Mesoscopic constitutive relations for dilute polymer solutions

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Abstract

A novel approach to the dynamics of dilute solutions of polymer molecules under flow conditions is proposed by applying the rules of mesoscopic nonequilibrium thermodynamics (MNET). The probability density describing the state of the system is taken to be a function of the position and velocity of the molecules, and on a local vector parameter accounting for its deformation. This function obeys a generalized Fokker-Planck equation, obtained by calculating the entropy production of the system, and identifying the corresponding probability currents in terms of generalized forces. In simple form, this coarse-grained description allows one to derive hydrodynamic equations where molecular deformation and diffusion effects are coupled. A class of non-linear constitutive relations for the pressure tensor are obtained. Particular models are considered and compared with experiments.

Key words: Fokker-Planck equations; FENE models; Polymer solutions; Non-Newtonian Phenomena; Constitutive relations.

1 Introduction

The statistical study of chain models of polymer molecules [1,2,3] have led to a collection of constitutive relations for the description of the elastic properties of polymer solutions [4,5], known as FENE dumbbell models, in which the restoring force depends on the end-to-end vector of the chain. By avoiding phenomena related to the fine structure of the polymer molecules, those models depict an intuitive picture of the physics involved in the molecule deformation [6], and reproduce non-Newtonian phenomena, such as birefringent pipes [7], negative wake [8] and cusp formation [9].

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Numerical simulations of molecular chain models have shown that the FENE approximation is useful to describe systems under flow conditions, for which the largest relaxation time of the polymer dominates the dynamics of the molecule, but are inaccurate for molecules under unsteady flow conditions in which molecules can explore faster relaxation modes [10]. Although simulations predict a more realistic restoring force, they are unable to describe its evolution in terms of a simple mathematical formulation for arbitrary flows, legitimizing the search for a simple description which captures short time scale physics.

In this paper, a theoretical framework originally proposed in Ref. [11,13] has been adopted to cope with the main features of dilute polymer suspensions under stationary flow. A coarse-grained description of the system dynamics is given in terms of a Fokker-Planck equation for the probability density depending on the parameters accounting for the motion of the polymer center of mass, and a single vector parameter (called the distortion vector) accounting for its elastic deformation. The Fokker-Planck equation can be constructed after invoking probability conservation, calculating the entropy production in the phase space of the system and following the scheme of mesoscopic non-equilibrium thermodynamics [12]. Moreover, it can be used to formulate a hydrodynamic description in terms of the evolution equations for the moments of the probability. Application to particular cases can be performed by incorporating different models for the Onsager tensor coefficients and the finite-size of the molecules [14].

The paper is organized as follows. In Sec. 2, the derivation of the generalized Fokker-Planck equation is presented. In Sec. 3, the evolution equations for the moments of the probability are derived, and in Sec. 4, are applied to obtain constitutive relations for the pressure tensor in particular cases. Sec. 5 is devoted to summarize our main results.

2 Fokker-Planck equations

The system under study, a dilute polymer solution, will be regarded as a polymer ‘gas’ suspended in a Newtonian solvent under stationary flow conditions given by $v_0(r)$. The description of this system can be carried out in terms of a Fokker-Planck equation.

As a first approximation, the state of the polymer gas can be characterized by the positions $r$ and instantaneous velocities $u$ of the center of mass of the polymer molecules [11,13,14,15], and by the vector $R$ characterizing the gross distortion and orientation of the molecule [3,6]. Here, it is assumed that the molecule segments explore different configurations much faster than the vari-
ations in the gross distortion due to the local velocity gradient, i.e. molecules are distorted instantaneously with the fluid element in which they are embed-
ded. Notice that, unlike in the conventional approaches [3], here we introduce
the velocity \( u \) as an independent variable necessary to determine the nonequi-
librium state of the system at the conditions imposed by the velocity gradient.
In the dilute regime, the description of the state of the system can be carried
out in terms of the single molecule probability density \( f(r, u, R, t) \), normalized
to the number of molecules and satisfying the continuity equation
\[
\frac{\partial f}{\partial t} + \nabla \cdot (uf) = -\frac{\partial}{\partial u} \cdot [fV_u] - \frac{\partial}{\partial R} \cdot [fV_R],
\]
(1)
where \( V_u \) and \( V_R \) are unknown streaming velocities in \( u \) and \( R \) subspaces [13,14,15].

