

COMMUNICATIONS

Thermodynamically consistent reptation model without independent alignment

Hans Christian Öttinger^{a)}

ETH Zürich, Department of Materials, Institute of Polymers and Swiss FIT Rheocenter, CH-8092 Zürich, Switzerland

Antony N. Beris

Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

(Received 26 October 1998; accepted 2 February 1999)

The Poissonian character of the reversible part of nonequilibrium dynamics is exploited here in order to determine a dynamically consistent expression for a reptation model without the independent alignment assumption. It is shown that the previously proposed form by Doi and Edwards for such a model is compatible with the GENERIC formalism of nonequilibrium thermodynamics [Phys. Rev. E **56**, 6620 (1997); **56**, 6633 (1997)] only after two changes are made: (a) the production term in the evolution equation involves an average of the orientation dyadic \mathbf{uu} over the entire internal phase space, and (b) the extra stress tensor involves an additional term, qualitatively different from the one representing the original Doi–Edwards expression. The predictions of the new model for the stress after double shear strain with flow reversal are shown to be realistic, demonstrating irreversibility effects, in contrast to the model with the independent alignment approximation. © 1999 American Institute of Physics. [S0021-9606(99)52314-3]

I. INTRODUCTION

The reptation model^{1–3} represents without a doubt the most successful *a priori* model of the rheological behavior of polymer melts. However, in its simplest and most widely used form several assumptions are made. Among those, the independent alignment (IA) assumption for the segments of the reptating chain² is particularly important. For example, with IA the chain deforms reversibly in double-step strain with flow reversal which is contrary to several experimental findings.^{4–7} Consequently, several models without IA have been developed.^{8–13} However, even within the microscopic approach within which reptation models without IA have been developed, the resulting model equations are not derived completely and/or with a unique fashion. For example, no changes were proposed for the stress tensor expression over that corresponding to the model derived with the IA approximation.¹² This raises questions, though, regarding the internal consistency of the model since, given the close connection between stress and dynamics, one typically expects changes in the first to accompany changes in the second.^{14,15}

Thus the need emerges for a further consideration of the reptation model without the IA approximation. In particular, we use here the recently developed GENERIC formalism of nonequilibrium thermodynamics^{15,16} as a guide in completing the missing steps in the model development. In particular, we explore the Poissonian structure of the reversible (convective) component of the equations in order to ascertain the validity of the production term in the evolution equation

for the distribution function, as well as in order to deduce the appropriate form for the stress tensor. This Poissonian structure is a common characteristic of the reversible dynamics of Hamiltonian systems and has been the subject of an extensive investigation for both discrete and continuum systems—see the recent book by Marsden and Ratiu¹⁷ and references therein.

II. MODEL EQUATIONS

The main variable of the reptation model is the distribution function $f(\mathbf{u}, s, \mathbf{r}, t)$, which expresses the distribution of \mathbf{u} and s at a given position \mathbf{r} and time t . The term \mathbf{u} is a unit vector and s represents a location along the chain, more like a dimensionless “tag” normalized between 0 and 1, positions corresponding to the two ends of the polymer chain. For simplicity in the following we will omit the position and time from the arguments of the variables and we will only include the orientation and the s parameter when there is an intermediate integration and thus a risk for confusion. The “rigorous” model without the IA approximation was originally proposed to be represented by the following convection-diffusion equation:¹²

$$\frac{\partial f}{\partial t} = -\mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} - \frac{\partial}{\partial \mathbf{u}} \cdot \left(f(\mathbf{1} - \mathbf{uu}) \mathbf{u} : \frac{\partial \mathbf{v}}{\partial \mathbf{r}} \right) + \frac{1}{\lambda} \frac{\partial^2 f}{\partial s^2} - \frac{\partial}{\partial s} \left[\frac{\partial \mathbf{v}}{\partial \mathbf{r}} : \hat{\boldsymbol{\tau}} f \right] + \frac{\partial \mathbf{v}}{\partial \mathbf{r}} : \mathbf{uu} f, \quad (1)$$

where λ is the reptation time scale, \mathbf{v} is the velocity, and $\hat{\boldsymbol{\tau}}$ is defined as

^{a)}Electronic mail: hco@ifp.mat.ethz.ch

$$\hat{\boldsymbol{\tau}}(s) = \int_{1/2}^s ds' \int d^3u f(\mathbf{u}, s') \mathbf{u} \mathbf{u}. \quad (2)$$

Note that in deriving Eq. (1) the polymer mass density (which may or may not be considered a constant depending on the problem) has been factored out from the distribution function f which is normalized pointwise to a constant value taken equal to unity, $\int_0^1 f(\mathbf{u}, s) d^3u ds = 1$.

