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Original Contributions

Extended irreversible thermodynamics, generalized hydrodynamics, kinetic theory, and rheology*)

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Abstract: The gist of extended irreversible thermodynamics and generalized hydrodynamics is presented within the context of rheology of complex molecules (e.g., polymers) in this paper. Then, the constitutive equation for stress developed for polyatomic fluids in a previous paper is applied to rheology of polymeric fluids. This constitutive equation is fully consistent with the thermodynamic laws. It is shown that the collision bracket integrals appearing in the constitutive equation can be recast in terms of friction tensors of beads and equilibrium force-force correlation functions if the momentum relaxation is much faster than the configuration relaxation and there exist such relaxation times. The force-force correlation functions reduce to those related to the mean square radius of gyration of the polymer if the Hookean model is taken for forces. By treating the recast collision bracket integrals in the constitutive equation as empirical parameters, we analyze some experimental data on shear rate and elongation rate dependence of polymeric melts and obtain excellent agreement with experiment. We show that the empirical parameters can be related to the zero shear rate viscosity and the ratio of the secondary to the primary normal stress coefficient. Therefore, for the plane Couette flow geometry considered in the paper, the constitutive equation is completely specified by the limiting material functions at zero shear rate and relaxation times.

Key words: Irreversible thermodynamics; kinetic theory; polymers; generalized hydrodynamics

1. Introduction

Macroscopic processes in matter must be subject to thermodynamic laws and any rational development of theory of macroscopic processes should be founded on such laws. As a science of flow in matter, rheology should not be an exception, but a survey of literature in the field would quickly reveal that the mainstream efforts [1–3] in the field have been carried on without paying due attention to the question since rheology is developed pretty much detached from the discipline of thermodynamics. There, however, has been in the past a theory of Coleman et al. [4] in which viscous phenomena are looked at from the standpoint of rational thermodynamics. More recently, there is a movement [5, 6] to extend linear irreversible thermodynamics to nonlinear regimes. The theory is known as extended irreversible thermodynamics (EIT) and it provides a logical framework in which to examine rheology fully subject to the thermodynamic principles. In EIT constitutive equations for stress, heat flux and diffusion fluxes are empirically postulated subject to the second law of thermodynamics. Being empirical, they do not provide molecular representations of various parameters appearing in them and the theory based on them consequently loses the important connection with molecular constitutions of the substances examined, which is essential to understanding macroscopic behavior of the substances. Recently, one of us (BCE) has reported [7, 8] on a kinetic theory of dense polyatomic fluids as a generalization of the generalized Boltzmann equation for dense simple fluids [9]. The kinetic equation is irreversible under a relatively general condition and forms the sta-

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tistical mechanical basis for irreversible thermodynamics. It is shown possible to derive from the kinetic equation various constitutive equations necessary for constructing a theory of extended irreversible thermodynamics for dense polyatomic fluids. In this paper those constitutive equations are applied to polymeric liquids, and some formal relations are obtained for collision bracket integrals appearing in them to lay foundations for statistical mechanical studies of rheology of polymers. We remark that the kinetic equation referred to in this paper is not a Kirkwood diffusion equation for polymers [10], which is often referred to as a kinetic equation in rheology of polymeric fluids. The latter equation contains phenomenological parameters in the form of friction coefficients. The kinetic equation, namely, the generalized Boltzmann equation does not have such parameters. We have shown in a previous paper [8] that the Kirkwood diffusion equation is contained in the kinetic theory on which the present paper is based. The kinetic equation used here is qualitatively different from the Liouville equation employed in the phase space kinetic theory of Bird et al. [1]. An important difference is that the generalized Boltzmann equation is irreversible since it breaks the time reversal invariance, whereas the Liouville equation does not. Another important difference is in the dissipation term [see (18) and (22) below] in the constitutive equations which the phase space kinetic theory does not have since the Liouville equation does not have a collision term that accounts for collisional dissipation of energy. These differences are crucial points of departure in the phase space kinetic theory and the present kinetic theory that determine whether the thermodynamic laws may be incorporated into the theory of rheology or not, and whether the differential constitutive equations exist or not in a way consistent with the thermodynamic laws.

On the basis of the assumption that the momentum relaxation is much faster than the configuration relaxation, it is possible to show that the collision bracket integrals appearing in the constitutive equation can be expressed in terms of friction tensors of beads, equilibrium force-force correlation functions, and the ratio of momentum and configuration relaxation times. The collision bracket integrals so calculated are second-rank tensors which will be called material tensors and contract with the stress tensors of various species in the polymeric liquids. Since the material tensors are not isotropic in general, the constitutive equation is generally anisotropic. To test the utility of the constitutive equation calculated, it will then be made semiempirical and applied to study strain rate dependences of elongation and shearing phenomena in polymeric fluids. In fact, it will be shown that elongation viscosity, shear viscosity, and normal stress coefficients can collectively and in mutually consistent fashion determine the constitutive equation for stress for a given material. We analyze the shear rate dependence of viscosity, primary normal stress coefficient and unidirectional elongation viscosity for some polymer melts and obtain excellent agreement with experiment.

This paper is organized as follows: In Section 2 extended irreversible thermodynamics and generalized hydrodynamics are briefly reviewed in order to present the gist of the ideas and the essential equations involved in the subjects. Then, stress and diffusion flux evolution equations, namely, the constitutive equations for stress and diffusion fluxes for polymers are presented along with the associated entropy production and approximate solutions to the consistency conditions. In Section 4 the collision bracket integrals appearing in the stress and diffusion flux evolution equations are cast into forms that include more readily recognizable quantities such as friction tensors, etc. The end result of the calculations made in this section is a stress evolution equation containing friction tensors and a quantity closely related to the mean square radius of gyration, both of which may be treated as empirical parameters. If they are treated as such, then the stress evolution equation (i.e., the constitutive equation for stress) becomes semiempirical. The reader who is not interested in the statistical mechanical foundations of the stress evolution equation may skip Section 4 and proceed to Section 5 where a semiempirical treatment is given of the stress evolution equation developed in Section 4. The semiempirical constitutive equation is applied to plane Couette flow and elongation flow and comparison is made with experiment in Section 5. In Section 6 formal comparison is made between the present constitutive equation and other ones existing in the literature, and concluding remarks are made.

2. Extended irreversible thermodynamics and generalized hydrodynamics

Linear irreversible thermodynamics [11] is founded on the pair of assumptions that the local equilibrium formula for entropy change remains valid – the local equilibrium hypothesis – and linear thermodynamic force – flux relations hold for constitutive equations together with the Onsager reciprocal relations for phenomenological coefficients in the constitutive equations. At the level of hydrodynamics, linear irreversible thermodynamics gives rise to classical hydrodynamic equations: Navier-Stokes, Fourier and diffusion equations together with the equation of continuity. Therefore, it is correct to say that classical hydrodynamics is implied by linear irreversible thermodynamics, and inasmuch as the latter is a theory holding near equilibrium as is well recognized, classical hydrodynamics may be regarded as a theory dealing with flow phenomena near equilibrium. The distance of the state of a system from equilibrium may be characterized by the magnitude of thermodynamic forces which drive nonequilibrium processes, and when that magnitude is sufficiently large the system may be said to be far from equilibrium. We will generically call a system *removed far from equilibrium* when the constitutive equations for stresses, heat flux, and diffusion fluxes (simply, fluxes) are required to be nonlinear with respect to the thermodynamic forces driving them. Unlike the linear thermodynamic force – flux relations well known in linear irreversible thermodynamics, the constitutive equations in such a situation can in general be differential equations rather than algebraic equations and, furthermore, nonlinear. Such constitutive equations, as we will see, give rise to hydrodynamic equations which extend the classical hydrodynamic equations, and we will call hydrodynamics described by the generalized form of equations *generalized hydrodynamics*. Extended irreversible thermodynamics is an outcome of the desire that the constitutive equations for fluxes and any other macroscopic observables conform to the thermodynamic laws. There are different versions of EIT, the majority of which is usually phrased in the framework of linear theory, but a nonlinear version [12] is essential if EIT is to be useful for understanding natural phenomena occurring far from equilibrium, since the constitutive equations must be, by necessity, nonlinear for such phenomena.

The local equilibrium hypothesis of linear irreversible thermodynamics assumes that the local entropy density $\mathscr{S}$ of a fluid is a function of conserved variables such as the internal energy density $\mathscr{E}$, mass density ϱ or specific volume v, and concentrations or mass fractions c_a, $a = 1,2,\ldots,r$. The set $(\mathscr{S}, \mathscr{E}, v, c_a\colon a = 1,2,\ldots,r)$ is called the equilibrium Gibbs space. In EIT this equilibrium Gibbs space is extended to include stress tensors $\boldsymbol{P}_a$, heat fluxes $\boldsymbol{Q}_a$, mass fluxes $\boldsymbol{J}_a$, and other macroscopic variables appropriate and necessary for description of macroscopic phenomena of interest. These additional nonconserved variables will be denoted $\Phi_a^{(\alpha)}$, $a = 1,2,\ldots,r$, $\alpha = 1,2,\ldots,l$, and the extended set $(\mathscr{S}, \mathscr{E}, v, c_a, \Phi_a^{(\alpha)}\colon a = 1,2,\ldots,r;\ \alpha = 1,2,\ldots,l)$ will be called nonequilibrium Gibbs space or, simply, Gibbs space. Then, the entropy density $\mathscr{S}$ obeys the differential form [6, 12]

$$T d\mathscr{S} = d\mathscr{E} + p\,dv - \sum_{a=1}^{r} \hat{\mu}_a dc_a + \sum_{a=1}^{r} \sum_{\alpha=1}^{l} X_a^{(\alpha)} \odot d\hat{\Phi}_a^{(\alpha)} \ , \tag{1}$$

where T is the temperature, p is the pressure, $\hat{\mu}_a$ is the chemical potential per unit mass of species a, and $\hat{\Phi}_a^{(\alpha)} = \Phi_a^{(\alpha)}/\varrho$. Since $\Phi_a^{(\alpha)}$ and $X_a^{(\alpha)}$ can be scalars, vectors or tensors, the symbol $\odot$ means taking an appropriate scalar product of the vectors or tensors involved. In the phenomenological theory the quantities T^{-1}, p, $\hat{\mu}_a$, and $X_a^{(\alpha)}$ must be determined by constitutive relations, such as the caloric equation of state, equation of state, etc., which characterize the material of interest. Here the differentials are interpreted as substantial derivatives in the frame moving at the fluid velocity $\boldsymbol{u}$. Then, the evolution of $\mathscr{S}$ is described through the Gibbs equation, whose time variation is determined by the balance equations for conserved variables and the constitutive equations for non-conserved variables. They are:

$$\varrho \frac{dv}{dt} = \nabla \cdot \boldsymbol{u} \quad \text{or} \quad \frac{\partial \varrho}{\partial t} = -\nabla \cdot \varrho \boldsymbol{u} \quad (v = 1/\varrho) \ , \tag{2}$$

$$\varrho \frac{d}{dt} c_a = -\nabla \cdot \boldsymbol{J}_a \ , \quad (1 \le a \le r) \ , \tag{3}$$

$$\varrho \frac{d\boldsymbol{u}}{dt} = -\nabla \cdot \boldsymbol{P} \ , \tag{4}$$

$$\varrho \frac{d\mathscr{E}}{dt} = -\nabla \cdot \boldsymbol{Q} - \boldsymbol{P} : \nabla \boldsymbol{u} \ , \tag{5}$$

$$\varrho \frac{d}{dt} \hat{\Phi}_a^{(\alpha)} = Z_a^{(\alpha)} + \Lambda_a^{(\alpha)} \ , \quad (1 \le a \le r, 1 \le \alpha \le l) \ , \tag{6}$$

where

$$\boldsymbol{P} = \sum_{a=1}^{r} \boldsymbol{P}_a \ , \tag{7a}$$

$$\boldsymbol{Q} = \sum_{a=1}^{r} \boldsymbol{Q}_a \ , \tag{7b}$$

$\Phi^{(\alpha)}_a$:

$$\Phi^{(1)}_a = [\boldsymbol{P}_a]^{(2)}$$

$$= \text{traceless symmetric part of } \boldsymbol{P}_a \ , \tag{8a}$$

$$\Phi^{(2)}_a = \Delta \equiv \tfrac{1}{3}\operatorname{Tr}\boldsymbol{P}_a - p_a$$

$$= \text{excess trace part of } \boldsymbol{P}_a \ , \tag{8b}$$

$$\Phi^{(3)}_a = \boldsymbol{Q}'_a$$

$$= \boldsymbol{Q}_a - \hat{h}_a\boldsymbol{J}_a = \text{net heat flux} \ , \tag{8c}$$

$$\Phi^{(4)}_a = \boldsymbol{J}_a \ , \quad \text{etc.}$$

$$= \text{diffusion (mass) flux} \ . \tag{8d}$$

Here $\boldsymbol{P}_a$ is the stress tensor of species a, $\boldsymbol{Q}_a$ its heat flux, p_a the partial pressure of species a and $\hat{h}_a$ the enthalpy of species a per unit mass. The terms $Z^{(\alpha)}_a$ are defined in Table 1 for $1 \le \alpha \le 4$, and the terms $\Lambda^{(\alpha)}_a$, which are called the dissipative terms, should be determined such that the entropy production in the system is always positive in conformation with the second law of thermodynamics. The entropy production is given by the formula [6, 9, 12]

$$\sigma = T^{-1} \sum_{a=1}^{r} \sum_{\alpha=1}^{l} X^{(\alpha)}_a \odot \Lambda^{(\alpha)}_a \ , \tag{9}$$

on which the local form of the second law of thermodynamics demands that

$$\sum_{a=1}^{r} \sum_{\alpha=1}^{l} X^{(\alpha)}_a \odot \Lambda^{(\alpha)}_a \ge 0 \ , \tag{10}$$

