Steady-state behavior of dilute polymers in elongational flow. Dependence of the critical elongational rate on chain length, hydrodynamic interaction, and excluded volume

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Synopsis

The steady-state properties of flexible polymer chains in solutions undergoing elongational flow have been studied using Brownian dynamics simulation. The coil–stretch transition is observed when the elongational rate, $\dot{\epsilon}$ exceeds a certain critical value $\dot{\epsilon}_c$. In this work, we describe in detail the simulation procedure and how to extract polymer dimensions, solution viscosity, and birefringence from the trajectories. Preliminary simulations involving no hydrodynamic interaction (HI) are used to check the simulation procedures by comparing their results with theoretical predictions for such an (unphysical) case. Afterwards, simulations with fluctuating nonaveraged HI are carried out to provide results comparable with experiments. After simulations with and without intramolecular potential, we arrive at a most important conclusion: the chain length dependence of $\dot{\epsilon}_c$ is the same in theta conditions as in good solvent conditions. Combining $\dot{\epsilon}_c$ with other solution properties such as the longest relaxation time, the intrinsic viscosity, and the radius of gyration, dimensionless compound quantities can be formulated. From our simulation results, we obtain numerical values for such quantities, which include the HI effect, and which are therefore useful for analyzing experimental data. © *1999 The Society of Rheology.* [S0148-6055(99)00602-1]

I. INTRODUCTION

When dilute solutions of flexible-chain polymers are subjected to flow, the macromolecular coils are deformed. Such deformation consists of orientation and/or stretching that can be observed experimentally as a change in properties that depends on the overall size of the coil or on the orientation of its segments. In some specific setups, it can be accepted that the flow rate at which the macromolecule is exposed is approximately constant in some region where it dwells for a sufficiently long time. The steady-state behavior of the polymer chains in such homogeneous flows can be characterized in terms of the dependence of the polymer properties on flow rate.

In shear flows, the dependence of polymer properties on flow rate $\dot{\gamma}$, is smooth: for instance the mean square radius of gyration depends on $\dot{\gamma}^2$. However, the dependence is remarkably different in elongational flows: as the elongational rate $\dot{\epsilon}$, increases the properties remain nearly unchanged and continue to show the nonflow values, until a certain critical value $\dot{\epsilon}_c$ is reached. In the vicinity of $\dot{\epsilon}_c$, the properties experience a very sharp,

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dramatic increase from the nonflow values, corresponding to the coil conformation, reaching nearly the values corresponding to a fully stretched chain.

This coil–stretch transition was theoretically predicted in the classical paper by De Gennes (1974), who improved and extended the pioneering work of Peterlin (1966). Some details of the DeGennes theory were later clarified and shown to be consequences of the mathematical approximation employed [Fan *et al.* (1989)]. The very interesting features of this phenomenom prompted the development of laboratory setups in which the transition could be experimentally observed [for a review of early studies, see the article by Keller and Odell (1985)]. The early theory predicted a basic yet simple relationship between the critical elongational rate and a characteristic time (the Rouse–Zimm longest relaxation time) τ_1 of the chain:

$$\dot{\epsilon}_c \tau_1 \approx 1. \tag{1}$$

However, the theory was based on a very simple dumbbell model, so that both its qualitative aspects as well as the quantitative results, such as the precise value of $\dot{\epsilon}_c \tau_1$ had to wait for more realistic chain models. A noteworthy result is the analytical expression of Bird *et al.* (1983) for arbitrarily long Rouse chains, which is a better conformational representation of a polymer chain than a simple dumbbell, although it still has important defects: infinite extensibility and, particularly, (see below) the omission of hydrodynamic interaction (HI).

In more recent years, the impossibility of deriving theoretically analytic results for realistic chain models has motivated the development of simulation procedures by a number of authors ([Acierno *et al.* (1974); Saab and Dotson (1987); Liu (1989); Zylka and Öttinger (1989); Larson (1990); Reese and Zimm (1990); van de Brule (1993); Hinch (1994); Keunings (1997); Rallison (1997); Andrews *et al.* (1998a,1998b); Agarwal *et al.* (1998)] to name just a few). More specifically, our group employed a Brownian dynamics algorithm with full inclusion of fluctuating hydrodynamic interaction, to simulate flexible chain models that can embody a variety of features. Such an approach has been applied to predict the properties in quiescent solutions [García Bernal *et al.* (1991); Rey *et al.* (1992)], in shear flow [López Cascales *et al.* (1992b); Knudsen *et al.* (1996a)] and in both steady [López Cascales and García de la Torre (1991b,1992b,1994)] and transient [Rey *et al.* (1992); Knudsen *et al.* (1996b)] elongational flows.

In the present work, we focus on the specific problem of steady, homogeneous elongational flow, and attempt to determine precisely the dependence of the critical elongational rate on chain length, including rigorously effects such as fluctuating HI and excluded volume. The dependence of $\dot{\epsilon}_c$ on chain length N, or molecular weight M can be expressed as a power law:

$$\dot{\epsilon}_c \propto N^a \propto M^a. \tag{2}$$

For ideal chains, $\tau_1 \propto M^{3/2}$, and so Eq. (2) predicts $a = -1.5$ for theta solvents. If Eq. (2) were valid for good solvent conditions, when $\tau_1 \propto M^{3\nu}$ with $\nu = 0.59$ [Ohta *et al.* (1982)], then we would obtain $a \approx -1.8$ in good solvents. From the earliest experimental realizations of the elongational flow of dilute polymer solutions [Farrell *et al.* (1980); Fuller and Leal (1980); Odell *et al.* (1985); Atkins *et al.* (1986); Brestkin *et al.* (1986)], a controversy has existed concerning the value of the scaling exponent a in Eq. (2). Such controversy persists even after more recent experiments [Menasveta and Hoagland (1991, 1992); Narh *et al.* (1992); Nguyen *et al.* (1995)]. While various authors have found $a = -1.5$ to be valid regardless of solvent quality, i.e., in both theta and good solvents [Farrell *et al.* (1980); Fuller and Leal (1980); Keller and Odell (1985); Odell *et al.* (1985); Menasveta and Hoagland (1991,1992); Narh *et al.* (1992)], others have reported

$a \approx -1.8$ in good solvents [Atkins *et al.* (1986); Brestkin *et al.* (1986); Nguyen *et al.* (1995)]. Some theoretical considerations have predicted a different scaling exponent in good solvents, ranging from $a = -1.8$ [Rabin (1985a)] to $a = -1.6$ [Rabin *et al.* (1985b)]. Interestingly, there is even a Monte Carlo simulation which predicts the abnormal result of $a = -2.3$ [Mansfield and Rakesh (1989)]. Evidently, the results are conflicting. Since excluded volume can easily be included in Brownian dynamics, another reason for undertaking this work was to throw some light on this controversy using this simulation technique. Actually, this possibility has been developed by Andrews *et al.* (1998a) in a very recently published article, which, in several regards, is complemented by our work.

From the chain length dependence of $\dot{\epsilon}_c$, we attempt to determine a precise value for the compound quantity $\dot{\epsilon}_c \tau_1$ [Eq. (1)], including rigorously the HI effect. We also formulate and evaluate the combination of $\dot{\epsilon}_c$ with the intrinsic viscosity and the combination newly proposed in this article of $\dot{\epsilon}_c$ with the radius of gyration. We try to extract experimental estimates for these combinations from measurements in the literature, and compare them to our predictions.

II. THEORY, MODELS, AND METHODS

A. Models for polymer and flow

We consider a dilute polymer solution in a steady, homogeneous elongational flow with a velocity field given by

$$v_x = -\tfrac{1}{2}\dot{\epsilon}x; \quad v_y = -\tfrac{1}{2}\dot{\epsilon}y; \quad v_z = \dot{\epsilon}z \tag{3}$$

which is an appropriate idealization of the field produced by the opposing jets device pioneered by Keller, Odell, and co-workers [Pope and Keller (1978); Keller and Odell (1985)].