The Fokker-Planck equation describing the dynamics of the system follows
from the explicit expressions of \( V_u \) and \( V_R \). These can be obtained using the
MNET formalism which introduces the Gibbs entropy postulate [16,11,13]
\[
s(t) = -k_B \int C \ln \frac{f}{f_{eq}} dudR + s_{eq},
\]
(2)
where \( k_B \) is the Boltzmann constant, \( s \) and \( s_{eq} \) are the entropy per mass unit
and the entropy at local equilibrium of a given reference state, respectively.
\( C \equiv m f / \rho \) represents the mass fraction of polymer molecules with a given \( u \n\) and \( R \), \( m \) the molecule mass and \( \rho \) the mass density field, given by
\[
\rho(r, t) = \int mfdudR.\]
(3)

The probability density \( f_{eq} \) characterizing the system at the reference state is
given by
\[
f_{eq}(r, u, R) = e^{\frac{m}{k_B T}[\mu_B + \frac{1}{2}(u-v_0)^2 - FR]},
\]
(4)
where \( T \) is the temperature of the heat bath, \( \mu_B \) is the local equilibrium
chemical potential and \( \frac{1}{2}(u - v_0)^2 \) the kinetic energy of diffusion per unit
mass. The last term in the argument of the exponential function, \( F \cdot R \), is
the work exerted by the bath on the molecule in order to attain a distortion
\( R \). Here \( F \) is the restitutive force per unit mass of the molecule thought as a
springy body.

The Gibbs entropy postulate (2) is consistent with the Gibbs equation [17,13]
\[
T \delta s = \delta e - p \delta \rho^{-1} - \int \mu \delta C dudR,
\]
(5)
where \( e \) is the internal energy per unit mass, \( p \) is the pressure and \( \mu \) the nonequilibrium chemical potential. The last term of Eqn. (5) is reminiscent of the one corresponding to a mixture in which the components are specified by two continuum indexes \((u, R)\). Eqns. (1)-(5) can be used to obtain the explicit expressions for the streaming velocities \( V_u \) and \( V_R \), by calculating the entropy production \( \sigma \) of the system in the \((r, u, R)\)-space, and taking into account the evolution equation for \( C \) [15]. The mass continuity equation is given by

\[
\frac{d\rho}{dt} = -\rho \nabla \cdot v, \tag{6}
\]

where \( v(r, t) \) is the average velocity field of the molecules defined by

\[
v(r, t) = \int uCdudR, \tag{7}
\]

and the convective derivative given by \( \frac{d}{dt} = \frac{\partial}{\partial r} + v \cdot \nabla \). After taking the time derivative of the Gibbs equation (5) and integrating by parts, assuming that probability fluxes vanish at the boundaries, one obtains the entropy balance equation

\[
\rho \frac{ds}{dt} = -\nabla \cdot J_s + \sigma. \tag{8}
\]

In writing this equation, we have identified the entropy flow \( J_s \)

\[
J_s \equiv -k_B \int (u - v) f(\ln f - 1)du dR \tag{9}
- \frac{1}{T} \int (u - v) fF \cdot RdudR - \frac{m}{2T} \int (u - v) f(u - v)^2 dudR,
\]

the entropy production

\[
\sigma \equiv -\frac{m}{2T} \int fV_u \cdot \frac{\partial \mu}{\partial u} dudR - \frac{m}{2T} \int fV_R \cdot \frac{\partial \mu}{\partial R} dudR \tag{10}
- \frac{m}{2T} \int f(u - v) \cdot \nabla (u - v_0)^2 dudR,
\]

and assumed that the elastic force \( F \) is independent of \( r \) and \( u \). The incorporation of \( R \) into the description, introduces elastic contributions to both the entropy flow and the entropy production in Eqns. (9) and (10). They represent a novel ingredient not considered in previous MNET analysis (see, for example, Ref. [13,14,15]).
After taking variations of Eqn. (2) and comparing with Eqn. (10), one arrives at the explicit expression of the nonequilibrium chemical potential

$$\mu \equiv \frac{k_B T}{m} \ln f + \frac{1}{2}(u - v_0)^2 + F \cdot R.$$  

(11)