Table 1. $Z^{(\alpha)\#}_a$

$\alpha = 1$	$-\nabla\cdot\psi^{(1)}_a - 2[\boldsymbol{J}_a d_t \boldsymbol{u}]^{(2)} - 2[\boldsymbol{P}_a\cdot\nabla\boldsymbol{u}]^{(2)} + [\boldsymbol{V}^{(2)}_a]^{(2)}$
$\alpha = 2$	$-\nabla\cdot\psi^{(2)}_a - \frac{2}{3}\boldsymbol{J}_a\cdot d_t\boldsymbol{u} - \frac{2}{3}\boldsymbol{P}_a : \nabla\boldsymbol{u} + \frac{1}{3}\boldsymbol{V}^{(2)}_a : \boldsymbol{U}$
$\alpha = 3$	$-\nabla\cdot\psi^{(3)}_a - \boldsymbol{J}_a d_t\hat{h}_a - d_t\boldsymbol{u}\cdot(\boldsymbol{P}_a - p_a\boldsymbol{U})$ $-\boldsymbol{Q}'_a\cdot\nabla\boldsymbol{u} - \varphi^{(3)}_a : \nabla\boldsymbol{u} + \boldsymbol{V}^{(3)}_a - \boldsymbol{P}_a\cdot\nabla\hat{h}_a$
$\alpha = 4$	$-\nabla\cdot\boldsymbol{P} + c_a\nabla\cdot\boldsymbol{P} - \boldsymbol{J}_a\cdot\nabla\boldsymbol{u} + \boldsymbol{V}^{(4)}_a$

\# The notation is the same as in [8], to which the definitions of the symbols are referred. In the modified moment method on which the present theory is based, the higher moments $\psi^{(\alpha)}_a$ and $\varphi^{(3)}_a$ are neglected when only the first 13 moments plus diffusion fluxes are taken into consideration. Note that $d_t \equiv d/dt$.

the equality holding only when $X^{(\alpha)}_a = 0$ for all a and α. The dissipative terms $\Lambda^{(\alpha)}_a$ are generally nonlinear functions of $X^{(\alpha)}_a$ or, ultimately, of variables $(v, T, c_a, \hat{\Phi}^{(\alpha)}_a)$. Thus, the condition (10) imposes a restriction on possible choice for the dissipative terms $\Lambda^{(\alpha)}_a$, and this restriction means that the flux evolution equations (or the constitutive equations) (6) cannot be arbitrary, but must conform to condition (10) if the flux evolution is to be consistent with the second law of thermodynamics. It can be also shown that the entropy flux $\boldsymbol{J}_s$ is given by the formula [6, 9, 12]

$$\boldsymbol{J}_s = \sum_{a=1}^{r} (\boldsymbol{Q}_a - \hat{\mu}_a\boldsymbol{J}_a)/T + \boldsymbol{J}_{sn} \ , \tag{11}$$

where the nonclassical part $\boldsymbol{J}_{sn}$ of the entropy flux is defined by the equation [6]

$$\nabla\cdot\boldsymbol{J}_{sn} + T^{-1} \sum_{a=1}^{r} \sum_{\alpha=1}^{l} [Z^{(\alpha)}_a \odot X^{(\alpha)}_a + \Phi^{(\alpha)}_a \odot \chi^{(\alpha)}_a] = 0 \ . \tag{12}$$

In (12) the thermodynamic forces $\chi^{(\alpha)}_a$ are defined as follows:

$$\chi^{(1)}_a = -[\nabla\boldsymbol{u}]^{(2)} \ , \tag{13a}$$

$$\chi^{(2)}_a = -\nabla\cdot\boldsymbol{u} \ , \tag{13b}$$

$$\chi^{(3)}_a = -\nabla\ln T \ , \tag{13c}$$

$$\chi^{(4)}_a = -\nabla_T\hat{\mu}_a + v_a\nabla p \ , \tag{13d}$$

where the subscript T to ∇ means keeping T fixed and $v_a = 1/\varrho_a$. Equations (13a–d) define the thermodynamic force for shear, dilatation, heat conduction and diffusion, respectively. The nonclassical entropy flux $\boldsymbol{J}_{sn}$ defined in (12) should vanish in the case of linear irreversible processes, since in that case

$$Z^{(\alpha)}_a \odot X^{(\alpha)}_a + \Phi^{(\alpha)}_a \odot \chi^{(\alpha)}_a = 0 \ . \tag{14}$$

and there cannot be a nonclassical current possible near equilibrium. The reason for this is that $Z^{(\alpha)}_a$ is proportional to $\chi^{(\alpha)}_a$ while $X^{(\alpha)}_a$ is proportional to $-\Phi^{(\alpha)}_a$ such that (14) holds. In the rheological context, such a situation arises in the case of the Maxwell fluid [13] if $X^{(1)}_a$ is taken as

$$X^{(1)}_a = -\Phi^{(1)}_a/2p_a \ . \tag{15}$$

The set of evolution equations for thermodynamic state of a system in the Gibbs space is complete if the evolution equation for entropy density is added to the set (2) – (6). Such an equation is obtained by substituting (2), (3), (5), and (6) into the extended Gibbs relation (1) and using the definitions of entropy production (9) and entropy flux (11) and (12):

$$\varrho \frac{d}{dt} \mathscr{S} = -\nabla \cdot J_s + \sigma \ , \tag{16}$$

which is simply the entropy balance equation. When the set of evolution Eqs. (2) – (6) is appended with various constitutive relations such as the caloric equation of state for T^{-1} or specific heat (C_v), the equation of state for p, and the equations for $\hat{\mu}_a$ and $X_a^{(\alpha)}$:

$$C_v \ = C_v(\mathscr{E}, v, c_a, \hat{\Phi}_a^{(\alpha)}) = C_v(T, v, c_a, \hat{\Phi}_a^{(\alpha)}) \ , \tag{17a}$$

$$p \ = p(\mathscr{E}, v, c_a, \hat{\Phi}_a^{(\alpha)}) = p(T, v, c_a, \hat{\Phi}_a^{(\alpha)}) \ , \tag{17b}$$

$$\hat{\mu}_a \ = \hat{\mu}_a(\mathscr{E}, v, c_a, \hat{\Phi}_a^{(\alpha)}) = \hat{\mu}_a(T, v, c_a, \hat{\Phi}_a^{(\alpha)}) \ , \tag{17c}$$

$$X_a^{(\alpha)} = X_a^{(\alpha)}(\mathscr{E}, v, c_a, \hat{\Phi}_a^{(\alpha)}) = X_a^{(\alpha)}(T, v, c_a, \hat{\Phi}_a^{(\alpha)}) \ , \tag{17d}$$

the formal mathematical structure of generalized hydrodynamics is complete and a fluid dynamic formalism thus is in place for systems where nonlinear processes occur removed far from equilibrium.

The formalism constructed up to this point is phenomenological since there is no reference to the molecular constitution of matter and statistical mechanical theory for the evolution Eqs. (2) – (6) and (16) and constitutive relations (17 a – d) which contain material parameters. These equations can be given statistical mechanical foundations [8, 9] by means of the generalized Boltzmann equation for dense fluids, monatomic or polyatomic.

3. Evolution equations for stress and diffusion fluxes of polymers

The balance Eqs. (2) – (5) for conserved variables and the constitutive Eqs. (6) for nonconserved variables have been derived in a general setting from the generalized Boltzmann equation for dense polyatomic fluids in [8]. Here we shall take only the stress and diffusion flux evolution equations and cast them into appropriate forms necessary for studying rheology of polymeric liquids. This truncation of the Gibbs space is permissible under the assumptions that the fluid is incompressible and the temperature is maintained uniform so that there is no heat conduction. This second assumption is often too restrictive and sometimes unrealistic since there can be considerable viscous heating arising from flow of the substance, but it is taken to make analysis simpler than otherwise. There is, however, no problem to remove these assumptions and carry out a more general investigation.

The polymers will be assumed to be monodisperse, but the polydispersity can be taken into account quite easily in the present formalism by simply increasing the number of independent species, since the formalism is already for a mixture.

3.1 Preliminary

Before presenting the evolution equations, it is useful to define the notation used below. We will reserve italic lower case letters a, b, c, etc., for species, subscripts i, j, k, etc., for molecules of a species, and subscripts q, r, s, t, etc., for monomers in a species which are treated as if they are a single atom or a group. Thus, the set (aiq) stands for the qth monomer in the ith molecule (polymer) of species a. With this code for subscripts, we define the following:

$$\boldsymbol{r}_{aiq;bks} = \boldsymbol{r}_{aiq} - \boldsymbol{r}_{bks}$$
$$= \text{relative distance between } (aiq) \text{ and } (bks) \ ,$$

$$\dot{\boldsymbol{r}}_{aiq} = d\boldsymbol{r}_{aiq}/dt = \text{velocity of } (aiq) \ ,$$

$$V_{aiq;bks}$$
$$= \text{potential energy between } (aiq) \text{ and } (bks) \ ,$$

$$\boldsymbol{F}_{aiq;bks} = -(\partial V_{aiq;bks}/\partial \boldsymbol{r}_{aiq;bks})$$
$$= \text{force between } (aiq) \text{ and } (bks) \ ,$$

$$F^{(2)}_{aiq;bks} = -(r^{-1}_{aiq;bks}\partial/\partial r_{aiq;bks})^2 V_{aiq;bks} \ ,$$

$$\mathscr{C}_{aiq} = \dot{\boldsymbol{r}}_{aiq} - \boldsymbol{u} = \text{peculiar velocity of } (aiq) \ ,$$

$$h^{(1)}_{aiq} = m_{aq}[\mathscr{C}_{aiq}\mathscr{C}_{aiq}]^{(2)} + \frac{1}{2}\sum_{b=1}^{r}\sum_{k \in b}^{N_b}\sum_{\substack{s \in k \\ (aiq \neq bks)}} [\boldsymbol{F}_{aiq;bks}\boldsymbol{r}_{aiq;bks}]^{(2)} \ ,$$

$$h^{(4)}_{aiq} = m_{aq}\mathscr{C}_{aiq} \ ,$$

where m_{aq} is the mass of the qth monomer and $[A]^{(2)}$

denotes the traceless symmetric part of second rank tensor $\boldsymbol{A}$:

$$[\boldsymbol{A}]^{(2)} = \tfrac{1}{2}(\boldsymbol{Q}+\boldsymbol{A}^{t}) - \tfrac{1}{3}\boldsymbol{U}\mathrm{Tr}\boldsymbol{A} \ , \ (\boldsymbol{U} = \text{unit tensor}) \ .$$

In what follows, we use the angular brackets ⟨⟩ to denote integration over the phase space volume, $F^{(N)}(t)$ for the distribution function obeying the generalized Boltzmann equation and $F^{(N)}_{eq}$ the equilibrium distribution function.

3.2 *Evolution (constitutive) equations and entropy production*

Since the fluid is assumed to be incompressible and non-heat-conducting, it is not necessary to consider the heat flux and the excess trace part Δ_a of the stress tensor, but only the traceless symmetric part $\Pi_a \equiv [\boldsymbol{P}_a]^{(2)}$ and the diffusion fluxes; see (8a) and (8b) for the definitions of the symbols. The reader is referred to [8] for statistical mechanical definitions of various macroscopic variables appearing in (2)–(6). The statistical-mechanically derived evolution equations for $\hat{\Pi}_a = \Pi_a/\varrho$ and $\boldsymbol{J}_a$ are as follows:

$$\varrho \frac{d}{dt}\hat{\Pi}_a = -2[\boldsymbol{J}_a d_t \boldsymbol{u}]^{(2)} - 2[\boldsymbol{P}_a \cdot \nabla \boldsymbol{u}]^{(2)} + [\boldsymbol{V}_a^{(2)}]^{(2)} + \Lambda_a^{(1)} \ , \tag{18}$$

$$\varrho \frac{d}{dt}\hat{\boldsymbol{J}}_a = -\nabla\cdot(\boldsymbol{P}_a - c_a \boldsymbol{P}) - \boldsymbol{P}\cdot\nabla c_a - \boldsymbol{J}_a\cdot\nabla\boldsymbol{u} + \boldsymbol{V}_a^{(4)} + \Lambda_a^{(4)} \ , \tag{19}$$

where

$$d_t\boldsymbol{u} = d\boldsymbol{u}/dt \ ,$$

$$\hat{\boldsymbol{J}}_a = \boldsymbol{J}_a/\varrho \ ,$$

$$\boldsymbol{V}_a^{(2)} = \Bigg\langle \frac{1}{2} \sum_{i\in a}^{N_a} \sum_{q\in i} \sum_{\substack{b=1 \\ (aiq \neq bks)}}^{r} \sum_{k\in b}^{N_b} \sum_{s\in k} [\{\boldsymbol{F}_{aiq;bks}\dot{\boldsymbol{r}}_{aiq;bks}\} + \boldsymbol{F}^{(2)}_{aiq;bks}\dot{\boldsymbol{r}}_{aiq;bks}\cdot\boldsymbol{r}_{aiq;bks}\boldsymbol{r}_{aiq;bks}\boldsymbol{r}_{aiq;bks}] \times \delta(\boldsymbol{r}_{aiq} - \boldsymbol{r})F^{(N)}(t)\Bigg\rangle \ , \tag{20}$$

$$\boldsymbol{V}_a^{(4)} = \Bigg\langle \frac{1}{2} \sum_{i\in a}^{N_a} \sum_{q\in i} \sum_{\substack{b=1 \\ (aiq \neq bks)}}^{r} \sum_{k\in b}^{N_b} \sum_{s\in k} \boldsymbol{F}_{aiq;bks} \times [\delta(\boldsymbol{r}_{aiq} - \boldsymbol{r}) + \delta(\boldsymbol{r}_{biq} - \boldsymbol{r})]\boldsymbol{F}^{(N)}(t)\Bigg\rangle \ , \tag{21}$$

and to the first cumulant approximation and under the assumptions stated earlier in this section the dissipation terms are given by the formula

$$\Lambda_a^{(\alpha)} = (g\beta)^{-1} \sum_{c=1}^{r} \mathbb{R}_{ac}^{(\alpha\alpha)} \odot X_c^{(\alpha)} q_e(X) \ . \tag{22}$$