The polymer molecules are modeled as bead-and-spring chains. The simplest model is the Rouse chain composed of Gaussian (Hookean) springs with a force law $\mathbf{F}(\mathbf{Q}) = -H\mathbf{Q}$, where the spring constant is $H = 3kT/b^2$, and $b^2 = \langle Q^2 \rangle$ is the mean square spring length. The failure of the Gaussian chain to predict finite extensibility is removed in an improved model, the chain of finitely extensible nonlinear elastic (FENE) springs. In this model the spring force is given by Bird *et al.* (1987):

$$\mathbf{F}(\mathbf{Q}) = -\frac{H}{1-\left(\dfrac{Q}{Q_{\max}}\right)^2}\mathbf{Q}, \tag{4}$$

where $\mathbf{Q}$ is the spring vector and $Q_{\max}$ is the maximum spring length. At low elongation, Eq. (4) reduces to the force law of the Hookean spring given above, where the spring constant is formulated now in terms of $b^2 = \langle Q^2 \rangle_0$, i.e., the mean square spring length at the limit of low elongation (in our case, in the absence of flow).

Polymer chains with intramolecular interactions can be simulated by Brownian dynamics by introducing interaction forces between non-neighboring beads, calculated from appropriate intramolecular potentials. Physically, a most adequate choice is the Lennard-Jones (LJ) potential,

$$V = 4\epsilon_{\mathrm{LJ}}\left[\left(\frac{\sigma_{\mathrm{LJ}}}{r_{ik}}\right)^{12} - \left(\frac{\sigma_{\mathrm{LJ}}}{r_{ik}}\right)^{6}\right], \tag{5}$$

where r_{ik} is the distance between beads i and k, and ϵ_{LJ} and σ_{LJ} are the Lennard-Jones parameters.

Computationally, the LJ potential has a disadvantage in Brownian dynamics simulation: due to its very steep behavior below σ_{LJ}, the simulation is only feasible with quite small time steps. This circumstance has been noted by several workers [Rey *et al.* (1992); Andrews *et al.* (1998a)]. Thus, in order to account for excluded-volume (EV) effect in good-solvent conditions, we have employed a purely repulsive potential [López Cascales and García de la Torre (1991a); Rey *et al.* (1992); Knudsen *et al.* (1996a)] given by

$$V(r_{ik}) = \begin{cases} Ae^{-\alpha r_{ik}} r_{ik} \leq r_c \\ 0 \quad r_{ik} > r_c \end{cases} . \tag{6}$$

This potential has the advantage of being "softer" than the LJ potential at short distances. With the proper choice of parameters, $A = 75.0$, $\alpha = 4$, and $r_c = 0.152$ (in reduced units), this potential has been shown to predict the proper power-law dependence of polymer dimension on chain length, i.e., $\langle r^2 \rangle_0$ or $\langle s^2 \rangle_0$ proportional to $N^{1.2}$.

Polymer chains in theta solvents can be in principle simulated as "ideal" chains in which intramolecular interactions are simply absent. Chain dimensions and some simple solution properties are adequately predicted in this way [García de la Torre *et al.* (1982); García Bernal *et al.* (1990)]. However, a correct description of the theta state requires the simultaneous effect of balanced attractive and repulsive contributions. For an interesting discussion in this regard, see Milchev *et al.* (1993). Thus, Andrews *et al.* (1998a) have employed a Morse potential as proposed by Milchev *et al.* (1993). In this work, we have recourse to the original Lennard-Jones potential, although at the cost of spending much computing time. The parameterization of the LJ potential for various solvent conditions has been described by Freire, Rey and their co-workers. For good solvents, the parameters are taken as $\epsilon_{LJ} = 0.1$ and $\sigma_{LJ} = 0.8$, which reproduce properly the dependence of polymer dimensions, intrinsic viscosity, and translational diffusion, $\langle S^2 \rangle \propto N^{1.2}$, $D_t \propto N^{-0.6}$, and $[\eta] \propto N^{0.8}$, approximately [Rey *et al.* (1987a)]. The theta state of LJ chains has been found for $\epsilon_{LJ} = 0.3$ and $\sigma_{LJ} = 0.8$ [Freire *et al.* (1986b)], with proportional properties $\langle S^2 \rangle \propto N$, $[\eta] \propto N^{0.5}$, and $D_t \propto N^{-0.5}$ [Freire *et al.* (1986b)]. Finally, following Andrews *et al.* (1998a), we include in our work the case of bad solvents, in the so-called collapsed or globule conformation of the chains. This condition is described by a LJ potential with $\epsilon_{LJ} = 1.0$ and $\sigma_{LJ} = 0.8$ [Rey *et al.* (1987b)].

B. Polymer properties

From the long trajectories generated as described below, we obtain polymer properties as averages over values calculated for instantaneous conformations sampled along the trajectory. More particularly, we consider the radius of gyration, the intrinsic elongational viscosity, and the birefringence. The two former are calculated from well-known expressions, but for the birefringence of FENE chains we have devised a specific procedure which is described below.

The mean square radius of gyration $\langle s^2 \rangle$ can be expressed as

$$\langle s^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle S_i^2 \rangle,$$

where $\mathbf{S}_i = \mathbf{r}_i - \mathbf{r}_c$, with $\mathbf{r}_i$ and $\mathbf{r}_c$ being the position vector of bead i and of the center of mass, respectively.

The intrinsic elongational viscosity is defined as $[\bar{\eta}] = (\bar{\eta} - 3\eta)/(3\eta_s c)$ at the limit of very low mass concentration c, where $\bar{\eta}$ is the elongational viscosity of the solution and $3\eta_s$ is the Trouton value for the elongational viscosity of the solvent, η_s being the solvent shear viscosity. From the Kramers form of the stress tensor [Bird *et al.* (1987)], and recalling that the number concentration of the polymer is $n = cN_A/M$, where M is the molecular weight, we obtain:

$$[\bar{\eta}] = \frac{N_A}{3\eta_s M \dot{\epsilon}} \sum_{j=1}^{N-1} \langle F_j^x Q_j^x - F_j^z Q_j^z \rangle. \tag{7}$$

The property most commonly used to monitor the coil–stretch transition is birefringence Δn, which we intend to describe by taking into account the finite extensibility of the subchains that comprise the molecule, i.e., the FENE springs in the model. The optical anisotropy of the polymer subchains represented by the springs increases as they stretch, but reaches a finite limit, as the FENE spring elongation does. As a consequence, the whole chain has a limiting or maximum birefringence Δn_∞. In the relationship between anisotropy and elongation [Treloar (1975)], the inverse Langevin function takes place in a similar manner as in the force–elongation relationship. In the latter case, a simplifying approximation for the inverse Langevin function leads to the FENE spring law. Although some authors [Carrington *et al.* (1997)] have employed a different, more accurate approximation in the anisotropy–elongation relationship, the coherence between the two treatments requires the use of the same approximation. Then, the resulting expression for the birefringence is [Kobe and Wiest (1993)]:

$$\frac{\Delta n}{\Delta n_\infty} = \frac{1}{(N-1)Q_{\max}} \sum_{j=1}^{N-1} \langle Q_{j,z}^2 - Q_{j,x}^2 \rangle. \tag{8}$$

Actually, this expression has been used in previous studies of birefringence of bead and spring chains [Kobe and Wiest (1993); Andrews *et al.* (1998a), and (1998b)].

