temperature. In contrast to the end-to-end distance and the density, the radius of gyration only seems to satisfactorily exhibit the predicted power law $\langle r_{nm}^2 \rangle / \langle S^2 \rangle \sim N^{1/3}$ (Fig. 3). Presumably for much larger $N$ the “collapse transition” becomes more pronounced; but this is outside the scope of the present computer possibilities. The expected asymptotic behavior has been indicated in Fig. 3 by the broken curves. Indeed, the fact that for $T < \theta$ the change to a different polymer state takes place is supported by the structure function [Fig. 4(c)]: at temperatures, $T < \theta$ $S(k)$ exhibits a behavior that is very different from a power law holding at $T \geq \theta$ indicating a “phase transition.” It should be noted that the qualitative features of $S(k)$ at low temperatures seem to be independent of size [compare left- and right-hand parts of Fig. 4(c)].

These aspects of the low-temperature behavior of the present polymer model are supported by the calculated average internal distances (Fig. 5) and the specific heat (Fig. 6). Similar numerical investigations on internal distances\(^24\) and the specific heat\(^4\) have been performed on lattice polymers.

In Fig. 5 we present a $\log-\log$ plot of the mean square internal distances [Eq. (9a)] normalized by the number of bonds by which the $m$th and the $n$th bead are separated. In Fig. 5(a) the effects of temperature and finite chain length on the internal distances are demonstrated. For the sake of simplicity we have restricted the distances between the first and the $n$th bead. The influence of this special choice on the general features is discussed in Fig. 5(b): the effects of the free ends of the chain on the internal distance distribution do not change the qualitative features seen in Fig. 5(a).

It is commonly assumed that at high temperatures ($T > \theta$) the internal distances exhibit a swollen behavior\(^38\)

$$\langle r_{nm}^2 \rangle / |n - m| \sim |n - m|^{-\nu \omega} \quad \text{if} \quad |n - m| > L_c$$

(36a)

($\nu \approx 0.6$) and an ideal behavior

$$\langle r_{nm}^2 \rangle / |n - m| = \text{const.} \quad \text{if} \quad |n - m| < L_c,$$

(36b)

where the “critical chemical distance” $L_c$ is given by

$$L_c \approx \left( \frac{\theta}{T - \theta} \right)^2$$

(36c)

if the Ginzburg criterion of critical phenomena

$$\left( \frac{T - \theta}{\theta} \right)^{\gamma} \gg N^{1/2}$$

(36d)

holds. Comparing these predictions with our calculations [Fig. 5(a)], we do not find agreement. Certainly, one can argue that conditions (36c) and (36d) do not hold for the size of system we investigated and one should find the asymptotic behaviors (36a) and (36b) at larger $N$; our results do not, however, support the conjecture that internal distance are able to change drastically if one investigate larger systems. Moreover, we cannot see evidence that larger systems will exhibit a zero initial slope as predicted by Eq. (36b).

The behavior of $\langle r_{nm}^2 \rangle$ is understood as follows. At short bond distances $|n - m|$, the repulsive forces dominate leading to a swollen short-range part of the chain: $\langle r_{nm}^2 \rangle > |n - m|$ for $|n - m| \lesssim 3$. This picture holds approximately for all temperatures. At larger values of $|n - m|$ the behavior depends strongly on temperature. At temperature $T = \theta$ the repulsive forces swell the coil as far as the intramolecular forces between distant parts of the chain becomes negligible. So at large bond distances $|n - m|$ the chain exhibits ideal behavior $\langle r_{nm}^2 \rangle / |n - m| = \text{const.}$ [compare temperatures $k_B T / \epsilon = 5$ and 3.7 in Fig. 5(a); other similar high temperature curves have been omitted]. At temperature $T < \theta$ the attractive forces become more important; one observes a gradual collapse (coil–globule transition) of the polymer which becomes the more pronounced as the system enlarges.

In Fig. 5(c) we show the temperature dependence of the second-nearest-neighbor and fourth-nearest-neighbor correlations for $N = 15$. The typical high-temperature correlations ($k_B T / \epsilon = 3.7, 1.0$) are isotropic along the chain, whereas the typical low-temperature correlations ($k_B T / \epsilon = 0.16$) are essentially anisotropic along the chain. One only observes a change from the coil state (high temperatures) to the globular state (low temperatures) within the small temperature region, where the specific heat exhibits a maximum (at $k_B T / \epsilon = 0.3$ for $N = 16$; compare Fig. 6). The correlations of the $|n - m|$ th nearest neighbor with $|n - m| > 4$ and for $N = 15$ and $N = 63$ exhibit similar behavior to that shown in Fig. 5(c) and have been omitted for the sake of clarity.
In Fig. 6 the internal energy per bead \( \langle E \rangle / (N + 1) \epsilon \) (13) and the corresponding specific heat per bead \( C / (N + 1) \kappa_B \) (19) have been plotted for various temperatures and for systems of various size, e.g., \( N = 7, 15, 31, 63 \). The specific heat exhibits a maximum at low temperatures which is shifted slightly to higher temperatures with increasing chain length. The finite size effects are too serious to confirm the predicted logarithmic divergence at the \( \theta \) point\(^{34,12} \); but our results are consistent with these predictions. At \( T = 0 \) the specific heat remains finite according to the equipartition law\(^{35} \)

\[
C / (N + 1) \kappa_B \bigg|_{T=0} = 1 - 5/2(N+1),
\]

which is asserted by our calculations (Fig. 6). This supports the reliability of our Monte Carlo calculations at low temperatures.

