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On the derivation of macroscopic models for compressible viscoelastic fluids using the generalized bracket framework ☆

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ABSTRACT

The generalized bracket framework is used to derive a family of compressible viscoelastic models. The framework accounts for both reversible and non-reversible dynamics and ensures that the derived models are consistent with the laws of thermodynamics. The most general compressible forms of the UCM and Oldroyd B models are derived. For these models the elastic strain energy is taken to be that for a Hookean material. Nonlinear elastic strain energy functionals are also considered and used to derive new viscoelastic models. The viscometric behaviour of these models is investigated and model predictions are compared with experimental data for Boger fluids and mLLDPE.

1. Introduction

The ability to predict the flow of non-isothermal viscoelastic fluids is important in many processes in the polymer industry. Over the last 70 years many significant contributions to the study and characterization of a vast collection of polymeric materials have been made. However, theoretical advances in modelling non-isothermal viscoelastic fluids have developed at a more gradual pace.

A plethora of constitutive equations for modelling viscoelastic fluids under incompressible and isothermal conditions exist in the literature. However, derivation of suitable models for compressible and non-isothermal flow problems have received far less attention [5]. In many numerical investigations bespoke rheological models are crafted to suit specific flow problems and therefore are not applicable to more general problems. In polymer processing applications, such as injection moulding and high-speed extrusion, the pressure and flow rate may be large. Furthermore polymer melt flow generally happens at high temperatures where flow parameters and dynamics are a direct result of thermodynamic relationships between state variables. Hence, compressible and non-isothermal effects within the viscoelastic regime may become important and influence resulting flow phenomena.

Early work to account for temperature dependence of data used the principle of time-temperature superposition [43] to superimpose mechanical property data at different temperatures by means of an experimentally determined shift factor. This was based on extensive experimental evidence of creep and recovery in polymeric liquids and allowed data obtained at one temperature to be used to infer those at another. Of course, this is an empiricism that is not universally valid. Nevertheless, the approach works well for many liquids over a wide range of temperatures. The assumption here is that temperature is a control variable and that a given experiment is performed under isothermal conditions. Unfortunately, it is not sufficient only to possess knowledge of how the material properties depend on temperature since in many processing applications such as injection moulding, film blowing and wire coating, significant temperature gradients perpendicular to the flow direction arise due to viscous heating. The spatial variation of the material parameters requires a more sophisticated modelling approach than simply time-temperature superposition in order to describe the flow of polymeric liquids more generally. Thus it is necessary to develop a set of evolution equations that are fully non-isothermal and universally valid. This is a formidable mathematical modelling challenge.

Coleman and Noll [10,11] introduced the concept of a simple fluid in which the stress tensor and heat flux vector at a given material point are expressed as functions of the history of these quantities with diminishing influence as one travels into the past. In this theory the stress tensor and heat flux vector fields of the simple fluid depend on functionals of the deformation gradient and temperature, which are required to satisfy certain continuity and smoothness conditions in order to facilitate mathematical analysis. The complexity of the functionals has meant that the approach has only been implemented in the simplest of situations and so its applicability has been rather limited - for example, to linear viscoelasticity. Its restriction to fluids with fading memory also means that the theory excludes Newtonian fluids [44] and all models that explicitly contain a solvent viscosity since the Newtonian fluid is recovered as the relaxation time tends to zero.

Marucci [36] developed a kinetic model for non-isothermal polymeric solutions based on Hookean dumbbell theory. The spring factor in this non-isothermal theory is assumed to vary linearly with temper-

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☆ Information on the data underpinning the results presented here, including how to access them, can be found in the Cardiff University data catalogue at 10.17035/d.2019.0069612855 or as a clickable web link http://doi.org/10.17035/d.2019.0069612855.

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ature. Gupta and Metzner [27] noted that the additional term in the constitutive equation that accounts for non-isothermal effects has the wrong sign compared with experimental data. They suggested a correction to the model in which the constant stiffness parameter is replaced by a variable stiffness parameter which decays algebraically as temperature increases.

Using an empirical dependence of viscosity on temperature the resulting constitutive equation was used as the basis for numerical simulations by Luo and Tanner [35] and McClelland and Finlayson [37] of film blowing and extrusion, respectively. Wiest [49] extended these ideas to the Rouse model and generalized them to models with a discrete spectrum of relaxation times. However, the resulting constitutive equations are restricted to fluids with a low degree of elasticity which means that they are not particularly suitable for use in many polymer processing situations in which elastic effects are just as important as thermal effects. Sugeng et al. [46] proposed a non-isothermal generalization of the PTT constitutive equation. However, it is restricted to incompressible fluids and suffers from the difficulty in modelling spatial temperature variations in the kinetic theory.

The governing equations for fluid motion consist of balance laws governing mass and momentum transfer as well as a constitutive equation relating stress and strain and an equation of state coupling thermodynamic variables (pressure, density and temperature). Several approaches exist for deriving classes of models that conform to fundamental principles in physics. Thermodynamic approaches are particularly desirable since they are based on fewer physical assumptions.

The observed macroscopic behaviour of a viscoelastic material is a result of interactions at the microscopic level. A significant difficulty in developing mathematical models for complex fluids is how to consistently abstract microscopic information to the macroscopic level of description. Practical considerations usually mean that the laws of thermodynamics are compromised. Nowhere is this more apparent than in the use of the incompressibility constraint. Invoking incompressibility eliminates the need to define pressure in terms of other thermodynamic variables such as density and temperature and instead defines it as a Lagrange multiplier [5]. However in many industrial processes involving viscoelastic flows such as oil recovery and polymeric injection moulding, high pressure/temperature variation occurs. In these situations the incompressibility assumption is unphysical and results in the irretrievable loss of important thermodynamic information. Nguyen et al. [40] showed that compressible effects play a significant role in the prediction of flow during microscopic injection moulding. For example, density variations of over 10% were predicted when using the compressible generalised Newtonian model.

There have been a number of advances in the development of models for compressible viscoelastic fluids as well as nonisothermal flows [5]. Compressible and non-isothermal extensions to Maxwell models have been proposed by Belblidia et al. [3] and Wilmanski et al. [50]. However, the availability of compressible forms of other models is rather limited. The limitations of the UCM/Oldroyd-B models, especially with regard to extensional flow problems, compel us to consider a wider range of constitutive laws. Ad-hoc models for capturing thermorheological behaviour of polymer melts/polymer solutions usually result in weak and contradictory predictions. Extending isothermal models to non-isothermal ones is nontrivial and necessitates adherence to thermodynamic relations. The aim of this paper is to derive models capable of capturing a wide range of viscoelastic phenomena.

Peters [41] developed a framework for deriving so-called ‘semi-empirical’ differential models for nonisothermal flows. Importantly the constitutive equations discussed by Peters were derived from an energy equation. The thermodynamic admissibility of a model can be assessed by use of the Clausius–Duhem inequality.

The earliest work on a bracket framework for describing fluids began in the late 1980s [45]. The Hamiltonian/Poisson description of continua provided an elegant and computationally powerful tool for analysing the behaviour of large particle systems. However progress was hindered as it was only able to describe conservative systems and therefore frictionless flows. The development of a bracket modelling dissipative phenomena enabled the applicability of bracket fluid models to be extended to engineering problems.

The dynamics of any real fluid system can be divided into two categories: reversible and irreversible. Deformation of purely elastic materials is a reversible process: mechanical energy is stored and can be released into mechanical energy again. Deformation of viscous materials is irreversible: mechanical energy is entirely dissipated. For viscoelastic materials, mechanical energy is partly stored in elastic energy and partly dissipated [6]. In addition to the partitioning of elastically stored and dissipated energy, two different ways of storing elastic energy in a viscoelastic material have to be distinguished: entropy and energy elasticity.

In the generalised bracket description each of the terms in the equations governing state variables are delineated from derivatives of the Helmholtz free energy. The reversible or conservative dynamics are captured by the (continuous) Poisson bracket: a bilinear, antisymmetric operator that satisfies the Jacobi identity. The irreversible dynamics (viscosity, relaxation) is described by the dissipative bracket. Beris and Edwards [4] combined the two to create the generalised bracket as a means for deriving equations for general fluid systems. The underlying mathematical structure of the generalised bracket in association with the Hamiltonian/Helmholtz free energy provide powerful tools for developing properly structured equations.

This paper is primarily concerned with the modelling of compressible viscoelastic fluids by means of the generalised bracket and energy/entropy formulation. The main contribution is the derivation of a compressible version of the FENE model which also captures strain hardening behaviour. An incompressible form of this model was implemented by Garduño et al. [17]. A compressible and nonisothermal generalisation of this model is derived in this paper. In the generalised bracket approach, the second strain hardening regime is modelled by prescribing a non-zero form of the stick/slip tensor. This ensures that strain hardening effects can be captured whilst the solvent viscosity remains constant. Additionally compressible, nonisothermal Maxwell-type viscoelastic models derived using the generalised bracket are compared to several models proposed in the literature. The differences that exist between them highlight the necessity for models to be derived from a powerful theoretical framework that account for compressibility and thermal effects. The aim is to derive models for viscoelasticity that are consistent with thermodynamics, thus avoiding ad-hoc modifications to existing models to account for compressible and thermal effects. Examples from the literature are discussed within this context.

This paper is organised as follows. Section 2 provides an overview of the fundamental principles of thermodynamics and the derivation of general governing equations using the generalised bracket formulation. Compressible isothermal and non-isothermal forms of the Oldroyd-B model derived using the generalized bracket formulation are presented in Section 3. Section 4 will emphasize key differences between the compressible models derived using thermodynamic considerations and some of the models that are have been proposed in the literature. In Section 5 viscoelastic models based on nonlinear elastic strain energy formulations are discussed. The main contribution is a new non-isothermal and compressible version of the FENE model that is derived within the generalized bracket framework. Section 6 will then present a viscometric analysis of the behaviour of the new model, specifically shear and extensional viscosities. A summary of the paper is then provided in Section 7.

2. The generalised bracket formulation

The continuum mechanics description of fluid dynamics involves modelling fluids based upon separate conservation principles. In the thermodynamic approach conservation laws for thermodynamic state variables are derived directly from the first and second laws of thermodynamics, thus reducing the number of assumptions used [4]. In this section we briefly review the generalised bracket and the underlying mathematical principles that govern transport phenomena in fluids. The central idea in this approach is that the dynamics of an arbitrary functional, F, are governed by the evolution equation

$$\frac{dF}{dt} = \{[F, H]\} \tag{2.1}$$

where $\{[\cdot, \cdot]\}$ is the generalised bracket and H is the energy of the system, Ω. The generalised bracket is itself composed of two sub-brackets

$$\{[F, G]\} = \{F, G\} + [F, G] \tag{2.2}$$

where F and G are arbitrary functionals over Ω. The first bracket, $\{\cdot, \cdot\}$, is the Poisson bracket which describes the conservative dynamics of the system. The second bracket $[\cdot, \cdot]$ describes the dissipative processes, specifically viscous dissipation, relaxation and non-affine motion. The Poisson bracket has been used in descriptions of particle systems since the development of Hamiltonian mechanics [29]. The Poisson bracket formulation of Hamiltonian mechanics was originally developed for discrete particle systems. The application of Poisson bracket formalism to continuous systems began with Clebsch [8] who proposed a representation of the fluid velocity in a form that facilitates a canonical Hamiltonian description. In this case a variational description of the incompressible Euler equations of fluid mechanics was derived. The use of potentials to represent vector fields has a history that transcends the familiar potential decomposition of electricity and magnetism. The aim is to represent the fluid velocity in a form that facilitates a canonical Hamiltonian description. The Poisson bracket can be expressed in terms of these potentials. Arnold [2] discovered the relationship between the Lagrangian and Eulerian descriptions of an incompressible fluid in group theoretic terms and introduced the Poisson bracket for expressing the kinematics of the velocity field. The Poisson bracket for continuous media was developed further by Morrison and Greene [38] and Edwards and Beris [15], for example.

Fundamental to this approach is the formulation of the total energy of a fluid system. One can express the total energy (the Hamiltonian) as

$$H = \int_{\Omega} h(\rho, \mathbf{u}, s, \mathbf{C})\, d\Omega = \int_{\Omega} [K(\rho, \mathbf{u}) + \hat{u}(\rho, s) + w(\mathbf{C})]\, d\Omega \tag{2.3}$$

In the absence of any field potential the total energy, h, of the system is divided into three parts: kinetic energy, K, internal energy, $\hat{u}$, and elastic energy, w, where ρ is the density, $\mathbf{u}$ is the velocity vector, s is the entropy and $\mathbf{C}$ is the conformation tensor. Furthermore, when considering dissipative processes, one has to consider the effects of mechanical degradation and loss of available energy. Temporal evolution of the system depends on the energy available to be converted into mechanical work. As a result the total energy is replaced by the *total available energy* or Helmholtz free energy

$$A = \int_{\Omega} (h - sT)\, d\Omega = \int_{\Omega} \left[\frac{\mathbf{m} \cdot \mathbf{m}}{2\rho} + w(\mathbf{C}) + \hat{u}(\rho, s(\rho, \mathbf{C}, T)) - s(\rho, \mathbf{C}, T)T \right] d\Omega \tag{2.4}$$

where $\mathbf{m} = \rho\mathbf{u}$ is the momentum vector and T is the temperature. The governing equations for a compressible and nonisothermal fluid system are then determined by taking derivatives of A with respect to dynamic state variables. To introduce the formulation, we begin by considering the dynamics of non-dissipative systems.