This is a highly nonlinear function of fluxes which will be found essential for appropriate description of experimental data; see Section 5 below. The curly brackets {} in (20) mean symmetrizing the dyadic product, and other symbols are defined by the formulas

$$g = (m_r/2k_B T)^{1/2}/(nd)^2 \ , \tag{23a}$$

$$\beta = 1/k_B T \ , \tag{23b}$$

where m_r denotes a mean reduced mass suitably defined, $\boldsymbol{k}_B$ the Boltzmann constant, n the number density and d a mean size parameter for the mixture (e.g., the length of a monomer),

$$q_e(X) = \sinh\kappa/\kappa \ , \tag{24a}$$

$$\kappa(X) = \left[\sum_{a=1}^{r}\sum_{c=1}^{r}\sum_{\alpha} X_a^{(\alpha)} \odot \mathbb{R}_{ac}^{(\alpha\alpha)} \odot X_c^{(\alpha)}\right]^{1/2} , \tag{24b}$$

and finally

$$\mathbb{R}_{ac}^{(\alpha\alpha)} = \beta^2 g \sum_{j\in a}^{N_a} \sum_{\substack{q\in j \\ (ajq\neq cks)}} \sum_{k\in c}^{N_c} \sum_{s\in k} \langle h_{ajq}^{(\alpha)} \delta(\boldsymbol{r}_{ajq} - \boldsymbol{r}) \times iT^{(N)} h_{cks}^{(\alpha)} \boldsymbol{F}_{eq}^{(N)} \rangle \ . \tag{24b}$$

This is the collision bracket integral which contains the molecular information on the substance in question and gives the transport coefficient in terms of molecular parameters. In (25) $i = \sqrt{-1}$ and $T^{(N)}$ is the N particle collision operator obeying the classical Lippmann-Schwinger equation [14–17] described below. It must be noted that the constitutive Eqs. (18) and (19) are in a fixed reference frame, but they can be put into the corotating frame of reference form if the method reported in a previous paper [18] on the subject is applied. One can also use the rules formulated there [18] to convert a fixed frame of reference form to the corotating form. It is important to note that we have neglected as a way of closure the terms involving moments of higher order than those corresponding to the first 13 moments in the constitutive equations. One may approximate $X_a^{(\alpha)}$ such that

$$X_a^{(1)} = -\Pi_a/2p_a \;, \tag{26a}$$

$$X_a^{(4)} = -J_a/\varrho_a \;, \tag{26b}$$

which result when the consistency condition [8] is solved to the lowest order approximation. In this approximation, $\kappa(X)$ becomes a quadratic function of Π_a and J_a and its square is simply proportional to the Rayleigh-Onsager dissipation function. In this connection it is worthwhile to note that the entropy production corresponding to the form $\Lambda_a^{(\alpha)}$ as in (22) is [9]

$$\sigma = k_B g^{-1} \kappa \sinh \kappa \;, \tag{27}$$

which becomes the linear irreversible thermodynamic form – the Rayleigh-Onsager dissipation function if the hyperbolic function is approximated with κ to the lowest order. Note that κ is small near equilibrium where the fluxes are small in magnitude. We remark that σ is always positive as required by the second law of thermodynamics.

The material properties of a substance manifest themselves in the collision bracket integrals $\mathbb{R}_{ac}^{(\alpha\alpha)}$ which in the context of the present paper are related to shear viscosity and diffusion coefficients. Therefore, treating them as empirical parameters, we can make the theory semiempirical. This line of approach will be taken in Section 5. As a matter of fact, putting the kinetic-theory-based constitutive equations into forms that can be readily made semiempirical is one of the major goals in this paper since that way the constitutive equations can eventually bridge experimental data to molecular pictures through the kinetic theory underlying them, namely, the constitutive equations.

To see the significance of the constitutive Eqs. (18) and (19) and the meanings of the collision bracket integrals in (22), let us linearize (18) and (19) with respect to fluxes with $X_c^{(\alpha)}$ defined by (26a, b) and take their steady state forms. Then we get the linear equations

$$\sum_{c=1}^{r} \mathbb{R}_{ac}^{(11)}\colon \Pi_c/2p_c = -2g\beta p_a [\nabla u]^{(2)} \;, \quad (1 \le a \le r) \;, \tag{28a}$$

$$\sum_{c=1}^{r} \mathbb{R}_{ac}^{(44)} \cdot J_c/\varrho_c = -g\beta c_a p \nabla \ln c_a \;, \quad (1 \le a \le r) \;, \tag{28b}$$

which are seen to be in the same forms as for linear constitutive relations in linear theory of transport processes. Therefore, the inverse of $\mathbb{R}_{ac}^{(\alpha\alpha)}$ is related to the linear transport coefficient for process α, namely, shear viscosity and diffusion coefficients. In the next section we recast the constitutive Eq. (18) into a form that can be readily used semiempirically by assuming some parameters such as friction tensors, etc., as empirical parameters. The reader not interested in the statistical mechanical foundations of such a semiempirical constitutive equation may pass over Section 4 and proceed directly to Section 5 where a semiempirical treatment is given of the constitutive equation recast in a self-contained manner.

4. Collision bracket integrals

The collision bracket integrals can be calculated by means of a cluster expansion [19] in which the N particle collision operator is expanded into a density series whose coefficients are made up with irreducible cluster collision operators of two, three particles, etc. Such an expansion yields transport coefficients in a density series similar to the virial expansion for pressure, but is not most suitable for dense polymeric liquids, except for dilute solutions. Here, we will explore another approach which we believe is more suitable for dense polymeric liquids.

To cast the evolution equations into more suitable forms and also to see their connection to the more conventional equations based on the Brownian motion model in rheology of polymers, we would like to examine the collision bracket integrals and cast them in terms of friction tensors that appear in the Brownian motion model [1, 20]. To begin with, let us recall that $T^{(N)}$ obeys the Lippmann-Schwinger equation [14–17]

$$T^{(N)}(z) = \mathscr{L}_1^{(N)} - \mathscr{L}_1^{(N)} \mathscr{R}_0(z) T^{(N)}(z) \;, \tag{29a}$$

where $\mathscr{L}_1^{(N)}$ is the interaction Liouville operator of the system, and

$$\mathscr{R}_0(z) = (\mathscr{L}_0^{(N)} - z)^{-1} \;, \quad (z = i\varepsilon, \varepsilon > 0) \tag{29b}$$

is the resolvent operator for N free particles. Here $\mathscr{L}_0^{(N)}$ is the free Liouville operator of the system consisting of $N = \sum_{c=1}^{r} N_c$ molecules where N_c is the number of molecules of species c. The integral Eq. (29a) for $T^{(N)}$ can be recast into the equivalent form

$$T^{(N)}(z) = \mathscr{L}_1^{(N)} - \mathscr{L}_1^{(N)} \mathscr{R}(z) \mathscr{L}_1^{(N)} \, , \tag{30}$$

where $\mathscr{R}(z)$ is the full resolvent operator for the system defined by

$$\mathscr{R}(z) = (\mathscr{L}^{(N)} - z)^{-1} \, , \tag{31}$$

with $\mathscr{L}^{(N)} = \mathscr{L}_0^{(N)} + \mathscr{L}_1^{(N)}$ denoting the full Liouville operator for the system. The equivalence of (29a) and (30) is well known in scattering theory [21]. Now, recalling that $\mathscr{L}_1^{(N)}$ is a differential operator of momentum and observing that the operation of $\mathscr{L}_1^{(N)}$ gives rise to an odd function of momenta in the collision integral (25) and thus yields a vanishing contribution, we obtain

$$\mathbb{R}_{ac}^{(\alpha\alpha)} = -i\beta^2 g \sum_{j\in a}^{N_a} \sum_{\substack{q\in j \\ (ajq \neq cks)}} \sum_{k\in c}^{N_c} \sum_{s\in k} \langle h_{ajq}^{(\alpha)} \delta(\boldsymbol{r}_{ajq} - \boldsymbol{r}) \times \mathscr{L}_1^{(N)} \mathscr{R}(z) \mathscr{L}_1^{(N)} h_{cks}^{(\alpha)} F_{eq}^{(N)} \rangle \, . \tag{32}$$

This collision bracket integral will be recast into more suitable forms for studying the evolution of diffusion fluxes and stress.

4.1 Collision bracket integrals for diffusion flux evolution

Since the interaction Liouville operator is given by the formula

$$\mathscr{L}_1^{(N)} = i \sum_{a=1}^{r} \sum_{j\in a}^{N_a} \sum_{q\in j} (\partial V / \partial \boldsymbol{r}_{ajq}) \cdot (\partial / \partial \boldsymbol{p}_{ajq}) \, , \tag{33}$$

by performing integration by parts, we obtain from (32) in the case of $\alpha = 4$ (i.e., diffusion)

$$\mathbb{R}_{ac}^{(44)} = -i\beta^2 g \sum_{j\in a}^{N_a} \sum_{\substack{q\in j \\ (ajq \neq cks)}} \sum_{k\in c}^{N_c} \sum_{s\in k} \langle \delta(\boldsymbol{r}_{ajq} - \boldsymbol{r}) \boldsymbol{F}_{ajq} \times \mathscr{R}(z) \boldsymbol{F}_{cks} F_{eq}^{(N)} \rangle \, , \tag{34}$$

where

$$\boldsymbol{F}_{aiq} = \sum_{b=1}^{r} \sum_{\substack{j\in b \\ (aiq \neq bjs)}}^{N_a} \sum_{s\in j} \boldsymbol{F}_{aiq;bjs} \, , \tag{35}$$

namely, the force on $q \in i$ of species a. The resolvent operator may be written as

$$-i\mathscr{R}(z) = \int_0^\infty dt \exp\left[-it(\mathscr{L}^{(N)} - z)\right] \, . \tag{36}$$

Since the evolution operator $\exp(-it\mathscr{L}^{(N)})$ propagates the phases of the operand to those of time t, the collision bracket integral in (34) can be written in a more insightful form as follows:

$$\mathbb{R}_{ac}^{(44)} = \beta^2 g \sum_{j\in a}^{N_a} \sum_{\substack{q\in j \\ (ajq \neq cks)}} \sum_{k\in c}^{N_c} \sum_{s\in k} \int_0^\infty dt \langle \boldsymbol{F}_{ajq} \boldsymbol{F}_{cks}(t) \rangle_{eq} \, , \tag{37}$$

where

$$\langle \ldots \rangle_{eq} = V^{-1} \int dx^{(N)} \ldots F_{eq}^{(N)} \, . \tag{38}$$

Note that we have approximated the delta function in the long wavelength limit by the formula

$$\delta(\boldsymbol{r}) = V^{-1}[1 + O(V^{-1/3})] \tag{39}$$

since the delta function is coarse-grained. In the form of (37) the collision bracket integral $\mathbb{R}_{ac}^{(44)}$ is seen to be related to the friction tensor defined by [22, 23]

$$\zeta_{ac} = \beta \int_0^\infty dt \langle \boldsymbol{F}_a \boldsymbol{F}_c(t) \rangle_{eq} \, , \tag{40}$$

where

$$\boldsymbol{F}_a = \sum_{i\in a}^{N_a} \sum_{q\in i} \boldsymbol{F}_{aiq} \, , \tag{41}$$

and similarly for $\boldsymbol{F}_c$. Thus we find [24]

$$\mathbb{R}_{ac}^{(44)} = \beta g \zeta_{ac} \, . \tag{42}$$

A completely molecular theory would require evaluation of friction tensors ζ_{ac} in (40) by some statistical mechanical methods. Since the diffusion flux $\boldsymbol{J}_a$ can be written as

$$\boldsymbol{J}_a = \varrho_a(\boldsymbol{u}_a - \boldsymbol{u}) \, , \tag{43}$$

where $\boldsymbol{u}_a$ is the mean velocity of species a, the evolution equation of the diffusion flux (19) can be written in the form

$$\varrho_a \frac{d}{dt}(\boldsymbol{u}_a - \boldsymbol{u}) = \underline{-\nabla \cdot ((\boldsymbol{P}_a - c_a \boldsymbol{P}) - \varrho_a(\boldsymbol{u}_a - \boldsymbol{u}) \cdot \nabla \boldsymbol{u}}$$

$$\underline{+\nabla \cdot [\varrho_a(\boldsymbol{u}_a - \boldsymbol{u})(\boldsymbol{u}_a - \boldsymbol{u})] - \boldsymbol{\Pi}_a \cdot \nabla c_a}$$

$$-p\nabla c_a + V_a^{(4)} - \sum_{c=1}^{r} \zeta_{ac}\cdot(u_c - u)q_e \ , \tag{44}$$

for which we have used the approximation (26b) for $X_a^{(44)}$. The first four underlined terms on the righthand side of (44) are nonlinear contributions arising from hydrodynamic interactions of species a when its surroundings flow at velocity $\boldsymbol{u}$, subject to stress Π applied. (Note that $\Pi = \sum_{c=1}^{r} \Pi_c$.) Equation (44) is a macroscopic equation of motion for species a and, apart from the terms related to the hydrodynamic interactions (i.e., those underlined by the broken line), is rather intimately related to the Brownian motion model in the existing theories of polymer solutions. To see this connection, let us put $q_e = 1$, which holds near equilibrium where the fluxes are small in magnitude. If we, moreover, ignore the underlined terms in (44), then

$$\varrho_a \frac{d}{dt}(u_a - u) = -p\nabla c_a + V_a^{(4)} - \sum_{c=1}^{r} \zeta_{ac}\cdot(u_c - u) \ . \tag{45}$$

