

## Modified reptation model

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(Received 31 August 1994)

We consider a modification of the Doi-Edwards [*The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986)] and Curtiss-Bird [*Dynamics of Polymeric Liquids, Vol. 2, Kinetic Theory* (Wiley-Interscience, New York, 1987), 2nd ed.] models for polymer melts in which the effect of constraint release or partially anisotropic Brownian motion is introduced through a stochastic force in the time-evolution equation for the orientation of inner chain segments. A thermodynamically consistent expression for the stress tensor is proposed. In the linear viscoelastic regime, the results for the moduli are very similar to those predicted by double reptation. In the nonlinear viscoelastic regime, the model describes the rheological behavior in an objective manner. The shear-rate dependence of the viscosity obtained from the modified reptation model is more realistic than the Doi-Edwards prediction.

PACS number(s): 61.25.Hq, 47.50.+d, 61.41.+e, 62.10.+s

### I. INTRODUCTION

Concentrated polymer solutions and polymer melts constitute extremely complex many-particle systems. For that reason, it is unquestionably important to make both ingenious and far-reaching assumptions in describing the dynamics of polymers in such undiluted systems. A widely and successfully applied class of molecular models for the polymer dynamics in concentrated solutions and melts relies on the notion of reptational motion [1]. The first reptation theory for the rheology of undiluted polymers was developed by Doi and Edwards [2]. The Doi-Edwards model is based on the assumption that each polymer in a highly entangled system moves ("reptates") in a tube formed by other polymers. A systematic kinetic theory for polymer melts has been developed by Curtiss and Bird [3]. In their derivation of a diffusion equation for the polymer dynamics, Curtiss and Bird use anisotropic friction tensors to describe the hindrance of sideway motions of the polymers in concentrated systems. These anisotropic friction tensors express essentially the same physical idea as the constraining tube in the Doi-Edwards model.

In this paper, we introduce a modified reptation model which accounts for the effect of constraint release (Doi-Edwards picture) or partially anisotropic Brownian motion (Curtiss-Bird picture). The formulation of the model is based exclusively on simplicity and various consistency criteria (fluctuation-dissipation theorem, material objectivity, thermodynamic consistency). While the proposed dynamics has been considered before, the expression for the stress tensor deviates from that previously suggested. After introducing the model and discussing the basic assumptions we derive a memory-integral expression for the stress tensor from which we obtain the linear viscoelastic behavior and the zero-shear-rate viscosity. The relaxation modulus is very similar to the one obtained from the idea of double reptation so that the modified

model may be regarded as an extension of double reptation into the regime of nonlinear viscoelasticity. As an example of a nonlinear viscoelastic property, we discuss high-precision simulation results for the shear-rate-dependent viscosity and its asymptotic behavior at high shear rates. Furthermore, it is shown how polydisperse melts can be modeled.

### II. FORMULATION OF THE MODEL

The variables used in the Doi-Edwards and Curtiss-Bird models to characterize polymer configurations are a unit vector  $\mathbf{U}$  and a real number  $S$  in the interval  $[0, 1]$ . The unit vector  $\mathbf{U}$  describes the direction of the polymer chain at the position  $S$  within the chain, where the label  $S$  varies from 0 to 1 in going from one chain end to the other. The reptation dynamics is usually formulated in terms of a diffusion equation for the configurational distribution function. We here rely on a stochastic formulation of reptation dynamics in which  $\mathbf{U}$  and  $S$  are stochastic processes, where these time-dependent random variables can be determined from stochastic differential equations supplemented by suitable initial and boundary conditions [4,5].