For the internal programming of the Brownian dynamics simulation and the presentation of results, it is convenient to employ reduced, dimensionless quantities (denoted hereafter with an asterisk). Dimensions, energy and force are reduced by b, kT, and kT/b, respectively, and reduced time is given by

$$t^* = t/(\zeta b^2/kT). \tag{9}$$

The elongational rate is made dimensionless recalling that it is a reciprocal of time:

$$\dot{\epsilon}^* = \dot{\epsilon}(\zeta b^2/kT). \tag{10}$$

In dimensionless reduced form, $\langle s^{*2} \rangle = \langle s^2 \rangle / b^2$ and

$$[\bar{\eta}]^* = \left(\frac{1}{3}\right) \frac{6\pi\sigma^*}{\dot{\epsilon}^*} \sum_{j=1}^{N-1} \langle F_j^{*x} Q_j^{*x} - F_j^{*z} Q_j^{*z} \rangle, \tag{11}$$

where $\sigma^* = \sigma/b$. Finally, we note that the ratio $\Delta n/\Delta n_\infty$ is obviously dimensionless.

C. Existing theories: combination of critical elongational rate and longest relaxation time

The simple free-draining description, in which HI is neglected, has the virtue of providing analytical results for the case of the Gaussian chain, with Hookean springs. For example, the end-to-end distance is given by [Bird *et al.* (1983); López Cascales and García de la Torre (1991b)]:

$$\frac{\langle r^2\rangle}{Nb^2} = 1+\frac{2\lambda_H^2\dot{\epsilon}^2}{N(N+1)}\times\sum_{m=1,\text{odd}}^{N-1}\frac{\cos^2 M}{\sin^2 M(\sin^2 M+\lambda_H\dot{\epsilon})(\sin^2 M-\lambda_H\dot{\epsilon})}, \tag{12}$$

where $M = m\pi/2N$ and $\lambda_H = (1/12)(\zeta b^2/kT)$. From this expression, it is easily seen that $\langle r^2\rangle$ goes to infinity when $\dot{\epsilon}$ reaches the critical value

$$\dot{\epsilon}_c = \lambda_H^{-1}\sin^2\left(\frac{\pi}{2N}\right), \tag{13}$$

which for sufficiently high N can be approximated by

$$\dot{\epsilon}_c = \frac{\pi^2 kT}{\zeta b^2}\frac{3}{N^2} \quad \text{(no-HI)} \tag{14}$$

or, in the reduced form defined in Eq. (10),

$$\dot{\epsilon}_c^* = 3\pi^2/N^2 \quad \text{(no-HI)}. \tag{15}$$

From the earliest studies of the elongational flow of polymer solutions, it has been a common practice to relate the elongation rate $\dot{\epsilon}$ with the longest relaxation time τ_1 [Keller and Odell (1985)]. The product $\dot{\epsilon}\tau_1$ is a dimensionless quantity that is sometimes referred to as the Deborah number.

For the free-draining case, in the limit of large N, we have [Bird *et al.* (1987)]:

$$\tau_1 = \frac{\zeta b^2 N^2}{6\pi^2 kT} \quad \text{(no-HI)} \tag{16}$$

or

$$\tau_1^* = \frac{N^2}{6\pi^2} \quad \text{(no-HI)}. \tag{17}$$

Then the critical value of the product is:

$$\dot{\epsilon}_c\tau_1 = \tfrac{1}{2} \quad \text{(no-HI)}. \tag{18}$$

Although in the analysis of experimental data they may be of no use or simply misleading, the no-HI theoretical results are very useful for testing the simulation procedures. For applications to real cases, the hydrodynamic interaction effect must be introduced in some way. A previous, quantitative, theoretical, determination of $\dot{\epsilon}\tau_1$ was made by Magda *et al.* (1988), employing a procedure in which fluctuating hydrodynamic interaction is replaced by a configurational average. Furthermore, the τ_1 value to which they refer is that obtained with the preaveraging approximation. These authors found that the coil–stretch transition takes place when $\dot{\epsilon}/\lambda_0 \simeq 2$, where $\lambda_0^{-1} \simeq 4\tau_1$, τ_1 being the Zimm birefringence–viscoelastic relaxation time. Their precise numerical values are $\dot{\epsilon} = 2.17\lambda_0$ and $\lambda_0^{-1} = 4.1\tau_1$, which yield $(\dot{\epsilon}_c\tau_1)_{\text{pre}} = 0.53$, where the notation $(\ldots)_{\text{pre}}$ stands for preaveraging.

In the presentation and discussion of results for $\dot{\epsilon}_c\tau_1$ one must be careful because of a possible confusion over τ_1. From the earliest works [Zimm (1956), Stockmayer (1967)] it has been known that two alternative forms of the relaxation times can be formulated, one referring to the relaxation times that determine dielectric relaxation and denoted as τ_k', following Stockmayer (1967), while the other form of the relaxation times is involved in birefringence and viscoelasticity, which we denote as τ_k, following Zimm (1956). Our τ_1 is the longest of the birefringence/viscoelastic relaxation times. The τ_k'

times are related to the time decay of the first-order Legendre polynomial of the angle subtended by two successive orientations of some characteristic vector, separated by a given time, while the τ_k's are those which take place in the decay of the second-order Legendre polynomial. As a consequence, it follows that $\tau_1' = 2\tau_1$. It is evident that the two types of relaxation times can be confused because of notation. This happens even in standard monographs: thus, Yamakawa (1971) adheres to the Zimm–Stockmayer notation that we have used, while Doi and Edwards (1986) employ τ_1 (unprimed) when referring to the dielectric relaxation times.

D. Brownian dynamics simulation

The dynamics of the polymer chains is monitored from trajectories of individual molecules obtained by Brownian dynamics simulation. We employ a modification of the Ermak and McCammon algorithm [Ermak and McCammon (1978)] proposed by Iniesta and García de la Torre (1990) that includes the displacement due to solvent flow. Each step is taken twice, and the positions of the beads $\mathbf{r}_i$ after the time step Δt are calculated from the previous ones, $\mathbf{r}_i^0$, according to the following equations:

$$\mathbf{r}' = \mathbf{r}^0 + \frac{\Delta t}{kT}\mathbf{D}^0 \cdot \mathbf{F}^0 + \Delta t(\nabla_r \mathbf{D})^0 + \Delta t \mathbf{v}^0 + \mathbf{R}^0, \tag{19}$$

and

$$\mathbf{r} = \mathbf{r}^0 + \frac{\Delta t}{kT}\frac{1}{2}(\mathbf{D}^0 \cdot \mathbf{F}^0 + \mathbf{D}' \cdot \mathbf{F}') + \Delta t \frac{1}{2}[(\nabla_r \mathbf{D})' + (\nabla_r \mathbf{D})^0] + \Delta t \frac{1}{2}(\mathbf{v}^0 + \mathbf{v}') + \mathbf{R}', \tag{20}$$

where $\mathbf{r}$ is the generalized ($3N$ dimensional) position vector containing the three coordinates of the position vectors $\mathbf{r}_i$ of all the beads. Similarly $\mathbf{F}$ and $\mathbf{v}$ are the generalized vectors for forces and flow velocities at $\mathbf{r}$. Note that the forces at each bead are the resultants of the forces at the springs attached to that bead, i.e., $\mathbf{F}_i = -\mathbf{F}(\mathbf{Q}_{i-1}) + \mathbf{F}(\mathbf{Q}_i)$, except $\mathbf{F}_1 = \mathbf{F}(\mathbf{Q}_1)$, and $\mathbf{F}_N = -\mathbf{F}(\mathbf{Q}_{N-1})$. $\mathbf{D}$ is the generalized $3N \times 3N$ diffusion tensor. Equation (19) is for the predictor substep, which takes into account the quantities corresponding to the previous conformation $\mathbf{r}^0$ denoted by the 0 superscript. In this step, an estimate $\mathbf{r}'$ of the following conformation is obtained, and the necessary quantities are evaluated. The next substep is the corrector, which is calculated as indicated in Eq. (20), again from the previous conformation $\mathbf{r}^0$, but using quantities that are the mean of those at $\mathbf{r}^0$ and $\mathbf{r}'$. Although the step in our predictor–corrector procedure is equivalent to two Ermak–McCammon steps and subsequently takes about twice the CPU time of the latter, longer time steps are possible and lead to an increase in efficiency [Chirico and Langowski (1992); Ottinger (1996)]. Owing to its pseudosecond-order construction, the algorithm is particularly suited for systems with linear flow fields and forces like those in the present problem.