We may treat $\boldsymbol{u}$, p, ϱ_a and ζ_{ac} as phenomenological parameters. The lefthand side of this equation is the inertia term in the frame of reference moving at velocity $\boldsymbol{u}$, the first term on the righthand side, which may be written as

$$-p\nabla c_a = -c_a p\nabla \ln c_a = -p_a \nabla \ln c_a \ , \tag{46}$$

the diffusion term arising from the Brownian motion of species a; the second term is the force on species a (see (21) for the definition of $V_a^{(4)}$), and the third term is the friction term. Equation (45) is thus comparable, almost one to one, to the equation of motion (Langevin equation) for a polymer bead in the well known Brownian motion model [1, 20]

$$m_q \ddot{r}_q = -\zeta_q(\dot{r}_q - u_q) - k_B T \frac{\partial}{\partial r_q} \ln \Psi + F_q \ , \tag{47}$$

where m_q is the mass, u_q is the fluid velocity at the location of the qth bead, F_q is the force on the bead, Ψ is the configuration distribution function, and ζ_q is the bead friction constant. The Langevin Eq. (47) is a molecular equation of motion, and a postulate, which contains macroscopic, phenomenological parameters such as the friction constant and the fluid velocity, and *these parameters are not determined within the framework of the theory of Brownian motion.* The Langevin equation is easier to comprehend for particles of a macroscopic size such as colloidal particles or pollens, but the applicability to molecules of the notion of macroscopic friction, the Einstein relation and the Stokes-Einstein relation is open to question, as often discussed in the literature [25]. Such a question would not arise in the case of (45) or (44) since these are macroscopic equations for the mean velocity of a molecule: *Eq. (45) says that the mean motion of a molecule obeys approximately a Langevin equation.* We consider this difference between two Langevin Eqs. (45) and (47) as being significant.

The Einstein relation between the diffusion and friction terms is implied by (45) since it gives rise to a set of linear thermodynamic force-flux relations when

$$\varrho_a \frac{d}{dt}(u_a - u) \approx V_a^{(4)} \ , \tag{48}$$

which means

$$\sum_{c=1}^{r} \zeta_{ac}\cdot(u_c - u) = -p\nabla c_a \ , \quad (1 \le a \le r) \ . \tag{49}$$

This relation defines the diffusion tensor which may be given in terms of the friction tensor as follows:

$$\boldsymbol{D} = k_B T \zeta^{-1} \ , \tag{50}$$

where

$$\zeta = \begin{pmatrix} \zeta_{aa} & \zeta_{ab} & \cdots \\ \zeta_{ba} & \zeta_{bb} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \ . \tag{51}$$

This relation establishes the Einstein relation between diffusion and friction tensors for polymeric fluids or polyatomic fluids in general and thereby makes it possible to connect the constitutive equation for stress in the present kinetic theory to the one in the Brownian motion model, as we will show later. The Einstein relation (50) was shown to hold for dense simple fluids in [24].

4.2 Collision bracket integrals for stress evolution

The method used in Sect. 4.1 can be applied to calculate the collision bracket integrals for stress evolution. If $\alpha = 1$ is taken in the general formula for $\mathbb{R}_{ac}^{(\alpha\alpha)}$ in (33) (i.e., for the traceless symmetric part of the stress) and integration by parts is performed, the stress counterpart of $\mathbb{R}_{ac}^{(44)}$ is obtained:

$$\mathbb{R}_{ac}^{(11)} = (4\beta^2 g/V) \sum_{i\in a}^{N_a} \sum_{q\in i} \underset{(aiq \neq cks)}{\sum_{k\in c}^{N_c} \sum_{s\in k}} \int_0^\infty dt \times \langle [\mathscr{C}_{aiq}\boldsymbol{F}_{aiq}]^{(2)} [\mathscr{C}_{cks}(t)\boldsymbol{F}_{cks}(t)]^{(2)} F_{eq}^{(N)} \rangle . \quad (52)$$

To make further progress, we recast the integrand in (52) as follows:

$$\begin{aligned}
[\mathscr{C}\boldsymbol{F}]_{kl}^{(2)} [\mathscr{C}(t)\boldsymbol{F}(t)]_{mn}^{(2)} &\equiv [\mathscr{C}\boldsymbol{F}]_{kl}^{(2)} [\mathscr{C}^t \boldsymbol{F}^t]_{mn}^{(2)} \\
&= \tfrac{1}{4}(\mathscr{C}_k \mathscr{C}_m^t F_l F_n^t + \mathscr{C}_l \mathscr{C}_m^t F_k F_n^t \\
&\quad + \mathscr{C}_k \mathscr{C}_n^t F_l F_m^t + \mathscr{C}_l \mathscr{C}_n^t F_k F_m^t) \\
&\quad - \tfrac{1}{6}(\mathscr{C}_p \mathscr{C}_m^t F_p F_n^t + \mathscr{C}_p \mathscr{C}_n^t F_p F_m^t)\delta_{kl} \\
&\quad - \tfrac{1}{6}(\mathscr{C}_k \mathscr{C}_p^t F_l F_p^t + \mathscr{C}_l \mathscr{C}_p^t F_k F_p^t)\delta_{mn} \\
&\quad + \tfrac{1}{9} \mathscr{C}_p \mathscr{C}_q^t F_p F_q^t \delta_{kl}\delta_{mn} ,
\end{aligned} \quad (53)$$

where the Einstein summation convention is used for repeated indices standing for the cartesian components of the vectors and $\mathscr{C}^t = \mathscr{C}(t)$, etc. Therefore, (53) indicates that the collision bracket integral $\mathbb{R}_{ac}^{(11)}$ consists of momentum and force correlations. The force correlations are intimately related to the configuration distribution of the system, and the configuration relaxes to its equilibrium form at a characteristic rate. If the fluid is dilute the configuration relaxation time should be comparable to the momentum relaxation time since both momentum and configuration equilibrium will be achieved by comparable numbers of collisions for a dilute fluid. In other words, the configuration relaxation is as facile as the momentum relaxation in the case of gases. However, if the fluid is dense (i.e., a liquid), the momentum relaxation will be much faster than the configuration relaxation. Therefore, the density of the fluid determines the mode of evaluation used for the time correlation functions appearing in (52).

Let us now observe that the equilibrium distribution function $F_{eq}^{(N)}$ is factorizable into the momentum and configuration distribution function

$$F_{eq}^{(N)} = F_m^{(N)}(\mathscr{C}) F_c^{(N)}(r) , \quad (54)$$

and the momentum and configuration correlation function can be calculated separately with the corresponding distribution function. Thus, we define

$$\langle \mathscr{C}_k \mathscr{C}_m^t \rangle \equiv \langle \mathscr{C}_k \mathscr{C}_m(t) \rangle = \int dp^{(N)} \mathscr{C}_k \mathscr{C}_m(t) F_m^{(N)}(\mathscr{C}) , \quad (55)$$

$$\langle F_l F_n^t \rangle \equiv \langle F_l F_n(t) \rangle = V^{-1} \int dr^{(N)} F_l F_n(t) F_c^{(N)}(r) . \quad (56)$$

Therefore, when taken average, (53) becomes

$$\begin{aligned}
&\langle [\mathscr{C}\boldsymbol{F}]_{kl}^{(2)} [\mathscr{C}(t)\boldsymbol{F}(t)]_{mn}^{(2)} F_{eq}^{(N)} \rangle \\
&= \tfrac{1}{4}[\langle \mathscr{C}\mathscr{C}(t)\rangle_{km} \langle \boldsymbol{F}\boldsymbol{F}(t)\rangle_{ln} + \langle \mathscr{C}\mathscr{C}(t)\rangle_{lm} \langle \boldsymbol{F}\boldsymbol{F}(t)\rangle_{kn} \\
&\quad + \langle \mathscr{C}\mathscr{C}(t)\rangle_{kn} \langle \boldsymbol{F}\boldsymbol{F}(t)\rangle_{lm} + \langle \mathscr{C}\mathscr{C}(t)\rangle_{ln} \langle \boldsymbol{F}\boldsymbol{F}(t)\rangle_{km}] \\
&\quad - \tfrac{1}{6}[\langle \mathscr{C}\mathscr{C}(t)\rangle_{pm} \langle \boldsymbol{F}\boldsymbol{F}(t)\rangle_{pn} \\
&\quad + \langle \mathscr{C}\mathscr{C}(t)\rangle_{pn} \langle \boldsymbol{F}\boldsymbol{F}(t)\rangle_{nm}]\delta_{kl} \\
&\quad - \tfrac{1}{6}[\langle \mathscr{C}\mathscr{C}(t)\rangle_{kp} \langle \boldsymbol{F}\boldsymbol{F}(t)\rangle_{lp} \\
&\quad + \langle \mathscr{C}\mathscr{C}(t)\rangle_{lp} \langle \boldsymbol{F}\boldsymbol{F}(t)\rangle_{kp}]\delta_{mn} \\
&\quad + \tfrac{1}{9}\langle \mathscr{C}\mathscr{C}(t)\rangle_{pq} \langle \boldsymbol{F}\boldsymbol{F}(t)\rangle_{pq} \delta_{kl}\delta_{mn} .
\end{aligned} \quad (57)$$

Let us assume that the momentum correlation function relaxes with relaxation time τ_a:

$$\begin{aligned}
\langle \mathscr{C}_{aiq} \mathscr{C}_{cks}(t) \rangle &= \exp(-t/\tau_a) \langle \mathscr{C}_{aiq} \mathscr{C}_{cks} \rangle \\
&= \tfrac{1}{3}\exp(-t/\tau_a) \langle \mathscr{C}_{aiq} \cdot \mathscr{C}_{aiq} \rangle \boldsymbol{U} \delta_{ac}\delta_{ik}\delta_{qs} \\
&= (k_B T/m_{aq}) \exp(-t/\tau_a) \boldsymbol{U} \delta_{ac}\delta_{ik}\delta_{qs} .
\end{aligned} \quad (58)$$

By applying (58) to (57), we obtain the collision bracket integral $\mathbb{R}_{ac}^{(11)}$ in the following form:

$$\begin{aligned}
\mathbb{R}_{ac}^{(11)} : X_c^{(1)} = 4\beta^2 g \sum_{i\in a}^{N_a} \sum_{q\in i} m_{aq}^{-1} \int_0^\infty dt \exp(-t/\tau_a) \\
\times \{ [\langle \boldsymbol{F}_{aiq}\boldsymbol{F}_{aiq}(t)]^{(2)} \rangle \cdot X_a^{(1)}]^{(2)} \\
+ \tfrac{1}{3}\langle \boldsymbol{F}_{aiq} \cdot \boldsymbol{F}_{aiq}(t) \rangle X_a^{(1)} \} \delta_{ac} .
\end{aligned} \quad (59)$$

If we further assume that there exists a configuration relaxation time τ_f such that

$$\langle \boldsymbol{F}_{aiq}\boldsymbol{F}_{aiq}(t) \rangle = \exp(-t/\tau_f) \boldsymbol{G}_{aiq} , \quad (60\text{a})$$

$$\boldsymbol{G}_{aiq} \equiv \langle \boldsymbol{F}_{aiq}\boldsymbol{F}_{aiq} \rangle , \quad (60\text{b})$$

where $\boldsymbol{G}_{aiq}$ is an equilibrium force correlation function, then from (59) follows the formula

$$\mathbb{R}_{ac}^{(11)}:X_c^{(1)} = 4\beta^2 g \sum_{i\in a}^{N_a} \sum_{q\in i} m_{aq}^{-1}\left(\frac{\tau_a\tau_f}{\tau_a+\tau_f}\right)$$
$$\times\{[\boldsymbol{G}_{aiq}]^{(2)}\cdot X_a^{(1)}]^{(2)}$$
$$+\tfrac{1}{3}X_a^{(1)}\,\mathrm{Tr}\,\boldsymbol{G}_{aiq}\}\delta_{ac}\ . \tag{61}$$