In the following, a modified version of the Doi-Edwards and Curtiss-Bird models is defined through modified time-evolution equations for  $\mathbf{U}_t$  and  $S_t$ . The simplest modification of the traditional reptation models is obtained by adding a stochastic term to the usually deterministic differential equation for  $\mathbf{U}_t$ . Then, the process  $\mathbf{U}$  satisfies the stochastic differential equation

$$d\mathbf{U}_t = (\delta - \mathbf{U}_t \mathbf{U}_t) \cdot \left[ \boldsymbol{\kappa}(t) \cdot \mathbf{U}_t dt + \frac{\pi \bar{\epsilon}}{(3\lambda)^{1/2}} d\mathbf{W}_t \right] - \frac{\pi^2 \bar{\epsilon}^2}{3\lambda} \mathbf{U}_t dt, \quad (1)$$

where  $\kappa(t)$  is the transposed velocity-gradient tensor,  $\lambda$  is a characteristic time constant, namely the so-called disengagement or reptation time,  $\bar{\epsilon}$  is a real number related to the reptation coefficient  $\epsilon'$  of Ref. [3], and  $\mathbf{W}_t$  represents a three-dimensional Wiener process. As a Gaussian stochastic process, the Wiener process is completely characterized by its first and second moments,  $\langle \mathbf{W}_t \rangle = \mathbf{0}$ ,  $\langle \mathbf{W}_t \mathbf{W}_{t'} \rangle = \min(t, t') \delta$  [6,7]. The term  $\kappa(t) \cdot \mathbf{U}_t$  in Eq. (1), which occurs also in the traditional reptation models, expresses the fact that the vector  $\mathbf{U}_t$  tends to follow the flow field. A randomizing effect, which is expressed in terms of the Wiener process, is superimposed. The transverse projection operator  $(\delta - \mathbf{U}_t \mathbf{U}_t)$  is introduced such that the dynamics preserves the property of being a unit vector. Since the stochastic differential equation (1) involves multiplicative noise (i.e.,  $d\mathbf{W}_t$  is multiplied by a configuration-dependent term), its interpretation is delicate. We here adopt the Itô interpretation of Eq. (1) [6,7]. In Itô calculus, the additional deterministic contribution in the second line of Eq. (1) is necessary in order to preserve the length of  $\mathbf{U}_t$ .

Equation (1) is the time-evolution equation for a rigid dumbbell with time constant  $\lambda^{\text{rd}} = \lambda/(\pi^2 \bar{\epsilon}^2)$  [6]. The usual deterministic differential equation for  $\mathbf{U}$  is recovered for  $\bar{\epsilon} = 0$ . The remaining dynamical equations are chosen exactly as in the original Doi-Edwards and Curtiss-Bird models. In other words, the process  $S$  is the solution of the following stochastic differential equation,

$$dS_t = \sqrt{\frac{2}{\lambda}} dW'_t, \quad (2)$$

where  $W'$  is another Wiener process which is independent of  $\mathbf{W}$ .

The only coupling between the two processes  $\mathbf{U}$  and  $S$  arises through the boundary conditions. Whenever the process  $S$  reaches one of the boundaries of its range,  $\mathbf{U}$  no longer follows the flow field but rather is chosen as a randomly oriented unit vector; 0 and 1 constitute

reflecting boundaries for the process  $S$ .

A physical interpretation of the dynamics of  $\mathbf{U}$  and  $S$  has been offered in previous papers [4,5]. A better understanding of the mathematical implications of the stochastic differential equations of motion can be gained through time-discretized approximations which are the starting point of simulation algorithms [6] (see below). On the level of diffusion equations, the idea of introducing noise into the time-evolution equation for  $\mathbf{U}$  has been suggested previously. Indeed, after a suitable redefinition of parameters, the stochastic differential equations formulated here are equivalent to the diffusion equation (19.3-26) of Ref. [3]. In the spirit of the Curtiss-Bird model, the new term involving  $\bar{\epsilon}$  results from a superposition of the equilibration-in-momentum-space and reptation assumptions for the Brownian forces on a chain in a concentrated system. In the spirit of the Doi-Edwards model, this term may be regarded as a constraint release mechanism which allows configurational relaxation to take place not only at the chain ends (for other descriptions of constraint release, see Ref. [8] and the references given on p. 238 and p. 282 of Ref. [2]). Since the release of constraints occurs through the reptational motion of surrounding chains forming a tube, and hence occurs on the same time scale as the reptation of a probe chain, the parameter  $\bar{\epsilon}$  should be a number of order one. In particular, we assume  $\bar{\epsilon}$  to be independent of molecular weight. For polymers which are long enough to be massively entangled we then expect  $\bar{\epsilon}$  to be a universal number.