2.1. Equilibrium thermodynamics: The Poisson bracket

The Poisson bracket is introduced by considering the dynamics of reversible processes. A reversible process is one in which the system remains in equilibrium and entropy is constant. Consider a closed system, Ω, with boundary $\partial\Omega$. The system has an internal energy, U, which as we will see is related to the heat energy, Q, of the system. The change of internal energy of a system is given by the heat energy transmitted into the system plus work done, W, by the surroundings on the fluid body

$$dU = dQ + dW \tag{2.5}$$

The infinitesimal change in heat energy is given by $dQ = TdS$ and the work done by the system is $dW = -pdV$. Substituting these relations into (2.5) yields the fundamental equation of thermodynamics. For some closed system, Ω the change in energy is determined by the equation

$$dU = TdS - pdV \tag{2.6}$$

where p is the pressure exerted onto the surrounding wall, $\partial\Omega$, and V is the volume of Ω. The fundamental Eq. (2.6) forms the basis for the definition of pressure (see Section 2.2). The fundamental equation governing non-dissipative fluid transport is given by

$$\frac{dF}{dt} = \{F, H\} \tag{2.7}$$

where F is some observable (functional) defined over Ω.

The bracket $\{\cdot, \cdot\}$ is anticommutative, distributive and satisfies the Jacobi identity. Importantly, if any function, ϕ is constant over phase space then $\{f, \phi\} = 0$ for any f. The continuous Poisson bracket in *Lagrangian* coordinates is given by

$$\{F, H\}_L = \int_{\Omega} \left[\frac{\delta F}{\delta \Gamma} \frac{\delta H}{\delta \Pi} - \frac{\delta F}{\delta \Pi} \frac{\delta H}{\delta \Gamma} \right] d^3 r \tag{2.8}$$

where $\Gamma(\mathbf{r}, t)$ and $\Pi(\mathbf{r}, t)$ are the *Lagrangian* position and momentum vector fields, respectively [4]. Assume that for a viscoelastic medium the observable F is a function of the state variables we wish to model, specifically $\rho(\mathbf{x}, t)$, $\mathbf{m}(\mathbf{x}, t) := \rho\mathbf{u}(\mathbf{x}, t)$, $s(\mathbf{x}, t)$ and $\mathbf{C}(\mathbf{x}, t)$. Use of a chain rule expansion yields

$$\frac{dF}{dt} = \int_{\Omega} \left[\frac{\delta F}{\delta \rho} \frac{\partial \rho}{\partial t} + \frac{\delta F}{\delta \mathbf{m}} \cdot \frac{\partial \mathbf{m}}{\partial t} + \frac{\delta F}{\delta s} \frac{\partial s}{\partial t} + \frac{\delta F}{\delta \mathbf{C}} : \frac{\partial \mathbf{C}}{\partial t} \right] d\Omega \tag{2.9}$$

In order to obtain working equations, Eq. (2.8) must be expressed using a (Cartesian) fixed coordinate frame. An expansion of derivative terms in Eq. (2.8) yields

$$\frac{\delta F}{\delta \boldsymbol{\Gamma}} = \int_{\Omega} \left[\frac{\delta F}{\delta \rho} \frac{\delta \rho}{\delta \boldsymbol{\Gamma}} + \frac{\delta F}{\delta \mathbf{m}} \frac{\delta \mathbf{m}}{\delta \boldsymbol{\Gamma}} + \frac{\delta F}{\delta s} \frac{\delta s}{\delta \boldsymbol{\Gamma}} + \frac{\delta F}{\delta \mathbf{C}} \frac{\delta \mathbf{C}}{\delta \boldsymbol{\Gamma}} \right] d\Omega \tag{2.10}$$

$$\frac{\delta F}{\delta \boldsymbol{\Pi}} = \int_{\Omega} \left[\frac{\delta F}{\delta \rho} \frac{\delta \rho}{\delta \boldsymbol{\Pi}} + \frac{\delta F}{\delta \mathbf{m}} \frac{\delta \mathbf{m}}{\delta \boldsymbol{\Pi}} + \frac{\delta F}{\delta s} \frac{\delta s}{\delta \boldsymbol{\Pi}} + \frac{\delta F}{\delta \mathbf{C}} \frac{\delta \mathbf{C}}{\delta \boldsymbol{\Pi}} \right] d\Omega \tag{2.11}$$

Substituting Eqs. (2.10) and (2.11) into Eq. (2.8) and applying integration by parts utilizing the no-slip boundary conditions on $\partial\Omega$, the Eulerian form of the continuous bracket is derived.

$$\begin{aligned}
\{F, H\}_E = &- \int_{\Omega'} \left[\frac{\delta F}{\delta \rho} \nabla_j \left(\rho \frac{\delta H}{\delta m_j} \right) - \frac{\delta H}{\delta \rho} \nabla_j \left(\rho \frac{\delta F}{\delta m_j} \right) \right] d\Omega \\
&- \int_{\Omega'} \left[\frac{\delta F}{\delta m_k} \nabla_j \left(m_k \frac{\delta H}{\delta m_j} \right) - \frac{\delta H}{\delta m_k} \nabla_j \left(m_k \frac{\delta H}{\delta m_j} \right) \right] d\Omega \\
&- \int_{\Omega'} \left[\frac{\delta F}{\delta s} \nabla_j \left(s \frac{\delta H}{\delta m_j} \right) - \frac{\delta H}{\delta s} \nabla_j \left(s \frac{\delta F}{\delta m_j} \right) \right] d\Omega \\
&- \int_{\Omega'} \left[\frac{\delta F}{\delta C_{ij}} \nabla_k \left(C_{ij} \frac{\delta H}{\delta m_k} \right) - \frac{\delta H}{\delta C_{ij}} \nabla_k \left(C_{ij} \frac{\delta F}{\delta m_k} \right) \right] d\Omega \\
&- \int_{\Omega'} C_{ki} \left[\frac{\delta H}{\delta C_{ij}} \nabla_k \left(\frac{\delta F}{\delta m_j} \right) - \frac{\delta F}{\delta C_{ij}} \nabla_k \left(\frac{\delta H}{\delta m_j} \right) \right] d\Omega \\
&- \int_{\Omega'} C_{kj} \left[\frac{\delta H}{\delta C_{ij}} \nabla_k \left(\frac{\delta F}{\delta m_i} \right) - \frac{\delta F}{\delta C_{ij}} \nabla_k \left(\frac{\delta H}{\delta m_i} \right) \right] d\Omega
\end{aligned} \tag{2.12}$$

For further details on the coordinate transformation for the continuous Poisson bracket (2.8)–(2.12) see Beris and Edwards [4]. Substituting (2.9) and (2.12) into Eq. (2.7) general dynamic equations for ρ, $\rho\mathbf{u}$, s and $\mathbf{C}$ can be established by comparing coefficients in the expansion. In order to complete the process however, one must establish an expression for the energy functional (Hamiltonian/Helmholtz free energy) in terms of the dynamic variables that have been specified. The simplest form of this expression is obtained through a decomposition of energy into kinetic and stored/potential energy. In the absence of potential fields (gravity/electromagnetism) the Helmholtz free energy can be categorised into two parts: kinetic and internal energy. Beris and Edwards [4] include further discussion of field energy potential terms that can be modelled relatively easily using this method. Classical forms of the expressions for K and $\hat{u}$ are used. Taking derivatives of Eq. (2.3) we obtain

$$\begin{aligned} \frac{\delta H}{\delta \mathbf{m}} &= \frac{\mathbf{m}}{\rho} = \mathbf{u} \qquad \frac{\delta H}{\delta s} = T \\ \frac{\delta H}{\delta \rho} &= -\frac{\mathbf{m}\cdot\mathbf{m}}{2\rho^2} + \frac{\partial \hat{u}}{\partial \rho} \end{aligned} \tag{2.13}$$

This equation demonstrates that derivatives with respect to the components of structural variable $\mathbf{C}$ are solely dependent on the expression for strain-energy, w, that is chosen. Substituting these expressions into (2.12) and comparing coefficients we obtain the system of equations for non-dissipative compressible viscoelastic flow

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= -\nabla\cdot(\rho\mathbf{u}) \\ \frac{\partial s}{\partial t} &= -\nabla\cdot(s\mathbf{u}) \\ \rho\frac{\partial \mathbf{u}}{\partial t} &= -\nabla p - \rho\mathbf{u}\cdot\nabla\mathbf{u} + 2\nabla\cdot\left(\mathbf{C}\cdot\frac{\partial H}{\partial \mathbf{C}}\right) \\ \frac{\partial \mathbf{C}}{\partial t} &= -\nabla\cdot(\mathbf{u}\mathbf{C}) + \nabla\mathbf{u}\cdot\mathbf{C} + \mathbf{C}\cdot\nabla\mathbf{u}^T \end{aligned} \tag{2.14}$$

Pressure is automatically defined as a function of the dynamic variables and derivatives of the Helmholtz free energy density h:

$$p := \rho\frac{\partial h}{\partial \rho} + \mathbf{m}\cdot\frac{\partial h}{\partial \mathbf{m}} + s\frac{\partial h}{\partial s} + \mathbf{C} : \frac{\partial h}{\partial \mathbf{C}} - h. \tag{2.15}$$

The first three equations in (2.14) represent the conservation of mass, entropy (for non-dissipative processes) and momentum (in the absence of diffusion). The non-dissipative description of fluid motion contains no viscous or relaxation terms, hence the viscous stress tensor and relaxation terms in the conformation tensor equation do not appear. Another significant feature of the continuous Poisson bracket is that the material and upper convected derivatives are the natural time derivatives that arise in the derivation of the balance law for $\mathbf{u}$ and $\mathbf{C}$, respectively. The last equation in (2.14) is equivalent to the vanishing Truesdell derivative of $\mathbf{C}$, hence material objectivity is satisfied from the outset.

In the case of non-dissipative systems, the total available energy and total energy are equivalent. Distinctions between the two only become important when considering the dynamics of entropy producing systems in which mechanical energy is degraded. The system Eq. (2.14) is adequate for describing compressible fluids such as liquid helium and other so-called superfluids that exhibit no dissipative phenomena (viscosity/relaxation). When modelling particle systems that permit dissipative phenomena, irreversible (non-equilibrium) thermodynamic processes also need to be modelled.

2.2. Non-equilibrium thermodynamics: The dissipative bracket

When describing conservative systems the underlying assumption is that the time scale for changes in the system are large when compared to the time scale of changes of internal variables. If we intend to model systems that exhibit relaxation/dissipation on time scales similar to those of the system it is no longer sufficient to assume that the dynamics of the system variables are reversible. All real viscoelastic fluids exhibit dissipative behaviour in the form of viscous dissipation and stress relaxation, with both effects decreasing the amount of energy available to be converted into mechanical work.