Compared with the traditional reptation model (with IA), the above diffusion equation has two additional terms, the last two terms that appear on the right-hand side of Eq. (1). The first of those represents a rescaling of s due to the retraction (or expansion) of the chain within the confining tube. The second of the last two terms in Eq. (1) is introduced in order to conserve the normalization of f in time. However, this expression is not unique. In addition to the expression used in Eq. (1), there are at least two more expressions, E1 and E2, that one can come up with easily

$$E1 = + \frac{\partial \mathbf{v}}{\partial \mathbf{r}} : \left(\int \mathbf{u}' \mathbf{u}' f(\mathbf{u}', s) d^3u' \right) f(\mathbf{u}, s), \quad (3)$$

or

$$E2 = + \frac{\partial \mathbf{v}}{\partial \mathbf{r}} : \left(\int_0^1 \int \mathbf{u}' \mathbf{u}' f(\mathbf{u}', s') d^3u' ds' \right) f(\mathbf{u}, s). \quad (4)$$

Note that, for consistency, if expression E2 is chosen the appropriate boundary conditions in s for f are

$$f(\mathbf{u}, s) = \tilde{f}(s) \frac{1}{4\pi} \delta(|u| - 1), \quad s = 0, 1 \quad (5)$$

with

$$\tilde{f}(s) \equiv \int f(\mathbf{u}, s) d^3u. \quad (6)$$

The function \tilde{f} , which is the probability density that a chain segment is found at position s and hence represents the monomer distribution along the chain contour, satisfies the additional boundary conditions

$$\left\{ \frac{\partial \mathbf{v}}{\partial \mathbf{r}} : [\hat{\boldsymbol{\tau}}(1) - \hat{\boldsymbol{\tau}}(0)] [1 - \tilde{f}(s)] - \frac{2}{\lambda} \frac{\partial \tilde{f}(s)}{\partial s} \right\} \Bigg|_{s=0} = 0, \quad (7)$$

$$\left\{ \frac{\partial \mathbf{v}}{\partial \mathbf{r}} : [\hat{\boldsymbol{\tau}}(1) - \hat{\boldsymbol{\tau}}(0)] [1 - \tilde{f}(s)] + \frac{2}{\lambda} \frac{\partial \tilde{f}(s)}{\partial s} \right\} \Bigg|_{s=1} = 0. \quad (8)$$

The traditional boundary conditions for the original reptation model are recovered if we consider the additional constraint $\tilde{f}(s) = 1$, $s = 0, 1$ which, however, needs not apply when expression E2 is chosen.

The main question that arises is therefore which one, if any, of the above expressions is better to use? In addition, Doi and Edwards have not proposed any changes in the expression that they gave for the stress tensor, $\boldsymbol{\tau}$, for the rigorous model, over that corresponding to the original reptation model with IA^{12,15}

$$\boldsymbol{\tau} = N n_p k_B T [-\mathbf{1} + 3[\hat{\boldsymbol{\tau}}(1) - \hat{\boldsymbol{\tau}}(0)]], \quad (9)$$

where N is the number of polymer segments in a chain and n_p the number density of chains. Nevertheless, it is usually

expected to see changes in the expression for the stress tensor once changes are brought in the evolution equation of the structure, given their close interrelationship.^{14,15}

III. HAMILTONIAN STRUCTURE

To address both of the above issues, we have developed here a Hamiltonian reformulation of the governing equations for the reptation model without IA. According to the GENERIC formalism, the governing equations should be of the form

$$\frac{\partial x}{\partial t} = L \cdot \frac{\delta E}{\delta x} + M \cdot \frac{\delta S}{\delta x}, \quad (10)$$

where x is the vector of the independent variables, which in this case corresponds to $x = \{\rho, \mathbf{M}, \epsilon, f(\mathbf{u}, s)\}$ with ρ denoting the polymer mass density, $\mathbf{M} = \rho \mathbf{v}$ the linear momentum density vector, and ϵ the energy density; E and S are the total energy and entropy functionals, respectively, and L and M are two matrix linear operators. The two contributions to the time evolution of x generated by the energy E and the entropy S in Eq. (10) are called the reversible and irreversible contributions to GENERIC, respectively. Using the energy as the generator of reversible dynamics is inspired by Hamilton's description of conservative systems, and using the entropy as the generator of irreversible dynamics is inspired by the Ginzburg-Landau formulation of relaxation equations.