Let us now define friction tensors in analogy to (40) as follows:

$$\zeta_{aiq} = \beta\int_0^\infty dt\,\langle \boldsymbol{F}_{aiq}\boldsymbol{F}_{aiq}(t)\rangle\ , \tag{62}$$

and evaluate them under the assumption (60). We then obtain

$$\zeta_{aiq} = \beta\,\boldsymbol{G}_{aiq}\tau_f\ . \tag{63}$$

As mentioned before, as the density increases, the configuration relaxation gets increasingly slower than the momentum correlation which relaxes faster with increasing density since the collisions become more frequent between the molecules, and hence, the force correlation function is expected to relax much more slowly compared with the momentum correlation function. That is, as the density increases, the force correlation function relaxation time τ_f becomes much larger than the momentum correlation function relaxation time τ_a. Their density dependence therefore may be written as

$$\tau_a = \tau_a^0\exp(-\delta n)\ ,$$
$$\tau_f = \tau_f^0\exp(\nu n)\ ,$$

where τ_a^0 and τ_f^0 are the low density relaxation times and δ and ν are constant parameters. Here, we will take $\delta=\nu$ as a model. Since τ_a and τ_f are comparable at low densities, we may also take $\tau_a^0=\tau_f^0\equiv\tau_m$. Then we find in the density regime of liquids

$$\frac{\tau_a\tau_f}{\tau_a+\tau_f}\approx\tau_a=\tau_m^2/\tau_f\ .$$

Since from (63)

$$1/\tau_f=\beta\zeta_{aiq}^{-1}:\boldsymbol{G}_{aiq}\ ,$$

we finally obtain from (61) the formula

$$\mathbb{R}_{ac}^{(11)}:X_c^{(1)} = 4g\beta^3\tau_m^2 \sum_{i\in a}^{N_a}\sum_{q\in i}(m_{aq}^{-1}\zeta_{aiq}^{-1}:\boldsymbol{G}_{aiq})$$
$$\times\{[[\boldsymbol{G}_{aiq}]^{(2)}\cdot X_a^{(1)}]^{(2)}+\tfrac{1}{3}X_a^{(1)}\,\mathrm{Tr}\,\boldsymbol{G}_{aiq}\}\delta_{ac}. \tag{64}$$

If τ_f is calculated from (63) by taking trace, then there holds the relation

$$\mathbb{R}_{ac}^{(11)}:X_c^{(1)} = 4g\beta^3\tau_m^2 \sum_{i\in a}^{N_a}\sum_{q\in i}(\mathrm{Tr}\,\boldsymbol{G}_{aiq}/m_{aq}\,\mathrm{Tr}\,\zeta_{aiq})$$
$$\times\{[[\boldsymbol{G}_{aiq}]^{(2)}\cdot X_a^{(1)}]^{(2)}+\tfrac{1}{3}X_a^{(1)}\,\mathrm{Tr}\,\boldsymbol{G}_{aiq}\}\delta_{ac}. \tag{65}$$

Either one of (64) and (65) is acceptable for our purpose, but we will use (64). To see the physical significance of $\boldsymbol{G}_{aiq}$, let us assume that the polymer is a Hookean chain. Then $\boldsymbol{F}_{aiq}$ is seen to be proportional to the distance between neighboring beads and therefore *$\boldsymbol{G}_{aiq}$ is related to the mean square radius of gyration*. For this, we calculate $\boldsymbol{F}_{aiq}$ more explicitly. According to the definition of $\boldsymbol{F}_{aiq}$ (35), in the Hookean chain model

$$\boldsymbol{F}_{aiq}=\sum_{\substack{s\in i\\(s\neq q)}} H_a\boldsymbol{r}_{aiq;ais}+\boldsymbol{F}'_{aiq}\ , \tag{66}$$

where H_a is the spring constant and $\boldsymbol{F}'_{aiq}$ denotes the force due to other polymers and the solvent if the system is a solution:

$$\boldsymbol{F}'_{aiq}=\sum_{b=1}^{r}\sum_{\substack{j\in b\\(j\neq i)}}^{N_b}\sum_{s\in j}\boldsymbol{F}_{aiq;bjs}\ . \tag{67}$$

Clearly, the Hookean term (i.e., the first term) on the righthand side of (66), when substituted into $\boldsymbol{G}_{aiq}$, would give rise to the equilibrium mean square radius of gyration. This clearly means that the viscosity is intimately related to the mean square radius of gyration or the end-to-end distance.

Returning to (64), we observe that, since the molecules of a species are identical, the subscript i may be dropped from the quantities in (64), and the sum over i may be replaced by the factor N_a so as to write (64) in the form

$$\begin{aligned}\mathbb{R}_{ac}^{(11)}:X_c^{(1)} &= 4g\beta^3\tau_m^2 N_a \sum_{q\in a} (m_{aq}^{-1}\zeta_{aq}^{-1}:\boldsymbol{G}_{aq}) \\ &\quad\times\{[[\boldsymbol{G}_{aq}]^{(2)}\cdot X_a^{(1)}]^{(2)}+\tfrac{1}{3}X_a^{(1)}\,\mathrm{Tr}\,\boldsymbol{G}_{aq}\}\delta_{ac} \\ &= 4g\beta^3\tau_m^2 N_a \sum_{q\in a} (m_{aq}^{-1}\zeta_{aq}^{-1}:\boldsymbol{G}_{aq}) \\ &\quad\times[\boldsymbol{G}_{aq}\cdot X_a^{(1)}]^{(2)}\delta_{ac}\ , \end{aligned} \tag{68}$$

and similarly for (65). Here we have dropped the subscript i referring to molecule $i\in a$ from ζ_{aiq} and G_{aiq} since the sum over i is replaced with N_a. The results obtained above for $\mathbb{R}_{ac}^{(11)}$ show that the viscosity is proportional to the friction tensor of beads and inversely proportional to approximately the square of the mean size of the polymer.

We now consider the tensor $V_a^{(2)}$ appearing in (18). This is a term that has been neglected in the previous semiempirical studies [26] of non-Newtonian viscosity on the ground that it belongs to the physically unmeasured set of macroscopic variables, which is complementary to the Gibbs variable set chosen compatibly with the 13-moment method. Strictly speaking, no current experiment appears to measure such quantities, and the truncation scheme within the framework of 13 moments seems to justify the neglect. However, if we assume that beads are stretched or compressed by flow of the medium under shear, then to an approximation it is possible to write [1, 20]

$$\dot{r}_{aiq;bks} = \dot{r}^0_{aiq;bks} + \gamma\cdot r_{aiq;bks}\ , \tag{69}$$

where $\dot{r}^0_{aiq;bks}$ is the velocity when $\gamma = 0$, and

$$\gamma = \nabla\boldsymbol{u}\ . \tag{70}$$

From the strict statistical mechanical viewpoint (69) is arguable and must be regarded as an assumption since it presumes that the particles are imbedded in a continuum liquid which is sheared at shear rate γ. In a strictly statistical theory all the species should be put on an equal molecular footing. If not, for example, the friction tensors appearing in (68) must be regarded as phenomenological quantities. The assumption (69) is commonly used in polymer solution theories [1, 20] and is not unreasonable, especially if the solvent is regarded as a continuum liquid and the velocity evolution is decoupled from the constitutive equation for stress as will be done below. However, in the case of a single component polymer melt the notion of continuum liquid for the solvent is not present, and the status of the assumption becomes a little murky. We note that the assumption is, nevertheless, used in the case of polymer melts as is evident from the literature; see [1] and [20]. On substitution of (69), $V_a^{(2)}$ can be written as

$$\boldsymbol{V}_a^{(2)} = 2\gamma\cdot\boldsymbol{W}_a\ , \tag{71}$$

where

$$\begin{aligned}\boldsymbol{W}_a = \frac{1}{2}\Big\langle\frac{1}{2}\sum_{i\in a}^{N_a}\sum_{q\in i}\sum_{\substack{b=1\\(ajq\neq bks)}}^{r}\sum_{k\in b}^{N_b}\sum_{s\in k} &[\{\boldsymbol{F}_{aiq;bks}\boldsymbol{r}_{aiq;bks}\} \\ &+\boldsymbol{F}^{(2)}_{aiq;bks}\boldsymbol{r}_{aiq;bks}\cdot\boldsymbol{r}_{aiq;bks}\boldsymbol{r}_{aiq;bks}\boldsymbol{r}_{aiq;bks}] \\ &\times\delta(\boldsymbol{r}_{aiq}-\boldsymbol{r})F^{(N)}(t)\Big\rangle\ . \end{aligned} \tag{72}$$

This is the work done to stretch the molecules in the flow field, in excess of the equilibrium contribution. Note that the equilibrium velocity term at $\gamma = 0$, therefore, does not contribute. In the isothermal condition this work must be equal to the Helmholtz work function, $\mathscr{A}_a$. Thus, we assert that

$$\boldsymbol{W}_a = -\mathscr{A}_a\boldsymbol{U}\ ,$$

and therefore,

$$\boldsymbol{V}_a^{(2)} = -2\mathscr{A}_a\gamma = -2\mathscr{A}_a[\nabla\boldsymbol{u}]^{(2)}\ . \tag{73}$$

According to the extended Gibbs relation and also the kinetic theory underlying the present work, $\mathscr{A}_a$ must be a bilinear function of $X_a^{(1)}$ and $\Phi_a^{(1)}$:

$$\mathscr{A}_a = -X_a^{(1)}:\Phi_a^{(1)} \tag{74}$$

for the shear part in which we are interested here. The $X_a^{(1)}$, to the lowest order approximation, is given by (26a), and it would yield $\mathscr{A}_a$ in the form

$$\mathscr{A}_a = \Phi_a^{(1)}:\Phi_a^{(1)}/2p_a = \Pi_a:\Pi_a/2p_a\ . \tag{75}$$

This approximate form, however, is not sufficient for some nonlinear processes in complex liquids, and the solution in (26a) must be improved. Before pursuing this aim, we summarize the constitutive equation for stress Π_a within the validity of (68):

$$\begin{aligned}\varrho\frac{d}{dt}\hat{\Pi}_a = -2[d_t\boldsymbol{u}\boldsymbol{J}_a]^{(2)} - 2[\boldsymbol{P}_a\cdot\nabla\boldsymbol{u}]^{(2)} + 2(X_a^{(1)}:\Pi_a) \\ \times[\nabla\boldsymbol{u}]^{(2)} + 4p_{\mathrm{a}}^2\zeta_a^{-1}[\mathscr{R}_a\cdot X_a^{(1)}]^{(2)}q_e(X)\ ,\end{aligned} \tag{76}$$

where

$$\zeta_a^{-1}\,\mathcal{R}_a = (\beta^2\tau_m^2 N_a/p_a^2)\sum_{q\in a} m_{aq}^{-1}(\zeta_{aq}^{-1}:\boldsymbol{G}_{aq})\boldsymbol{G}_{aq}\ , \tag{77}$$

ζ_a being a suitably chosen mean value of ζ_{aq}. Equation (77) defines the material tensor that we have alluded to in the Introduction. We may now treat these material tensors $\zeta_a^{-1}\,\mathcal{R}_a$ as empirical parameters and interpret rheological data with (76). The constitutive Eq. (76) is in a decoupled form since it is for species a only, whereas in the original Eq. (18) the stress tensors for different species are coupled. This decoupling is traceable to the relaxation time approximation (58) for the momentum correlation functions. This weakness can be removed if the collision bracket integrals are computed directly from (52); this is the price paid for a more physically transparent form for $\mathbb{R}_{ac}^{(11)}$. It must be noted that (76) is in a fixed frame of reference. If a corotating frame of reference is used and if the diffusion term is neglected to an approximation, then it takes the form

$$\begin{aligned}\varrho\frac{d}{dt}\hat{\Pi}_a = &-2p_a[\nabla\boldsymbol{u}]^{(2)} - 2[\Pi_a\cdot[\nabla\boldsymbol{u}]^{(2)}]^{(2)}\\ &-[\omega,\Pi_a] + 2(X_a^{(1)}:\Pi_a)[\nabla\boldsymbol{u}]^{(2)}\\ &+4p_a^2\zeta_a^{-1}[\,\mathcal{R}_a\cdot X_a^{(1)}]^{(2)}q_e(X_a^{(1)})\ ,\end{aligned} \tag{78}$$

where ω is the vorticity tensor defined as

$$\omega = [\nabla\boldsymbol{u} - (\nabla\boldsymbol{u})^t]/2\ , \tag{79}$$

$$[\omega,\Pi_a] = \omega\cdot\Pi_a - \Pi_a\cdot\omega\ . \tag{80}$$

If the term containing the vorticity on the right member of (78) is transferred to the lefthand side of the equation, then the left member becomes the Jaumann derivative [18, 27] of $\hat{\Pi}_a$, and the constitutive equation becomes corotational. We will use this constitutive equation to study some aspects of non-Newtonian polymeric liquids by treating the material tensors $\zeta_a^{-1}\,\mathcal{R}_a$ as phenomenological parameters.