Since the Poisson bracket is only suitable for modelling conservative dynamics it is necessary to derive an additional bracket to model irreversible dynamics. Early work on the combination of Hamiltonian and dissipative dynamics is due to Dzyaloshinskii and Volovick [14], Grmela [20], Kaufman [32], Morrison [39] and Grmela [19]. The concept of the dissipation bracket was introduced by Grmela [19]. The first application of the generalized bracket formulation in rheology appeared in Grmela [21] where the Poisson bracket without the s variable was introduced. A review of the recent development and applications of the generalized bracket formulation can be found in Grmela [23]. Beris & Edwards [15] introduced the unified bracket used in this paper. The internal dynamics of a viscoelastic fluid system is completely described by Eq. (2.7) with A being the Helmholtz free energy. Unlike the Poisson bracket an exact expression for the dissipation bracket $[F, G]$ cannot be derived from an equivalent discrete binary operator applicable to kinetic modelling of particle systems and so is only makes sense when a continuum approximation is used. Constraints and degeneracy conditions are imposed to ensure the non-decrease of entropy (second law of thermodynamics). For the generalized bracket we must also ensure that $dH/dt = 0$

$$\frac{dH}{dt} = \{H, H\} + [H, H] = 0 \Rightarrow [H, H] = 0$$

This arises by assuming the system is isolated, or at least surrounded by an adiabatic wall [4]. Additionally the entropy functional, S, must satisfy

$$\frac{dS}{dt} = \{S, H\} + [S, H] \geq 0$$

which in turn means $[S, H] \geq 0$ as $\{S, H\} = 0$. Throughout this paper we will use the Boltzmann definition of entropy (see Grmela and Carreau [24] and Beris and Edwards [4] for further details)

$$S(\rho, \mathbf{C}, T) = \int_\Omega s(\rho, \mathbf{C}, T)\, d\Omega = \int_\Omega \frac{\alpha\rho k_b}{2} \log\det\left(\frac{K\mathbf{C}}{\rho k_b T}\right) d\Omega \tag{2.16}$$

where α is the mass fraction, k_b is the Boltzmann constant, K is the spring constant. The total mass of the system $\mathcal{M}$ is conserved where

$$\mathcal{M} \equiv \int_\Omega \rho\, d\Omega,$$

Therefore

$$\frac{d\mathcal{M}}{dt} = \{\mathcal{M}, H\} + [\mathcal{M}, H] = 0,$$

and hence $[\mathcal{M}, H] = 0$. Moreover, the Hamiltonian must be generalised in the non-equilibrium nonisothermal case to account for *mechanical degradation*. Not all of the energy (represented by the Hamiltonian) is ‘available’ to be used for work in a nonisothermal system that is not in thermal equilibrium. Instead a fraction of the total energy, proportional to temperature and entropy, cannot be used. The Helmholtz free energy A replaces the Hamiltonian as the generating functional used in Eq. (2.7). Given two observables, F and G operating on Ω, the most general form of the dissipation bracket, obeying the first and second laws of thermodynamics, is given by

$$\begin{aligned} [F, G] = \int_\Omega \Bigg[&\Xi\left(L\left[\frac{\delta F}{\delta \omega}, \nabla\frac{\delta F}{\delta w}\right]; \frac{\delta G}{\delta w}; \frac{\delta G}{\delta w}\right) \\ &- \frac{1}{T}\frac{\delta F}{\delta s}\Xi\left(L\left[\frac{\delta G}{\delta \omega}, \nabla\frac{\delta G}{\delta w}\right]; \frac{\delta G}{\delta w}; \frac{\delta G}{\delta w}\right)\Bigg] d\Omega \end{aligned} \tag{2.17}$$

where $\omega = (\rho, \dots, \mathbf{m})$ is a vector containing the dynamic variables, $L[\,\cdot\,]$ denotes that Ξ is linear with respect to its arguments and Ξ is given by

$$\Xi = \Sigma_{i,j}\left[\hat{A}_{ij}\frac{\delta F}{\delta w_i}\frac{\delta G}{\delta w_j} + \hat{B}_{ijk}\frac{\delta F}{\delta w_i}\nabla_k\left(\frac{\delta G}{\delta w_j}\right)\right.$$

$$+\hat{C}_{ijk}\nabla_k\left(\frac{\delta F}{\delta w_i}\right)\frac{\delta G}{\delta w_j}+\hat{D}_{ijkl}\nabla_k\frac{\delta F}{\delta w_i}\nabla_l\frac{\delta G}{\delta w_j}\Bigg] \tag{2.18}$$

Eq. (2.17) represents the most general expression possible for a dissipation bracket consistent with the first and second laws of thermodynamics. In Eq. (2.17), $\hat{A}_{ij}$, $\hat{B}_{ijk}$, $\hat{C}_{ijk}$, $\hat{D}_{ijkl}$ are phenomenological coefficient matrices, which depend on the dynamic variables of the system. Beris and Edwards [4] discuss the general forms that these coefficient matrices take when used for modelling a range of fluids and composite rheological materials. Most well-known viscoelastic models can be derived by specifying a non-zero form of each phenomenological tensor. In Section 5 we consider nonisotropic behaviour and therefore propose nonzero forms of all four tensors. However Eq. (2.17) needs to be expressed in order to give physical meaning to each of the coefficient matrices. For a general viscoelastic fluid the dissipation bracket takes the form

$$\begin{aligned}
[F,H] = &-\int_\Omega Q_{ijkl}\nabla_i\left(\frac{\delta F}{\delta m_j}\right)\nabla_k\left(\frac{\delta H}{\delta m_l}\right)d\Omega \\
&+\int_\Omega \frac{1}{T}\frac{\delta F}{\delta s}Q_{ijkl}\nabla_i\left(\frac{\delta H}{\delta m_j}\right)\nabla_k\left(\frac{\delta H}{\delta m_l}\right)d\Omega \\
&-\int_\Omega \Lambda_{ijkl}\frac{\delta F}{\delta C_{ij}}\frac{\delta H}{\delta C_{kl}}\,d\Omega \\
&+\int_\Omega \frac{1}{T}\frac{\delta F}{\delta s}\Lambda_{ijkl}\frac{\delta H}{\delta C_{ij}}\frac{\delta H}{\delta C_{kl}}\,d\Omega \\
&-\int_\Omega L_{ijkl}\left(\nabla_i\frac{\delta F}{\delta m_j}\frac{\delta G}{\delta C_{kl}}-\nabla_i\frac{\delta G}{\delta m_j}\frac{\delta F}{\delta C_{kl}}\right)d\Omega \\
&-\int_\Omega \alpha_{ij}\nabla_i\left(\frac{\delta F}{\delta s}\right)\nabla_k\left(\frac{\delta H}{\delta s}\right)d\Omega \\
&+\int_\Omega \frac{1}{T}\frac{\delta F}{\delta s}\alpha_{ij}\nabla_i\left(\frac{\delta H}{\delta s}\right)\nabla_k\left(\frac{\delta H}{\delta s}\right)d\Omega
\end{aligned} \tag{2.19}$$

where $\boldsymbol{\Lambda}$ and $\mathbf{Q}$ are fourth-order relaxation and viscosity tensors, respectively, $\mathbf{L}$ represents non-affine interactions between the velocity gradient and conformation tensor fields and $\boldsymbol{\alpha}$ is the thermal conductivity matrix.

The forms that the two dissipative tensors can take vary significantly due to the limited number of assumptions used in this formulation. Most importantly $\boldsymbol{\Lambda}$, $\mathbf{Q}$ and $\mathbf{L}$ have to satisfy the Onsager reciprocal relations and frame indifference principles (which ensure that $[\cdot,\cdot]$ is non-negative definite). The generalised bracket for general non-isothermal viscoelastic fluids is thus obtained by adding Eqs. (2.19) to (2.12). Expanding the left-hand side of Eq. (2.1) using the chain rule and then comparing like terms with the right-hand side of Eqs. (2.19) and (2.12) we obtain the differential form of the governing equations for the state variables

$$\frac{\partial\rho}{\partial t}+\nabla\cdot(\rho\mathbf{u})=0 \tag{2.20}$$

$$\rho\left(\frac{\partial\mathbf{u}}{\partial t}+\mathbf{u}\cdot\nabla\mathbf{u}\right)=-\nabla p+\nabla\cdot\mathbb{T} \tag{2.21}$$

$$\begin{aligned}
\frac{\partial s}{\partial t}+\nabla\cdot(s\mathbf{u}) = &\frac{1}{T}\mathbf{Q}::\left(\nabla\mathbf{u}\otimes\nabla\mathbf{u}\right)+\frac{1}{T}\nabla\cdot(\boldsymbol{\alpha}T\nabla T) \\
&+\frac{1}{T}\boldsymbol{\Lambda}::\left(\frac{\delta H}{\delta\mathbf{C}}\otimes\frac{\delta H}{\delta\mathbf{C}}\right)
\end{aligned} \tag{2.22}$$

$$\overset{\triangledown}{\mathbf{C}}+(\nabla\cdot\mathbf{u})\mathbf{C}=-\boldsymbol{\Lambda}:\frac{\delta H}{\delta\mathbf{C}}+\mathbf{L}:\nabla\mathbf{u} \tag{2.23}$$

where the upper-convected derivative of $\mathbf{C}$ is defined as

$$\overset{\triangledown}{\mathbf{C}}=\frac{D\mathbf{C}}{Dt}-\nabla\mathbf{u}\cdot\mathbf{C}-\mathbf{C}\cdot\nabla\mathbf{u}^T$$

and the extra-stress tensor, $\mathbb{T}$, is given by

$$\mathbb{T}=\mathbf{Q}:\nabla\mathbf{u}+2\frac{\delta H}{\delta\mathbf{C}}\cdot\mathbf{C}+\mathbf{L}:\frac{\delta H}{\delta\mathbf{C}} \tag{2.24}$$

Eqs. (2.20)–(2.23) is a generalization of single conformation tensor viscoelastic fluid models. Constitutive equations are derived by specifying the forms of the Hamiltonian (Helmholtz free energy in the case of nonisothermal fluids) and tensors $\boldsymbol{\Lambda}$, $\mathbf{Q}$ and $\mathbf{L}$ (for further discussion of the general governing Eqs. (2.20)–(2.23), see [4] p. 328–335).

2.3. *The energy balance equation*

A generalised form of the energy balance equation can be derived from Eqs. (2.20)–(2.23). The time derivative of the Helmholtz free energy is given by

$$\frac{Da}{Dt}=\frac{D}{Dt}\left(\frac{\rho}{2}\mathbf{u}\cdot\mathbf{u}+\hat{a}(\rho,s,\mathbf{C})\right) \tag{2.25}$$

Taking the derivative of $\hat{a}$ with respect to t yields

$$\frac{D\hat{a}}{Dt}=\frac{\partial\hat{a}}{\partial\rho}\frac{D\rho}{Dt}+\frac{\partial\hat{a}}{\partial s}\frac{Ds}{Dt}+\frac{\partial\hat{a}}{\partial\mathbf{C}}:\frac{D\mathbf{C}}{Dt} \tag{2.26}$$

It can be shown, via substitution of (2.22) into Eq. (2.26), that in the absence of external thermal energy potential, the equation for internal energy is given by

$$\frac{D\hat{a}}{Dt}+(\nabla\cdot\mathbf{u})\hat{a}=\nabla\cdot\mathbf{q}+\hat{\boldsymbol{\sigma}}:\nabla\mathbf{u} \tag{2.27}$$

where

$$\hat{\boldsymbol{\sigma}}=\mathbb{T}-p\mathbf{I} \tag{2.28}$$

and $\mathbf{q}=-\boldsymbol{\alpha}\nabla T$. The thermal conductivity matrix, $\boldsymbol{\alpha}$, is a function of the conformation stress, to the extent dictated by the Cayley–Hamilton theorem (see [4] p. 331)

$$\boldsymbol{\alpha}=a_1\mathbf{I}+a_2\mathbf{C}+a_3\mathbf{C}\cdot\mathbf{C} \tag{2.29}$$

where scalar coefficients a_1, a_2 and a_3 are, in general, functions of the invariants of the conformation stress [4]. To ensure nonnegative entropy production, the following conditions must hold:

$$a_1\geq 0,\quad a_3\geq 0,\quad a_2\geq -2\sqrt{a_1a_3} \tag{2.30}$$

Note that the conditions found in Eq. (9.1–6) of the book of Edwards and Beris [16] are incorrect.

The body of theoretical and experimental work suggests thermal conductivity in polymeric fluids is anisotropic under flowing conditions [4,28]. Experiments on cross-linked elastomers show a significant enhancement in thermal conductivity in the direction of stretch for natural rubber subjected to uniaxial elongation [47]. Moreover, Cocci and Picot [9] and Picot et al. [42] showed that, for polymeric liquids, thermal conductivity in the direction of strain of the macromolecule was much higher than perpendicular to it. For dilute polymer solutions Van den Brule [48] defined a_1 as the anisotropic thermal conductivity of the solvent and a_i $i\in\{2,3\}$ are given by

$$a_2=\frac{3\zeta}{2m}\alpha\rho k_b \qquad a_3=0 \tag{2.31}$$

where m is the mass of the polymer and ζ is the friction coefficient. A detailed review of the theory behind the derivation of the energy equation was given by Dressler et al. [12].

The nascent field of theoretical non-isothermal rheology contains several controversies that need to be resolved in relation to nonequilibrium thermodynamics. The controversies arise when considering complex fluids and nonlinear time evolution far from equilibrium. The questions that need to be addressed are: what are the additional state variables, what is the physical meaning and role of time evolution of concepts such as nonequilibrium entropy and nonequilibrium temperature.

Grmela et al. [25] chose two extra fields, one describing mechanical deformation of the macromolecules and the other describing the entropy flux. Grmela [22] argues that it is reasonable to expect that the governing equations on all levels of description possess a common structure that guarantees that their solutions agree with the experimentally observed compatibilities with equilibrium thermodynamics and between the two levels of description. It is clear that in nonequilibrium thermodynamics, rheology plays an important role and there remains much to be accomplished. However, in the present paper we focus on the influence of viscoelasticity on the energy equation and ignore, for the present, the possible inclusion of internal variables.