Once obtained the entropy production $\sigma$ (Eqn. (10)) and identified the nonequilibrium chemical potential $\mu$ (Eqn. (11)) conjugated to the probability density defined over the phase space of the system, one can assume linear relationships between fluxes and forces, of the form [11,13,14,15,16]

$$fV_u = -fL_{uu} \cdot \frac{\partial \mu}{\partial u} - fL_{ur} \cdot \frac{\partial \mu}{\partial R} - fL_{ur} \cdot (u - v_0) \cdot (\nabla v_0)^T,$$  

(12)

$$fV_R = -fL_{Ru} \cdot \frac{\partial \mu}{\partial u} - fL_{RR} \cdot \frac{\partial \mu}{\partial R} - fL_{Rr} \cdot (u - v_0) \cdot (\nabla v_0)^T,$$  

(13)

where $(\nabla a)_{ij} = \frac{\partial a}{\partial x_i}$ and the Onsager coefficient matrices $L_{ij}$ satisfy the generalized Onsager relations [18]. Notice that unlike the usual framework of nonequilibrium thermodynamics given in r-space [17], in the MNET formalism, the linear relationships (13) are formulated in the $(r, u, R)$-space [16,11]. This assumption will lead, in general, to nonlinear constitutive relations in the physical space $r$ after a contraction of the description [14]. Finally, substituting equations (12) and (13) into the continuity equation (1), one obtains

$$\frac{\partial f}{\partial t} + \nabla \cdot (uf) =$$

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$$\left[ C_1 \cdot (u - v_0)f + \frac{k_B T}{m} L_{uu} \cdot \frac{\partial f}{\partial u} + L_{ur} \cdot \left( Ff + \frac{k_B T}{m} \frac{\partial f}{\partial R} \right) \right]$$

$$+ \frac{\partial}{\partial R} \left[ C_2 \cdot (u - v_0)f + \frac{k_B T}{m} L_{Ru} \cdot \frac{\partial f}{\partial u} + L_{RR} \cdot \left( Ff + \frac{k_B T}{m} \frac{\partial f}{\partial R} \right) \right],$$  

(14)

which constitutes the Fokker-Planck equation describing the evolution of the system at mesoscopic level. We have also defined the tensors

$$C_1 \equiv L_{uu} + L_{ur} \cdot \nabla v_0 \quad \text{and} \quad C_2 \equiv L_{Ru} + L_{RR} \cdot \nabla v_0.$$  

(15)

From these relations it follows that, in general, the transport coefficients may depend on the imposed velocity gradient, implying the breaking of the fluctuation-dissipation theorem at mesoscopic level, and incorporating non-Newtonian behavior [14,15].
3 Dynamics of the molecular distortion under flow conditions.

The equation describing the dynamics of the distortion of a single molecule can be obtained averaging over \( u \) the Fokker-Planck equation (14). Assuming that the Onsager coefficients do not depend on \( u \), one obtains the equation

\[
\frac{\partial g}{\partial t} + \nabla \cdot (v_R g) = \frac{\partial}{\partial R} \left[ C_2 \cdot (v_R - v_0) g + \mathbb{L}_{RR} \cdot \left( F g + \frac{k_BT}{m} \frac{\partial g}{\partial R} \right) \right], \tag{16}
\]

which governs the evolution of \( g(r, R, t) = \int f du \), that represents the probability of finding a molecule with a given distortion \( R \) at a point \( r \) at time \( t \).