The $X_a^{(1)}$ in (78) should be determined from the consistency condition [8] which, in the case of shear alone, takes the form

$$Z_a^{(1)}:X_a^{(1)} + \Pi_a:\chi = 0\ , \tag{81}$$

where

$$\chi \equiv \chi_a^{(1)} = -[\nabla\boldsymbol{u}]^{(2)}\ . \tag{82}$$

Since $Z_a^{(1)}$ is identified from (78) with the formula

$$Z_a^{(1)} = 2p_a\chi + 2[\Pi_a\cdot\chi]^{(2)} - [\omega,\Pi_a] - 2(X_a^{(1)}:\Pi_a)\chi\ , \tag{83}$$

substitution into (81) yields an equation for $X_a^{(1)}$:

$$\begin{aligned}&[2p_a\chi + 2[\Pi_a\cdot\chi]^{(2)} - [\omega,\Pi_a] - 2(X_a^{(1)}:\Pi_a)\chi]:X_a^{(1)}\\ &\quad+\Pi_a:\chi = 0\ .\end{aligned} \tag{84}$$

We now look for $X_a^{(1)}$ in the form

$$X_a^{(1)} = f\Pi_a\ , \tag{85}$$

where f is a scalar function of Π_a. Substituting (85) into (84) and solving the quadratic equation for f resulting thereby, we obtain f as follows:

$$f = -1/2p_a\phi \tag{86}$$

$$\begin{aligned}\phi = \frac{1}{2}\Bigg\{&1 + \frac{[\Pi_a\cdot\chi]^{(2)}:\Pi_a - \frac{1}{2}[\omega,\Pi_a]:\Pi_a}{p_a\Pi_a:\chi}\\ &+\left[\left(1 + \frac{[\Pi_a\cdot\chi]^{(2)}:\Pi_a - \frac{1}{2}[\omega,\Pi_a]:\Pi_a}{p_a\Pi_a:\chi}\right)^2\right.\\ &\left.+\frac{2\Pi_a:\Pi_a}{p_a^2}\right]^{1/2}\Bigg\}\ .\end{aligned} \tag{87}$$

We have chosen the negative branch of the solution of the quadratic form. Therefore, in the asymptotic limit of large $||\Pi_a||$ the factor ϕ is proportional to Π_a and, thus, $X_a^{(1)}$ exhibits a plateau independent of Π_a, while $X_a^{(1)}$ in the limit of small $||\Pi_a||$ is linear with respect to $||\Pi_a||$ as in (26a). These two different limiting behaviors of $X_a^{(1)}$ suggest that the non-equilibrium part of the Helmholtz work function behaves differently at the two limits, namely,

$$\mathscr{A}_a = \Pi_a:\Pi_a \quad \text{near} \quad ||\Pi_a|| = 0 \tag{88a}$$

$$\sim(\Pi_a:\Pi_a)^{1/2} \quad \text{as} \quad ||\Pi_a||\to\infty\ . \tag{88b}$$

If (26a) is used for $X_a^{(1)}$ and (78) is linearized with respect to $[\nabla\boldsymbol{u}]^{(2)}$ or Π_a, then it reduces to a Maxwell-type equation for stress evolution

$$\varrho\frac{d}{dt}\hat{\Pi}_a = -2p_a[\nabla\boldsymbol{u}]^{(2)} - 2p_a\zeta_a^{-1}[\,\mathcal{R}_a\cdot\Pi_a]^{(2)}\ . \tag{89}$$

It is perhaps worthwhile to point out that in this form the stress evolution equation is not necessarily isotropic unless the tensor $\mathscr{R}_a$ is isotropic, but it is not isotropic in the case of nonspherical fluids for which polymeric liquids are probably the most extreme examples. This equation generalizes the Maxwell equation for stress in the sense that the tensor $\mathscr{R}_a$ is not a constant times the unit tensor. If we assume that $\zeta_a^{-1}\,\mathscr{R}_a = \lambda_a^{-1}U$ where λ_a is a scalar with dimension of time (e.g., relaxation time), then (89) becomes a Maxwell model for stress tensor Π_a. A similar remark applies to the constitutive Eq. (78), which can be shown to reduce to some existing constitutive equations if some approximations are made and the material tensor is isotropic.

5. Application: semiempirical treatment of the constitutive equation

To make this section self-contained for those who are not interested in the statistical mechanical foundations, we reproduce the constitutive Eq. (78) which will be used semiempirically by treating the friction constants and $\mathscr{R}_a$ therein as empirical parameters. Thus, we take the constitutive equation for the stress tensor as follows:

$$\begin{aligned}\varrho\frac{d}{dt}\hat{\Pi}_a = {} & -2p_a[\nabla \boldsymbol{u}]^{(2)} - 2[\Pi_a\cdot[\nabla \boldsymbol{u}]^{(2)}]^{(2)} \\ & - [\omega,\Pi_a] + 2(X_a^{(1)}:\Pi_a)[\nabla \boldsymbol{u}]^{(2)} \\ & + 4p_a^2\zeta_a^{-1}[\mathscr{R}_a\cdot X_a^{(1)}]^{(2)}q_e(X_a^{(1)}) \ , \qquad (90)\end{aligned}$$

where $X_a^{(1)}$ is given by (85) with the accompanying Eqs. (86) and (87); ζ_a is the mean friction constant for species a and $\mathscr{R}_a$ is an empirical tensor coefficient. These parameters $\mathscr{R}_a$ and ζ_a in (90) can be in principle computed from their statistical mechanical formulas defined in the previous section. Their calculation requires solution of a many particle problem for polymers of distributed configurations and, hence, is not trivial to perform; it would require further intensive theoretical work. However, in the meantime, it should be useful and, in fact, important to test if the stress and its shear rate dependence given by the constitutive Eq. (90) is sensible from the experimental viewpoint. To this end we may treat the parameters as empirical ones and, by solving (90) suitably, obtain the stress tensors as a function of shear rate and other parameters to compare with experimental data. Since the constitutive equations are derived from a kinetic equation, this approach is semiempirical. We will show that the parameters in (90) can be determined from the information on the zero – shear – rate data for a substance and, hence, the nonlinear behavior can be predicted entirely in terms of the limiting material functions – viscosity and normal stress coefficients – at the zero shear rate.

In this paper, we consider two cases of flow: 1) plane Couette flow geometry where the flow is in the x direction while the velocity gradient is in the y direction and the z direction is neutral; and 2) undirectional elongation in the x direction. We will assume the fluid is of a single component.

5.1 Plane Couette flow

We consider laminar flow of a polymeric liquid in the plane Couette flow geometry just mentioned. Then, the only nonvanishing velocity gradient is $\partial u_x/\partial y$, which we will denote by the shear rate γ.

$$\gamma = \partial u_x/\partial y \ . \qquad (91)$$

This gives rise to the following:

$$[\nabla \boldsymbol{u}]^{(2)} = \tfrac{1}{2}\begin{pmatrix} 0 & \gamma & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \ , \qquad (92\text{a})$$

$$\omega = \tfrac{1}{2}\begin{pmatrix} 0 & -\gamma & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (92\text{b})$$

in matrix representation. Since the fluid is assumed to be of a single component, we will drop the subscript a for species from the variables and the parameters and use the following abbreviations to simplify the notation:

$$\Omega = \mathscr{R}/\zeta \ , \qquad (93\text{a})$$

$$X \equiv X^{(1)} = -\Pi/2p\phi \ , \qquad (93\text{b})$$

$$\begin{aligned}\Pi = \Pi_{xy} \ , \quad & N_1 = \Pi_{xx} - \Pi_{yy} \ , \\ & N_2 = \Pi_{yy} - \Pi_{zz} \ , \qquad (93\text{c})\end{aligned}$$

where ϕ is defined by (87). The three equations in (93c) give the shear stress, the primary, and the secondary normal stress difference defined according to the currently accepted convention, respectively. It is also convenient to define

$$\Omega_1 = \Omega_{xx} - \Omega_{yy} \ , \quad \Omega_2 = \Omega_{yy} - \Omega_{zz} \ , \quad \Omega_t = \mathrm{Tr}\,\boldsymbol{\Omega} \ . \tag{94}$$

Note that the tensor $\boldsymbol{\Omega}$ is related to force – force correlation functions and is symmetric. If different cartesian components of the forces are statistically uncorrelated, then the off-diagonal components of $\boldsymbol{\Omega}$ vanish. In this paper, we will consider this case only. For the plane Couette flow geometry in question there are three components of the stress tensor: Π, N_1 and N_2, and their evolution equations can be easily obtained from (90):

$$\begin{aligned} \varrho \frac{d}{dt}\hat{\Pi} = {} & -p\gamma - \tfrac{1}{3}(N_1+N_2)\gamma \\ & -(p\phi)^{-1}[\tfrac{1}{3}(N_1^2+N_2^2+N_1N_2)+\Pi^2]\gamma \\ & -pC_s\Pi q_e/\phi \ , \end{aligned} \tag{95a}$$

$$\varrho \frac{d}{dt}\hat{N}_1 = 2\gamma\Pi - 2p(C_{11}N_1 + C_{12}N_2)q_e/\phi \ , \tag{95b}$$

$$\varrho \frac{d}{dt}\hat{N}_2 = -2\gamma\Pi - 2p(-C_{21}N_1 + C_{22}N_2)q_e/\phi \ , \tag{95c}$$

where the various coefficients are defined as follows:

$$C_s = \tfrac{1}{3}(\Omega_1 + 2\Omega_2 + 2\Omega_t) = \Omega_{xx} + \Omega_{yy} \ , \tag{96a}$$

$$C_{12} = \tfrac{1}{3}\Omega_1 = \tfrac{1}{3}(\Omega_{xx} - \Omega_{yy}) \ , \tag{96b}$$

$$C_{21} = \tfrac{1}{3}\Omega_2 = \tfrac{1}{3}(\Omega_{yy} - \Omega_{zz}) \ , \tag{96c}$$

$$C_{11} = \tfrac{1}{3}(\Omega_t + \Omega_1 + \Omega_2) = \tfrac{1}{3}(2\Omega_{xx} + \Omega_{yy}) \ , \tag{96d}$$

$$C_{22} = \tfrac{1}{3}(\Omega_t - \Omega_1 - \Omega_2) = \tfrac{1}{3}(\Omega_{yy} + 2\Omega_{zz}) \ , \tag{96e}$$

$$\hat{\Pi} = \Pi/\varrho \ , \quad \hat{N}_i = N_i/\varrho \ , \quad (i = 1,2) \ . \tag{97}$$

Here the nonlinear factor q_e is given as follows:

$$\begin{aligned} q_e &= q_e(\Pi, N_1, N_2) \\ &= \sinh \kappa(\Pi, N_1, N_2)/\kappa(\Pi, N_1, N_2) \ , \end{aligned} \tag{98}$$

with κ given by the form

$$\begin{aligned} \kappa = {} & (\beta g/3)^{1/2}\phi^{-1}[(\Omega_1 + 2\Omega_2 + 2\Omega_t)\Pi^2 \\ & + \tfrac{1}{3}(2\Omega_1 + \Omega_2 + 2\Omega_t)N_1^2 + \tfrac{2}{3}(\Omega_t + \Omega_1 - \Omega_2)N_1N_2 \\ & + \tfrac{1}{3}(2\Omega_t - \Omega_1 - 2\Omega_2)N_2^2]^{1/2} \ , \end{aligned} \tag{99a}$$

$$\begin{aligned} \phi = \frac{1}{2}\Bigg\{ 1 + \frac{2(N_1+2N_2)}{3p} + \Bigg[\left(1 + \frac{2(N_1+2N_2)}{3p}\right)^2 \\ + \frac{2}{3p^2}(N_1^2 + N_2^2 + N_1N_2) + \frac{4\Pi^2}{p^2}\Bigg]^{1/2}\Bigg\} \ . \end{aligned} \tag{99b}$$

For the flow geometry in question the lefthand sides of (95 a – c) vanish at the steady state and the constitutive equations become coupled nonlinear algebraic equations:

$$\begin{aligned} & p\gamma + \tfrac{1}{3}(N_1+N_2)\gamma \\ & \quad + (p\phi)^{-1}[\tfrac{1}{3}(N_1^2+N_2^2+N_1N_2)+\Pi^2]\gamma \\ & \quad + pC_s\Pi q_e/\phi = 0 \ , \end{aligned} \tag{100a}$$

$$2\gamma\Pi - 2p(C_{11}N_1 + C_{12}N_2)q_e/\phi = 0 \ , \tag{100b}$$

$$2\gamma\Pi + 2p(-C_{21}N_1 + C_{22}N_2)q_e/\phi = 0 \ . \tag{100c}$$

When these coupled nonlinear algebraic equations are solved for Π, N_1 and N_2, the nonlinear shear viscosity and the primary and secondary normal stress coefficients can be determined as functions of γ, p, C_s, etc. In particular, we will show that C_s, C_{11}, etc., can be given in terms of zero-shear-rate material functions and, thus, (100 a – c) contain no other parameters except for γ, p, T, g, and density. Before proceeding to do this, we examine the limiting behavior of (100 a – c) in the limit of vanishing shear rate. Since Π, N_1, and N_2 become small as the shear rate γ diminishes in magnitude, we may set ϕ and q_e equal to unity and drop the second and the third term in (100 a) which are nonlinear. Note that the normal stress differences are of second order in γ and, hence, the first term in (100 b, c) must be kept in the equations. We then obtain from (100 a – c) the set of linear equations

$$\Pi = -\eta_0\gamma \ , \tag{101a}$$

$$C_{11}N_1 + C_{12}N_2 = -\eta_0\gamma^2/p \ , \tag{101b}$$

$$-C_{21}N_1 + C_{22}N_2 = \eta_0\gamma^2/p \ , \tag{101c}$$

where

$$\eta_0 = 1/C_S \ , \tag{102}$$

the Newtonian viscosity. Note that the shear stress Π is decoupled from the rest of the set and, therefore,

η_0 is determined immediately. Solving (101 b) and (101 c), we obtain the normal stress differences:

$$N_1 = -\frac{\eta_0}{p}\left(\frac{C_{22}+C_{12}}{C_{11}C_{22}+C_{12}C_{21}}\right)\gamma^2 \ , \tag{103a}$$

$$N_2 = \frac{\eta_0}{p}\left(\frac{C_{11}-C_{21}}{C_{11}C_{22}+C_{12}C_{21}}\right)\gamma^2 \ , \tag{103b}$$

from which the normal stress coefficients are identified:

$$\Psi_1^0 = \frac{\eta_0}{p}\left(\frac{C_{22}+C_{12}}{C_{11}C_{22}+C_{12}C_{21}}\right) \ , \tag{104a}$$

$$\Psi_2^0 = -\frac{\eta_0}{p}\left(\frac{C_{11}-C_{21}}{C_{11}C_{22}+C_{12}C_{21}}\right) \ . \tag{104b}$$

The Ψ_1^0 and Ψ_2^0 are the primary and the secondary normal stress coefficient at zero shear rate, respectively. These zero-shear-rate values of viscosity and normal stress coefficients (material functions) in (102) and (104a, b) allow us to determine in terms of the three zero-shear-rate material functions the five parameters C_s, C_{11}, C_{22}, C_{12} and C_{21} which are given in terms of three parameters Ω_{xx}, Ω_{yy} and Ω_{zz} or, equivalently, Ω_1, Ω_2 and Ω_t.