Compatible with the physics of the polymer melt and the set of independent variables used here are the following energy and entropy functionals:

$$E = \int \left(\epsilon + \frac{1}{2\rho} M^2 \right) d^3r, \quad (11)$$

$$S = \int \left(s(\rho, \epsilon) - k_B N n_p \right. \\ \left. \times \int_0^1 \int \delta(|u| - 1) p(\hat{\mathbf{u}}, s) \ln p(\hat{\mathbf{u}}, s) d^3u ds \right) d^3r,$$

where $\hat{\mathbf{u}} = \mathbf{u}/|u|$ and $p(\hat{\mathbf{u}}, s, \mathbf{r}, t)$ is a normalized probability defined as

$$p(\hat{\mathbf{u}}, s) = \frac{\int_0^\infty f(\hat{\mathbf{u}}|u', s) |u'|^2 d|u'|}{\int_0^1 \int f(\mathbf{u}', s') d^3u' ds'}. \quad (12)$$

Note that the use of the normalized probability p is necessary if no constraints are placed *a priori* on f , which is the case followed here since it considerably simplifies the analysis. The normalized probability p not only normalizes f (which, by the way, it is important to do explicitly here in order to get the correct expressions for the Volterra derivatives of the entropy functional) but it also removes the singular dependence that this function has emerging from the fact that f is nonzero only on the surface of a unit sphere in \mathbf{u} space and therefore it is proportional to $\delta(|u| - 1)$.

The definitions given by Eqs. (11) and (12) are essential, among other things, for the correct evaluation of the functional derivative

$$\frac{\delta S}{\delta f} = -k_B N n_p \left[\ln p(\hat{\mathbf{u}}, s) - \int_0^1 \int \ln p(\hat{\mathbf{u}}', s') f(\mathbf{u}', s') d^3 u' ds' \right], \quad (13)$$

which is needed in the derivations that follow.

Once the energy and entropy functionals are specified, the main task of demonstrating a GENERIC structure reduces in constructing matrix linear operators L and M possessing the proper structure and being compatible with the governing set of equations. The structure properties of the linear operator matrices are^{15,16} the degeneracy conditions

$$L \cdot \frac{\delta S}{\delta \mathbf{x}} = 0; \quad M \cdot \frac{\delta E}{\delta \mathbf{x}} = 0, \quad (14)$$

the Poissonian structure of the reversible operator L , and the positive definiteness and symmetry of the dissipative (irreversible) operator M . For the L operator to be Poissonian, the corresponding bilinear bracket $\{F, G\}$ defined for two arbitrary functionals F, G as^{15,16}

$$\{F, G\} = \frac{\delta F}{\delta \mathbf{x}} \cdot L \cdot \frac{\delta G}{\delta \mathbf{x}}, \quad (15)$$

must be a Poisson bracket,¹⁴⁻¹⁶ i.e., it must be antisymmetric, $\{F, G\} = -\{G, F\}$, and it must satisfy the Jacobi identity

$$\{F, \{G, H\}\} + \{G, \{H, F\}\} + \{H, \{F, G\}\} = 0, \quad (16)$$

where F , G , and H are three arbitrary functionals. Of all those properties, the most difficult to satisfy is the Jacobi identity. However, at the same time, this is the one that can be used to advantage to guide us on which of many possible alternative expressions is the one to be preferred, as the one that satisfies this very stringent requirement whose origin can be traced to the Hamiltonian structure of the reversible dynamics. This has been used in a number of applications, a recent one and relevant to this work being the selection of a closure relationship in polymer dynamics.¹⁸ The Jacobi identity is the property used here in order to guide us in the selection of the appropriate production term [last term in Eq. (1)] in the reptation model without IA.

The starting point for the formulation of the operator matrices L and M is the form that they have in the reptation model without IA, since that is already available.¹⁵ Thus, we need to focus exclusively here on the changes needed to bring the additional terms in the governing equations [last two terms in Eq. (1)]. Moreover, as those terms reflect changes in the reversible component of the dynamics (representing convective effects) those are represented by two corresponding additional terms in the reversible linear operator L , the irreversible one, M , remaining unchanged from the reptation model without IA.¹⁵ The explicit expressions for the new terms in L are given in the Appendix. Once the new terms are in place, a lengthy but straightforward check demonstrates that, among the three alternatives indicated only one results in an L matrix operator with a Poissonian structure, namely the second alternative, E2, presented in Eq. (4).

