THE THERMO-MECHANICS OF RATE-TYPE FLUIDS

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ABSTRACT. In this short paper a brief review is provided concerning the modeling of the thermo-mechanical response of rate type fluid models. Recently, two different approaches have been used to develop thermodynamically compatible rate type fluid models, one that assumes the Helmholtz potential and the other the Gibbs potential for the fluids. These two perspectives are complimentary, not all models that can be modeled within the first procedure can be obtained from the second one, and vice-versa. The two approaches greatly enlarge the arsenal of a modeler and most models that are used can be derived within the purview of these two approaches. More importantly, the two methodologies lead to interesting and useful new models which can be used to describe the behavior of materials that have hitherto defied proper description.

1. Introduction. Constitutive relations within the context of classical continuum mechanics that have been developed to describe the response of fluids can be broadly classified into three categories: differential type, rate type and integral type constitutive relations, based on the mathematical structure of the constitutive relations. These categories are not mutually exclusive in that a particular relation could belong to more than one category, for example one could describe a Maxwell fluid (see Maxwell [17]) either by means of a rate type relation or an integral type relation. This short survey concerns the development of thermodynamically compatible rate type fluid models. Specifically, attention is focused on two different approaches which however share a quintessential aspect in common, namely from amongst a class of admissible constitutive relations, a choice is made by demanding that the rate of entropy production be maximal. Such a requirement automatically satisfies the second law in that the rate of entropy production is non-negative. The maximization picks one amongst many rates of entropy productions that meet the second law of thermodynamics that are candidates for describing the material under consideration. In one of the approaches we start by assuming a form for the specific Helmholtz potential for the fluids while in the other approach we start by assuming a form for the specific Gibbs potential. In general, the two approaches are not equivalent; we cannot use a Legendre transformation to obtain the results for one approach from that for the other. In fact, for certain bodies, we cannot even define a specific Helmholtz potential, while a Gibbs potential can be defined, and vice-versa. While the Helmholtz potential approach leads very easily to the eponymous classical models due to Maxwell [17], Burgers [4] and Oldroyd [19], the Gibbs

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potential approach leads directly to models wherein the material moduli depend upon the stress and thus such a perspective is particularly convenient to develop models wherein the material moduli depend upon the mean normal stress\(^1\).

A simple mechanical analog suffices to show the non-equivalence of the two methodologies. Consider the physical system comprising of a linear or non-linear spring in parallel with an inextensible string, depicted in Fig. 1a), whose response relation is portrayed in Fig. 1b). For this physical system, we cannot define a specific Helmholtz potential. We also note for such a system, the stress cannot be expressed as a function of strain (to be more accurate, the force as a function of the elongation); the strain on the other hand can be expressed as a function of the stress (to be more accurate, the force as a function of the elongation). Next, consider the response relation given in Fig. 2, such a response cannot be obtained naturally within a framework that is based on a Gibbs potential approach. For the response of a material depicted in Fig. 3, one can neither define a Helmholtz potential nor a Gibbs potential.

![Figure 1. A Helmholtz potential cannot be defined for this system.](image)

At the heart of the two different perspectives are two different standpoints; whether to treat the stress or an appropriate kinematical variable as the primitive. Usually, the Gibbs potential is expressed as a function of the stress in addition to other variables such as temperature, etc., while the Helmholtz potential is assumed to be a function of appropriate kinematical quantities such as the deformation gradient, velocity gradient, or other kinematical quantities, and other variables such as the temperature. Within the context of classical Newtonian mechanics, it seems that one approach has a firmer philosophical footing than the other, for the following reason. In classical mechanics, stress is the cause, and kinematics is the effect\(^2\). Thus, it would seem that the assuming a constitutive relation for the Gibbs

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\(^1\)While the approach used by Málek and Rajagopal [15], wherein they define a Helmholtz potential for the fluid, can yield some specific models wherein the material modulus depends on the stress, such as the viscosity depending upon the pressure, the procedure used in the paper cannot lead to the general implicit models of the type developed in the paper by Rajagopal and Srinivasa [33] using the Gibbs potential.

\(^2\)While Truesdell ([37]) observes that: “A constitutive equation is a relation between forces and motions. In popular terms, force is applied to a body to “cause” it to undergo a motion, and the
potential might be the more natural way to go. However, as we have mentioned earlier, it is not even possible to unambiguously define a Gibbs potential dependent on the stress for certain physical systems. Also, within the context of classical Newtonian mechanics, while force can be considered the cause and kinematics the effect, it might not be possible to define the kinematics explicitly in terms of the force/stress, only implicit relations between the stress and kinematics being possible. What one needs is to develop a general thermodynamic potential which reduces to the Helmholtz potential or the Gibbs potential depending upon the problem on hand, but such a thermodynamic potential is not available.