Since there are three independent material functions η_0, Ψ_1^0 and Ψ_2^0, (102) and (104a, b) can be used to find Ω_1, Ω_2 and Ω_t in terms of η_0, Ψ_1^0 and Ψ_2^0. It is easy to show the following quadratic form determines them within a sign:

$$A\Omega_2^2 + B\Omega_2 + C = 0 \ , \tag{105}$$

where with abbreviations

$$\alpha_1 = p\Psi_1^0/\eta_0 \ , \tag{106a}$$

$$\alpha_2 = p\Psi_2^0/\eta_0 \ , \tag{106b}$$

$$\theta = \alpha_2/\alpha_1 \ , \tag{107}$$

the coefficients are defined as follows:

$$A = -3(1+2\theta)^2 \ , \tag{108a}$$

$$B = \frac{3}{\eta_0}(1+10\theta+7\theta^2) + \frac{9}{\alpha_1}(1-\theta) \ , \tag{108b}$$

$$C = -\frac{9}{\eta_0^2}\left[\theta(2+\theta) + \frac{\eta_0}{\alpha_1}(1-\theta)\right] \ . \tag{108c}$$

Then, Ω_1 and Ω_t are given by the formulas

$$\Omega_1 = -\frac{2(1+2\theta)\Omega_2 - 3\eta_0^{-1}(1+\theta)}{1-\theta} \ , \tag{109a}$$

$$\Omega_t = -\frac{3\eta_0^{-1} - (2+\theta)\Omega_2}{1-\theta} \ . \tag{109b}$$

This shows that η_0, Ψ_1^0, and Ψ_2^0 determine the parameters Ω_1, Ω_2, and Ω_t and, consequently, the constitutive equations (95a – c), apart from a molecular parameter (i.e., a monomer size parameter) contained in the factor g appearing in κ; see (99a) and 23a). The unidirectional elongation data will further restrict them as we will show below.

5.2 *Unidirectional elongation*

Since we have considered a plane Couette flow, the appropriate elongation flow to consider is a unidirectional flow in the x direction. If the elongation rate is denoted $\dot{\varepsilon}$, then the velocity components are $u_x = \dot{\varepsilon}x$, $u_y = -\frac{1}{2}\dot{\varepsilon}y$ and $u_z = -\frac{1}{2}\dot{\varepsilon}z$. This means that

$$\nabla u = \tfrac{1}{2}\dot{\varepsilon}\begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \ , \tag{110a}$$

$$\omega = 0 \ . \tag{110b}$$

The stress tensor is diagonal:

$$\Pi = \begin{pmatrix} \Pi_{xx} & 0 & 0 \\ 0 & \Pi_{yy} & 0 \\ 0 & 0 & \Pi_{zz} \end{pmatrix} \ . \tag{111}$$

Moreover, since $\Pi_{yy} = \Pi_{zz}$ by symmetry of the flow geometry, there is only one nonvanishing normal stress difference

$$N_1 = \Pi_{xx} - \Pi_{yy} \equiv N \ . \tag{112}$$

In this case, we find

$$\Pi : \Pi = \tfrac{2}{3}N^2 \ , \tag{113a}$$

$$[\Pi \cdot \nabla u]^{(2)} = \tfrac{1}{6}\dot{\varepsilon}N\begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \ . \tag{113b}$$

The evolution equation for N is then easily obtained from (78) in the following form:

$$\varrho \frac{d}{dt}\hat{N} = -3p\dot{\varepsilon} - \dot{\varepsilon}N - (p\phi)^{-1}\dot{\varepsilon}N^2 - (p/\phi)C_e N q_e(N) \ , \tag{114}$$

where

$$C_e = \tfrac{2}{3}(\Omega_t + \Omega_1 + \Omega_2) = 2\Omega_{xx} + \Omega_{yy} \ , \tag{115}$$

$$q_e(N) = \sinh\kappa(N)/\kappa(N) \ , \tag{116a}$$

with $\kappa(N)$ given by the expression

$$\kappa(N) = [(2\beta g)^{1/2}/3\phi](\Omega_1 + \Omega_t)^{1/2}N \ , \tag{116b}$$

$$\phi = \frac{1}{2}\left\{1 + \frac{N}{3p} + \left[\left(1 + \frac{N}{3p}\right)^2 + \frac{4N^2}{3p^2}\right]^{1/2}\right\} \ . \tag{116c}$$

It is important to remark that since the steady state equation for $N_2 = \Pi_{yy} - \Pi_{zz}$ is

$$\left[\dot{\varepsilon} - \frac{2p}{3\phi}(\Omega_t - \Omega_1 - \Omega_2)q_e\right]N_2 + \frac{2p}{3\phi}\Omega_2 N_1 = 0 \ , \tag{117}$$

the fact that $N_2 = 0$ demands that

$$\Omega_2 = 0 \ . \tag{118}$$

Therefore, if this condition did not hold, the coefficient C_e should have read

$$C_e = \tfrac{2}{3}(\Omega_t + \Omega_1 + \Omega_2) \ . \tag{119}$$

This condition (118) necessary for unidirectional elongation, therefore, puts a further restriction on the constitutive Eqs. (95a – c) for shear experiment discussed on Sect. 5.1 and only two material parameters will be necessary to determine Ω_t and Ω_1. We will return to this question shortly.

We observe that $\kappa(N)$ tends toward a constant independent of N as $|N| \to \infty$. This means that the associated entropy production, which is proportional to $\kappa \sinh\kappa$, tends to a plateau value in the limit.

At the steady state the normal stress difference is given by the algebraic equation

$$\dot{\varepsilon}N + (p\phi)^{-1}\dot{\varepsilon}N^2 + (p/\phi)C_e N q_e(N) = -3p\dot{\varepsilon} \ . \tag{120}$$

The solution of this algebraic equation defines the elongation viscosity η_e through the relation

$$N = -\eta_e\dot{\varepsilon} \ , \tag{121}$$

where η_e generally depends on $\dot{\varepsilon}$. As in the case of shear, it is useful to consider the vanishing $\dot{\varepsilon}$ limit where (118) can be linearized. We put q_e and ϕ equal to unity in the limit of vanishing $\dot{\varepsilon}$ and drop the nonlinear terms to obtain the linear equation

$$C_e N = -3\dot{\varepsilon} \ , \tag{122}$$

from which we obtain the zero-elongation-rate elongation viscosity η_e^0:

$$\eta_e^0 = 3/C_e \ . \tag{123}$$

It is experimentally known that

$$\eta_e^0 = 3\eta_0 \ , \tag{124}$$

where η_0 is the shear viscosity at zero shear rate. Therefore, it is useful to examine to what extent this relation is met by (102) that holds for the shear viscosity. Since with (118) $C_s = (2\Omega_t + \Omega_1)/3 = \eta_0^{-1}$, we find

$$\eta_e^0 = 3\eta_0/(1 + \eta_0\Omega_1/3) \ . \tag{125}$$

Thus, the relation (124) holds rigorously in the vanishing limit of Ω_1. Since from (109a)

$$\Omega_1 = -3(1+\theta)/\eta_0(1-\theta) \ , \tag{126}$$

we find

$$\eta_e^0 = 3\eta_0(\theta - 1)/2\theta \ . \tag{127}$$

Note that θ is negative and generally less than unity. Therefore, η_e^0 is generally larger than $3\eta_0$. If $\theta = -1$, that is, if $\Psi_2^0 = -\Psi_1^0$, then we have (124) identically satisfied. The reverse is also true: that is, if $\Omega_1 = \Omega_2 = 0$, then $\theta = -1$. Therefore, one wonders if the relation (124) holds only in the cases where the condition $\theta = -1$ holds, which is guaranteed if

$$\Omega_1 = \Omega_2 = 0 \ . \tag{128}$$

The physical meaning of this condition is that the differences in the force-force correlations are equal in the primary and secondary directions. Presumably, this condition is, at least approximately, met by the systems studied in many cases, but it it possible that the condition may be broken in general if there is present a small term arising from an anisotropy of force-force correlation functions making up the material tensor $\mathscr{R}$: for example, $\Omega_2 = 0$, i.e., $\Omega_{yy} = \Omega_{zz}$, but $\Omega_1 = \Omega_{xx} - \Omega_{yy} \neq 0$ although small, the consequence of which is already seen in (127) or (126).

To assess this situation from the angle of the existing phenomenological theories, let us take a couple of models well known in rheology: the corotational Maxwell and Jeffreys models [1]. Both models predict $\eta_e^0 = 3\eta_0$, but at the same time a fixed value of $-1/2$ for $\theta = \Psi_2^0/\Psi_1^0$. However, for some materials the fixed ratio of $\theta = -1/2$ is not satisfactory since the value of θ may not necessarily be equal to $-1/2$. Therefore, if one wishes to account for an experimental θ value different from $-1/2$, one then will have to either abandon the model or suitably modify it. Let us take the latter approach and see if a consistent picture emerges from a modified model. We take the corotational Jeffreys model [1] and make the scalar inverse relaxation time an anisotropic tensor Λ as follows:

$$\varrho \frac{d}{dt} \hat{\Pi} = -2p\gamma - \lambda_2 \frac{D}{Dt}\gamma - [\omega, \Pi] - p\Lambda \cdot \Pi \ , \quad (129)$$

where λ_2 is a constant, D/Dt denotes the corotational (Jaumann) time derivative and Λ is a tensor:

$$\Lambda = \begin{pmatrix} \Lambda_1 & 0 & 0 \\ 0 & \Lambda_2 & 0 \\ 0 & 0 & \Lambda_3 \end{pmatrix} \ . \quad (130)$$

Here, the diagonal components stand for the xx, yy, and zz components of Λ. If $\Lambda_1 = \Lambda_2 = \Lambda_3$, then (129) becomes the corotational Jeffreys model in the present system of notation. As in the case of the corotational Jeffreys and Maxwell models, (129) does not yield all the steady constitutive equations for stress components (e.g., Π_{zz} in the case of plane Couette flow). Nevertheless, it is possible to determine the shear viscosity and the normal stress coefficients. Especially, for the flow geometries considered here, we find the following zero-shear-rate material functions:

$$\eta_0 = \Lambda_1^{-1} \ , \quad (131\text{a})$$

$$\Psi_1^0 = \eta_0 (1 - \lambda_2 \Lambda_1)(\Lambda_1 + \Lambda_2)/p\Lambda_1\Lambda_2 \ , \quad (131\text{b})$$

$$\Psi_2^0 = -\eta_0 (1 - \lambda_2 \Lambda_1)(2\Lambda_1 - \Lambda_2)/p\Lambda_1\Lambda_2 \ . \quad (131\text{c})$$

Therefore,

$$\theta = \Psi_2^0/\Psi_1^0 = -(2 - \Lambda_2/\Lambda_1)/(1 + \Lambda_2/\Lambda_1) \ . \quad (132)$$

In the case of $\Lambda_1 = \Lambda_2$ (i.e., an isotropic Λ), we obtain $\theta = -1/2$ as predicted [1] by the corotational Jeffreys model. The same model yields the zero-shear-rate elongation viscosity η_e^0 in the form

$$\eta_e^0 = 3\eta_0/(2 - \Lambda_2/\Lambda_1) \ , \quad (133)$$

which becomes $\eta_e^0 = 3\eta_0$ if $\Lambda_1 = \Lambda_2$, i.e., if $\theta = -1/2$. The same conclusion can be drawn in the case of the corotational Maxwell model, namely, if $\lambda_2 = 0$ in (129). Other models can be made similarly anisotropic by introducing an anisotropic stress relaxation time tensor, and it should not come as a surprise if they yielded basically the same conclusion as above. The basic physics underlying an anisotropic inverse relaxation time or a material tensor $\boldsymbol{\Omega}$ is that each stress component has a characteristic relaxation time, and different characteristic relaxation times are not necessarily equal to each other if the interaction forces are anisotropic, as is generally the case for polyatomics. This does not seem to be so unrealistic a view, and in this viewpoint and if one takes the opinion that the same constitutive equation must describe two different flow configurations for the same substance, e.g., plane Couette flow and elongational flow as in the present section, then one is compelled to choose between the θ value that is fixed at $-1/2$, and a violation of the Trouton relation $\eta_e^0 = 3\eta_0$, since they are not simultaneously satisfied. We believe that experiments must resolve this question regarding the two limiting laws.