A proper description of polymer hydrodynamics requires an adequate representation of HI. For this purpose the diffusion tensor is expressed in terms of the Oseen tensor $\mathbf{T}_{ij}$ as $\mathbf{D}_{ij} = kT\mathbf{T}_{ij}$ [Yamakawa (1971)], which is evaluated for each conformation. Thus, our description of HI is properly fluctuating, thus avoiding any type of averaging approximation. If hydrodynamic interaction is neglected, the results may not be of application to dilute polymer solutions, as it is in our case. However, the no-HI case is still of interest since simple analytical results are available from theory and can be used for testing the simulation procedures. If HI is neglected, we set $\mathbf{D}_{ij} = \mathbf{0}$ in Eqs. (19) and

(20). For the bead friction we use a Stokes coefficient $\zeta = 6\pi\eta_s\sigma$, where $\sigma = 0.257b$, which corresponds to a HI parameter $h^* = 0.25$.

E. Simulation procedures

The very strong effect of the coil–stretch transition on polymer properties means that it is easy to determine $\dot{\epsilon}_c$ by computer simulation. The case of Gaussian chains is particularly simple because they are infinitely extensible. In a computer experiment, a single Gaussian chain, which is initially in a coiled conformation, is submitted to an elongational flow of fixed $\dot{\epsilon}$, and some property (say, the end-to-end distance or the gyration radius) is monitored during the simulation. If $\dot{\epsilon} > \dot{\epsilon}_c$, the chain will sooner or later suffer transition and will rapidly and limitlessly grow in size. In a short simulation time the Cartesian coordinates increase so sharply that an overflow results with the subsequent abortion of the computer execution. Thus $\dot{\epsilon}_c$ can be bracketed in a series of simulation experiments with different $\dot{\epsilon}$ in which the computer program is either running for a sufficiently long time or aborts by overflow. While refining the determination, i.e., very close to $\dot{\epsilon}_c$, the single-molecule run was repeated a few times, with different starting conformations. This procedure was iterated, thus reducing the interval in which $\dot{\epsilon}_c$ is located until it has a width smaller than 5%.

For FENE chains a similar strategy can be employed, although in this case the computer program does not stop itself since dimensions and coordinates are always kept limited. A practical criterion has to be imposed to check for coil–stretch transition. For instance, we say that the transition is taking place if the end-to-end distance r reaches half its limiting value for the fully extended chain $r_{max}/2 = (N-1)Q_{max}/2$. We tried other criteria for checking transition; for example, if chain dimensions are regarded in terms of their order of magnitude (on a logarithmic scale), the criterion used may be that $\ln(r^2)$ reaches the mid value between $\ln[(N-1)b^2]$ and $\ln[(N-1)^2Q_{max}^2]$. In practice, we found that various transition criteria gave indistinguishable results for $\dot{\epsilon}_c$, which is perhaps to be expected given the extreme sharpness of the transition.

Besides determining $\dot{\epsilon}_c$, in a second stage of our study we attempted to calculate the variation of polymer properties with $\dot{\epsilon}$, below $\dot{\epsilon}_c$, and for FENE chains above $\dot{\epsilon}_c$. For this purpose, the properties of a chain were monitored during very long simulations with fixed $\dot{\epsilon}$. The heading portion of the trajectory was rejected in order to eliminate any dependence on the initial conformation. This portion amounts to about one fifth of the total trajectory length, and is sufficiently long to ensure that the molecule eventually undergoes transition to the final state corresponding to the $\dot{\epsilon}$ value of the flow to which it is submitted. For the conformations displayed by the molecule along the remaining length of the trajectory, the polymer properties are calculated and averaged. In a steady-state regime, this average over successive conformations of a single molecule is equivalent to the instantaneous average over a sample of molecules. The number of conformations for which the properties in Figs. 1–3 were evaluated is typically 50 000. The properties are usually determined with errors of about 3%–5%, except the low-rate birefringence, which as it is very close to zero is not important (the bar errors are not appreciably larger than the size of the data points themselves, mostly in the logarithmic scales). Due to the sharpness of the transition, such small errors do not affect the detection of $\dot{\epsilon}_c$.

In some simulations with FENE chains the initial conformation was not a coil. Instead, the simulation was started with very stretched conformations generated with springs nearly aligned with the elongational direction of the flow and with spring lengths close to Q_{max}.

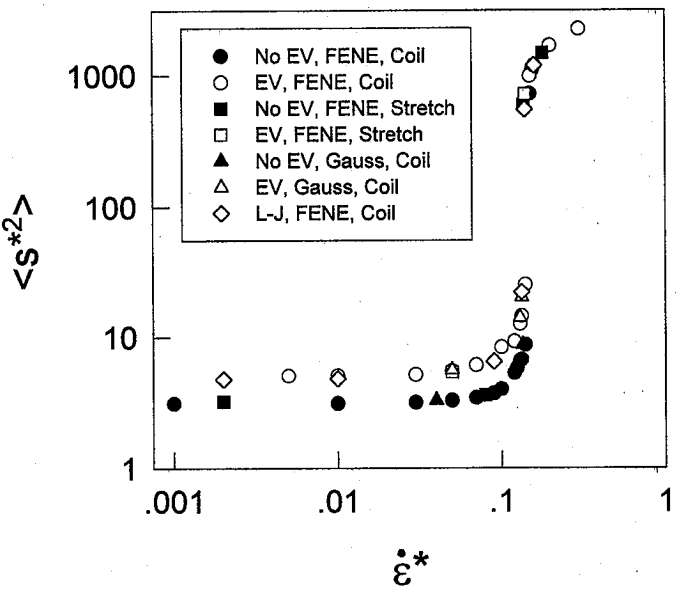

FIG. 1. Dimensionless mean square radius of gyration $\langle s^{*2} \rangle$ vs dimensionless elongational rate $\dot{\epsilon}^*$ for chains of $N = 20$ with HI. Chains were started from the coil state (coil) or the stretched state (stretch). Chain springs were Gaussian (Gauss) or FENE. Excluded volume was either absent (no-EV), represented by the soft potential (EV) or by the Lennard-Jones potential (LJ).

III. RESULTS AND DISCUSSION

A. Dependence of properties on elongational rate

Figure 1 displays the results for steady-state values of the mean square radius of gyration as a function of the applied elongational rate, for chains of 20 beads and hydrodynamic interaction. A number of cases have been included in Fig. 1. Thus, we consider both FENE and Gaussian chains with the same $\langle s^2 \rangle_0$ in the absence of flow. (Obviously, the Gaussian chains cannot be studied beyond $\dot{\epsilon}_c$). Most simulations were started with the molecule in a coil conformation, although we also carried out a few simulations in which

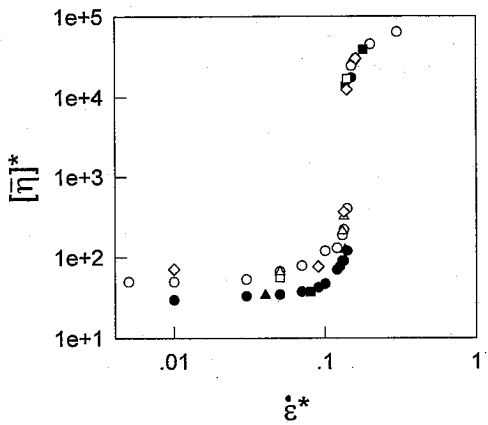

FIG. 2. The same as in Fig. 1, for the dimensionless elongational intrinsic viscosity $[\bar{\eta}]^*$.