The last term in equation (16) contains the thermal fluctuations and elastic contributions. Here, we have introduced the average velocity \( v_R = g^{-1} \int u f du \). The term \( C_2 \cdot (v_0 - v_R) \) represents a drag force on the molecule. We will assume that it is proportional to \( R \) times the characteristic stress given by the velocity gradient imposed by the heat bath. Thus, at first order in \( R \), one has \( C_2 \cdot (v_R - v_0) \approx -C_2 \cdot R \cdot \nabla v_0 \). Notice that averaging equation (16) over \( R \), an equation for the distortion vector distribution resembling known equations for dilute suspensions of polymers is obtained [19].

From equation Eqn. (16), we can compute the evolution equation for the average distortion field \( \langle R \rangle(r, t) \)

\[
\langle R \rangle(r, t) = \frac{1}{n} \int R g dR, \tag{17}
\]

and for the second moment field \( A(r, t) \)

\[
A(r, t) = \langle R R \rangle = \frac{1}{n} \int R R g dR, \tag{18}
\]

which can be interpreted as the moment of inertia tensor of the molecule [5]. In these equations, \( n(r, t) = \int g dR \) is the particle density satisfying the continuity equation \( \frac{\partial n}{\partial t} = -\nabla \cdot [n v(r, t)] \), obtained by averaging (16) over \( R \).

Taking the time derivative of Eqn. (17) and using (16), after integrating by parts one obtains

\[
\frac{d\langle R \rangle}{dt} = \frac{1}{n} \nabla \cdot [n (A - \langle R \rangle \langle R \rangle) \cdot \nabla v_0] + C_2 \cdot \langle R \rangle \cdot \nabla v_0 - \mathbb{L}_{RR} \cdot \langle F \rangle, \tag{19}
\]

where \( \langle F \rangle = n^{-1} \int F g dR \) is the average elastic force depending on \( r \) and \( t \) through the average value \( \langle R \rangle(r, t) \). The first term in the right-hand side of Eqn. (19) contains the standard deviation \( \sqrt{\langle A - \langle R \rangle \langle R \rangle \rangle} \) of the \( R \) distribution.
In the case of a narrow distribution this term can be neglected, reducing our equation to the one obtained in Ref. [6].

Following a similar procedure, from Eqs. (16) and (18) it is possible to obtain the evolution equation for $A$

$$\frac{dA}{dt} - 2 [A \cdot \nabla v_0]^s = 2 \left\{ \mathbb{L}_{RR} \cdot \left[ \frac{k_B T}{m} \mathbb{I} - \langle FR \rangle \right] \right\}^s$$

$$+ 2 \left[ L_{Rr} \cdot \left( \nabla v_0 \cdot \nabla v_0^T \right) \cdot A \right]^s$$

(20)

where the super index $s$ stands for the symmetric part of a tensor, $\mathbb{I}$ is the identity tensor and we have chosen $L_{Ru} = \mathbb{I}$ in (15), to obey the material frame indifference condition for (20), [19]. Thus, the left-hand side of this equation is an Oldroyd time derivative. The first term in the right-hand side represents the elastic contribution, comprising the thermal fluctuations of the monomers ($\frac{k_B T}{m}$), and their spatial restrictions due to the fact that they constitute a chain ($\langle FR \rangle$). The last term in Eqn. (20) is a genuine nonlinear contribution in $\nabla v_0$ arising from contracting the description from the mesoscopic ($r, u, R$)-space to the physical $r$-space. Moreover, in this equation, we have neglected contributions arising from higher order moments of the distribution since their characteristic relaxation times are at least one order of magnitude smaller than the one corresponding to $\langle R \rangle$ and $A$ (see, for example, [15]).