motion “caused” differs according to the nature of the body. In continuum mechanics the forces of interest are contact forces, which are specified by the stress tensor $T$, he and others land up specifying constitutive relations for the stress in terms of the motion, that is the cause in terms of the effect, instead of the effect in terms of the cause, as it ought to be. Of course, the response of the material might be complicated enough wherein one can only specify a relation between the effect and the cause. There is also the possibility that one might not know which is the cause and which the effect. There is also the point of view that all one can specify are relationship between events. We cannot get into philosophical discussions here. However, specifying the cause in terms of the effect seems at variance with sound philosophy.
Our interest here is primarily in the development of rate type models to describe the viscoelastic response of fluids. However, the general procedures that are being discussed are not restricted to the development of models for viscoelastic behavior of materials. It has been used to develop models for elastic bodies (see Rajagopal and Srinivasa [32]), classical plasticity (see Rajagopal and Srinivasa [24, 25]), twinning of solids (Rajagopal and Srinivasa [23]), phase changes that include solid to solid and solid to liquid/liquid to solid phase transitions (Rajagopal and Srinivasa [26], Barot et al. [1], Heida et al. [12]), single crystal super alloys (Prasad, Rao and Rajagopal [20], Prasad and Rajagopal [21]) viscoelastic fluids (Rajagopal and Srinivasa [27, 28], Krishman and Rajagopal [14]), transition from viscoelastic fluid to viscoelastic solid (Kannan and Rajagopal [13]), fluid mixtures (Málek and Rajagopal [16]), crystallization of polymers (Rao and Rajagopal [36]), chemically reacting viscoelastic solids (Kannan and Rajagopal [13]), granular materials and capillarity (Heida and Málek [10] and Heida et al. [11]), attesting to the framework’s versatility.

2. Kinematics. Let \( \mathcal{B} \) denote the abstract body\(^3\) and let \( \kappa_R \) and \( \kappa_t \) denote the reference and current placers, respectively, of the body that locate the body in a three dimensional Euclidean Space, namely the configurations \( \kappa_R(\mathcal{B}) \) and \( \kappa_t(\mathcal{B}) \), respectively. Let \( P \in \mathcal{B} \) denote a typical material particle, and let

\[
X = \kappa_R(P), \quad x = \kappa_t(P),
\]

(1)

denote the same material point \( P \) in the reference and current configurations. By the motion of the body we mean a mapping \( \chi_{\kappa_R} : \mathcal{B} \times \mathbb{R} \rightarrow \mathcal{E} \) such that

\[
x = \chi_{\kappa_R}(X, t)
\]

(2)
denotes the position of the particle in the current configuration corresponding to the point \( X \) in the reference configuration, at time \( t \). We shall assume that the motion is invertible and so

\[
X = \chi_{\kappa_R}^{-1}(x, t).
\]

(3)

We shall also assume that the motion is sufficiently smooth to make all the derivatives that we take to be meaningful. Thus any scalar, vector or tensor function defined over the abstract body and time can be expressed as

\[
\phi = \hat{\phi}(P, t) = \hat{\phi}(X, t) = \phi(x, t).
\]

(4)

\(^3\)We shall not concern ourselves with a rigorous definition of what is meant by a body, placer, configuration, etc. The notion of a body, placer, etc., are not the main object of this discourse, and the precision in the definition of these notions is not germane to what is being discussed. It is sufficient for our purpose to think of a body as a set of points that is endowed with a measure and a topology. In addition to the usual mathematical description of a body that can be found in books such as Truesdell [37], we shall see later that to meaningfully define what is meant by a body that captures the physical necessities of being a body one needs to know the various natural configurations that the body is capable of being in. That is, it is not sufficient to merely endow a set of “particles” with properties such as mass, etc; one must also know the class of configurations that are “natural” to the body in that these are configurations that the body can exist in when there are no external stimuli to the body; that is we need to know the “natural configurations” associated with this abstract set of particles. We shall discuss this issue later. It is also worth remarking that the classical notion of a body does not seem to be well suited to describe several important problems that arise in natural philosophy wherein one seems to need a set that is without points that is endowed with a topology and a measure. That is, we need to develop the notion of topology associated with bodies that do not have points (which has been done), and more importantly the calculus that goes with it.
We shall use the following notation to express the various derivatives that we shall use:
\[
\dot{\phi} = \frac{d\phi}{dt}, \quad \frac{\partial\phi}{\partial t}, \quad \frac{\partial\phi}{\partial X}, \quad \frac{\partial\phi}{\partial x} = \frac{\partial\dot{\phi}}{\partial t}, \quad \frac{\partial\dot{\phi}}{\partial X}, \quad \text{and} \quad \frac{\partial\dot{\phi}}{\partial x} = \frac{\partial\ddot{\phi}}{\partial x}. \tag{5}
\]

We denote the displacement \( u \) through
\[
u = x - X. \tag{6}
\]

The deformation gradient \( F_{\kappa R} \) is defined through
\[
F_{\kappa R} = \frac{\partial X_{\kappa R}}{\partial X}. \tag{7}
\]