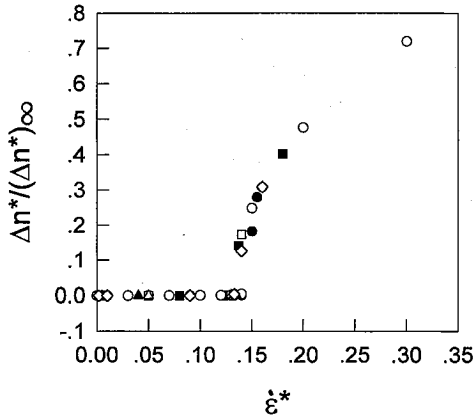

FIG. 3. Variation of the normalized birefringence $\Delta n^*/\Delta n_\infty^*$ with $\dot{\epsilon}^*$. Same code as in Fig. 1.

the initial conformation was close to full extension. The most important aspect of Fig. 1 is the inclusion of chains both without and with excluded-volume effects. The former case represents in an approximate manner theta conditions (a more detailed representation will be used later), and for the latter case that represents good-solvent conditions, two possibilities are considered, namely the Lennard-Jones and the soft types [Eqs. (5) and (6), respectively].

The steady-state view of the coil–stretch transition is clearly seen in Fig. 1 as a very sharp change in $\langle s^2 \rangle$, which increases by several orders of magnitude when the elongational rate reaches a critical value $\dot{\epsilon}_c^* = 0.13$. The essential finding is that $\dot{\epsilon}_c$ is the same for chains with and without excluded volume. In the vicinity of $\dot{\epsilon}_c$, the two families of data merge into a single family. Above $\dot{\epsilon}_c$, $\langle s^2 \rangle$ does not depend on EV, as one might expect for a chain that is stretched by the flow itself, although the point to note is that the transition takes place at the very same $\dot{\epsilon}_c$.

Moreover, $\dot{\epsilon}_c$ is the same for infinitely (Gaussian) and finitely (FENE) extensible chains. Although the behavior of the models above $\dot{\epsilon}_c$ is determined by their extensibility, the value of $\dot{\epsilon}_c$ is governed by the chain properties in the coiled (no-flow) state. We also note that the steady-state values on both sides of $\dot{\epsilon}_c$ are the same (as is to be expected) regardless of whether the initial chain is coiled or stretched.

In Fig. 2 we display the elongational rate dependence of the intrinsic elongational viscosity. We note the existence of a "Newtonian plateau" in which $[\bar{\eta}]$ is independent of flow rate. In other regards, the aspect of Fig. 2 is the same as that for $\langle s^2 \rangle$ in Fig. 1. Our Fig. 2 has the same aspect as a previous result of Kobe and Wiest (1993) for chains without intramolecular interactions, and of Andrews *et al.* (1998a) for the good solvent case. Finally, Fig. 3 depicts the results obtained for the birefringence Δn normalized to the value of a totally stretched chain Δn_∞ (so that as $\dot{\epsilon} \to \infty$, $\Delta n/\Delta n_\infty \to 1$). Ignoring other details, we focus on the main feature of Figs. 1–3, which is the sharp change in properties when $\dot{\epsilon}^*$ reaches the critical value $\dot{\epsilon}_c^*$, which is the same for all the properties.

The essential conclusion from this part of our work is that the inclusion of intramolecular interaction does not change $\dot{\epsilon}_c$, whose value is the same for both theta and excluded-volume, good solvent conditions. (It is also interesting to note that the two different ways to account for excluded-volume effects in good solvent conditions give equivalent results). As commented in Sec. I, there is some controversy between some authors who obtain different scaling exponents, $a = -1.5$ for theta solvents and -1.5

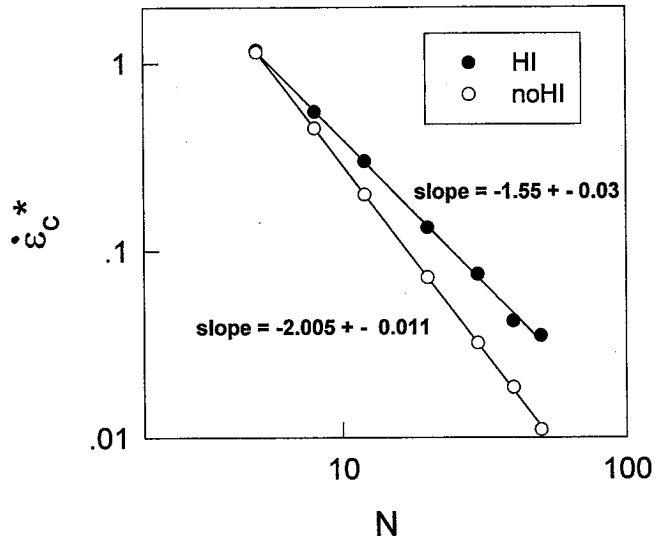

FIG. 4. Variation of the dimensionless critical elongational rate $\dot{\epsilon}_c^*$ with chain length N. Results for FENE chains without EV.

$> a > -1.8$ in good solvents, and other authors who obtain the same value, $a = -1.5$ for both theta and good solvents. Our conclusion gives support to the latter. This situation will be explored in more detail later on.

B. Critical elongational rate: chain length dependence and combination with the longest relaxation time

On the assumption that the critical elongational rate is practically the same for chains with excluded-volume expansion as for ideal, Gaussian chains, we present now the results of the chain-length dependence for the latter case in which intramolecular interactions are absent.

We first carried out a simulations to determine $\dot{\epsilon}_c^*$ without HI, in order to check the result with the available theoretical results. The results presented in Fig. 4 give a scaling relationship of $\dot{\epsilon}_c^* = (28.6 \pm 0.3) N^{-2.005 \pm 0.011}$, which is in very good agreement with the well-known result in the absence of HI, Eq. (15). Such accordance with theory lends important support to our simulation procedures. Next, we carried out simulations including HI. The results for $\dot{\epsilon}_c^*$ are plotted versus N in Fig. 4. A least squares fit gives the result $\dot{\epsilon}_c^* = (14.1 \pm 1.1) N^{-(1.55 \pm 0.03)}$. This is in agreement with the scaling law observed for polymer chains in theta solvents, $\dot{\epsilon}_c^* \propto M^{-3/2}$ [Keller and Odell (1985); Cathey and Fuller (1990)].

From the earliest studies of the elongational flow of polymer solutions, it has been a common practice to relate the elongation rate $\dot{\epsilon}$ with the longest relaxation time τ_1 [Keller and Odell (1985)]. The quantity $\dot{\epsilon}_c \tau_1$ can be also fully determined from our Brownian dynamics simulation. In a previous work [Navarro *et al.* (1995)] the longest relaxation time was obtained by Brownian dynamics simulation of the decay of electric birefringence. In the no-HI case, we obtained $\tau_1^* = C_\tau N^2$, with $C_\tau = 0.0167$, which compared very well with $C_\tau = 1/(6\pi^2) = 0.0169$ from Eq. (17). In the present work if the chain length exponent is forced to be exactly 2, we obtain $\dot{\epsilon}_c^* = C_\epsilon N^{-2}$ with C_ϵ

$= 28.8$, which is in very good agreement with $C_\epsilon = 3\pi^2 = 29.6$ according to Eq. (15). Also, combining the two simulations in the no-HI case, we have $\dot{\epsilon}_c\tau_1 = 0.489$, which is in very good agreement with the theoretical results in Eq. (18). The goodness of the agreement is particularly relevant if one considers the rather complicated procedures required for the simulation and that independent simulations for two properties are involved. This, we feel, lends value to our Brownian dynamics simulation methodology.