### 3.1 Evolution equation for the pressure tensor.

At hydrodynamic level, the presence of polymer molecules modifies the stress field of the flow by adding stresses due to elastic and Brownian motion fluctuations. These contributions can be calculated by averaging our description over the instantaneous velocity $u$ and the distortion vector $R$ of the polymer molecules and using the definitions

$$\mathbb{P}^K = m \int (u - v)(u - v) f du dR,$$  

(21)

and

$$\mathbb{P}^E = -\frac{m}{2} \int (FR + RF) f du dR,$$  

(22)

where $\mathbb{P}^K$ and $\mathbb{P}^E$ are the kinetic and elastic contributions of the suspended phase to the total pressure tensor, respectively, [20,21].
The equations for the pressure tensor contributions can be obtained from the evolution equations for the moments of the probability density $f$ and the Fokker-Planck equation (14). Contributions from third and higher order moments of the hydrodynamic hierarchy have been neglected [15]. For the kinetic contribution, using Eqns. (14), (15) and (21), one obtains the evolution equation

$$\frac{dP^K}{dt} + 2 \left[ P^K \cdot (C_1 + \nabla \mathbf{v}_0) \right]_s = 2 \frac{k_B T}{m} \rho (C_1 - L_{ur} \cdot \nabla \mathbf{v}_0)^s. \tag{23}$$

The time derivative in equation (23) accounts for memory effects in a similar fashion as Maxwell like models do [19]. For times $t \gg [C_1 + \nabla \mathbf{v}_0]_{ij}^{-1}$, the time derivative in equation (23) can be neglected, giving an algebraic system of equations for the components of $P^K$ that can be solved for any imposed flow. Eqn. (23) incorporates contributions to the stresses arising from the flow inhomogeneities through $\nabla \mathbf{v}_0$. These contributions have not been considered in previous descriptions where Brownian stresses were assumed to be given by $P^K \simeq \frac{k_B T}{m} \rho I$, [2]. To simplify the computation of the elastic contribution to the pressure tensor, in the following we will consider that the elastic force $\mathbf{F}$ is proportional to $\mathbf{R}$ with a proportionality coefficient $\xi_0 \tilde{F}$, where $\tilde{F}$ is a dimensionless function of $tr(\mathbf{A})$ giving the form of the spring law, and $\xi_0$ is the characteristic spring restitution coefficient per unit mass. Therefore, the elastic contribution is $P^E = -\xi_0 \tilde{F} \rho \mathbf{A}$ and its evolution is related to equation (20).

We will now proceed to express the evolution equations (20) and (23) in dimensionless form. In the absence of an externally imposed flow, equation (20) suggests that $\mathbf{A}$ scales with $k_B T/m \xi_0$. Therefore, we will scale length with $\sqrt{k_B T/4m \xi_0}$, time with the inverse of the shear rate $\dot{\gamma}$ and pressure with $\eta_0 \dot{\gamma}$, where $\eta_0$ is the solvent viscosity. Since the Onsager coefficient $L_{RR}$ represents the mobility, it will be scaled with the inverse of the characteristic friction coefficient per unit mass, say $\beta$, [3]. The coefficient $L_{Rr}$ will be scaled with $\beta/\xi_0$ as it characterizes the coupling between the distortion of the molecule and the drag forces, see Eq. (13). Thus, the evolution equation (20) takes the dimensionless form

$$\frac{d\mathbf{A}}{dt} - 2 [\mathbf{A} \cdot \nabla \mathbf{v}_0]^s = \frac{2}{D} \left[ L_{RR} \cdot (I - \tilde{F} \mathbf{A}) \right]^s + 2D \left[ L_{Rr} \cdot (\nabla \mathbf{v}_0 \cdot \nabla \mathbf{v}_0^T) \cdot \mathbf{A} \right]^s, \tag{24}$$

where $D = \dot{\gamma} \beta / \xi_0$ is the Deborah number. In similar form, the dimensionless evolution equation for $P^K$ is given by

$$\frac{dP^K}{dt} + 2 \left( P^K \cdot \nabla \mathbf{v}_0 \right)^s = \frac{2c}{D} \left( \frac{D^*}{D} C_1 - L_{ur} \cdot \nabla \mathbf{v}_0 \right)^s - 2D^* \left( P^K \cdot C_1 \right)^s, \tag{25}$$
where \( c = \rho k_B T / \eta m \xi_0 \) is a measure of the concentration of polymers, \( D^* = \beta^2 / \xi_0 \) is a dimensionless parameter that compares viscous dissipation and molecule relaxation times. We have scaled the friction tensor \( C_1 \) with \( \beta \). Finally, notice that the dimensionless elastic contribution to the pressure tensor is

\[
P^E = -\frac{c \tilde{F}}{2D^*} \mathbf{I}.
\]