2.4. *Summary of the generalised bracket method*

In this section we have presented the theory underlying the generalised bracket method for deriving viscoelastic fluid models, and described important properties of the Poisson and dissipative brackets. The generalised bracket method is modular and can be summarised as follows:

- **Module 1**: Choose variables that characterise the state of the system, i.e mass density, ρ, momentum, $\mathbf{m} = \rho\mathbf{u}$, entropy, s and conformation stress **C**. It is at this stage that the continuum approximation is made.
- **Module 2**: Choose a form of the energy and entropy (or Helmholtz free energy) functional. Throughout this paper we use the standard Marrucci definition of entropy (Eq. (2.16)). The constitutive equation depends on the elastic strain energy and entropy functionals. We consider both linear and nonlinear strain energy formulations when developing the various models detailed in the next sections.
- **Module 3**: Choose the form of the phenomenological tensors in the dissipative bracket, ensuring that the dissipative tensors satisfy the Onsager reciprocal relations and the resulting constitutive equation satisfies Hulsen's theorem. In this paper we make use of the 'non-affine' tensor (Beris and Edwards) to derive a new model for Boger fluids.

These three modules provide a framework for deriving thermodynamically consistent models for transport in viscoelastic fluids. In the following sections compressible forms of the UCM and Oldroyd-B models are derived thermodynamically via this bracket formalism. The equations given by Eqs. (2.20)–(2.23) provide the most general description for thermodynamically consistent compressible models.

3. The compressible Oldroyd-B model

Maxwell-type fluids can be modelled within the generalised bracket framework. The Oldroyd-B model is essentially an extension of the UCM model that is able to provide a mathematical description of fluids with a (Newtonian) solvent constituent in addition to an elastic or polymeric component. First of all, it is necessary to specify the form of the Helmholtz free energy. Given a Helmholtz free energy of the form (2.3) the system of equations for mass, momentum, entropy and constitutive law are given by Eqs. (2.20)–(2.23). For an Oldroyd-B fluid the extra stress tensor is assumed to comprise polymeric and solvent contributions. In order to capture these two contributions, nonzero forms of $\boldsymbol{\Lambda}$ and **Q** need to be specified [4].

3.1. *Isothermal compressible Oldroyd B model*

In the first instance we consider the isothermal case where the fluid parameters (viscosities, relaxation time) are assumed to be independent of temperature. The components of the relaxation tensor are given by

$$\Lambda_{ijkl} = \frac{1}{2\alpha\rho K\lambda_2}(\delta_{jl}C_{ik} + \delta_{jk}C_{il} + \delta_{il}C_{jk} + \delta_{ik}C_{jl}) + \frac{2}{3nK}\left(\frac{1}{\lambda_0} - \frac{1}{\lambda_2}\right)\delta_{ij}C_{kl} \tag{3.1}$$

where λ_0 and λ_2 are the relaxation times of the fluid, α is the mass fraction of the polymer [12] and K is the spring factor. Essentially λ_0 and λ_2 represent the trace and the traceless stress relaxation, respectively.

The expression for $\boldsymbol{\Lambda}$ given by Eq. (3.1) satisfies the Onsager reciprocal relations and is non-negative definite. For the purposes of this paper we will only consider fluids characterised by a single relaxation time i.e. $\lambda_0 = \lambda_2 = \lambda$. In general these material parameters are functions of temperature i.e. $\lambda = \lambda(T)$.

Eq. (3.1) is one of many forms that $\boldsymbol{\Lambda}$ can take. The only strict requirement is that the equation for the conformation tensor ensures $\mathbf{C}(\mathbf{x}, t)$ is non-negative definite $\forall t > 0$. We have chosen this form as it is one of the simpler expressions for relaxation. In reality both the viscosity and relaxation time of a fluid will be functions of pressure and temperature with relationships being uniquely determined for each specific material. The most general form of the viscosity tensor is given by

$$Q_{ijkl} = \mu_s(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \eta_s(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) + \kappa'_s\delta_{ij}\delta_{kl} \tag{3.2}$$

To satisfy frame indifference (principle of objectivity), η_s has to be set to zero so that

$$Q_{ijkl} = \mu_s(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \kappa'_s\delta_{ij}\delta_{kl} \tag{3.3}$$

where μ_s is the shear viscosity and $\kappa'_s = \kappa_s - \frac{2}{3}\mu_s$ is the 'second viscosity'. Using κ'_s instead of the *bulk viscosity* κ_s permits the separation of gradient and divergence free terms in the Newtonian viscosity.

Eq. (3.3) provides the most general form of a fourth order viscosity tensor that satisfies the principle of frame indifference and the Onsager reciprocal relations [4]. The subscript 's' denotes that **Q** is normally associated with the viscosity of the solvent (Newtonian) component of the fluid. The polymeric viscosity and relaxation time of the fluid are related through the general elastic modulus, defined

$$G(\rho, T) = \alpha\rho k_b T = \mu_p(\rho, T)/\lambda(T) \tag{3.4}$$

where α is the polymeric mass fraction, k_b is the Boltzmann constant $\mu_p(\rho, T)$ is the polymeric viscosity and $\lambda(T)$ is the relaxation time. In the case of isothermal flow the temperature is constant. The Helmholtz free energy density is given by the sum of the kinetic and internal energy (elastic strain energy, chemical potential etc.) less a *degradation term* proportional to the Boltzmann entropy and temperature (for more details on the relationship between the Hamiltonian and Helmholtz free energy and relationships between the derivatives of the two functionals see Beris and Edwards [4])

$$A[\rho, \rho\mathbf{u}, T, \mathbf{C}] = \int_\Omega a(\rho, \rho\mathbf{u}, T, \mathbf{C})\, d\Omega = \int_\Omega \left(\frac{\rho\mathbf{u}\cdot\rho\mathbf{u}}{2\rho} + \hat{a}(\rho, T, \mathbf{C})\right) d\Omega \tag{3.5}$$

where

$$\hat{a} = \hat{a}_0(\rho, T) + \frac{\alpha\rho K}{2}(tr\mathbf{C} - 3) - \frac{\alpha\rho k_b T}{2}\log\det\left(\frac{\mathbf{C}K}{\rho k_b T}\right) \tag{3.6}$$

The additional term, $\hat{a}_0(\rho, T)$, in Eq. (3.5) represents the Helmholtz free energy density for the fluid in the 'rest' state (i.e. not depending on **C**) of a fluid. It then follows that

$$\frac{\delta A}{\delta\mathbf{C}} = \frac{\alpha\rho K}{2}\mathbf{I} - \frac{\alpha\rho k_b T}{2}\mathbf{C}^{-1} \tag{3.7}$$

Substituting (3.7) and (3.1) into the equation for the conformation tensor in (2.22) we can write

$$\boldsymbol{\Lambda} : \frac{\delta A}{\delta\mathbf{C}} = \frac{1}{\lambda}\mathbf{C} - \frac{1}{\lambda}\frac{\alpha\rho k_b T}{K}\mathbf{I}, \tag{3.8}$$

thus obtaining a dynamic equation for the conformation tensor

$$\overset{\triangledown}{\mathbf{C}} + (\nabla\cdot\mathbf{u})\mathbf{C} = -\frac{1}{\lambda}\left(\mathbf{C} - \frac{G}{\alpha K}\mathbf{I}\right) \tag{3.9}$$

Eq. (2.24) becomes

$$\mathbb{T} = 2\mu_s(T)\mathbb{D} + \kappa'_s(T)(\nabla\cdot\mathbf{u})\mathbf{I} + \alpha K(T)\mathbf{C} - \alpha\rho k_b T\mathbf{I} \tag{3.10}$$

The extra stress can be divided into solvent, $\boldsymbol{\tau}_s$, and polymeric, $\boldsymbol{\tau}_p$, parts where $\mathbb{T} = \boldsymbol{\tau}_s + \boldsymbol{\tau}_p$.The equation for the polymeric part of the extra stress is given by

$$\boldsymbol{\tau}_p = \alpha K(T)\mathbf{C} - \alpha\rho k_b T\mathbf{I} \tag{3.11}$$

Note that $\mathbf{C} \equiv \rho\mathbf{c}$ where ρ is the density and $\mathbf{c}$ is the kinematic conformation tensor. Conservation of mass can be written

$$\frac{D\rho}{Dt} + \rho(\nabla\cdot\mathbf{u}) = 0 \tag{3.12}$$

Using Eqs. (3.9) and (3.12) the constitutive equation in terms of the kinematic conformation tensor can be derived

$$\lambda(T)\overset{\triangledown}{\mathbf{c}} + \mathbf{c} = \frac{k_b T}{K(T)}\mathbf{I} \tag{3.13}$$

Writing Eq. (3.11) in terms of the kinematic conformation stress

$$\boldsymbol{\tau}_p = \alpha\rho K(T)\mathbf{c} - \alpha\rho k_b T\mathbf{I} \tag{3.14}$$

and taking the upper convected derivative of (3.14) we obtain

$$\overset{\triangledown}{\boldsymbol{\tau}}_p = \alpha\frac{D\rho}{Dt}K\mathbf{c} + \alpha\rho K\overset{\triangledown}{\mathbf{c}} - \alpha\rho k_b T\overset{\triangledown}{\mathbf{I}} - \alpha\frac{D\rho}{Dt}k_b T\mathbf{I}. \tag{3.15}$$

Eliminating the material derivative of ρ using Eq. (3.12) yields

$$\overset{\triangledown}{\boldsymbol{\tau}}_p = \alpha\rho K\overset{\triangledown}{\mathbf{c}} - \alpha\rho k_b T\overset{\triangledown}{\mathbf{I}} - (\nabla\cdot\mathbf{u})[\alpha\rho K\mathbf{c} - \alpha\rho k_b T\mathbf{I}].$$

This equation can be simplified using Eq. (3.14) to give

$$\overset{\triangledown}{\boldsymbol{\tau}}_p + (\nabla\cdot\mathbf{u})\boldsymbol{\tau}_p = \alpha\rho K\overset{\triangledown}{\mathbf{c}} - \alpha\rho k_b T\overset{\triangledown}{\mathbf{I}} \tag{3.16}$$

and finally we arrive at the constitutive equation for the polymer stress

$$\lambda\left(\overset{\triangledown}{\boldsymbol{\tau}}_p + (\nabla\cdot\mathbf{u})\boldsymbol{\tau}_p\right) + \boldsymbol{\tau}_p = 2\lambda\alpha\rho k_b T\mathbb{D} \tag{3.17}$$

Eq. (3.17) represents the most general form of constitutive equation for a compressible Oldroyd-B fluid with a single relaxation time. However, this equation is not in a form that can be used in any practical sense to obtain numerical approximations to viscoelastic flow problems. In order to reduce the equations to a more tractable form we write down the constitutive equations for the solvent and polymeric contributions to $\mathbb{T}$

$$\begin{aligned} &\boldsymbol{\tau}_s = 2\mu_s\mathbb{D} + \kappa_s'(\nabla\cdot\mathbf{u})\mathbf{I} \\ &\lambda\overset{\triangledown}{\boldsymbol{\tau}}_p + (1 + \lambda(\nabla\cdot\mathbf{u}))\boldsymbol{\tau}_p = 2\mu_p\mathbb{D} \end{aligned} \tag{3.18}$$

When the incompressibility condition ($\nabla\cdot\mathbf{u} = 0$) is imposed and defining the polymer viscosity $\mu_p = \lambda\alpha\rho k_b T$, we recover the incompressible form of the Oldroyd-B constitutive law given by

$$\begin{aligned} &\boldsymbol{\tau}_s = 2\mu_s\mathbb{D} \\ &\lambda\overset{\triangledown}{\boldsymbol{\tau}}_p + \boldsymbol{\tau}_p = 2\mu_p\mathbb{D} \end{aligned} \tag{3.19}$$

Eq. (3.18) represents the constitutive equation for an isothermal compressible Oldroyd-B fluid with relaxation time independent of $\mathbf{C}$. The system given by Eqs. (2.20)–(2.23) is also capable of modelling viscoelastic fluids with a spectrum of relaxation times. We now consider the extension of Eq. (3.18) to the nonisothermal case when the fluid parameters are functions of temperature.

3.2. Nonisothermal and compressible Oldroyd B model

For the nonisothermal case we consider the fluid parameters to be temperature dependent i.e. $\mu_s = \mu_s(T)$, $\mu_p = \mu_p(\rho, T)$ $\lambda = \lambda(T)$. The relaxation tensor is given by

$$\Lambda_{ijkl} = \frac{1}{2\alpha\rho K(T)\lambda(T)}(\delta_{jl}C_{ik} + \delta_{jk}C_{il} + \delta_{il}C_{jk} + \delta_{ik}C_{jl}) \tag{3.20}$$

In several instances in the literature the spring factor is assumed to have a linear dependence on temperature,

$$K(T) = k_b T\mu \tag{3.21}$$

where μ is a constant dependent on the equilibrium extension of the polymers. Linear dependence of the spring factor on temperature was addressed by Gupta and Metzner [27], who pointed out that when Eq. (3.21) is used the resulting constitutive model could not adequately describe experimental data. We will consider the spring factor to be a general function of temperature to be determined empirically.