5.3 *Comparison with experiment*

A simple fluid version of the present theory has been extensively tested [26] against shear flow data for a simple fluid and polymeric solutions. However, no comparison was made for polymer melts. The present extended formulation is intended to encompass a wider range of polymeric fluids in various flow configurations. In this section, to see the utility of the constitutive Eqs. (100a) – (100c) and (120) developed, comparison is carried out for three different polymeric melts in steady shear and unidirectional flow experiments for viscosity and primary normal stress coefficients. For this purpose, we adjust the zero-shear-rate material functions to experimental values and solve the nonlinear constitutive equations numerically. In addition to them, we define the following parameters appearing in the factor κ:

$$\tau = (\beta g/3)^{1/2} \ , \tag{134a}$$

$$\tau_e = p(3\beta g/\eta_0)^{1/2} \ , \tag{134b}$$

and adjust them empirically. The τ is used for shear viscosity and normal stress coefficients, while τ_e is used for elongation viscosity. We remark that τ and τ_e are not independent parameters since one can be related to the other. Therefore, there are four parameters for a set of four (non-Newtonian) material functions, η_e, η, Ψ_1 and Ψ_2 for which the γ and $\dot{\varepsilon}$ dependence is calculated. The results of calculation are presented in Figs. 1 – 3 for some polymer melts.

We first consider the case [28] of shear flow of a commercial polystyrene melt of molecular weight $M_w = 240000$. The relevant equations for this case are (100a) – (100c). The coefficients C_{ij} are all fixed in terms of zero-shear-rate material functions, namely, η_0, Ψ_1^0 and Ψ_2^0, as described in Sect. 5.1. The only remaining unknown parameter τ is adjusted to $\tau = 0.035$ s. In Fig. 1, we present comparisons of experimental data on the shear viscosity and the primary normal stress coefficient of a polystyrene melt [28] just mentioned. The values of the material functions are: $\eta_0 = 1.26 \times 10^5$ Pa s; $\Psi_1^0 = 3.98 \times 10^6$ Pa s^2; and $\Psi_2^0 = -7.94 \times 10^4$ Pa s^2. The open triangles and the open circles are the experimental data, and the solid curves are theoretical. Note that there are no data reported for the secondary normal stress coefficient for the melt. The agreement is quite satisfactory between theory and experiment. Laun et al. [28] fitted their data with an empirical constitutive equation with 18 parameters (nine relaxation times and a corresponding number of weight factors). In the present approach there are only four parameters – three zero shear rate material functions and τ.

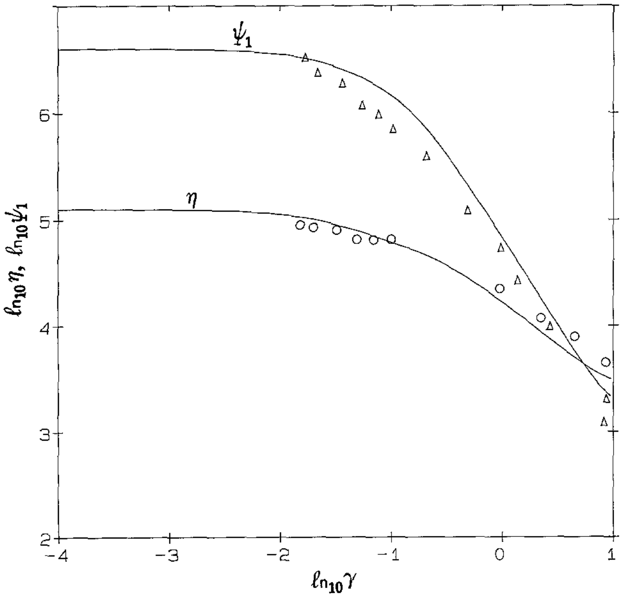

Fig. 1. Shear viscosity (η) and primary normal stress coefficient (Ψ_1) vs shear rate (γ) for a polystyrene melt. The open triangles and the open circles are experimental data by Laun et al. [28], and the solid curves are theoretical. $\tau = 0.035$ s, $\eta_0 = 1.259 \times 10^5$ Pa s, $\Psi_1^0 = 3.98 \times 10^6$ Pa s^2, and $\Psi_2^0 = -7.94 \times 10^4$ Pa s^2.

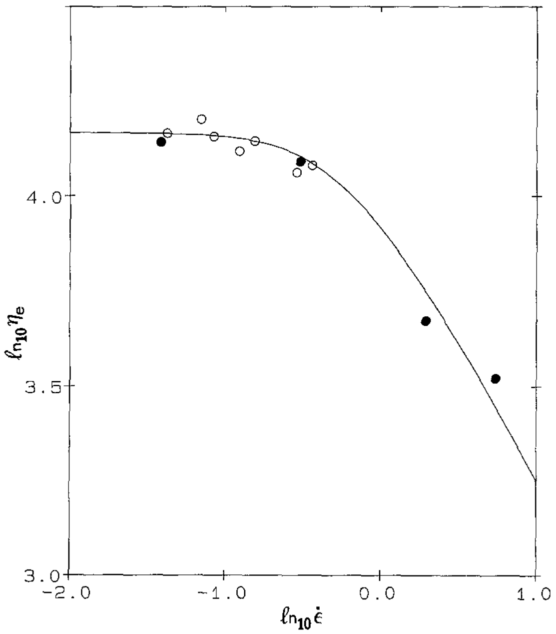

Fig. 2. Elongation viscosity vs elongation rate for a high-density polyethylene melt. The data are from Münstedt and Middleman [29]. $\tau = 18$ s, $\eta_0 = 4953.12$ Pa s, and $\theta = -1$. The zero $\dot{\varepsilon}$ elongation viscosity is equal to $3\eta_0$, as predicted by the Trouton relation.

There are two experiments considered in the case of unidirectional extensional flow at constant elongation rate. Calculations are carried out on the basis of (120) with C_e fixed in terms of the zero elongation rate viscosity satisfying the Trouton relation [cf. (124)]. Therefore, we are considering the case of $\theta = -1$. The parameter τ is empirically adjusted. In Fig. 2, we present comparison of the theoretical prediction for elongation rate dependence of elongation viscosity with experimental data reported by Münstedt and Middleman [29] on a high-density polyethylene (HDPE) melt. The filled circles are the data obtained by a bubble-collapse method and the open circles are the data acquired with a universal extensional rheometer. With the value of $\tau_e = 70$ and $\eta_0 =$

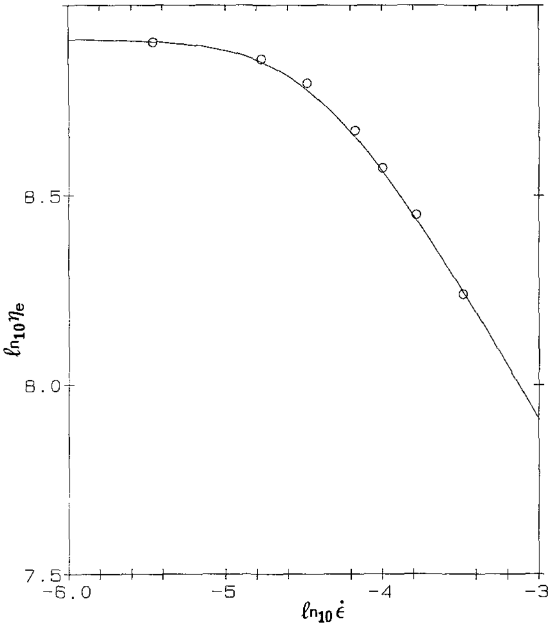

Fig. 3. Elongation viscosity vs elongation rate for uncrosslinked polyisobutylene. The experimental data are from Peng [30]. $\tau = 70$ s, $\eta_0 = 2.72 \times 10^8$ Pa s, and $\theta = -1$. The zero $\dot{\varepsilon}$ elongation viscosity is equal to $3\eta_0$, as predicted by the Trouton relation.

4953.12 Pa s the theoretical prediction is shown to agree with experiment rather well. In Fig. 3, we present comparison for uncrosslinked polyisobutylene (the data were obtained by Peng [30]). In this case, $\tau_e = 18$ and $\eta_0 = 2.72 \times 10^8$ Pa s. Agreement between experiment and theory is suprisingly good.

These comparisons of experimental data and theoretical predictions for shear rate or elongation rate dependence of material functions indicate that, when treated empirically, the constitutive equation for stress derived from kinetic theory provides a molecular basis to study more deeply some questions of significance to rheology of polymers. The present study indicates that some important rheological material functions may possibly be represented by a single universal constitutive equation, provided that the limiting material functions (i.e., zero-shear-rate and zero-elongation-rate viscometric functions) are appropriately given by either an empirical means or a molecular theory. This optimistic expectation is based on the past studies made on the basis of similar constitutive equations for simple liquids [26b] and polymer solutions [26a], which also show good agreement between theory and experiment. In essence, the previous studies show that there exist rheological corresponding states [26a] for the materials examined. We emphasize that the nonlinear factor $q_e(X)$ is essential for good agreement between theory and experiment in the high γ and $\dot{\varepsilon}$ regime.

6. Discussion and concluding remarks

In this paper, we have shown that rheology can be phrased within the framework of extended irreversible thermodynamics, generalized hydrodynamics, and kinetic theory of polymeric liquids and polyatomic liquids in general. The constitutive equations for diffusion fluxes and stresses are cast in a form more easily amenable to physical interpretations and identifiable with some constitutive equations derived from the Brownian motion model. In principle, the material tensor in the constitutive equations can be calculated by means of statistical mechanical methods, starting from the statistical definition given in the main text. This part of the program is open and requires further intensive efforts. However, one may make the theory semiempirical by treating the material tensor as a set of empirical parameters, as we have done in Sect. 5. This can be a fruitful approach if one is willing to sacrifice one's urge to be completely molecular, since it still can provide some powerful means to investigate various flow properties of interesting substances without completely forgetting some molecular aspects of the constitutive equations involved. The present theory certainly provides theoretical machineries for both lines of approach, molecular and semiempirical.

We would like to remark that the treatment given to the constitutive equation to calculate the material functions is a kind of approximation, since the momentum balance equation is decoupled from the constitutive equation when a linear flow field is taken. This is the approach generally taken in rheology, but we would like to point out that it is not without limitations. Our study [31] in gas dynamics with the generalized hydrodynamic equations shows that effective viscosities obtained from the solutions of the generalized hydrodynamic equations are not only local, but also not necessarily the same as the values obtained from the constitutive equations under the assumption of a linear velocity field, namely, the kind of approach taken in rheology as mentioned above.

The constitutive equation (90) is different from those appearing in the literature, such as Tanner's [32], the FENE-*p* model [33], that of Acierno et al. [34], and the Phan-Thien-Tanner equation [35]. Tanner's constitutive equation is a modification of the Oldroyd B model [1] which can be obtained from a network theory. Its dissipation term corresponding to

$\Lambda^{(1)}$ in the present theory is linear. It is perhaps of interest to mention that the Oldroyd model can be obtained from the constitutive Eq. (18) by linearizing it with respect to $\boldsymbol{\Pi}$ (see [26b]). The FENE-*p* model is based on a diffusion equation (a Fokker-Planck equation) where the force is assumed to take a special form that prevents an infinite stretching of chains. This constitutive equation is different from the present one, not only in form, but also in its dynamical origin since it is based on a stochastic (Brownian motion) model. The constitutive equations of Acierno et al. and Phan-Thien et al. are based on a network theory, although there are considerable differences in form between them, owing to the fact that their treatments of the segment creation rate term are different. Both constitutive equations, however, are empirical, since they contain not only empirical parameters, but also an empirical function postulated for the segment destruction rate. It is worth noting that this postulated function, especially in the Phan-Thien-Tanner theory, makes the term that is equivalent to the dissipation term $\Lambda^{(1)}$ nonlinear in stress, although it appears to have nothing to do with the Rayleigh-Onsager dissipation function to which the dissipation term in the present theory gives rise in the small shear limit. The network theory used by Acierno et al. and Phan-Thien et al. has one aspect in common with the present theory: that is, the presence of creation and destruction rate terms for segments that remind us of the collision term in the generalized Boltzmann equation [8] underlying the constitutive Eq. (90), since the latter accounts for molecular population changes accompanying the changes in mechanical states due to molecular interactions. Unfortunately, the network theory is not subjected to the thermodynamic principles and, as a consequence, it is not clear if the constitutive equations obtained therein are consistent with the second law of thermodynamics.

In conclusion, the results by the present semiempirical treatment of the constitutive Eq. (90) not only indicate that its phenomenological utility is as good as any existing constitutive equations despite less parameters in it, but also are sufficiently encouraging as to warrant continued efforts to calculate parameters appearing in it by using some molecular models, and thereby, to better understand the molecular basis of polymeric rheology in a manner consistent with the thermodynamic laws. The underlying statistical mechanical theory provides means to pursue such an aim. The parameters in the present constitutive equation (90) can be completely determined by experimental data on zero shear rate viscosity and normal stress coefficients. This feature is of considerable potential interest since the limiting laws at $\gamma = 0$ determine the high shear rate and high elongation rate behavior of material functions. Therefore, the limiting law viscosity and normal stress coefficients are the ultimate material function necessary in rheology.

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