Brownian dynamics simulation of flexible polymer chains with excluded volume and hydrodynamic interactions. A comparison with Monte Carlo and theoretical results

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(*Received 24 May 1991; revised 23 August 1991; accepted 17 October 1991*)

The generation of Brownian dynamics trajectories for a flexible polymer constituted of statistical Gaussian units with intramolecular long-range (excluded volume) interactions is accomplished. The intramolecular interactions are described by relatively soft repulsive forces derived from an exponentially decaying potential with a cut-off distance. The validity of this method is satisfactorily tested through the comparison of a wide set of numerical results for equilibrium properties (different averaged dimensions and internal distances, and the end-to-end distance distribution factor) with Monte Carlo results from a model that includes the customary hard-spheres representation of excluded volume forces. Furthermore, the numerical values obtained in this study for the different properties are shown to agree with the scaling theories or Renormalization Group predictions. A transport property, the translational diffusion coefficient, is also obtained and included in the numerical analysis.

(Keywords: Brownian dynamics; excluded volume; hydrodynamic interactions)

INTRODUCTION

Brownian dynamics (BD) simulations constitute the best choice to obtain transport and dynamic properties of a polymer chain in a continuous solvent, since it permits the introduction of realistic hydrodynamic interactions (HI) between polymer units. In recent years, a considerable amount of numerical work has been directed to obtain these properties for Gaussian and worm-like chains[1–6]. Some studies have also been performed with models that include long-range intramolecular interactions[7,8]. However, these models do not consider HI effects and, therefore, the results are restricted to equilibrium properties only. Nevertheless, the introduction of HI implies an additional complication of the numerical method[1,2,9]. The computational problem is aggravated by the presence of long-range interactions, which require a careful choice of time steps. Unfortunately, we have verified that the combined use of small time steps with HI poses a severe limit on the feasibility of generating long trajectories.

In the present work, a model is examined in which the excluded volume interactions are described through a 'relatively soft' intramolecular potential added to a Gaussian chain. Employing this potential, we have found that we do not need any further reduction of the time length step with respect to the value that we have previously used for unperturbed chains[9]. This method has been shown to be clearly more efficient than our previous (not reported) initial attempts with HI and harder potentials, where the time steps had to be severely reduced. Of course, the validity of such a method is subordinated to the performance of the model to reproduce different properties that can also be checked through alternative computations. In particular, we have focused our test on the reproduction of the following equilibrium properties: the critical exponent ν, defined as $\langle S^2 \rangle = a^2 M^{2\nu}$, where $\langle S^2 \rangle$ is the quadratic mean radius of gyration for a chain with N units; the distribution function $F(R)$ of the end-to-end distance; internal averages between units as $\langle R_{ij}^{-1} \rangle$ and $\langle R_{ij}^2 \rangle$, that are useful for determining many properties through exact or approximate formulae. We have computed these properties with our method (including HI and the soft potential) and we have compared the results with theoretical predictions and also with values calculated through alternative Monte Carlo (MC) calculations performed for a model of Gaussian chains with a hard intramolecular potential between units. The excluded volume interactions are easily introduced in MC simulations, which correctly reproduce the equilibrium properties of polymers in dilute solutions, though they can describe only dynamics in tentative[10,11], not completely realistic, ways.

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0032-3861/92/163477-05

In addition to our study of purely static properties, a transport property, the diffusion coefficient D_t, is obtained from the mean quadratic displacement of the centre of masses along the trajectory, as the first application of the method to the evaluation of properties directly related with the HI problem. In these calculations, a preaveraged version of HI is introduced in order to perform a direct comparison of the BD results with numerical results derived from the preaveraged Kirkwood–Riseman theory.

METHOD

We consider a model for flexible chains with a long-range potential and generate BD trajectories according to the first-order Ermak and McCammon algorithm[1]. The model is built so that, in the absence of this potential, we have the basic Gaussian chain, where units are connected by harmonic springs between neighbours as 'entropic' soft short-range forces, so that the distance between them follows a Gaussian distribution, whose root mean square is defined as the statistical length b. Then, we have added long-range interactions between non-neighbouring units. As explained in the Introduction, a relatively soft potential is considered in which the same time step can be maintained as employed in our previous BD study of transport and dynamic properties for linear, ring and star Gaussian chains without long-range interactions[9,12] (whereas we have verified in preliminary tests with the same algorithm that the time steps should be shortened by a factor of 1/100 when the more common Lennard–Jones potential is used). We have used a repulsive potential of the form $A\,e^{-\beta R_{ij}}$, inspired by the repulsive component of some typical intermolecular potentials for small molecules. This potential has a finite value, even for $R_{ij} = 0$, that can be adjusted to achieve different intensities of the repulsive forces, and it can be made soft enough by choosing a particular value for the β parameter. In this way, the force between non-neighbouring units is introduced and BD simulations are performed following the same procedure described elsewhere for Gaussian chains of different lengths[9] (i.e. different number of statistical units N). As a marginal difference with respect to other models describing excluded volume effects, we do not consider that the long-range potential affects the interaction between neighbouring units.