The nondraining limit, with the hydrodynamic interaction properly accounted for as described above, is of relevance for practical use. In our simulations of electric birefringence decay [Navarro *et al.* (1995)], $\tau_1^* = C_\tau N^{3/2}$ with $C_\tau = 0.043$. In the present work, by setting the length dependence $\dot{\epsilon}_c^* = C_\epsilon N^{-3/2}$ (instead of $-3/2$ we obtained -1.55), we obtain $C_\epsilon = 11.7$. Combining the HI results of the two simulations, we arrive at $\dot{\epsilon}_c\tau_1 = 0.50$ as our final result.

The above commented result obtained by Magda *et al.* (1988), $(\dot{\epsilon}_c\tau_1)_{\text{pre}} = 0.53$, in which hydrodynamic interaction was somehow preaveraged, is remarkably close to that of our simulations, in which we have employed a fully fluctuating hydrodynamic interaction. Furthermore, in the absence of hydrodynamic interaction, the result was $(\dot{\epsilon}_c\tau_1)_{\text{noHI}} = 1/2$. It is really noteworthy that although each of the two properties ($\dot{\epsilon}_c$ and τ_1) depend strongly on HI, as manifested by different molecular-weight exponents, the product $(\dot{\epsilon}_c\tau_1)$ is practically independent of hydrodynamic interactions.

C. Compound quantities involving the critical elongational rate and the intrinsic viscosity or the radius of gyration

In addition to the commonly employed combination $\dot{\epsilon}_c\tau_1$, other compound quantities involving other simple solution properties can be formulated. One of them is the dimensionless quantity ν [López Cascales and García de la Torre (1991b)] combining $\dot{\epsilon}$ and the zero-shear intrinsic viscosity $[\eta]_0$. There is a simple relationship between the sum of the series of relaxation times which gives the intrinsic viscosity and the longest one, τ_1. This relationship reads

$$\tau_1 = K_{\tau\eta}\frac{M\eta_s[\eta]_0}{N_A kT}, \tag{21}$$

where $K_{\tau\eta}$ is a numerical constant. Thus, $\dot{\epsilon}$ and $[\eta]_0$ can be combined to form the dimensionless quantity

$$\nu = \frac{M\eta_s[\eta]_0}{N_A kT}\dot{\epsilon} = \dot{\epsilon}\tau_1/K_{\tau\eta}. \tag{22}$$

If hydrodynamic interaction is neglected [Bird *et al.* (1987)], we have

$$\tau_1 = \frac{6M[\eta]_0\eta_s}{\pi^2 N_A kT} \quad (\text{no}-\text{HI}) \tag{23}$$

and

$$[\eta]_0 = \frac{N_A\zeta b^2 N^2}{36\eta_s M} \quad (\text{no}-\text{HI}) \tag{24}$$

so that

$$K_{\tau\eta} = 6/\pi^2 \simeq 0.609\ldots \quad (\text{no}-\text{HI}). \tag{25}$$

Combining Eqs. (22), (25), and the no-HI result Eq. (18), we obtain

$$\nu_c = \pi^2/12 \simeq 0.82... \quad \text{(no-HI)}. \tag{26}$$

In a previous work [Navarro *et al.* (1995)] the quantity combining the longest relaxation time and the intrinsic viscosity was obtained by Brownian dynamics simulation. In the no-HI case we obtained $K_{\tau\eta} = 0.60$, which along with the present simulation result $\dot{\epsilon}_c\tau_1 = 0.489$ gives $\nu_c = 0.815$, which is in very good agreement with the theoretical results in Eq. (26). Similarly in our simulations with hydrodynamic interaction [Navarro *et al.* (1995)], we obtained $K_{\tau\eta} = 0.50$ and a combination of this with the present HI value, $\dot{\epsilon}_c\tau_1 = 0.50$ gives $\nu_c = 1.01$. It is again noteworthy that, as in the case of the combination $\dot{\epsilon}_c\tau_1$, the HI and no-HI results are rather close to each other.

In this article we propose one more dimensionless combination of $\dot{\epsilon}_c$ with a simple and common solution property, the unperturbed mean square radius of gyration, $R_g \equiv \langle s^2\rangle^{1/2}$:

$$K_{\epsilon R} = \frac{RT}{\eta_s R_g^3 \dot{\epsilon}_c}. \tag{27}$$

The definition has been made by analogy with two others dimensionless combinations of τ_1 with R_g and with $[\eta]$, that we defined in Navarro *et al.* (1995):

$$K_{\tau R} = \frac{RT}{\eta_s}\frac{\tau_1}{R_g^3}, \tag{28}$$

and

$$K_{\tau\eta} = \frac{RT}{\eta_s M}\frac{\tau_1}{[\eta]}. \tag{29}$$

The following combination of $K_{\epsilon R}$ with the other compound quantities follows easily:

$$K_{\epsilon R} = \frac{K_{\tau R}}{(\dot{\epsilon}_c\tau_1)} = \frac{6^{3/2}\Phi_0}{\nu_c} = \frac{K_{\tau R}}{K_{\tau\eta}\nu_c}, \tag{30}$$

where Φ_0 is the most famous dimensionless, universal compound quantity, the Flory constant involving the intrinsic viscosity and the radius of gyration

$$\Phi_0 = \frac{M[\eta]}{6^{3/2}R_g^3}. \tag{31}$$

We stress that $K_{\epsilon R}$ compound quantity (unlike to other combinations) is only meaningful when hydrodynamic interaction is included. With the $K_{\tau R}$ value from Navarrro *et al.* (1995) and the results for $\dot{\epsilon}_c\tau_1$ obtained above, we arrive at $K_{\epsilon R} = 3.6\times 10^{24}$.

The numerical values of the various dimensionless quantities employed or derived in this work, for both the no-HI and HI cases, are listed in Table I. All our results for the no-HI case compare very well with the results from analytic theories. This encouraging finding lends strong support to our simulation and computational procedures. We have attempted a comparison of the theoretical predictions for the numerical values of $\dot{\epsilon}_c\tau_1$, ν_c, and $K_{\epsilon R}$ in the HI case with some available experimental results. Nguyen *et al.* (1995) have characterized the molecular weight dependence of $\dot{\epsilon}_c$ of polystyrene in various solvents, including the theta solvent decalin. From their results, Nguyen *et al.* report $B \equiv \dot{\epsilon}_c\tau_1'$ to be $B \simeq 3$ in decalin, which they claim to be distinct from the result

TABLE I. Dimensionless compound quantities and constants.

	No-HI	Preave-HI	HI	Expt.
$\dot{\epsilon}_c\tau_1$	$\frac{1}{2} = 0.50...$	...	0.50[a]	1.5[b]
ν_c	$\frac{\pi^2}{12} = 0.82...$	...	1.01[a]	4.4[b]
$K_{\tau\eta}$	$\frac{6}{\pi^2} = 0.609...$	0.42[c]	0.5[d]	...
$K_{\tau R}\times 10^{24}$	...	1.76	1.8[d]	
$\Phi\times 10^{-23}$	...	2.82[e]	2.53[f]	2.5[f]
$K_{\epsilon R}\times 10^{-24}$	...	...	3.6[a]	2.3 ± 0.8[g]
				0.95[b]

[a]This work.
[b]Nguyen *et al.* (1995).
[c]Zimm (1956), Yamakawa (1970), and Hearst (1962).
[d]Navarro *et al.* (1995).
[e]Yamakawa (1970), Hearst (1962).
[f]García de la Torre *et al.* (1984), Freire *et al.* (1986b) and references therein.
[g]Menasveta and Hoagland (1992).

obtained by Magda *et al.* (1988) (which is quite close to our simulation result, as we have already described). The analysis of Nguyen *et al.* is somehow affected by the above mentioned existence of two notations and types of relaxation times. From Eq. (23) in Nguyen *et al.* (1995) and the numerical values used in it, it is clear that their B combines $\dot{\epsilon}_c$ with the "dielectric" relaxation time τ_1'. Thus, we have $\dot{\epsilon}_c\tau_1 = B/2 = 1.5$ for polystyrene in decalin, which is to be compared with the theoretical and simulation result $\dot{\epsilon}_c\tau_1 = 0.50$. The prediction is correct in order of magnitude and the agreement is not as poor as in the comparison with B, but still lacks quantitative value.