The relaxation tensor with components given by (3.20) was initially proposed by Dressler et al. [12]. Likewise the components of the viscous dissipation tensor are given by

$$Q_{ijkl} = \mu_s(T)(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \kappa_s'(T)\delta_{ij}\delta_{kl} \tag{3.22}$$

where $\kappa_s'(T) = \kappa_s(T) - \frac{2}{3}\mu_s(T)$. With temperature a non-constant variable, the upper convected derivative of (3.14) is given by

$$\overset{\triangledown}{\boldsymbol{\tau}}_p = \alpha\frac{D\rho}{Dt}K\mathbf{c} + \alpha\rho\frac{DK(T)}{Dt}\mathbf{c} + \alpha\rho K\overset{\triangledown}{\mathbf{c}} - \alpha\rho k_b T\overset{\triangledown}{\mathbf{I}} - \alpha\frac{D\rho}{Dt}k_b T\mathbf{I} - \alpha\rho k_b\frac{DT}{Dt}\mathbf{I} \tag{3.23}$$

Substituting Eq. (3.12) into (3.23) we obtain

$$\begin{aligned} \overset{\triangledown}{\boldsymbol{\tau}}_p &= \alpha\rho K\overset{\triangledown}{\mathbf{c}} - \alpha\rho k_b T\overset{\triangledown}{\mathbf{I}} + \left(-(\nabla\cdot\mathbf{u}) + \frac{D\ln K(T)}{Dt}\right)[\alpha\rho K\mathbf{c} - \alpha\rho k_b T\mathbf{I}] \\ &\quad + \left(\frac{D\ln K(T)}{Dt} - \frac{D\ln T}{Dt}\right)\alpha\rho k_b T\mathbf{I} \end{aligned}$$

Eliminating $\mathbf{c}$ using Eqs. (3.13) and (3.14) yields

$$\begin{aligned} &\lambda(T)\left(\overset{\triangledown}{\boldsymbol{\tau}}_p + \left((\nabla\cdot\mathbf{u}) - \frac{D\ln K(T)}{Dt}\right)\boldsymbol{\tau}_p + \alpha\rho k_b T\overset{\triangledown}{\mathbf{I}}\right) + (\boldsymbol{\tau}_p + \alpha\rho k_b T\mathbf{I}) \\ &= \alpha\rho k_b T\mathbf{I} + \left(\frac{D\ln K(T)}{Dt} - \frac{D\ln T}{Dt}\right)\alpha\rho k_b T\mathbf{I}, \end{aligned}$$

This equation contains additional terms due to the non-constant temperature and spring constant. With the inclusion of the solvent stress the constitutive law is given by

$$\begin{aligned} &\lambda(T)\overset{\triangledown}{\boldsymbol{\tau}}_p + \left[1 + \lambda(T)\left(\nabla\cdot\mathbf{u} - \frac{D\ln K(T)}{Dt}\right)\right]\boldsymbol{\tau}_p \\ &= G(\rho, T)\lambda(T)\left[2\mathbb{D} + \left(\frac{D\ln K(T)}{Dt} - \frac{D\ln(T)}{Dt}\right)\mathbf{I}\right] \\ &\boldsymbol{\tau}_s = 2\mu_s(T)\left(\mathbb{D} - \frac{1}{3}(\nabla\cdot\mathbf{u})\mathbf{I}\right) + \kappa(T)(\nabla\cdot\mathbf{u})\mathbf{I} \end{aligned} \tag{3.24}$$

Eq. (3.24) is a general form of the Oldroyd-B constitutive equation applicable to non-isothermal compressible flow problems. The functional dependence of the viscosity, relaxation time and spring constant are determined experimentally and are dependent on the particular polymer melt/solution under consideration. In the case of incompressible and isothermal flow the model reduces to Eq. (3.19).

4. Discussion of viscoelastic models

One of the major hurdles in the analysis of compressible flow of non-Newtonian fluids is the lack of universal agreement on the form of the governing equations. As a result the tendency has been to construct ad-hoc governing equations suitable for particular problems. Whilst being a crucial tool in engineering applications, this approach fails to provide equations consistent with fundamental principles in physics. Thus these models have limited applicability and cannot be applied to a wide range of viscoelastic flow problems.

4.1. Weakly compressible model [3]

Belblidia et al. [3] proposed a model for weakly compressible fluids. The constitutive equations for the solvent and polymeric contributions to the extra stress are given by

$$\begin{aligned} &\boldsymbol{\tau}_s = 2\mu_s\mathbb{D} + \mu_s\left(\frac{\kappa_s}{\mu_s} - \frac{2}{3}\right)(\nabla\cdot\mathbf{u})\mathbf{I} \\ &\lambda\overset{\triangledown}{\boldsymbol{\tau}}_p + \boldsymbol{\tau}_p = 2\mu_p\mathbb{D} \end{aligned} \tag{4.1}$$

respectively. The system of governing equations is closed using the equation of state

$$\frac{\tilde{p}+B}{\tilde{p}_0+B}=\left(\frac{\rho}{\rho_0}\right) \tag{4.2}$$

where $\tilde{p}=p-\frac{1}{3}\mathrm{tr}(\boldsymbol{\tau}_p+2\mu_s\mathbb{D})$ is the *augmented pressure*. This compressible viscoelastic model has been effective at simulating viscous flows at low Mach numbers. Several applications to polymer processing operations exist, such as injection moulding and high-speed extrusion where compressible effects are significant. The model used by Belblidia [3] has features that resemble the isothermal compressible Oldroyd-B model derived in Section 3. However, comparisons of Eqs. (3.18) and (4.1) show that additional compressible terms appear in the model derived using the generalized bracket formulation.

4.2. Model based on the Boltzmann equation approach

Wilmanski [50] derived a compressible viscoelastic model by taking moments of the phase density, f, which satisfies the Boltzmann equation

$$\frac{\partial f}{\partial t}+\mathbf{v}\cdot\frac{\partial f}{\partial \mathbf{x}}+\mathbf{b}^0\cdot\frac{\partial f}{\partial \mathbf{v}}=C[f,f] \tag{4.3}$$

where $\mathbf{x}$ and $\mathbf{v}$ are position and velocity fields of the continuum and C is the collision operator. The Boltzmann equation relies on some of the same fundamental assumptions that are used in the bracket theory, namely that the interactions between particles are reversible at the microscopic level (*microscopic reversibility*) and that interactions between particles occur one at a time. Starting from (4.3), universal balance laws of extended thermodynamics can be obtained with which to model viscoelasticity. The theory is based on the derivation of balance laws for modelling both viscous liquids and linear elastic solids [50]. For viscous heat-conducting fluids the equations governing the state variables of the system have the same structure as those governing the dynamics of ideal gases, albeit with slightly different conditions on some scalar coefficients. An additional condition ensuring the non-decrease of entropy is imposed in order to satisfy the second law of thermodynamics. With this in mind the following set of governing equations for the extra-stress and energy for a heat-conducting Maxwellian fluid are proposed

$$\begin{gathered}
\lambda_\sigma\left[\overset{\triangledown}{\mathbb{T}}+\frac{2}{3}(\mathbb{T}:\mathbb{D})\mathbf{I}\right]+\mathbb{T}=2\mu_e\mathbb{D}^D\\
\frac{De}{Dt}=-\nabla\cdot\mathbf{q}+\mathbb{T}:\nabla\mathbf{u}\\
\lambda_q\frac{D\mathbf{q}}{Dt}+\mathbf{q}=-\kappa\nabla T\\
\mathbb{T}=\boldsymbol{\sigma}^D\qquad p=-\frac{1}{3}\mathrm{tr}(\boldsymbol{\sigma})\qquad \rho=\rho(\boldsymbol{\sigma})
\end{gathered} \tag{4.4}$$

where e is the thermal energy, λ_σ is the stress relaxation time, λ_q is a thermal relaxation constant and κ is the (isotropic) thermal conductivity parameter. $\mathbf{A}^D$ denotes the trace free part of a tensor $\mathbf{A}$. The model of Wilmanski, unlike the GENERIC and bracket formulations, is based upon a general balance law that is itself derived from the Boltzmann equation. The extended thermodynamic technique used to derive (4.4) possesses additional modelling potential as it can be used to derive field equations in non-inertial (relativistic) coordinates and can be generalised to systems far from thermodynamic equilibrium.

4.3. Dressler model

Dressler et al. [12] provide a detailed thermodynamic analysis for generating models for polymeric liquids. The methodology used in the current paper and the analysis performed by Dressler et al. [12] are based on the principle that all thermodynamic systems are encompassed by a single mathematical structure of a general abstract equation.

Several nonisothermal extensions to well-established viscoelastic models are proposed in [12] and the discussion of GENERIC provides the best context for the models discussed in this paper. A key point to be emphasised is the discussion of the energy equation used to model heat flow commonly used in engineering heat analysis

$$\rho c\frac{DT}{Dt}=\mathbb{T}:\nabla\mathbf{u}-\nabla\cdot\mathbf{q}+\rho Q \tag{4.5}$$

where T is temperature, $\mathbf{q}=-\boldsymbol{\alpha}\nabla T$ is the heat flux vector field, c is the specific heat capacity and Q is external heat energy. Dressler et al. [12] point out that unless the internal energy is solely dependent on temperature (i.e. $u=u(T)$) Eq. (4.5) is inadequate for describing frictional heating behaviour in polymers and must be replaced by

$$\rho c\frac{DT}{Dt}=\boldsymbol{\sigma}:\mathbb{D}-\nabla\cdot\mathbf{q}+\rho Q-\rho\left.\frac{Du}{Dt}\right|_T \tag{4.6}$$

an important contribution in this work was the following nonisothermal generalisation of the Maxwell constitutive law

$$\begin{aligned}
&\lambda(T)\,\overset{\triangledown}{\mathbb{T}}+\left[1+\lambda(T)\left(\nabla\cdot\mathbf{u}-\frac{D\ln K(T)}{Dt}\right)\right]\mathbb{T}\\
&\quad=2\mu_p(T)\left[\mathbb{D}+\left(\frac{D\ln K(T)}{Dt}-\frac{D\ln T}{Dt}\right)\mathbf{I}\right]
\end{aligned} \tag{4.7}$$

Eq. (4.7) is the most sophisticated model presented in this section, and takes account of temperature dependence of the thermodynamic variables. Note that the relaxation time is defined by $\lambda(T)=\zeta/4K(T)$ where ζ is the friction coefficient and $K(T)$ is the temperature dependent elastic spring factor.

4.4. Other models for compressible viscoelasticity

There are many other models that have been proposed to describe compressibility in addition to those described in this section. Chakraborty and Sader [7] reviewed a number of constitutive equations for compressible viscoelastic flows in their linear limits. They were particularly concerned about the inability of earlier models to reproduce the response of linear mechanical vibrations of bipyramidal nanoparticles in simple liquids at high frequency (20 GHz). They show that only a recent model is able to recover all the required features of a linear viscoelastic flow and provide a rigorous foundation for the analysis of vibrating nanostructures in simple liquids. This highlights the importance of shear and compressional relaxation processes, as a function of flow geometry, and the impact of the shear and bulk viscosities on nanometer scale flows.

Huo and Yong [31] considered a compressible viscoelastic fluid model. Although the model has a convex entropy, the Hessian matrix of the entropy does not symmetrize the system of first-order partial differential equations due to the non-conservative terms in the constitutive equation. They show that the corresponding 1D model is symmetrizable, hyperbolic and dissipative and satisfies the Kawashima condition. They use these properties to prove the global existence of smooth solutions near equilibrium and justify the compatibility of the model with the Navier–Stokes equations.

Guaily [26] derived a temperature equation for polymeric fluids in which elasticity and compressibility effects appear explicitly. An advantage of this temperature equation is that it does not contain functions that depend on a particular choice of model for the polymer stress.

5. Nonlinear elastic models

For Maxwell-type models the elastic energy term in the Helmholtz free energy functional is linear in $\mathbf{C}$. However, for many rubber-like elastic solids and polymeric fluids empirical evidence would suggest that the elastic energy stored is a nonlinear function of $\mathbf{C}$. The generalised bracket method provides a path for deriving thermodynamically consistent models for viscoelastic fluids using nonlinear strain energy formula in the generating functional for the constitutive equation.