In the absence of flow,  $\mathbf{U}_t$  and  $S_t$  are uniform random variables on the unit sphere and on the interval  $[0, 1]$ , respectively. In other words,  $\mathbf{U}_t$  and  $S_t$  are distributed according to the Boltzmann distribution; this remark may be regarded as a verification of the fluctuation-dissipation theorem.

While the reptation dynamics formulated above has previously been introduced in an equivalent form in Ref. [3], the stress tensor expression considered here,

$$\boldsymbol{\tau}(t) = N n_p k_B T \left\{ \frac{1}{3} \delta - \langle \mathbf{U}_t \mathbf{U}_t \rangle - \epsilon \lambda \kappa(t) : \langle S_t (1 - S_t) \mathbf{U}_t \mathbf{U}_t \mathbf{U}_t \mathbf{U}_t \rangle - \bar{\epsilon} \lambda \kappa(t) : \langle \mathbf{U}_t \mathbf{U}_t \mathbf{U}_t \mathbf{U}_t \rangle \right\}, \quad (3)$$

deviates significantly from the one of Ref. [3]. In Eq. (3),  $N$  is the number of segments in each polymer molecule,  $n_p$  is the number density of polymers,  $k_B$  is Boltzmann's constant, and  $T$  is the absolute temperature. Furthermore,  $\epsilon$  is the link tension coefficient of the Curtiss-Bird model ( $0 \leq \epsilon \leq 1$ ) and  $\bar{\epsilon}$  is another dimensionless parameter.

In Ref. [3] the anisotropic term  $-\frac{1}{2} N n_p k_B T \pi^2 \bar{\epsilon}^2 \times \langle S_t (1 - S_t) \mathbf{U}_t \mathbf{U}_t \rangle$  appears in the stress tensor instead of the term above involving  $\bar{\epsilon}$ . Such a contribution, however, is inconsistent with a very general, systematic formulation of the time-evolution equations for nonequilibrium systems developed by Jongschaap [9,10] (this problem

does not occur for the original Curtiss-Bird model for which  $\bar{\epsilon} = 0$ ). On the other hand, additional terms proportional to  $\kappa(t)$  are not ruled out by Jongschaap's formalism. Although the validity of Jongschaap's formalism may be questioned we here adopt it as a thermodynamic consistency criterion. We hence keep the term proportional to the link tension coefficient  $\epsilon$  of the Curtiss-Bird model, and we add a simple new term proportional to  $\bar{\epsilon}$  such that for  $\bar{\epsilon} = 2/(\pi^2 \bar{\epsilon}^2)$  the stress tensor contribution of rigid dumbbells with dynamics given by Eq. (1) is recovered. Note that stress tensor contributions proportional to  $\kappa(t)$  lead to a violation of the stress-optical law, and that the coefficients  $\epsilon$  and  $\bar{\epsilon}$  should hence be small.

For the link-tension coefficient  $\epsilon$ , dynamic viscosity measurements indeed suggest that  $\epsilon$  should be small [3], and it has been argued theoretically that  $\epsilon$  should be of the order of  $1/N$  [5]. Experimental or theoretical estimates of the small parameter  $\bar{\epsilon}$  still need to be determined. Since the presence of the noise term in Eq. (1) is expected to reduce the decay of the viscosity with shear rate and to avoid the large recoil effects of the Doi-Edwards model,

small values of  $\epsilon$  and  $\bar{\epsilon}$  should be sufficient for predicting realistic material behavior.