Moreover, note that the L matrix not only provides for the distribution function equation, Eq. (1) with the alterna-

tive closure E2 provided by Eq. (4) replacing the original production term, last term in Eq. (1), but it can also be used to evaluate the corresponding form for the stress tensor.¹⁵ The antisymmetry of L and the first degeneracy condition in Eq. (14) are crucial for finding the stress tensor (see Appendix), which comes out to be (to within a multiple of the unit tensor that can be absorbed in the pressure)

$$\boldsymbol{\tau} = N n_p k_B T \int_0^1 \int [3 + \tilde{f}(0) - \tilde{f}(s)] \mathbf{u} \mathbf{u} f(\mathbf{u}, s) d^3 u ds. \quad (17)$$

Note that Eq. (17) includes two extra terms as compared to the expression provided for the original reptation model which was also used for the model without IA, Eq. (9). A consequence of these extra terms is discussed below in conjunction with the new model's predictions in a double-step strain experiment.

IV. KEY MODEL PREDICTION

The most important deficiency of the reptation model with IA is its prediction of stresses in flows with flow reversal. In order to verify that our new model without IA captures the irreversibility associated with flow reversal appropriately, we here consider the simple situation where, starting from equilibrium, we apply a shear step $-\gamma$ and, immediately after that, a shear step $+\gamma$. With the IA approximation, we fully recover the initial equilibrium configuration, so that the system is stress free after the instantaneous double-step strain. This result is clearly at variance with experimental findings,⁴⁻⁷ and Doi⁸ has shown how to obtain a more realistic prediction by avoiding the IA approximation. We here focus on the ratio $r(\gamma)$ of shear stresses immediately after an instantaneous double-step strain ($-\gamma$ and $+\gamma$) and after a single-step strain ($+\gamma$). While IA leads to $r(\gamma) = 0$, Doi's prediction⁸ based on direct arguments within the reptation picture is

$$r(\gamma) = 1 - A[\beta(\gamma)] \quad (18)$$

with

$$\beta(\gamma) = (1 + \gamma^2/3)^{-1/2}, \quad A(\beta) = \frac{4\beta \cos(\pi\beta/2)}{\pi(1 - \beta^2)}. \quad (19)$$

For the new model without IA, we determined the ratio $r(\gamma)$ by simulation. Actually, the first step strain can be treated exactly. After a single step, the distribution in s is still uniform, and the distribution of \mathbf{u} for any given s is simply determined by the appropriate rotations of an equilibrium ensemble of random unit vectors. This implies that the stress prediction of the new model in a single-step strain experiment coincides with the one obtained from the original DE model with IA, which is known to be realistic. With this initial configuration we apply the second step, where we can switch off the reptational diffusive motion in s because here we are interested only in the stress immediately after the rapidly performed double step. The probability density $\tilde{f}(s)$, defined in Eq. (6), after the double step is a constant larger than unity in the middle section of the chain, it then jumps to a value smaller than unity at some distance from the center,

and it increases to unity towards the chain ends. The inner portion of the chain, where $\tilde{f}(s)$ is constant, does not contribute to the stress (total strain zero after the two steps), but the chain parts near the ends clearly carry stress from deformations applied in the second step. For $\gamma=3$, after carefully eliminating the effects of ensemble size, number of time steps, and bin width in the histogram representation of $\tilde{f}(s)$, we obtain $r(3)=0.30$. If compared to Doi's prediction (18), (19), which leads to $r(3)=0.40$, the new model without IA clearly implies irreversibility in flow reversal of the right order of magnitude. Actually, with an improved approximation for the average chain stretching in Doi's approach, one obtains the even closer prediction $r(3)=0.34$.¹⁹ If the modification of the stress tensor had not been taken into account, we would have obtained the somewhat smaller value $r(3)=0.27$ from the new model.

We do not expect exact agreement between Doi's prediction⁸ and our result. The reason for this is that in our single segment approach, as in most other diffusion equations and constitutive equations, the Rouse time scale, being much shorter than the reptation time scale, is completely neglected. This implies that the step strains, while fast compared to reptation time scale, are slow compared to the unresolved Rouse time scale. In Doi's direct analysis,⁸ the step strains are assumed to be fast compared to both the reptation and Rouse time scales. The resulting difference is best seen in the effects discussed in the Appendix of Doi's paper.⁸ For melts of high-molecular-weight chains, both types of experiments could actually be performed. The assumption that the chain length relaxes on a negligibly short time scale is also the reason for the seemingly paradoxical effect that the convection mechanism fully accounts for the irreversibility in flow reversal.