From the experiments of Nguyen *et al.*, we have also tried to estimate ν_c. Using their data in the theta solvent decalin, with $\eta_s = 2.39\,\mathrm{mPa\,s}$ and $[\eta] = 2.34\times 10^{-3}M'^{0.53}\,\mathrm{m^3\,kg^{-1}}$ (M' in kg/mol), we calculate $[\eta] = 310\,\mathrm{cm^3/g}$ for $M = 10^7$ g/mol. From their graphed dependence of $\dot{\epsilon}_c$ on M we obtain [after correction $\dot{\epsilon}_c$(app) with the 0.7 factor] the value $\dot{\epsilon}_c = 1470\,\mathrm{s^{-1}}$ for the same molecular weight. Substituting these results into Eq. (22) we arrive at the result $\nu_c = 4.4$, in contrast with the simulation result, $\nu_c = 1.01$.

For a similar analysis of $K_{\epsilon R}$, we take the unperturbed dimensions of polystyrene from the compilation of Kurata and Tsunashima (1988). The constant $R_0/M^{1/2}$, where $R_0 \equiv \langle r^2\rangle_0^{1/2}$ is the mean square end-to-end distance takes on values that strongly depend on the source; we estimate $R_0/M^{1/2} = (700\pm 50)\times 10^{-4}$ nm. This amounts to writing $R_{g,0} = 2.85\times 10^{-9}M^{1/2}$ (cm). Again, for polystyrene/decalin theta system, from Fig. 15 of Nguyen *et al.* (1995), for what they call the "apparent" value, which shows a slope of -1.5, we obtain graphically $\dot{\epsilon}_c$(app) $= 6.7\times 10^{13}M^{-1.5}\,(\mathrm{s^{-1}})$ which is converted to $\dot{\epsilon}_c = 4.7\times 10^{13}M^{-1.5}\,(\mathrm{s^{-1}})$ by applying the correction factor 0.7 [Eq. (9) Nguyen *et al.* (1995)]. The solvent viscosity of decalin is $\eta_s = 0.0239$ P. From these data, using Eq. (27), we arrive at $K_{\epsilon R} = 0.95\times 10^{24}$.

Menasveta and Hoagland (1992) measured $\dot{\epsilon}_c$ of polystyrene in a good solvent, toluene, and found $\dot{\epsilon}_c \propto M^{-1.47\pm 0.03}$, which is in agreement with our finding that the scaling law is independent of solvent quality. If we fix a $-3/2$ scaling exponent, their data [Table I in Menasveta and Hoagland (1992)], with M and $\dot{\epsilon}_c$ as determined in their

laboratory, are fitted by $\dot{\epsilon}_c = (9.3 \pm 0.4) \times 10^{13} M^{-3/2}$. Combining this with molecular weight dependence of $R_{g,0}$, we obtain $K_{\epsilon R} = (2.0 \pm 0.5) \times 10^{24}$ from Eq. (27).

In judging the agreement between our simulation results for $\dot{\epsilon}_c \tau_1$, ν_c, or $K_{\epsilon R}$ and the estimates from experimental work, one should bear in mind that these compound quantities accumulates the possible experimental, theoretical, or computational deficiencies in the various properties, $\dot{\epsilon}_c$, τ_1, $[\eta]$, and $R_{g,0}$, each of which is the final result of elaborate experimental or computational processes. Thus, we find the values obtained from simulation agree with those derived from experimental data just in their order of magnitude, but not quantitatively. On the experimental side, it would be important that all the involved quantities, $\dot{\epsilon}_c$, τ_1, $[\eta]$, and $R_{g,0}$ were measured in the same laboratory, on the polymer/solvent/temperature system, etc. The availability of the numerical data for the dimensionless quantities reported in this work may stimulate such measurements.

D. Effect of solvent quality: excluded volume and intramolecular interactions

As noted in Sec. I, one of the intentions of this work was to shed some light on the existing controversy about the exponent a in the $\dot{\epsilon}_c$ vs M relationship, Eq. (2): some authors [Farrell *et al.* (1980); Fuller and Leal (1980); Keller and Odell (1985); Odell *et al.* (1985); Menasveta and Hoagland (1991,1992); Narh *et al.* (1992)], found that the exponent is the same, $a = -1.5$ for both theta solvents and good solvents, while others claim that in good solvents the exponent is different $a \approx -1.8$ [Atkins *et al.* (1986); Brestkin *et al.* (1986); Nguyen *et al.* (1995)]. According to our simulation results described above, the reduced $\dot{\epsilon}_c^*$ is the same, and follows a $N^{-1.5}$ dependency regardless of the introduction of the excluded-volume interactions proper of good solvent conditions, and this lends support to the first group of authors. The finding (using computer simulation) that a is the same for good solvents as for theta solvents is not exclusive of our work: in their very recent paper, Andrews *et al.* (1998a) carried out simulations without hydrodynamic interaction, obtaining $a = -2$ in good solvents, which is the same exponent predicted from the basic theory of the ideal chain [Eq. (14)] [Bird *et al.* (1983)]. Therefore, although their numerical value is influenced by the neglect of HI, it is clear that such a value is the same in the two conditions.

Nonetheless, the importance of this problem prompted us to carry out a deeper study of some aspects. First, in the previous calculations the theta state of the polymer molecules was represented by an ideal chain in which intramolecular interactions are simply absent. However, the theta state actually corresponds to a balance between simultaneous attractive and repulsive interactions [see for instance Rey *et al.* (1987b) or Milchev *et al.* (1993)]. Another aspect concerns the possible behavior of chains in bad solvents, below the theta state, where the polymer adopts the so-called collapsed or globular conformation. The information on this situation is scarce; Andrews *et al.* (1998a) have reported some simulations without HI, and it may be interesting to complement their results here.

For the two purposes, the inclusion of intramolecular interactions via the LJ potential is effective. In Sec. II of this article, we have described how the LJ potential is useful in describing all the cases regarding solvent quality: good, theta, and bad solvent with $\epsilon_{LJ} = 0.1$, 0.3, and 1.0, respectively, and $\sigma_{LJ} = 0.8$ in all cases. Thus, we invested large amounts of computer time carrying out Brownian dynamics simulations for LJ chains with the various values of the solvent-quality parameter.