### III. LINEAR VISCOELASTICITY

We next formulate the stress tensor in the form of a memory-integral expression,

$$\boldsymbol{\tau}(t) = Nn_p k_B T \left\{ \frac{1}{3} \boldsymbol{\delta} - \int_{-\infty}^t dt' \left[ \mu(t-t') \langle \mathbf{U}_t \mathbf{U}_t \rangle_{t'}^{\text{rd}} + [\epsilon \nu(t-t') + \bar{\epsilon} \mu(t-t')] \lambda \boldsymbol{\kappa}(t) : \langle \mathbf{U}_t \mathbf{U}_t \mathbf{U}_t \mathbf{U}_t \rangle_{t'}^{\text{rd}} \right] \right\}, \quad (4)$$

where

$$\mu(t) = \frac{8}{\lambda} \sum_{\substack{n=1 \\ n \text{ odd}}}^{\infty} e^{-n^2 \pi^2 t / \lambda}, \quad (5)$$

$$\nu(t) = \frac{16}{\pi^2 \lambda} \sum_{\substack{n=1 \\ n \text{ odd}}}^{\infty} \frac{1}{n^2} e^{-n^2 \pi^2 t / \lambda}, \quad (6)$$

and  $\langle \rangle_{t'}^{\text{rd}}$  denotes an average for rigid dumbbells which were at equilibrium for times previous to  $t'$  and have been exposed to the flow after  $t'$  [the time constant for these dumbbells is  $\lambda^{\text{rd}} = \lambda / (\pi^2 \bar{\epsilon}^2)$ ]. Note that the expression (4) is a rather formal result because the evaluation of the rigid dumbbell averages  $\langle \rangle_{t'}^{\text{rd}}$  is nontrivial. The importance of rigid dumbbell results for a modified reptation model with the same dynamics as considered here has previously been emphasized in Ref. [3].

Equation (4) is a convenient starting point for evaluating the relaxation modulus  $G(t)$ . Due to the presence of the prefactor  $\boldsymbol{\kappa}(t)$ , the fourth moments of  $\mathbf{U}_t$  can be replaced by their equilibrium values, and the linear viscoelastic limit of the second moments of rigid dumbbells can be found in Ref. [3] (from the results of Sec. 14.5 of Ref. [3], even the second-order memory-integral expansion can be constructed in a rigorous manner). One obtains for the relaxation modulus

$$G(t) = Nn_p k_B T \lambda \left[ \frac{1}{45} (\epsilon + 6\bar{\epsilon}) \delta(t) + \frac{1}{10} \nu(t) e^{-\bar{\epsilon}^2 \pi^2 t / \lambda} \right]. \quad (7)$$

The relaxation times following from Eq. (7) are of the form

$$\lambda_n = \frac{1 + \bar{\epsilon}^2}{n^2 + \bar{\epsilon}^2} \lambda_1, \quad \lambda_1 = \frac{\lambda}{(1 + \bar{\epsilon}^2) \pi^2}, \quad n \text{ odd}. \quad (8)$$

For increasing  $\bar{\epsilon}$ , the first relaxation time becomes less dominating, and the spectrum hence becomes more realistic. Note that the expression (7) for the relaxation modulus is closely related to the idea of double reptation which accounts for the fact that a constraint imposed by a surrounding chain on a probe chain can be removed by the reptational motion of either of the two chains [8]. According to double reptation, the noninstan-

taneous contribution to the modulus  $G(t)$  of the original Doi-Edwards model obtained for  $\epsilon = \bar{\epsilon} = 0$  is multiplied by  $G(t)/G(0)$ . A similar additional factor is here given by the time dependence of the relaxation modulus for rigid dumbbells with a comparable relaxation time, which is  $\exp\{-\bar{\epsilon}^2 \pi^2 t / \lambda\}$ . The success of double reptation suggests that a more realistic linear viscoelastic behavior should also result for the present modification of the original reptation models. While the idea of double reptation is limited to linear viscoelasticity, the model introduced in this paper allows the prediction of the rheological behavior also in the nonlinear regime.