From the point of view of thermodynamics, there are only a few constraints on the forms that the strain energy and relaxation tensor should take. This allows a number of potential models to be derived in a manner consistent with the first and second laws. In addition to mass and momentum conservation, further physical constraints exist on the conformation tensor, $\mathbf{C}(\mathbf{x}, t)$. The constraint that ensures thermodynamic consistency was proposed by Hulsen [30]. For the system of governing Eqs. (2.20)–(2.23), the evolution equation for $\mathbf{C}$ takes the form

$$\overset{\triangledown}{\mathbf{C}} + (\nabla\cdot\mathbf{u})\mathbf{C} + \mathbf{\Lambda} : \frac{\delta A}{\delta\mathbf{C}} - \mathbf{L} : \nabla\mathbf{u} = 0 \tag{5.1}$$

where

$$\mathbf{\Lambda} : \frac{\delta A}{\delta\mathbf{C}} = a_1(\mathbf{C})\mathbf{I} + a_2(\mathbf{C})\mathbf{C} + a_3(\mathbf{C})\mathbf{C}^2 \tag{5.2}$$

and $a_i(\mathbf{C})$ $i\in\{1, 2, 3\}$ are general functions of the *principal invariants* of $\mathbf{C}$ which ensures that $a_i(\mathbf{C})$ are objective or frame indifferent. Hulsen [30] examined the mathematical behaviour of the conformation tensor obeying (5.1) and provided a condition that ensures the consistency of a model for a given Hamiltonian/Helmholtz free energy. The following theorem summarizes this condition.

Theorem 5.1 (Hulsen [30]). *Given that C satisfies the differential equation given by (5.1) and C(x,0) is positive definite. Then if* $a_1(\mathbf{C}) < 0$ *and* $\nabla\mathbf{u}$ *finite, C remains positive definite for all* $t > 0$.

A proof and detailed discussion of Hulsen's sufficient condition theorem is included in the monograph of Beris and Edwards [4] (Section 8.1.5 B). To invoke Hulsen's theorem it is sufficient to analyse the behaviour of $a_1(\mathbf{C})$ for positive definite $\mathbf{C}$ [30] since satisfaction of the conditions in the theorem determines if a given strain energy/relaxation tensor model is *physically admissible*. Further investigation is needed in order to determine the well-posedness of the mathematical equations generated for given boundary conditions as well as how well the solutions to these equations compare to experimental data. We now derive a new viscoelastic model based on a hyperelastic strain energy formulation for viscoplastic materials.

5.1. Compressible Mooney–Rivlin type model

The literature concerning models for hyperelastic materials is rich with formulations for elastic strain energy density functions [13]. For both the UCM and Oldroyd-B models the elastic potential energy is that of a neoHookean material i.e. $w(\mathbf{C}) = \frac{\hat{\mu}}{2}(I_1(\mathbf{C}) - 3)$ where $\hat{\mu} = \alpha\rho K$. We now consider a fluid whose polymeric constituent behaves like a Mooney–Rivlin material i.e. instead of a strain energy directly proportional to $I_1(\mathbf{C})$ the strain energy depends on all three principal invariants

$$w(\mathbf{C}) = \frac{\mu_1}{2}\left(\frac{I_1(\mathbf{C})}{I_3(\mathbf{C})^{\frac{1}{3}}} - 3\right) + \frac{\mu_2}{2}\left(\frac{I_2(\mathbf{C})}{I_3(\mathbf{C})^{\frac{2}{3}}} - 3\right) + \kappa'_p(I_3(\mathbf{C})^{1/2} - 1)^2 \tag{5.3}$$

where μ_1 and μ_2 are parameters to be determined empirically. The first and second terms are associated with the stiffness of the polymeric constituent and the third term is a compressible term associated with the bulk viscosity. It is easy to verify that if $I_3(\mathbf{C}) = \det\mathbf{C} = 1$, $\mu_2 = 0$ and $\mu_1 = \alpha\rho K$, then (5.3) reduces to the strain energy for a Maxwell material. Taking the derivative of the Helmholtz free energy functional, with elastic strain energy defined by (5.3) we obtain

$$\begin{aligned}\frac{\delta A}{\delta\mathbf{C}} = &-\left(\kappa'_p(I_3^{1/2} - I_3) + \frac{\mu_1 I_1}{6I_3^{4/3}} + \frac{\mu_2 I_2}{3I_3^{5/3}} + \frac{G(T)}{2}\right)\mathbf{C}^{-1} \\ &+\left(\frac{\mu_1}{2I_3^{1/3}} + \frac{\mu_2 I_1}{2I_3^{2/3}}\right)\mathbf{I} - \frac{\mu_2}{2I_3^{2/3}}\mathbf{C}\end{aligned} \tag{5.4}$$

which we write in the form

$$\frac{\delta A}{\delta\mathbf{C}} = g_1(\mathbf{C})\mathbf{C}^{-1} + g_2(\mathbf{C})\mathbf{I} + g_3(\mathbf{C})\mathbf{C}$$

where

$$\begin{aligned}g_1(\mathbf{C}) &= -\left(\kappa'_p(I_3^{1/2} - I_3) + \frac{\mu_1 I_1}{6I_3^{4/3}} + \frac{\mu_2 I_2}{3I_3^{5/3}} + \frac{\alpha\rho k_b T}{2}\right) \\ g_2(\mathbf{C}) &= \left(\frac{\mu_1}{2I_3^{1/3}} + \frac{\mu_2 I_1}{2I_3^{2/3}}\right) \\ g_3(\mathbf{C}) &= -\frac{\mu_2}{2I_3^{2/3}}\end{aligned} \tag{5.5}$$

Using the expression given by Eq. (5.4) for the energy derivative and Eq. (3.1) for the relaxation we obtain

$$\begin{aligned}\mathbf{\Lambda} : \frac{\delta A}{\delta\mathbf{C}} = &\frac{2}{\alpha K}\left(\frac{1}{\lambda_0}g_1(\mathbf{C}) + \frac{1}{3}\left(\frac{1}{\lambda_0} - \frac{1}{\lambda_2}\right)\right. \\ &\left.\times\left[g_2(\mathbf{C})I_1(\mathbf{C}) + g_3(\mathbf{C})\big(I_1(\mathbf{C}) - 2I_2(\mathbf{C})\big)\right]\right)\mathbf{I} \\ &+ \frac{2}{\lambda_2\alpha K}g_2(\mathbf{C})\mathbf{C} + \frac{2}{\lambda_2\alpha K}g_3(\mathbf{C})\mathbf{C}^2\end{aligned} \tag{5.6}$$

where we have used the fact that $tr\mathbf{C}^2 = I_1(\mathbf{C}) - 2I_2(\mathbf{C})$. Consider once more the case when relaxation is described via a single relaxation time, λ. In this case Eq. (5.6) reduces to

$$\begin{aligned}\mathbf{\Lambda} : \frac{\delta A}{\delta\mathbf{C}} &= \frac{2}{\lambda\alpha K}g_1(\mathbf{C})\mathbf{I} + \frac{2}{\lambda\alpha K}g_2(\mathbf{C})\mathbf{C} + \frac{2}{\lambda\alpha K}g_3(\mathbf{C})\mathbf{C}^2 \\ &= a_1(\mathbf{C})\mathbf{I} + a_2(\mathbf{C})\mathbf{C} + a_3(\mathbf{C})\mathbf{C}^2\end{aligned} \tag{5.7}$$

Eq. (5.7) is of the form (5.2) and therefore by Theorem 5.1 the physical admissibility of the model depends on the behaviour of $a_1(\mathbf{C}) = \frac{2}{\alpha K}g_1(\mathbf{C})$. Substituting our strain energy expression into Eqs. (2.22) and (2.24), the governing equation for the conformation tensor is obtained

$$\overset{\triangledown}{\mathbf{C}} + (\nabla\cdot\mathbf{u})\mathbf{C} = -\frac{1}{\lambda\alpha K}\boldsymbol{\tau}_p \tag{5.8}$$

where

$$\mathbb{T} = 2\mu_s\mathbb{D} + \kappa_s(\nabla\cdot\mathbf{u})\mathbf{I} + \boldsymbol{\tau}_p \tag{5.9}$$

$$\boldsymbol{\tau}_p = 2g_1(\mathbf{C})\mathbf{I} + 2g_2(\mathbf{C})\mathbf{C} + 2g_3(\mathbf{C})\mathbf{C}^2 \tag{5.10}$$

Due to the additional complications introduced when $g_3 \neq 0$, Eq. (5.10) cannot be simplified further (i.e. $\mathbf{C}$ cannot be eliminated). However further constraints on μ_1 and μ_2 exist in order to ensure $\boldsymbol{\tau}_p = \mathbf{0}$ when $\mathbf{C}$ is at equilibrium. Using the Cayley–Hamilton Theorem, it can be shown that the right-hand side of the dynamic equation for the conformation tensor can be written in the form

$$\mathbf{\Lambda} : \frac{\delta A}{\delta\mathbf{C}} = -\left(\alpha_0 + \alpha_2\alpha_{01}^2\right)\mathbf{I} + \left(\alpha_1 + 2\alpha_{01}\alpha_2\right)\mathbf{C} - \alpha_2\mathbf{C}^2 \tag{5.11}$$

where α_i are functions of the invariants of $\mathbf{C}$ (and also functions of $g_i(\mathbf{C})$) [4]. The parameter α_{01} is specifically chosen to be the ratio α_0/α_1 so that $\mathbf{C} = \alpha_{01}\mathbf{I}$ at equilibrium [4] i.e.

$$\overset{\triangledown}{\mathbf{C}} + (\nabla\cdot\mathbf{u})\mathbf{C} = 0 \qquad \text{when} \quad \mathbf{C} = \alpha_{01}\mathbf{I} \tag{5.12}$$

5.2. Compressible nonisothermal FENE-P-type model

Recently, a new class of models has been proposed that displays both shear-thinning and considerable extensional-hardening behaviour with the aim of reproducing computationally the levels of drag enhancement that are measured experimentally for the flow of polymeric liquids past a sphere. Garduño et al. [17] proposed a new hybrid dissipative model based on a combination of FENE and White–Metzner models. An extensional viscosity that is strain-hardening was found to be a crucial component in the modelling. The viscosity ratio was also found to be an important factor for Boger fluids. The hybrid models were termed swanINNF(q). The proposed model however, is an ad hoc model since it was developed to possess certain behaviour by modifying existing models by including additional terms. In this section models with similar rheological properties that are suitable for describing nonisothermal compressible viscoelastic fluids are derived from thermodynamic considerations using the generalized bracket formulation with a nonlinear elastic strain energy.

The resulting model is similar to the swanINNFM(q) model of Garduño et al. [17]. However, additional terms appear in the formulation as a result of being derived from the general set of Eqs. (2.20)–(2.23). Although the additional terms do not play a significant role in viscometric flows, they may become important when predicting complex flows in 2D and 3D. The FENE-P model has been particularly successful at capturing the behaviour of polymeric liquids at large deformation rates. At the microscopic level the linear spring force law for Hookean dumbbells is replaced by an asymptotically increasing force that limits the extension of the dumbbells. The approximation introduced by Peterlin [33] averages the interactions between the dumbbells so that the elasticity can be described by a single conformation tensor. The closed form expression for the elastic energy is given by

$$w(\mathbf{C}) = -\frac{nKb(T)^2}{2T}\ln\left(1 - \frac{\mathrm{tr}\mathbf{C}}{b(T)}\right) \tag{5.13}$$

where $b(T) = R(T)^2$ is the square of the maximum extension of the dumbbell, which is taken to be temperature dependent. The Helmholtz free energy is given by

$$A = \int_\Omega \left[a_0(\rho, T) - \frac{\alpha\rho Kb(T)^2}{2T}\ln\left(1 - \frac{\mathrm{tr}\mathbf{C}}{b(T)}\right) - \frac{G(T)}{2}\ln(\det\mathbf{C})\right] d\Omega \tag{5.14}$$

The last term is the expression for the Boltzmann entropy. The expressions for $\mathbf{\Lambda}$ and $\mathbf{Q}$ remain the same as in Section 3 (Eqs. (3.20) and (3.22)). Consider the following nonzero expression for the non-affine tensor, $\mathbf{L}$,

$$L_{ijkl} = \frac{\psi(\dot\epsilon)}{2}\left\{C_{ik}\delta_{jl} + C_{il}\delta_{jk} + C_{jk}\delta_{il} + C_{jl}\delta_{ik}\right\} \tag{5.15}$$

where

$$\psi(\dot\epsilon) = \frac{\phi(\dot\epsilon) - 1}{2}, \qquad \phi(\dot\epsilon) = \cosh\left(\lambda_D\dot\epsilon\right), \tag{5.16}$$

and $\dot\epsilon = 3I_3(\mathbb{D})/I_2(\mathbb{D})$ is the generalised extension rate and λ_D is a dissipation parameter. The tensor $\mathbf{L}$, associated with non-affine motion (stick/slip) within the system, is a crucial ingredient in enabling the model to capture both shear thinning and strain hardening behaviour. Through modelling in this way we are able to deduce that strain hardening effects in the fluid are the result of nonlinear interactions between the conformation tensor and velocity gradient fields. Specifically, polymer chains 'stick' with respect to the solvent around them due to polymer chain entanglement. The evolution equation for the conformation tensor is given by

$$\lambda(T)\left[\overset{\triangledown}{\mathbf{C}} + (\nabla\cdot\mathbf{u})\mathbf{C}\right] = -\left[f(\mathrm{tr}\mathbf{C})\mathbf{C} - \frac{G(\rho, T)}{\alpha\rho K(T)}\mathbf{I}\right] + \lambda(T)\psi(\dot\epsilon)[\mathbf{C}\cdot\mathbb{D} + \mathbb{D}\cdot\mathbf{C}] \tag{5.17}$$

and the expression for the extra stress is

$$\mathbb{T} = 2\mu_s(T)\mathbb{D} + \kappa'(T)(\nabla\cdot\mathbf{u})\mathbb{I} + \frac{\phi(\dot\epsilon)\mu_p(\rho, T)}{\lambda(T)}(f(\mathrm{tr}\mathbf{C})\mathbf{C} - G(\rho, T)\mathbf{I}) \tag{5.18}$$