From numerical studies on lattices there is some evidence for a transition, possibly first order, at a temperature much lower than the \( \theta \) temperature.\(^{35,31} \) It has been proposed\(^{35} \) that this kind of transition and that on Bethe lattices\(^{14,15} \) is related to a liquid–solid transition of the segments. In the present model we found some evidence for such a transition. In our opinion the numerical results support the interpretation that the specific heat maximum is related to the liquid–solid transition.

C. Dynamic properties

Here we shall present dynamic results supplied by the dynamic Monte Carlo method used in the present work. As mentioned above the dynamics presented here simulate the so-called “free-draining limit”\(^{31,34} \) where all hydrodynamic effects are neglected.

In Figs. 7 and 8 we plotted the time dependence of the density correlation function \( \varphi_{dd}(t) \) [Eq. (20)] and the associated equilibrium relaxation time \( \tau_{\varphi} \) [Eq. (21)], respectively. As it is well known,\(^{21,24} \) in the absence of intramolecular forces the density relaxation time exhibits a power law in the asymptotic limit \( N \rightarrow \infty \),

\[
\tau_{\varphi} \propto N^z \quad (T = 0),
\]

which should also hold at the \( \theta \) point. If intramolecular forces are present the relaxation time exhibits a power law according\(^{35,34} \)

\[
\tau_{\varphi} \propto N^{z*} \quad (T > \theta),
\]

where the universal dynamic scaling exponent is proposed to be \( z = 2 + 1/\nu \) by means of phenomenological arguments\(^{32} \) which is consistent with predictions of an \( \epsilon = 4 - d \) expansion \( z = 4 - \epsilon/4 + \cdots \) (\( d \) is the dimensionality).\(^{34} \) Our results (Fig. 8) are consistent with the predictions (38) and (39); but investigations on larger systems have to be performed in order to ensure the accuracy of the proposed exponent \( z \).

Our calculations have supported evidence that Eq. (39) is valid only at \( T > \theta \). At temperatures below the \( \theta \) point the decay of density fluctuations is much faster than for \( T \geq \theta \), e.g., the relaxation time \( \tau_{\varphi} \) at \( T \leq \theta \) is substantially shorter than at \( T > \theta \): the global density is high enough to damp out the fluctuations very rapidly. From the data obtained in our calculations it is not clear whether or not a power law exists.

We have obtained more precise results by calculating the segment correlation function [Eq. (15)] (Fig. 9) which is of particular interest for quasielastic neutron scattering.\(^{35} \) In incoherent scattering \( (n = m) \) the results confirm the predicted\(^{35} \) initial \( -t^{1/2} \) behavior of segmental diffusion and the diffusional behavior \( -t \) for the center of gravity of the molecule at large times. In coherent scattering \( (n \neq m) \) the segment correlation function exhibits the same diffusional behavior \( -t \) at large times and a time-independent initial behavior.

IV. CONCLUDING REMARKS

It is clear that the freely jointed chain with Lennard–Jones interaction should not be regarded as a model that faithfully simulates real polymers. Also the dynamics introduced to calculate equilibrium quantities does not reproduce the time-dependent properties of real sys-

\[\text{FIG. 8. Temperature dependence and chain length dependence of the relaxation time \( \tau_{\varphi} \) [Eq. (21)] associated with \( \varphi_{dd}(t) \) shown in Fig. 7. The broken lines indicate the expected behavior for larger \( N \).}\]
systems. However, the model allows us to study various phenomena exhibited by real systems (e.g., coil state, collapse transition, globule state, etc.). Since the alternative analytical approaches are often still highly phenomenological and are restricted to studying only certain aspects, studies of the present model by Monte Carlo methods can be regarded as complementary and are expected to offer a better understanding of the various thermodynamic properties of a single polymer in dilute solution.

By Monte Carlo methods we have estimated the $\theta$ temperature of the present model $k_BT/\epsilon = 3.70 \pm 0.01$ and found consistency between their two definitions. Our results are consistent with the predicted scaling laws of various quantities as end-to-end distance, radius of gyration, density and structure function at temperature $T \geq \theta$. Especially, we found that for $T = \theta$ the mean size of the polymer coil exhibits the power law of the ideal random coil $\sim N^{3/2}$, but the detailed structure is different from the commonly supposed ideal random walk shape. The question if this is an artefact of the present model (e.g., the average length of the segments is assumed to be temperature independent) requires further investigations.

Due to finite size effects the predicted phase transition from the extended coil state to the dense globule state is replaced by a continuous "collapse transition." One observes a specific heat maximum at low temperature which is probably related to a liquid–solid transition.

The structure function $S(k)$ exhibits the expected power law $\sim k^{-1/\nu}$ at $T \geq \theta$, but gives a very different behavior at low temperatures. The calculations of the average internal distances support our other results, but are not consistent with phenomenological predictions given in the literature.$^{38}$

In conclusion, the Monte Carlo technique used in the present work provides the study of the dynamics in the so-called free-draining limit. At temperatures $T \geq \theta$ our results are consistent with analytical predictions, but exhibit a behavior at $T < \theta$ not yet found in other polymer models.

We are able to calculate various quantities of interest in the whole temperature region with reliable accuracy, but our results are limited to system size $N \geq 63$ which is, in some cases, not large enough to realize the desired asymptotic limiting behavior. Detailed studies on larger systems concerning special aspects of the present model are in preparation.

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