Eqns. (24), (25) and (26) represent the constitutive relations for a ”gas” of deformable particles embedded into a Newtonian heat bath. It is worth noticing that in this simple model we have characterized the internal dynamics of the particle by using the single vector parameter \( \mathbf{R} \), known as the gross distortion of the particle. In the following section, we will apply these equations to the case of a simple shear flows with different models for the restoring force of the particles and for the Onsager coefficients.

4 Applications

We will now proceed to consider the constitutive relation expressed in terms of the evolution equations (24) and (25) for particular forms of the Onsager coefficients, corresponding to simplified models of the suspended polymer molecules under shear flow conditions. With these simplifications, the constitutive relation reduces to models that, at first order in \( \nabla \mathbf{v}_0 \), resemble the known FENE models for polymer solutions.

The cases studied were a dumbbell, a dumbbell with an isotropic friction coefficient dependent on its gross distortion, and a dumbbell with a non-isotropic friction also dependent on the gross distortion of the molecule. Solutions are compared with experiments.

Dumbbells in a simple shear. In this case, the dimensionless Onsager coefficients \( \mathbb{L}_{RR} \) and \( \mathbb{L}_{ur} \) can be assumed to be isotropic and constant. In particular we will assume that \( \mathbb{C}_1 = \mathbb{L}_{RR} = \mathbb{I} \) and neglect non-linear terms in \( \nabla \mathbf{v}_0 \) by taking \( \mathbb{L}_{Rr} = 0 \). For spheres,

\[
\mathbb{L}_{ur} = \frac{ma^2 \beta^2}{6k_B T} \mathbb{I},
\]

where \( a \) is the radius of the sphere, [14]. Taking the radius \( a \) as the characteristic length scale \( \sqrt{k_B T / 4m \xi_0} \) of the particle one obtains \( \mathbb{L}_{ur} = \frac{D^*}{24} \mathbb{I} \).
Additionally, we will adopt the FENE spring law [3]

\[  \hat{F} = \frac{L^2}{L^2 - \text{tr}(A)}. \]  

(28)

For times \( t \gg [\mathbb{C}_1 + \nabla \mathbf{v}_0]^{-1} \), the time derivative in equations (24) and (25) can be neglected, leading to a set of algebraic equations for \( \mathbb{P}^k \) and \( \mathbb{A} \). Therefore, \( \mathbb{A} \) is a solution of a non-linear algebraic equation and its components are given by: \( A_{xx} = L^2(1 - A_{yy}) - 2A_{yy} \), \( A_{xy} = 2A_{yy}^2D \) and \( A_{zz} = A_{yy} \). With \( A_{yy} \) the real solution of

\[ 8D^2A_{yy}^3 + (3 + L^2)A_{yy} - L^2 = 0. \]  

(29)

The behavior of \( A_{xx} \) and \( A_{yy} \) as functions of \( D \) are common to FENE models [19]. For large values of \( D \), \( A_{xx} \) and \( A_{yy} \) will tend to \( L^2 \) and zero respectively. The solution to the elastic pressure tensor \( \mathbb{P}^E \) depends on \( \mathbb{A} \) and has no compact expression, therefore it is not shown here. Similarly, the components of the kinetic contribution to the pressure tensor are given by

\[ P_{xy}^K = -\frac{c}{2} \left( \frac{1}{24} + \frac{1}{D^*} \right) \]  

(30)

and

\[ P_{xx}^K - P_{yy}^K = \frac{cD}{2D^*} \left( \frac{1}{24} + \frac{1}{D^*} \right), \]  

(31)

whereas the dimensionless first normal stress difference is defined by

\[ N_1 = -D \left( P_{xx}^K - P_{yy}^K + P_{xx}^E - P_{yy}^E \right). \]  

(32)

The behavior of \( N_1 \) as a function of \( D \) reproduce the quadratic response of polymer solutions at low Deborah numbers observed in FENE models [4,22]. We have obtained two contributions to the shear stress: \( \sigma = -D(P_{xy}^K + P_{xy}^E) \). The contribution of the elastic part is similar to that of the usual FENE-P models [19]. A new contribution arises from the kinetic part and corresponds to that of a 'gas' of Brownian particles [15].