In the present simulations, we have also considered realistic HI that are introduced through a preaveraged tensor. This approximation, usual in simulation and theoretical calculations in unperturbed conditions[13], is not easily performed in the present conditions, since this tensor depends on $\langle R_{ij}^{-1} \rangle$, which remains unknown when excluded volume effects are considered. (A theoretical expression for $\langle R_{ij}^{-1} \rangle$ has been derived from the blob model[14]. In later sections, we discuss these results, and we also use our simulation values to define preaveraged HI tensors.)

We have found that a wide range of parameters A and β can yield appropriate values of the exponent ν corresponding to the scaling law for the radius of gyration previously mentioned. However, most of these parameters are not adequate, since they raise a clearly N-dependent value for the statistical quadratic average distance between neighbouring units along the chain skeleton, $(b')^2$, while we believe that, in an appropriate model, the N-dependent excluded volume effects should not change this distance in the working range of values of N. The only method that we have found to avoid this dependence consists of introducing a cut-off distance r_c for the excluded volume potential, so that:

$$U(R_{ij}) = \begin{cases} A\,e^{-\beta R_{ij}} & R_{ij} \leqslant r_c \\ 0 & R_{ij} > r_c \end{cases} \qquad (1)$$

This new parameter slightly complicates the mathematical form of the potential, because both the potential and its first derivative are no longer continuous. Nevertheless, the β parameter can be fitted so that discontinuities are not important.

With the final form of the repulsive potential given in equation (1) a certain range of parameters A, β and r_c are found that give a scaling exponent ν reasonably close to theoretical predictions, keeping the quadratic distance between neighbouring units of the model N independent. The value of ν is mainly determined by both parameters A and β (though A has a stronger influence), while r_c is directly related to the value of $(b')^2$. As a final result, we have established the set of parameters:

$$A = 75.0 \qquad \beta = 4 \qquad r_c = 2\sigma = 0.512$$

where σ is the Stokes friction radius of the statistical units of the model. (This is just an easy way to express r_c as a function of known magnitudes, and does not establish any physical relationship between excluded volume and hydrodynamic effects.) It should be mentioned that these parameter values also yield the highest correlation for linear $\log\langle S^2 \rangle$ *versus* $\log N$ fits. The values of the parameters indicated above are expressed in reduced units that were employed in previous BD simulations[9]: k_BT for energy and b for lengths (b being the statistical segment distance between neighbouring units in the equivalent Gaussian chain without intramolecular potential between non-neighbouring units). With these parameters, we could use the same simulation time step, $\Delta t^* = k_BT/(\xi b^2) = 0.01$ (where ξ is the friction coefficient of a unit), that was employed without the excluded volume potential[9]. For every chain with different N, we performed five different trajectories from different random number seeds, and have extended our calculations to 40000 steps per trajectory. Our final results are given as statistical means over the five samples.

MONTE CARLO CALCULATIONS

To check the results obtained through our BD program, we have also performed equilibrium MC simulations employing a purely repulsive hard-spheres potential. For every MC sample, we generated a linear Gaussian chain according to a simple method described before[15]. However, the MC sampling technique is different from that used previously. At every simulation step, we randomly choose a chain vector whose coordinates are randomly changed according to a Gaussian distribution of distances defined by b. Subsequently, we rotate the rest of the chain around this vector according to three randomly chosen Euler angles. This method, inspired by the Pivot algorithm[16], is very efficient in the generation of linear chains with excluded volume. Distances R_{ij} between all pairs of units are calculated after every step, the generated conformation being rejected if $R_{ij} < \sigma_{HS}$ for any pair ij ($|i - j| > 1$). The term σ_{HS} is the parameter characteristic of the hard-spheres potential, whose value