We carried out new determinations of $\dot{\epsilon}_c^*$ for varying N, with $\epsilon_{LJ} = 0.1$ and 0.3, with and without HI. The results are represented in Fig. 5. The series of points with $\epsilon_{LJ} = 0.3$, corresponding to the theta state, superimpose well with the data for the ideal

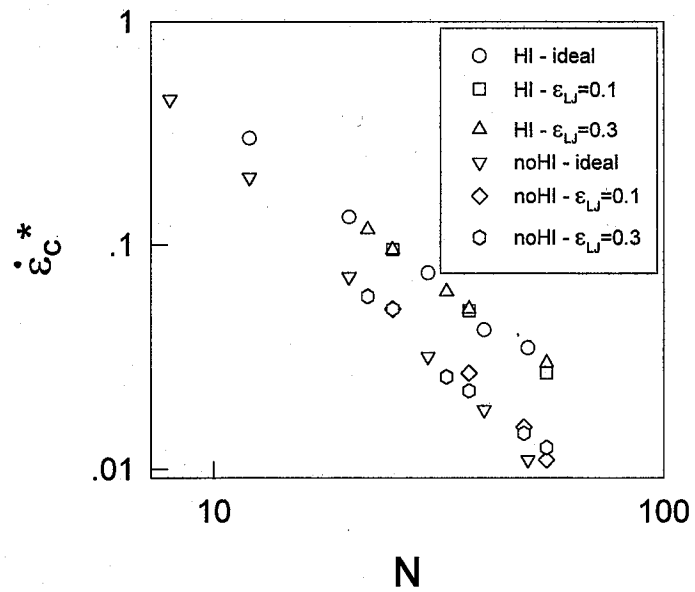

FIG. 5. Values of the reduced critical elongational rate $\dot{\epsilon}_c^*$ plotted vs chain length N for various cases with and without HI, and with choices for the intramolecular potential parameters corresponding to good and theta solvents.

chain. This demonstrates that, at least for the present purpose, there is no difference between the two ways of representing polymers in theta solvents. The new results for the good solvent conditions, $\epsilon_{LJ} = 0.1$, also superimpose well with the other two sets, following the same dependence with N. This confirms our previous finding that the dependence of the reduced $\dot{\epsilon}_c^*$ on N is the same, and therefore the exponent a must be the same for good solvents as for theta solvents.

In our LJ representation of intramolecular interactions, we follow the common practice [Freire *et al.* (1986a,1986b); Rey *et al.* (1987a,1987b); Milchev *et al.* (1993); Andrews *et al.* (1998a)] of gauging the solvent quality varying the potential parameter that gives the attractive part ϵ_{LJ} in our case. The above results indicate that the critical elongational rate is practically insensitive to ϵ_{LJ} for low or moderate values of this parameter. Then we proceeded carrying out more simulations with higher values of ϵ_{LJ}, reaching up to a value $\epsilon_{LJ} = 1.0$, representative of the collapsed conformations in bad solvents. The results, which are plotted in Fig. 6, provide a clear view of the influence of the solvent quality parameter in $\dot{\epsilon}_c^*$, which remains nearly unchanged in a wide region that covers the good solvent and theta solvent cases, but increase noticeably beyond that region, to reach values for the bad solvent case that are remarkably larger than for good solvents. This trend is also observed in the no-HI results of Andrews *et al.* (1998a).

To end with the present discussion, we turn back to the combination of the critical elongational rate with the longest relaxation time, in the form of the dimensionless product $\dot{\epsilon}_c \tau_1$, where τ_1 is the longest relaxation time of the chain (Rouse time, without HI; Zimm time with preaveraged HI, or a similar value with fluctuating HI). τ_1 is the longest of a series of times that characterize the dynamics of a polymer chain in its random coil conformation (as monitored, for instance, in dynamic light scattering of a quiescent solution), or in very slightly deformed conformations produced by weak external agents (shear flows or electric fields). All the workers, including ourselves, agree in

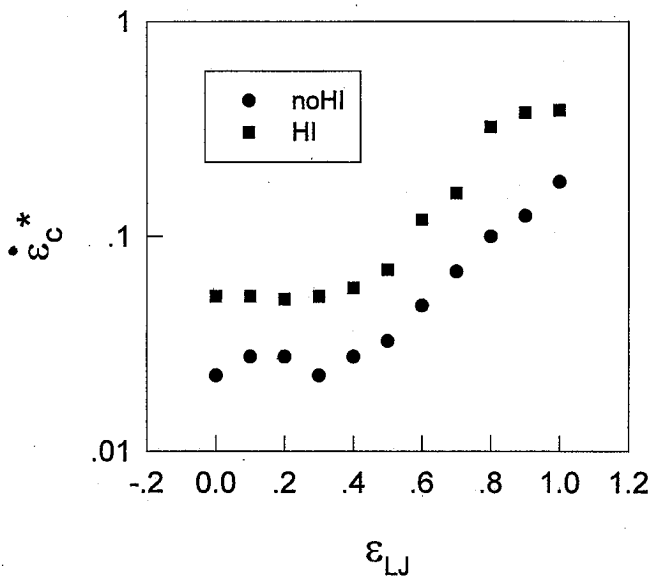

FIG. 6. Reduced critical elongational rate $\dot{\epsilon}_c^*$ for chains with $N = 37$ beads, for various values of the ϵ_{LJ} parameter of the LJ potential, covering from good to bad solvent conditions.

that excluded-volume effects in good solvent conditions produce a molecular weight dependence of approximately $\tau_1 \approx M^{-1.8}$. This is indeed predicted from renormalization group theory [Ohta *et al.* (1982)], and obtained from Brownian dynamics simulation of molecular relaxation of dynamic light scattering [Rey *et al.* (1991)].

On the other hand the relationship $\dot{\epsilon}_c \tau_1 \approx 1$ (now we know that the product is about 0.5) has been given a somehow universal validity, so that some authors identify the reciprocal of $\dot{\epsilon}_c$ with τ_1 in all instances. Under such premises, one should expect $\dot{\epsilon}_c \propto M^{-1.8}$, i.e., $a \approx -1.8$, and the result $a \approx -1.5$ found by various experimental workers and in our simulations would be considered to be contradictory.

In our opinion, the weakness in that rationale is the employment of the Rouse, Zimm (or improved Zimm) longest relaxation time as the characteristic time to define a Deborah number for elongational flow. Mathematically, the combination works well in theta conditions because in such a case $\dot{\epsilon}_c \propto M^{-1.5}$ and $\tau_1 \propto M^{1.5}$, with the obvious consequence that $\dot{\epsilon}_c \tau_1$ is a constant. However, on physical grounds, τ_1 may not be an adequate characteristic time in elongational flow. In the last years, the coil–stretch transition is being considered mainly as a dynamic, time-dependent phenomenom [Wiest *et al.* (1989); Liu (1989)]. The typical time of residence in the elongational flow required for a given polymer molecule to go from the coiled conformation to the stretched one is much longer than the Rouse–Zimm τ_1; this has been noticed in some computer simulations [López Cascales and García dela Torre (1992a); Agarwal *et al.* (1998)], and mostly in the remarkable experiments of Perkins *et al.* (1997). Also, the decay of properties from the values of the stretched state to those of the coil is governed by the dynamics of the chain in more or less stretched conformations, for which τ_1 is not meaningful. In summary, τ_1 does not provide an adequate time scale for coil–stretch processes in elongational flow. Therefore, the relevance that has been sometimes given to the combination $\dot{\epsilon}_c \tau_1$ is at least doubtful, and its use in predictions may be misleading.

IV. CONCLUDING REMARKS

In the present article, we have employed Brownian dynamics simulations to characterize the steady-state behavior of model polymer chains in elongational flow. We describe the calculation of various polymer properties, including the extensional viscosity and the optical birefringence. The critical elongational rate $\dot{\epsilon}_c$ is independent of whether or not intramolecular interactions are present: $\dot{\epsilon}_c$ is the same for excluded-volume chains as for theta chains. After determining the chain-length dependence of $\dot{\epsilon}_c$, we have been able to obtain precise values for $\dot{\epsilon}_c \tau_1$ and other dimensionless compound quantities.

We should point out that the coil–stretch transition, in addition to the steady-state aspect that we treat in this article, has dynamic aspects regarding how the properties respond to the inception or cessation of the flow. This includes not only the time dependence of bulk solution properties [Liu (1989); Wiest *et al.* (1989); López Cascales and García de la Torre (1992a)], but also the individual response of each chain in the sample [Perkins *et al.* (1997); Hernández Cifre and García de la Torre (1998)]. The Brownian dynamics methodology employed in this work is a promising tool for simulating such dynamic aspects.

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