In conclusion, the implementation of the Poissonian structure constraint in the formulation of the reptation model equations without the independent alignment approximation has led to a modified diffusion equation for the distribution function and to additional terms in the equation for the stress tensor. Albeit the uniqueness of the new model cannot be guaranteed, the approach followed has at least helped to select one and only one possible solution among three most natural options examined in this work (including two versions from the literature). Moreover, the new thermodynamically admissible model avoiding IA makes realistic predictions for the stress after double-step shear strain with flow reversal. This is the key test for the performance of a model without IA. A detailed and comprehensive evaluation of the model predictions in various flow situations is left to future work.

APPENDIX

All the reptation models considered in this paper differ only in the choice of the L operator. For the original Doi-Edwards model, the component of L coupling the configurational distribution function and the momentum density is (see Eqs. (58) and (116) of Ref. 15)

$$L_{42}^{\text{IA}} = - \left[\frac{\partial f}{\partial \mathbf{r}} \right] - \frac{\partial}{\partial \mathbf{u}} \cdot f(\mathbf{1} - \mathbf{u}\mathbf{u})\mathbf{u} \cdot \frac{\partial}{\partial \mathbf{r}}. \quad (\text{A1})$$

For the rigorous model without IA of Eq. (1), we have

$$L_{42} = L_{42}^{\text{IA}} - \frac{\partial}{\partial s} f \hat{\mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{r}} + f \mathbf{u}\mathbf{u} \cdot \frac{\partial}{\partial \mathbf{r}}, \quad (\text{A2})$$

whereas the modifications described by Eqs. (3) and (4) correspond to

$$L_{42}^{\text{E1}} = L_{42}^{\text{IA}} - \frac{\partial}{\partial s} f \hat{\mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{r}} + f \left(\int \mathbf{u}' \mathbf{u}' f(\mathbf{u}', s) d^3 u' \right) \cdot \frac{\partial}{\partial \mathbf{r}}, \quad (\text{A3})$$

$$L_{42}^{\text{E2}} = L_{42}^{\text{IA}} - \frac{\partial}{\partial s} f \hat{\mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{r}} + f \left(\int_0^1 \int \mathbf{u}' \mathbf{u}' f(\mathbf{u}', s') d^3 u' ds' \right) \cdot \frac{\partial}{\partial \mathbf{r}}. \quad (\text{A4})$$

In order to specify the full L operator [see Eq. (58) of Ref. 15] one needs the antisymmetry of L to obtain L_{24} , and the first degeneracy requirement in Eq. (14) to obtain the stress tensor occurring in the full L expression.¹⁵

¹ P. G. de Gennes, *J. Chem. Phys.* **55**, 572 (1971).

² M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. 2* **74**, 1789 (1978); **74**, 1802 (1978); **74**, 1818 (1978); **75**, 38 (1979).

³ C. F. Curtiss and R. B. Bird, *J. Chem. Phys.* **74**, 2016 (1981); **74**, 2026 (1981).

⁴ K. Osaki and M. Kurata, *Macromolecules* **13**, 671 (1980).

⁵ K. Osaki, S. Kimura, and M. Kurata, *J. Rheol.* **25**, 549 (1981).

⁶ D. C. Venerus and H. Kahvand, *J. Polym. Sci., Polym. Phys.* **32**, 1531 (1994).

⁷ E. F. Brown and W. R. Burghardt, *J. Rheol.* **40**, 37 (1996).

⁸ M. Doi, *J. Polym. Sci., Polym. Phys.* **18**, 1891 (1980).

⁹ M. Doi, *J. Polym. Sci., Polym. Phys.* **18**, 2055 (1980).

¹⁰ G. Marrucci and N. Grizzuti, *J. Non-Newtonian Fluid Mech.* **21**, 319 (1986).

¹¹ G. Marrucci, *J. Non-Newtonian Fluid Mech.* **21**, 329 (1986).

¹² M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).

¹³ H. C. Öttinger, *Stochastic Processes in Polymeric Fluids* (Springer, Berlin, 1996).

¹⁴ A. N. Beris and B. J. Edwards, *Thermodynamics of Flowing Systems with Internal Microstructure* (Oxford University Press, Oxford, 1994).

¹⁵ H. C. Öttinger and M. Grmela, *Phys. Rev. E* **56**, 6633 (1997).

¹⁶ M. Grmela and H. C. Öttinger, *Phys. Rev. E* **56**, 6620 (1997).

¹⁷ J. E. Marsden and T. S. Ratiu, *Introduction to Mechanics and Symmetry* (Springer, New York, 1994).

¹⁸ B. J. Edwards and H. C. Öttinger, *Phys. Rev. E* **56**, 4097 (1997).

¹⁹ D. C. Venerus (private communication).