Table 1 Dimensions resulting from BD and MC simulations for linear chains with intramolecular interactions

	BD		MC	
N	$\langle S^2\rangle/b^2$	$\langle R^2\rangle/b^2$	$\langle S^2\rangle/b^2$	$\langle R^2\rangle/b^2$
6	1.09 ± 0.02	5.7 ± 0.1	1.133 ± 0.002	6.06 ± 0.02
8	1.57 ± 0.04	8.7 ± 0.3	1.608 ± 0.003	8.99 ± 0.02
11	2.35 ± 0.05	13.8 ± 0.5	2.347 ± 0.007	13.59 ± 0.05
15	3.43 ± 0.06	21.0 ± 0.5	3.392 ± 0.009	20.16 ± 0.07
20	4.61 ± 0.05	29.2 ± 0.5	4.794 ± 0.008	28.98 ± 0.06
25	6.0 ± 0.30	36.0 ± 2.0	6.25 ± 0.010	38.09 ± 0.07
37	9.70 ± 0.20	64.0 ± 3.0	10.00 ± 0.030	61.60 ± 0.20

is chosen so that the average $\langle S^2\rangle$ for a chain obtained with this procedure is the same as the value calculated from a BD simulation of a chain with the same number of units, employing the model described in the previous section. The resulting parameter that adequately satisfies this criterion is $\sigma_{HS} = 0.56$, which is very close to the value of 0.55 proposed by Baumgärtner for the study of polymer chains in good solvent conditions[17].

For every chain, we have computed eight different MC samples, each composed of 50 000 conformations. Final MC results are presented as means and deviations over these samples.

RESULTS

Dimensions. Table 1 gives the results obtained from BD and MC simulations for the quadratic radius of gyration, $\langle S^2\rangle$, and the quadratic end-to-end distance, $\langle R^2\rangle$, for linear chains with the number of units ranging from $N = 6$ to 37. Differences between numerical uncertainties in both types of simulations are due to the size of the statistical sample considered, which is considerably larger in MC than in BD simulations. BD trajectories consume much more computer time than MC calculations, so that generation of longer trajectories is extravagant from a practical point of view.

A log–log fitting of $\langle S^2\rangle$ *versus* $N_G = (N-1)(1+1/N)$ yields the exponents $2\nu = 1.17 \pm 0.01$ for BD results and 1.175 ± 0.001 for MC results. The most precise theoretical estimation of this exponent, according to Renormalization Group theory[18], is $\nu = 0.588$ or $2\nu = 1.176$. On the other hand, a similar fitting of $\langle R^2\rangle$ *versus* $(N-1)$ (the number of connectors between neighbouring units in a linear chain) yields the exponents 1.20 ± 0.01 (BD) and 1.172 ± 0.002 (MC). The small difference observed in this case should be attributed to numerical uncertainties that are more important in the case of $\langle R^2\rangle$ than for $\langle S^2\rangle$ (as seen in *Table 1*).

Distribution function. The distribution function $F(R)$ of the end-to-end distance R is readily obtained from simulations by computing the histogram corresponding to an adequate grid of values of R. $F(R)$ is derived from the histogram by a proper normalization according to the total number of points (number of cycles in MC simulations or number of time steps in BD trajectories) and to the volume associated with the given checked grid interval. The results corresponding to a linear chain with $N = 20$ are shown in *Figure 1*. Taking into account the statistical fluctuations of the points, there is remarkable agreement between BD and MC results.

Figure 2 shows a direct comparison between BD results for $F(R)$ computed with and without excluded volume interactions (the latter obtained from trajectories calculated previously[9]). We include also in this figure the theoretical curve corresponding to a Gaussian chain with $N = 20$ statistical units. Clearly, Gaussian behaviour is not observed when repulsive interactions are introduced, a result that has already been reported[10,19]. Some other equations have been proposed for the distribution function of R when intramolecular interactions are present. Thus, we have included in *Figures 1* and *2* a theoretical curve[19] based on the scaling form derived by des Cloizeaux[20]:

$$F(R) = C\langle R^2\rangle^{-d/2}(R/\langle R^2\rangle^{1/2})^{\theta}\exp[-(KR/\langle R^2\rangle^{1/2})^{t}] \tag{2}$$