The success of the double reptation idea is truly spectacular when it is applied to polydisperse melts [8]. In that case, the time constants  $\lambda$  in Eqs. (1) and (2) should be sampled independently according to suitable probability distributions. The time constant  $\lambda$  of the surrounding chains occurring in Eq. (1) must be sampled according to the mass fraction of chains with the corresponding molecular weight [see Eqs. (19.3-25) of Ref. [3] for this correspondence between molecular weight and time constant]. The time constant  $\lambda$  of the reptating probe chain in Eq. (2) must be selected randomly according to the number fraction of chains with the corresponding molecular weight [notice that the selected molecular weight of the probe chain enters through the factor  $N$  in the stress tensor expression (3), too]. This simple procedure results in a rather involved mixing rule for nonlinear rheological properties due to the coupling of the time constants of molecules with different molecular weights in the stochastic differential equations of motion. The mixing rule given here differs crucially from the one implied by Eq. (19.3-26) of Ref. [3], which corresponds to having equal time constants  $\lambda$  in Eqs. (1) and (2).

### IV. VISCOSITY FUNCTION

The nonlinear rheological behavior of the new model suggested here satisfies the principle of material objectivity. This can be shown by analyzing the transformation behavior of the equation of motion (1) and of the stress tensor expression (3) under time-dependent rotations.

From the relaxation modulus (7) we obtain the zero-shear-rate viscosity

$$\eta_0 = \frac{1}{60} N n_p k_B T \lambda \left\{ \frac{12}{\pi^2 \bar{\epsilon}^2} \left[ 1 - \frac{\tanh(\pi \bar{\epsilon}/2)}{\pi \bar{\epsilon}/2} \right] + \frac{2}{3} \epsilon + 4 \bar{\epsilon} \right\}. \quad (9)$$

The simplest and most powerful method for investigating the modified reptation model proposed here are stochastic simulation techniques. Such simulations result from applying numerical integration schemes to the stochastic differential equations of motion (1) and (2) [4-6]. In the simplest simulation algorithm,  $\mathbf{U}_{t+\Delta t}$  is constructed from  $\mathbf{U}_t$  by adding  $\boldsymbol{\kappa}(t) \cdot \mathbf{U}_t \Delta t + \pi \bar{\epsilon} [\Delta t / (3\lambda)]^{1/2} \mathbf{W}$  to  $\mathbf{U}_t$ , where  $\mathbf{W}$  is a column vector formed out of three independent Gaussian random numbers with mean zero and variance unity; the result is then normalized to unity in order to obtain  $\mathbf{U}_{t+\Delta t}$ . In the limit  $\Delta t \rightarrow 0$ , this algorithm reproduces the dynamics described by the Itô stochastic differential equation (1) [6]. Similarly,  $\mathbf{S}_{t+\Delta t}$  is obtained by adding  $(2/\lambda)^{1/2} \mathbf{W}'$  to  $\mathbf{S}_t$ , where  $\mathbf{W}'$  is a further independent Gaussian random number with mean zero and variance one. When  $\mathbf{S}_{t+\Delta t}$  is not contained in  $[0, 1]$  it is reflected back into this interval and, whenever such a reflection happens,  $\mathbf{U}_{t+\Delta t}$  is replaced by a random unit vector. In order to obtain a higher-order algorithm one has to compensate for unobserved reflections [4,5].