**Isotropic non-constant friction.** In this case, the interaction between the molecule and the bath is modeled through a size dependent friction coefficient. We are assuming that the average shape of the molecule ranges from a sphere in quiescent liquid to a symmetrical spheroid with a principal axis \( L \) in the case of maximum distortion. In such case, the friction coefficient \( C_1 \) will be a tensorial
quantity. However, the ellipsoid will be considered to be aligned with the flow and, under this condition, the friction coefficient will be taken to be that of a spheroid in an axisymmetric unbounded flow given by

$$\beta = \beta_0 \frac{\sqrt{a^2 - b^2}}{(\alpha^2 + 1) \coth^{-1} \frac{\alpha}{\alpha - \alpha}},$$

(33)

where $\beta_0$ is now the Stokes friction coefficient, $a$ the principal spheroid axes along the flow, $b$ the perpendicular one and $\alpha = a/\sqrt{a^2 - b^2}$, [23]. Since in our formulation the molecule deformation is solely given by $R$, then $a \simeq \frac{1}{2} |R| = \frac{1}{2} \sqrt{tr(A)}$. Hence, the maximum value of $a$ is $\frac{1}{2} L$ and as a consequence, $\alpha$ ranges from $L/\sqrt{L^2 - 4b^2} > 1$ in the case of maximum deformation, to infinity in the case of a sphere (no deformation). From this consideration, it follows that $\coth^{-1} \alpha$ is never singular. Then, approximating $\coth^{-1} \alpha \simeq \frac{1}{\alpha} + \frac{1}{3\alpha^3}$, equation (33) becomes

$$\beta \simeq \frac{9}{32} \beta_0 \sqrt{tr(A)} \left[ 1 + \frac{4b^2}{3tr(A)} \right].$$

(34)

Notice that, by definition, $b$ must be a decreasing function of $tr(A)$, therefore, the second term in the approximation (34) must be negligible small as soon as the molecule model begins to experience some distortion. Now, by using Eqn. (34) the dimensionless evolution equation for the distortion tensor $A$ takes the form

$$\frac{dA}{dt} - A \cdot \nabla v_0 - \nabla v_0^T \cdot A = \frac{16}{9 \sqrt{tr(A)}} \frac{1}{D} \left( I - \tilde{F} A \right),$$

(35)

which constitutes a correction to the friction equivalent to those used in Refs. [24,5,6]. Notice that the dependence of the friction coefficient on $A$ introduces a non-linear coupling between Eqn. (35) and the corresponding evolution equation for $\mathbb{P}^K$. Solutions for $A$ and $\mathbb{P}^K$ can be obtained by following the procedure of the previous subsection.

Figure (1) shows a fit of the isotropic friction model to simple shear experiments with dilute micellar solutions in water [25]. Experiments were performed increasing the shear rate $\dot{\gamma}$ from zero in steps, the steps in shear rate were taken at an acceleration of $0.66 s^{-2}$. For shear rates over $100 s^{-1}$ the model overpredicts stresses. The kinetic contribution is responsible for the agreement for $\dot{\gamma}$ below $25 s^{-1}$ whereas the elastic contribution dominates for larger shear rates.