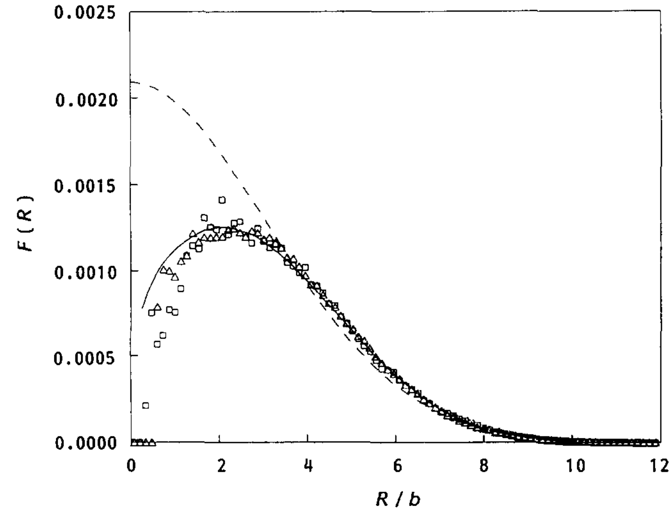

Figure 1 Comparison between distribution functions, $F(R)$, with intramolecular interactions computed via MC (△) and BD (□) simulations, for a linear chain with $N = 20$ units. The des Cloizeaux function, described in the text, is represented by a solid line. The broken line corresponds to a Gaussian distribution:

$$F(R) = \left[\frac{3}{2\pi(N-1)}\right]^{3/2}\exp\left[\frac{3R^2}{2(N-1)}\right]$$

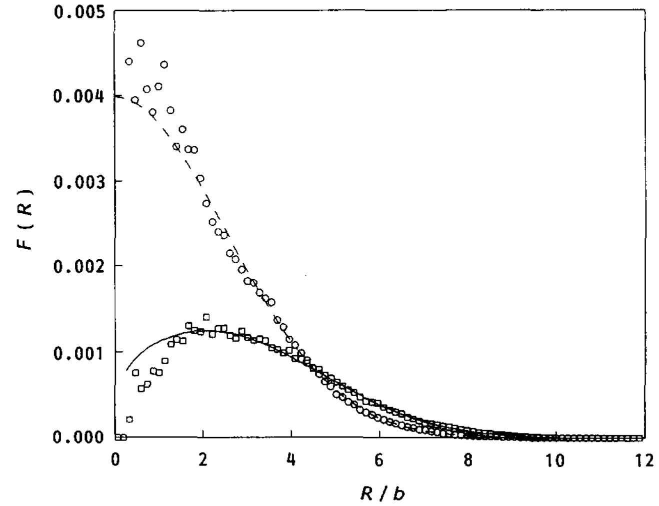

Figure 2 Comparison between $F(R)$ with (□) and without (○) intramolecular interactions, computed via BD simulations, for a linear chain with $N = 20$ units. The des Cloizeaux function is represented by a solid line. The broken line corresponds to a Gaussian distribution

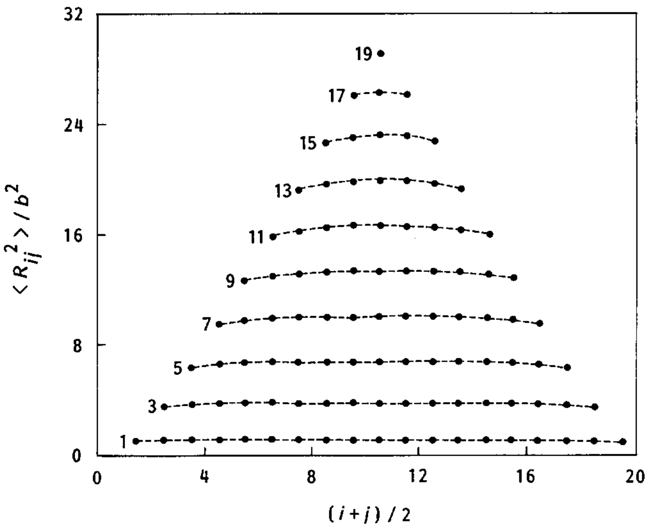

Figure 3 Average values of $\langle R_{ij}^2 \rangle$ *versus* the central position of the pair ij, $(i+j)/2$ for a linear chain with $N = 20$ units. The lines connect points with a given value of $|i-j|$, which is indicated by the numbers on the curves

where θ and t are related to critical exponents[21] and K is obtained from[19]:

$$K = \{\Gamma[(d+2+\theta)/t]/\Gamma[(d+\theta)/t]\}^{1/2} \quad (3)$$

so that, for space dimension $d = 3$ (which implies $\theta = 5/18$ and $t \simeq 5/2$), one obtains $K \simeq 1.08$. C is a normalization constant that is calculated from:

$$C = (1/4\pi)tK^{\theta+d}/\Gamma[(\theta+d)/t] \quad (4)$$

Good agreement between this function and both the BD and MC values can be observed.