In Fig. 1, the viscosity of the modified reptation model for  $\bar{\epsilon} = 1$ ,  $\epsilon = \bar{\epsilon} = 0$  obtained by high-precision simulations as a function of dimensionless shear rate  $\lambda \dot{\gamma}$  is compared to the corresponding result for the Doi-Edwards model ( $\epsilon = \bar{\epsilon} = \bar{\epsilon} = 0$ ). The fact that increasing  $\bar{\epsilon}$  leads to a smaller relaxation time  $\lambda_1$  [see Eq. (8)] implies that, for the modified model, deviations from the zero-shear-rate viscosity appear only at higher dimensionless shear rates  $\lambda \dot{\gamma}$ . In addition, the decay of the viscosity with shear rate is slower for the modified model. While for the Doi-Edwards model the asymptotic behavior of the viscosity is given by  $\eta(\dot{\gamma}) \propto \dot{\gamma}^{-3/2}$ , rigid-rod results imply [11]  $\eta(\dot{\gamma}) \propto \dot{\gamma}^{-4/3}$  for the modified model. For the new model, smaller values of  $\epsilon$  (or  $\bar{\epsilon}$ ) than usually assumed in the Curtiss-Bird model should hence prevent the viscosity from decreasing more rapidly than  $\dot{\gamma}^{-1}$  or, in other words, prevent the shear stress from being a nonmonotonic function of shear rate.

## V. SUMMARY

The modified reptation model obtained in this paper by introducing a stochastic force on the dynamical equation for the orientation of inner chain segments and by using a suitable stress tensor is more realistic than the original reptation models. The linear viscoelastic behavior of the new model is less dominated by a single relaxation time, which is a qualitative improvement, and the quantitative improvement should be very similar to that

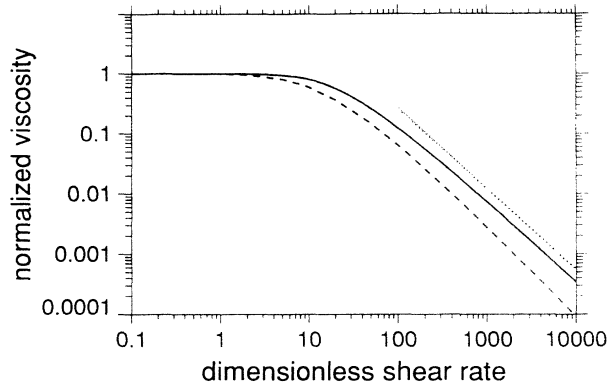


FIG. 1. The normalized viscosity as a function of the dimensionless shear rate  $\lambda \dot{\gamma}$  for the Doi-Edwards model (dashed line) and the modified reptation model for  $\bar{\epsilon} = 1$ ,  $\epsilon = \bar{\epsilon} = 0$  (continuous line). At high shear rates, the asymptotic viscosity curve for the new reptation model should possess the slope  $-4/3$  in the double logarithmic presentation; this slope is indicated by the dotted line.

obtained by the double reptation idea. In the nonlinear viscoelastic regime, which can easily be studied by computer simulations, the decay of the viscosity with shear rate is weakened and thus more realistic. In view of the additional mechanism for orientational relaxation, which acts not only at the chain ends, the modified model may be expected to perform better than the original reptation models when flows with strain reversal or recoil experiments are considered. A route for incorporating polydispersity effects which leads to new mixing rules has been described (in the linear viscoelastic regime, these mixing rules are known to be very successful). In fact, the most obvious deviations from previous reptation theories result for polydisperse melts. In formulating the model, the fluctuation-dissipation theorem, the principle of material objectivity, and a thermodynamic consistency criterion have been respected (the latter criterion is violated by a previous reptation model with the same dynamics). A more detailed discussion of the nonlinear viscoelastic behavior and mixing rules predicted by the modified reptation model and a detailed comparison with experimental results will be the subjects of forthcoming publications.

## ACKNOWLEDGMENTS

Financial support provided by the Swiss National Foundation for Scientific Research under Grant No. 20-36073.92 and generous allocations of CPU-time of the Swiss Federal Institute of Technology on the Cray Y-MP supercomputer are gratefully acknowledged.

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