Non-isotropic friction. Here we will take the friction tensor $C_1$ to be diagonal but non-isotropic. This case represents a more realistic model than the previous ones because it better accounts for the drag on a body with cylindrical
symmetry oriented with the flow, [23]. Thus, in a shear flow on the $x$ direction $L_{RR} = C_1^{-1}$, $L_{ur} = \frac{ma^2}{6k_BT} C_1 \cdot C_1$ and $L_{Rr} = 0$ for simplicity. Where the friction tensor will be modelled by

$$C_1 = \beta_0 \begin{bmatrix} \frac{9}{32} \sqrt{\text{tr}(A)} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (36)$$

Figure (2) shows a fit of the non-isotropic friction model to experiments with the same system [25] but in this case decreasing the shear rate $\dot{\gamma}$ to zero in steps at the same acceleration. For this model elastic stresses dominate at all shear rates. The models suggests that the difference between experiments arises from the possible configurations that the particles can explore in each case. The isotropic friction model best fits the stress behavior in the coil-stretch transition that occurs during shear rate growth. The residual stress at zero shear rate obtained in experiments (Figure (2)) suggests that particles have not reached a coiled configuration. This explains why the non-isotropic friction model reproduces the stress behavior in shear rate reduction.

Notice that, in this description, the dynamics of the molecule segments is not included. Therefore, the effect of hydrodynamic interactions between segments are not contained explicitly in the set of Onsager coefficients appearing in equations (12) and (13). If considered, these interactions will contribute to the rheology of the model by modifying the constitutive relations through a different set of Onsager coefficients. The aim of the present model was to estimate the collective effect of the molecule segments through a set of effective Onsager coefficients [27].

5 Conclusions

A novel approach to the description of the dynamics of dilute polymer solutions has been explored using the formalism of mesoscopic nonequilibrium thermodynamics in the simplified case of a single vector parameter characterizing the polymer configuration, common to FENE models.

The description has been carried out by formulating the laws of nonequilibrium thermodynamics after assuming valid the hypothesis of local equilibrium in phase space. By calculating the entropy production of the system, we have obtained general constitutive equations at mesoscopic level for the dissipative currents in $r$, $R$ and $u$ spaces. Using then probability conservation, a generalized Fokker-Planck equation describing the dynamics of the system has been
obtained.

A general closure to the governing equations for the hydrodynamics of this system model is derived from the Fokker-Planck equation. Those equations consist in two evolution equations for elastic and kinetic contributions to the pressure tensor. The evolution equation for the elastic stresses resembles known FENE models. The kinetic contribution, having no counterpart in the FENE models, enters into the hydrodynamic description due to the coupling between elastic and Brownian effects in the mesoscopic constitutive relations.

This method can generate a family of constitutive relations in configuration space depending on the modeled Onsager coefficients. Three examples were analyzed in the case of simple shear flow. In the first one, we have analyzed the dumbbell model with constant friction recovering the elastic behavior found in the FENE models [4]. In the second case, the friction of the molecule has been modeled with that of a spheroid aligned with the flow [24,26]. In this case we have obtained a steeper coil-stretch transition and good agreement with experiments of shear rate growth. In the last example we have considered the tensorial character of the Onsager coefficients by taking the non-isotropic friction tensor of a spheroidal particle aligned with the flow. This model is capable of describing the shear stress behavior in shear rate reduction experiments.

Given that the general constitutive equations here obtained can be reduced, with simple arguments, to models that predict experimental data, we are confident that further analysis can provide simple mathematical expressions for constitutive relations better approaching more complex situations. For example, in the case where configurational rates of change are relevant, the time change in the gross distortion of the molecule ought to be included in the description of the system, introducing an additional relaxation time.

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Fig. 1. Fit of experimental data (points) for the non-Newtonian shear stress versus the shear rate, using the isotropic friction model (line). The fit is made using $c\eta = 0.0038\text{kg/ms}$, $\beta = 3.5s^{-1}$, $\xi = 17s^{-2}$ and $L = 80$.

Fig. 2. Fit of experimental data (points) for the non-Newtonian shear stress versus the shear rate, using the non-isotropic friction model (lines). The fit is made using $c\eta = 0.025\text{kg/ms}$, $\beta = 5s^{-1}$, $\xi = 11s^{-2}$ and $L = 110, 140, 170$ starting from bottom.