In *Figures 1* and *2*, we can observe the depression in $F(R)$ appearing for small R, which is deferred to as a correlation hole in the end-to-end distance distribution function[21,22] and is due to excluded volume interactions. According to theoretical estimations based on equation (2) and the scaling law $\langle R^2 \rangle \sim (N-1)^{\nu}$, one obtains $F(R \rightarrow 0) \sim (N-1)^{-\varepsilon}$, with $\varepsilon \simeq 1.93$. We have computed this exponent by a log–log fitting of the values of the histogram (or normalized number of conformations) with $(R/b) < 1$ *versus* $(N-1)$, and have obtained an exponent $\varepsilon = 1.93 \pm 0.02$, so that the theoretical prediction is numerically verified.

Internal averages $\langle R_{ij}^2 \rangle$ *and* $\langle R_{ij}^{-1} \rangle$. The distribution momenta of internal distances between units, $\langle R_{ij}^n \rangle$, are of fundamental importance in accurately defining their distribution. However, our interest here is not to perform an exhaustive discussion of $F(R_{ij})$, but to check the results obtained from our BD model for averages with $n = 2$ and -1 that appear in the calculation of most properties of interest.

Figure 3 is a plot of $\langle R_{ij}^2 \rangle$ for a chain of $N = 20$ statistical units against the central position of the pair ij, $(i+j)/2$. The lines connect points of constant $|j-i|$ (constant distance, measured in number of intermediate connectors, along the chain backbone). As previously reported[11], there is a slight upward bending of the lines at their centre, indicating the existence of edge effects in the expansion of the chain. This is expected from physical considerations. The ends of a polymer chain are usually surrounded by fewer units than the beads at the centre of the chain; thus, the former are subjected to a smaller excluded volume force than the latter, and the corresponding expansion follows the same trend. (*Figure 3* shows data computed from MC simulations. BD trajectories give the same averages, but fluctuations due to statistical uncertainties are greater, as seen in *Table 1*, and the analysis of this subtle dependence on the position becomes problematic.)

For $|j-i| = 1$ we obtain the nearest neighbours quadratic distance for the expanded chain, $(b')^2$. The average value from BD trajectories of chains with different N is $(b')^2/b^2 = 1.091 \pm 0.003$, which represents about a 10% expansion with respect to unperturbed chains. This expansion is only 5% for the end connectors of the chains, and rises up to 15% at their middle points. These differences may not seem very important, but they may be responsible for some discrepancies observed between theoretical and simulation results for certain properties.

The popular blob theory[14] assumes a uniform expansion of the unperturbed chain when excluded volume interactions are introduced. In this case, the equilibrium distribution function $F(R_{ij})$ is still supposed to be the same as $F(R)$, so that $\langle R_{ij}^2 \rangle \sim |i-j|^{2\nu}$ (when a blob is considered to be equivalent to one unit of the simulation model). To check this point, we have computed $\langle R_{ij}^2 \rangle / |i-j|^{1.176}$ as a function of $|i-j|$ from our simulation results. We have observed that the resulting value of this ratio is not constant, but decreases with increasing $|i-j|$ for every chain. This implies again a non-uniform expansion of the chain. Thus, blob model theory is not consistent in this respect with our simulation results. However, more detailed information on longer chains would be desirable for adequate clarification of this point.