Note that, unlike the Oldroyd-B/UCM model this expression is nonlinear in **C**. Furthermore, it should be noted that the governing equation for the conformation stress now has nonlinear dependence on the velocity gradient through ϕ. This violates the general rule proposed by Beris and Edwards [4], however (i) this is not the first time this has been done [34] and (ii) the right-hand side of Eq. (5.17) satisfies Hulsen's sufficient condition theorem. We therefore conclude that this model fits within the generalised bracket framework and satisfies thermodynamic consistency. The governing equations in terms of the solvent and polymeric contributions to the extra stress $\mathbb{T}$ are given by

$$\begin{aligned}
&\boldsymbol{\tau}_s = 2\mu_s(T)\mathbb{D} + \kappa_s'(T)(\nabla\cdot\mathbf{u})\mathbf{I}\\
&(Z + \lambda(T)(\nabla\cdot\mathbf{u}))\boldsymbol{\tau}_p + \lambda(T)\overset{\triangledown}{\boldsymbol{\tau}}_p - \lambda(T)\left(\boldsymbol{\tau}_p + G(\rho, T)\mathbf{I}\right)\frac{D\ln Z}{Dt}\\
&\quad - \lambda(T)\psi(\dot\epsilon)[\boldsymbol{\tau}_p\cdot\mathbb{D} + \mathbb{D}\cdot\boldsymbol{\tau}_p] = \phi(\dot\epsilon)\mu_p(\rho, T)\\
&\left(2(\psi(\dot\epsilon) + 1)\mathbb{D} + \left(\frac{D\ln K(T)}{Dt} - \frac{D\ln T}{Dt}\right)\mathbf{I}\right)
\end{aligned} \tag{5.19}$$

where

$$Z = 1 + \frac{3}{b(T)}\left(1 + \frac{1}{3G(\rho, T)}\mathrm{tr}\boldsymbol{\tau}_p\right)$$

where we have used Eq. (3.4) to define $\mu_p(\rho, T)$. The constitutive equations represented by Eq. (5.19) is the bracket generated equivalent of the swanINNFM(q) with FENE-P base model. The key difference between the two models is that, by using a non zero **L** tensor, the additional terms in the constitutive equation can be derived in a manner consistent with the laws of thermodynamics. Additionally, when $\lambda_D = 0$ ($\phi \equiv 1$) we recover the nonisothermal FENE-P constitutive equation. This new model is constructed to be able to capture moderate shear thinning and *strain-hardening* at high extension rates, an experimentally observed characteristic of Boger fluids [18]. Eq. (5.19) is highly nonlinear in $\boldsymbol{\tau}_p$ making analytical solutions impossible for nontrivial flow problems. Future work is needed to develop efficient numerical schemes for finding solutions to benchmark viscoelastic flow problems. However, first we will analyse rheometrical properties of Eq. (5.19).

6. Viscometric behaviour

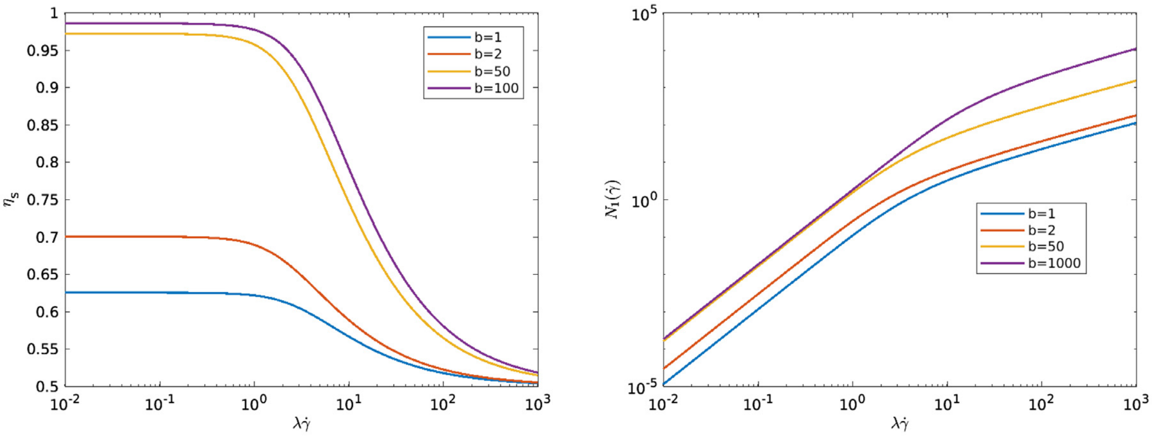
The rheological properties of constitutive models play an important role in terms of the type of behaviour that may be investigated using them. Two simple flows which provide insight into model behaviour are simple shear and uniaxial extension. The rheometric behaviour of the model with solvent viscosity fraction $\beta = \mu_0^s/\mu_0 = 0.5$ and $\lambda_0 = 1$ s is displayed in Figs. 1–3. The material parameters λ_0 and μ_0 are the relaxation time and viscosity of the fluid at the reference temperature, T_0. The quantities in the figures that follow are non-dimensionalised: shear and extensional viscosities using μ_0 and first normal stress difference using the rigidity modulus μ_0/λ_0.

For steady simple shear flow $\mathbf{u} = (u, v, w) = (\dot\gamma y, 0, 0)$ the shear viscosity and normal stress difference predictions of Eq. (5.19) are analysed. In Fig. 1 we present the shear viscosity and first normal stress difference under isothermal conditions with $T_0 = 293K$ for a range of values of the dimensionless maximum extensibility parameter b.Significant shear-thinning occurs at high shear rates particularly for large values of b. In contrast, the Oldroyd B model predicts a constant shear viscosity and a quadratic relationship between the first normal stress difference and shear-rate and a zero second normal stress difference.

The variation of viscosity with shear-rate and temperature for polymeric fluids can be described by a master curve. We use the Arrhenius model for the viscosities and relaxation time

$$\mu_p(T) = \mu_0^p k\exp(E_p/RT) \qquad \lambda(T) = \lambda_0 k\exp(E_p/RT) \tag{6.1}$$

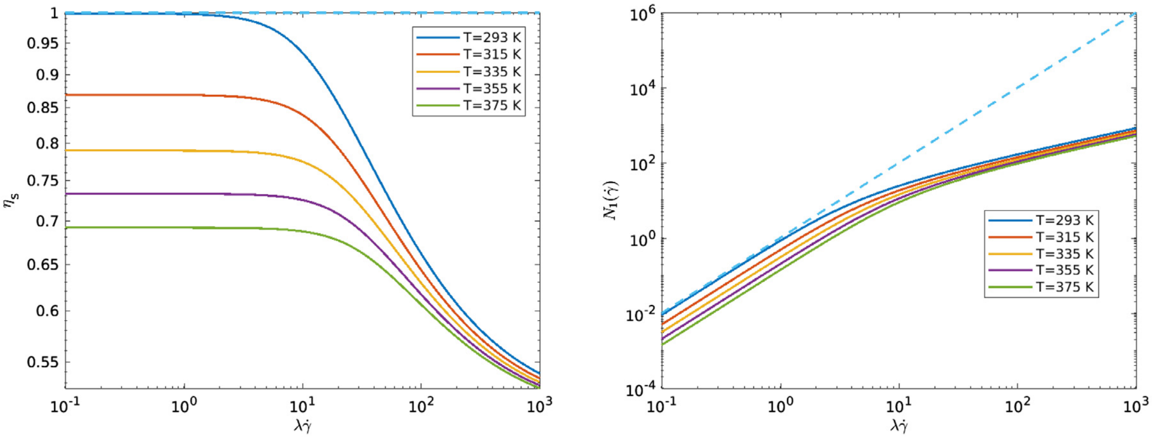
where $k = \exp(-E/RT_0)$ is a normalisation constant, R is the Boltzmann constant and E_p and E_s are the activation energies for the polymeric and solvent constituents, respectively. In Fig. 2 we present the influence of temperature on the shear properties of the model for $\beta = 0.5$, $\lambda_0 = 1$ s, $b = 50$, $E_s = 500$ J and $E_p = 5000$ J. The temperature thinning captured by Eq. (5.19) is also in qualitative agreement with experimental results in the literature on metallocene linear low density polyethylene (mLLDPE) [1].



(a)

(b)

Fig. 1. The effect of maximal chain extension, b, on (a) shear viscosity and (b) first normal stress difference for $\lambda_0 = 1$ s, $\mu_0^p/\mu_0 = 0.5$, $\mu_0^s/\mu_0 = 0.5$, $b = 50$, $E_s = 500$ J and $E_p = 5000$ J.



(a)

(b)

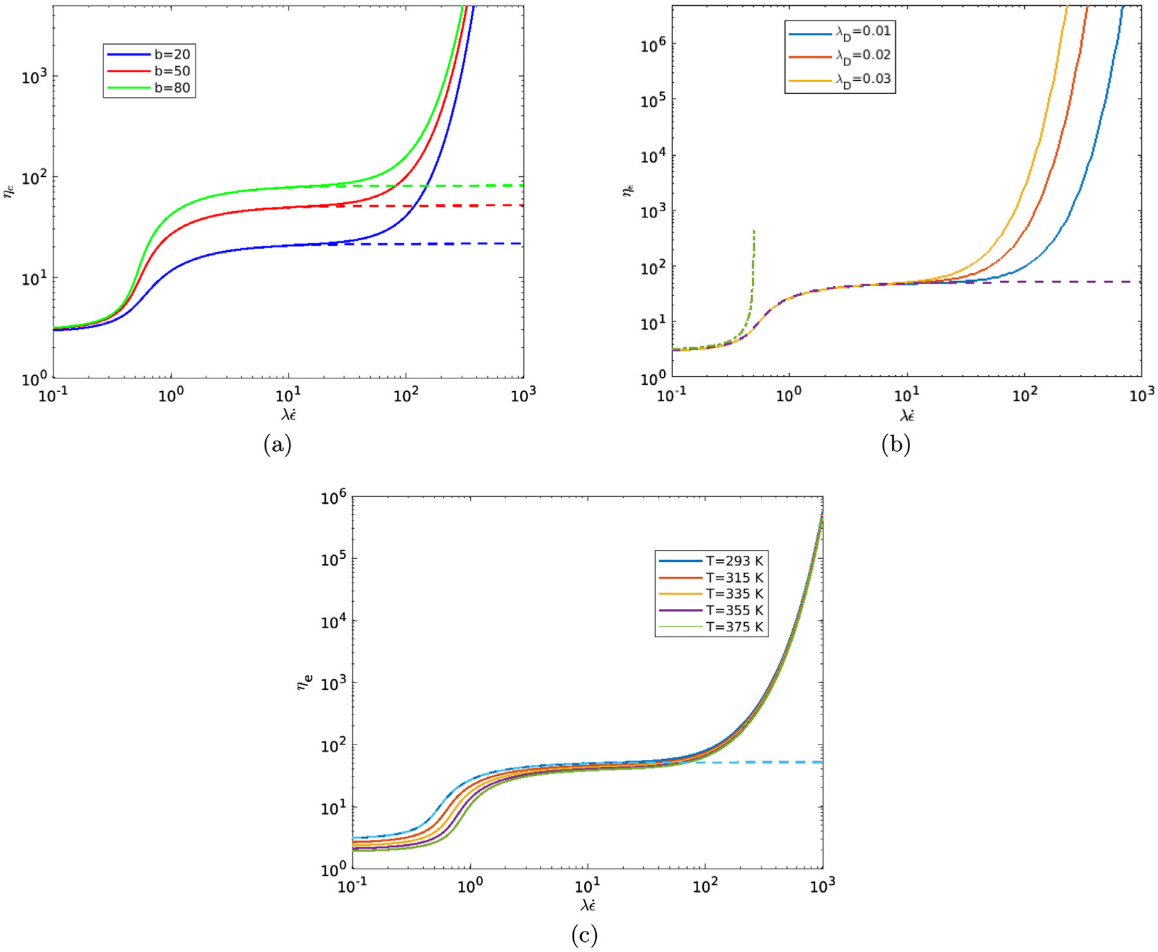
Fig. 2. The effect of temperature on (a) shear viscosity and (b) first normal stress difference; $\lambda_0 = 1$ s, $\mu_0^p/\mu_0 = 0.5$, $\mu_0^s/\mu_0 = 0.5$, $b = 50$, $E_s = 500$ J and $E_p = 5000$ J. The dashed line is the prediction of the Oldroyd B model.