Figure 4 shows the averages $\langle R_{ij}^{-1} \rangle$ *versus* the central position of the pair ij in the chain. We observe the same general features as in $\langle R_{ij}^2 \rangle$, that is, the expansion of the chain is not completely uniform. This may be relevant when HI are considered in the dynamics of a polymer chain in good solvent conditions. HI are usually represented through second-order tensors that depend on $1/R_{ij}$. Moreover, when, as frequently occurs, a

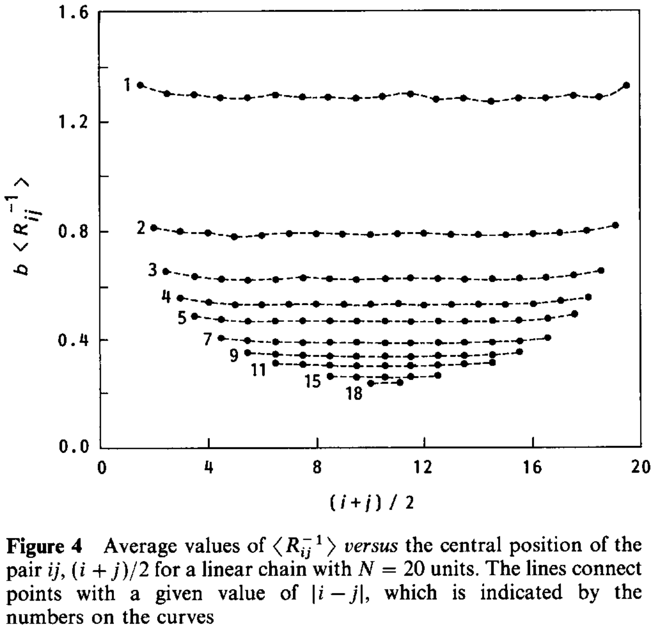

Figure 4 Average values of $\langle R_{ij}^{-1} \rangle$ *versus* the central position of the pair ij, $(i+j)/2$ for a linear chain with $N = 20$ units. The lines connect points with a given value of $|i-j|$, which is indicated by the numbers on the curves

Table 2 Diffusion coefficient (in reduced units) computed via BD simulations with intramolecular potential and preaveraged HI

N	D_t^*
6	0.352 ± 0.0030
8	0.305 ± 0.0030
11	0.250 ± 0.0020
15	0.208 ± 0.0030
20	0.1766 ± 0.0002
25	0.158 ± 0.0020

preaveraging representation of HI or other simplifying approximations are considered in theoretical developments[13], the average $\langle 1/R_{ij} \rangle$ plays an important role in the final expressions for different properties (as translational diffusion coefficients, relaxation times or dynamic light scattering cumulants).

Diffusion coefficient. As a first application of our model to non-equilibrium properties, we analysed the BD trajectories with excluded volume interactions to obtain the translational diffusion coefficient D_t of our chains. As in previous work[9], we computed D_t from the slope of the centre of masses quadratic displacement *versus* time. *Table 2* gives the results for the diffusion coefficient in reduced units ($D_t^* = \xi D_t / k_B T$). These results correspond to trajectories generated with the preaveraged Oseen tensor, calculated from previously computed values of the reciprocal averages, as:

$$\langle T_{ij} \rangle = T_{ij} \boldsymbol{I} = \frac{1}{6\pi\eta_0} \langle R_{ij}^{-1} \rangle \boldsymbol{I} \qquad (5)$$

for every pair ij, where $\boldsymbol{I}$ is a 3×3 unit tensor. This allows us to perform a direct comparison with the values calculated from the preaveraged Kirkwood–Riseman formula, which also employs the preaveraged tensor, according to the expressions:

$$D_t = \sum_{i}^{N} \sum_{j}^{N} [(H^{-1})_{ij}]^{-1} \qquad (6)$$

where

$$\begin{array}{ll} H_{ij} = 1 & \text{for } i = j \\ H_{ij} = < T_{ij} > & \text{otherwise} \end{array} \qquad (7)$$

We have verified that the results in *Table 2* (BD simulations with the preaveraged tensor) and those obtained from equations (5)–(7) are in excellent agreement. Differences are very small ($< 1\%$) when the internal averages used in equation (5) are (consistently) those obtained through the BD trajectories. A least-squares linear log–log fitting of D_t^* *versus* N provides the scaling law $D_t^* \sim N^{-(0.579 \pm 0.007)}$, while experimental data from good solvent dilute solutions[23–25] yield exponents in the range -0.55 to -0.68. A detailed discussion of the BD results for D_t and other transport and dynamical properties obtained with excluded volume chains and realistic preaveraged and also fluctuating HI is reported elsewhere[12].

ACKNOWLEDGEMENTS

This work was supported by Grants PB89-0093 (JJF) and PB87-0694 (JGT) from the Dirección General de Investigación Científica y Técnica. AR acknowledges a Fellowship from the Plan de Formación del Personal Investigador. We thank Professor M. Bishop, from Manhattan College and UMIST, for helpful discussions.

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