For uniaxial extensional flow $\mathbf{u} = (\dot{\epsilon}x, -\frac{\dot{\epsilon}}{2}y, -\frac{\dot{\epsilon}}{2}z)$ the extensional viscosity predictions of Eq. (5.19) are analysed. In Fig. 3(a) the influence of b on the extensional viscosity of both the model given by Eq. (5.19) and the FENE-P model is presented for $\lambda_D = 0.01$. In the case of the model given by Eq. (5.19) the dissipation parameter is given by $\lambda_D = 0.01$. After an initial strain-hardening regime the extensional viscosity of the FENE-P model reaches a plateau, whereas the model given by Eq. (5.19) predicts a second strain hardening regime at high shear rates ($\lambda_1\dot{\epsilon} \geq 10^2$). The second strain hardening regime is a viscoelastic effect which is almost certainly a result of coupling between polymer molecules that, under large enough strain-rate, cause the material stiffness to increase massively. The dissipation parameter λ_D determines the onset of the second strain hardening regime (see Fig. 3(b) where $\lambda_D = 0.01, 0.02, 0.03$). In Fig. 3(c) we see that temperature thinning effects on extensional viscosity are not significant and do not lead to qualitatively different behaviour.

7. Conclusions

In this paper the generalised bracket framework for establishing models for compressible non-isothermal flow of viscoelastic fluids has been presented and discussed. In the literature a number of ad-hoc modifications to incompressible Maxwell/Oldroyd models have been proposed [5] for modelling compressible viscoelastic fluids. Many of these violate the principles of thermodynamics and therefore are of limited applicability. The generalised bracket formulation eliminates the need to derive individual conservation laws by reducing the formulation of physical variable dynamics to a single master equation from which balance laws can be derived. The principles of thermodynamics are embedded in the master equation a priori. This approach provides a strong theoretical foundation from which a large range of valid (thermodynamically consistent) viscoelastic fluid models can be derived.

A compressible form of the Oldroyd-B model is derived using the elastic strain energy for a Hookean material. Several compressible Maxwell-type viscoelastic models from the literature have been reviewed and compared to the proposed model. We have demonstrated that clear distinctions exist between Maxwell-type models derived using the generalised bracket formulation and some ad-hoc models in the literature. A compressible nonisothermal form of the FENE-P model is derived using a nonlinear strain energy related to the FENE model. The resulting model displays both shear-thinning and strain-hardening behaviour in simple shear and uniaxial extensional flows, respectively. These are phenomena associated with polymeric fluids. The derivation of a particular model requires the specification of a strain energy, entropy and phenomenological tensors such as the viscosity and relaxation



(a) (b)

(c)

Fig. 3. The effect of (a) maximal chain extension, b, (for $\lambda_D = 0.01$), (b) dissipation parameter, λ_D, (c) temperature (for $b = 50$), on extensional viscosity for $\lambda_0 = 1$ s, $\mu_0^p/\mu_0 = 0.5$, $\mu_0^s/\mu_0 = 0.5$. The dashed line is the prediction of the FENE-P model.

tensors. Consistency with the laws of thermodynamics is ensured by this approach.

The viscometric behaviour of these models has been investigated and model predictions compared with experimental data for mLLDPE [1] and numerical results for Boger fluids [17,18]. Furthermore temperature thinning captured by Eq. (5.19) is also in agreement with experimental results in the literature [1]. In the future we would like to investigate the behaviour of specific polymer solutions and melts under nonisothermal/high pressure conditions, where the general model proposed in Section 5.2 will be able to provide an accurate description of the material consistent with thermodynamics.

A limiting factor of the generalised bracket formulation is the increased mathematical complexity introduced by the fourth order phenomenological tensors such as $\mathbf{\Lambda}$ and $\mathbf{Q}$, and the energy functional w($\mathbf{C}$). As we have demonstrated in this paper, constitutive equations derived via the generalized bracket formulation can become intractable unless further assumptions are made that reduce the complexity of the governing equations. Future work will use these models to solve suitable viscoelastic benchmark problems where compressible and non-isothermal effects are important. Comparisons will be made with analytical and numerical solutions, where they exist, and experimental measurements.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jnnfm.2019.02.006.

References

[1] B. Al-Shammari, T. Al-Fariss, F. Al-Sewailm, R. Elleithy, The effect of polymer concentration and temperature on the rheological behavior of metallocene linear low density polyethylene (mLLDPE) solutions, J. King Saud University-Eng. Sci. 23 (1) (2011) 9–14.

[2] V. Arnold, Sur la géométrie différentielle des groupes de lie de dimension infinie et ses applications à l'hydrodynamique des fluides parfaits, Annales de l'institut Fourier 16 (1) (1966) 319–361.

[3] F. Belblidia, I. Keshtiban, M. Webster, Stabilised computations for viscoelastic flows under compressible implementations, J. Non-Newtonian Fluid Mech. 134 (1) (2006) 56–76.

[4] A.N. Beris, B.J. Edwards, Thermodynamics of Flowing Systems with Internal Microstructure, Oxford University Press, 1994.

[5] P.C. Bollada, T.N. Phillips, On the mathematical modelling of a compressible viscoelastic fluid, Arch. Ration. Mech. An. 205 (1) (2012) 1–26.

[6] H. Braun, A model for the thermorheological behavior of viscoelastic fluids, Rheol. Acta 30 (6) (1991) 523–529.

[7] D. Chakraborty, J.E. Sader, Constitutive models for linear compressible viscoelastic flows of simple liquids at nanometer length scales, Phys. Fluids 27 (2015) 052002.

[8] A. Clebsch, Ueber die integration der hydrodynamischen gleichungen., J. Reine Angew. Math. 56 (1) (1859) 1–10.

[9] A. Cocci Jr, J. Picot, Rate of strain effect on the thermal conductivity of a polymer liquid, Polym. Eng. Sci. 13 (5) (1973) 337–341.

[10] B.D. Coleman, W. Noll, An approximation theorem for functionals, with applications in continuum mechanics, Arch. Ration. Mech. An. 6 (1) (1960) 355–370.
[11] B.D. Coleman, W. Noll, The thermodynamics of elastic materials with heat conduction and viscosity, Arch. Ration. Mech. An. 13 (1) (1963) 167–178.
[12] M. Dressler, B.J. Edwards, H.C. Öttinger, Macroscopic thermodynamics of flowing polymeric liquids, Rheol. Acta 38 (2) (1999) 117–136.
[13] A.D. Drozdov, Finite Elasticity and Viscoelasticity: A Course in the Nonlinear Mechanics of Solids, World Scientific, 1996.
[14] I. Dzyaloshinskii, G. Volovick, Poisson brackets in condensed matter physics, Ann. Phys. 125 (1980) 67–97.
[15] B.J. Edwards, A.N. Beris, Unified view of transport phenomena based on the generalized bracket formulation, Ind. Eng. Chem. Res. 30 (5) (1991) 873–881.
[16] B.J. Edwards, A.N. Beris, The dynamics of a thermotropic liquid crystal, Eur. J. Mech B/Fluids 11 (1992) 121–142.
[17] I. Garduño, H. Tamaddon-Jahromi, M. Webster, The falling sphere problem and capturing enhanced drag with Boger fluids, J. Non-Newtonian Fluid Mech. 231 (2016) 26–48.
[18] I. Garduño, H. Tamaddon-Jahromi, M. Webster, Flow past a sphere: predicting enhanced drag with shear-thinning fluids, dissipative and constant shear-viscosity models, J. Non-Newtonian Fluid Mech. 244 (2017) 25–41.
[19] M. Grmela, Bracket formulation of dissipative fluid mechanics equations, Phys. Lett. A 102 (1984) 355–358.
[20] M. Grmela, Particle and bracket formulations of kinetic equations, Contemp. Math. 28 (1984) 125–132.
[21] M. Grmela, Hamiltonian dynamics of incompressible elastic fluids, Phys. Lett. A 130 (1988) 81–86.
[22] M. Grmela, Comment on “thermodynamics of viscoelastic fluids: the temperature equation”, J. Rheol. 42 (1998) 1565–1567.
[23] M. Grmela, GENERIC Guide to the multiscale dynamics and thermodynamics, J. Phys. Comm. 2 (3) (2018) 032001.
[24] M. Grmela, P.J. Carreau, Conformation tensor rheological models, J. Non-Newtonian Fluid Mech. 23 (1987) 271–294.
[25] M. Grmela, D. Jou, J. Casas-Vázquez, Nonlinear and Hamiltonian extended irreversible thermodynamics, J. Chem.Phys. 108 (1998) 7937–7945.
[26] A. Guaily, Temperature equation for compressible polymeric fluids, Polymer 77 (2015) 305–311.
[27] R. Gupta, A. Metzner, Modeling of nonisothermal polymer processes, J. Rheol 26 (2) (1982) 181–198.
[28] S. Gupta, J.D. Schieber, D.C. Venerus, Anisotropic thermal conduction in polymer melts in uniaxial elongation flows, J. Rheol. 57 (2) (2013) 427–439.
[29] W.R. Hamilton, The Mathematical Papers of Sir William Rowan Hamilton, CUP Archive, 2000.
[30] M.A. Hulsen, A sufficient condition for a positive definite configuration tensor in differential models, J. Non-Newtonian Fluid Mech. 38 (1) (1990) 93–100.
[31] X. Huo, W.-A. Yong, Structural stability of a 1D compressible viscoelastic fluid model, J. Differ. Equations 261 (2016) 1264–1284, doi:10.1016/j.jde.2016.03.041.
[32] A.N. Kaufman, Dissipative Hamiltonian systems: a unifying principle, Phys. Lett. A 100 (8) (1984) 419–422.
[33] R. Keunings, On the Peterlin approximation for finitely extensible dumbbells, J. Non-Newtonian Fluid Mech. 68 (1) (1997) 85–100.
[34] A. Leygue, A. Beris, R. Keunings, A constitutive equation for entangled linear polymers inspired by reptation theory and consistent with non-equilibrium thermodynamics, J. Non-Newton. Fluid 101 (1–3) (2001) 95–111.
[35] X.L. Luo, R.I. Tanner, A computer study of film blowing, Polym. Eng Sci. 25 (1985) 620–629.
[36] G. Marrucci, The free energy constitutive equation for polymer solution from the dumbbell model, Trans. Soc. Rheol. 16 (1972) 321–330.
[37] M.A. McClelland, B.A. Finlayson, Heat transfer effects in extrudate swell of elastic liquids, J. Non-Newton. Fluid 27 (1988) 363–374.
[38] P.J. Morrison, The Maxwell-Vlasov equations as a continuous Hamiltonian system, Phys. Lett. A 80 (5) (1980) 383–386.
[39] P.J. Morrison, Bracket formulation for irreversible classical fields, Phys. Lett. A 100 (8) (1984) 423–427.
[40] Q. Nguyen, X. Chen, Y. Lam, C. Yue, Effects of polymer melt compressibility on mold filling in micro-injection molding, J. Micromech. Microeng. 21 (9) (2011) 095019.
[41] G.W. Peters, Thermorheological modelling of viscoelastic materials, Fluid Mech. A. 28 (1995). 21–21
[42] J. Picot, G. Goobie, G. Mawhinney, Shear-induced anisotropy in thermal conductivity of a polyethylene melt, Polym. Eng. Sci. 22 (3) (1982) 154–157.
[43] D.J. Plazek, Temperature dependence of the viscoelastic behavior of polystyrene, J. Phys. Chem-US 69 (10) (1965) 3480–3487.
[44] R. Rivlin, Review ofthe non-linear field theories of mechanics by C. Truesdell and W. Noll, J. Acoust. Soc. Am. 40 (1966) 1213.
[45] R. Salmon, Hamiltonian fluid mechanics, Annu. Rev. Fluid Mech. 20 (1) (1988) 225–256.
[46] F. Sugeng, N.P. Thien, R.I. Tanner, A study of non-isothermal non-Newtonian extrudate swell by a mixed boundary element and finite element method, J. Rheol. 31 (1987) 37–58.
[47] H. Tautz, Bestimmung der warmeleifahigkeit von kautschukvulkanisaten in abhangigkeit von der dehnung, Exp. Tech. Phys 7 (1959) 1–14.
[48] B. Van den Brule, P. Slikkerveer, Anisotropic conduction of heat caused by molecular orientation in a flowing polymeric liquid, Rheol. Acta 29 (3) (1990) 175–181.
[49] J.M. Wiest, Time-temperature superposition in nonisothermal flow, J. Non-Newtonian Fluid 27 (1988) 127–131.
[50] K. Wilmanski, Continuum Thermodynamics, World Scientific, 2008.