The displacement gradients \( \frac{\partial u}{\partial X} \) and \( \frac{\partial u}{\partial x} \) are related to the deformation gradient through
\[
\frac{\partial u}{\partial X} = F_{\kappa R} - I, \tag{8}
\]
and
\[
\frac{\partial u}{\partial x} = I - F_{\kappa R}^{-1}. \tag{9}
\]

The velocity is defined through
\[
v = \frac{\partial X_{\kappa R}}{\partial t}, \tag{10}
\]
the velocity gradient \( L \), and its symmetric part \( D \) and its skew part \( W \) through
\[
L = \frac{\partial v}{\partial x}, \quad D = \frac{1}{2} (L + L^T), \quad W = \frac{1}{2} (L - L^T). \tag{11}
\]

The Cauchy-Green stretch tensors \( B_{\kappa R} \) and \( C_{\kappa R} \) are defined through
\[
B_{\kappa R} := F_{\kappa R} F_{\kappa R}^T, \quad C_{\kappa R} := F_{\kappa R}^T F_{\kappa R}. \tag{12}
\]

The Green-St.Venant strain \( E \) and the Almansi-Hamel strain \( e \) are defined through
\[
E := \frac{1}{2} (C_{\kappa R} - I), \quad e := \frac{1}{2} (I - B_{\kappa R}). \tag{13}
\]

Figure 4 provides a depiction of the reference configuration, the current configuration and the natural configuration that is associated with the current configuration. Given the process class of interest, we shall assume that there is a unique natural configuration associated with the current configuration. We define the gradient of the mapping from the natural configuration (see Fig. 4) to the current configuration through
\[
F_{\kappa p(t)} := \frac{\partial X}{\partial X_{\kappa p(t)}}. \tag{14}
\]

The tensor \( G \), which is not necessarily the gradient of a function, is defined through
\[
G := F_{\kappa R} F_{\kappa p(t)}^{-1}. \tag{15}
\]

\(^4\)We shall follow the usual definition for the deformation gradient (see Truesdell and Noll [38]). However, there are some philosophical problems with regard to the usual definition that uses the reference configuration as merely a surrogate for the abstract body rather than requiring that the reference configuration is a configuration actually taken by the body.

\(^5\)Various measures of deformation have been introduced, e.g. by Cauchy [5], Green [8] and Finger [7]. See Truesdell [37]. Also, the Cauchy-Green stretch tensors that have been defined are the square of the stretch tensors that appear in the Polar Decomposition of the deformation gradient rather than stretch tensors.
In analogy to $\mathbf{L}$, we introduce $\mathbf{L}_{\kappa_p(t)}$ through

$$
\mathbf{L}_{\kappa_p(t)} := \dot{\mathbf{G}}^{-1}.
$$

(16)

We can define the tensors $\mathbf{B}_{\kappa_p(t)}$ and $\mathbf{C}_{\kappa_p(t)}$ through

$$
\mathbf{B}_{\kappa_p(t)} = \mathbf{F}_{\kappa_p(t)} \mathbf{F}^T_{\kappa_p(t)}, \quad \mathbf{C}_{\kappa_p(t)} = \mathbf{F}^T_{\kappa_p(t)} \mathbf{F}_{\kappa_p(t)}.
$$

(17)

Finally, we define the tensor $\mathbf{C}_{\kappa_R \rightarrow \kappa_p(t)}$ through

$$
\mathbf{C}_{\kappa_R \rightarrow \kappa_p(t)} := \mathbf{G}^T \mathbf{G}.
$$

(18)

It can then be shown (see Rajagopal and Srinivasa [27]) that

$$
\frac{\partial \rho_{\kappa_t}}{\partial t} + \text{div}(\rho_{\kappa_t} \mathbf{v}) = 0,
$$

(23)

where $\rho_{\kappa_t}$ denotes the density in the configuration $\kappa_t$.

**Balance of Mass:** The balance of mass takes the form

$$
\rho_{\kappa_t} \frac{d \mathbf{v}}{dt} = \text{div} \mathbf{T}_{\kappa_t} + \rho_{\kappa_t} \mathbf{b}_{\kappa_t},
$$

(24)

where $\mathbf{T}_{\kappa_t}$ is the Cauchy stress and $\mathbf{b}_{\kappa_t}$ the specific body force.
Balance of Angular Momentum: In the absence of body couples, the balance of angular momentum implies that the Cauchy stress is symmetric, i.e.,

$$T_{\kappa i} = T_{\kappa i}^T.$$ (25)

Balance of Energy: The local form of the balance of energy is

$$\rho_{\kappa t} \frac{d \varepsilon_{\kappa t}}{dt} = T_{\kappa i} \cdot L - \rho_{\kappa t} \nabla \theta_{\kappa t} + \rho_{\kappa t} r_{\kappa t},$$ (26)

where $\varepsilon_{\kappa t}$ is the specific internal energy, $q_{\kappa t}$ the heat flux vector, and $r_{\kappa t}$ is the specific radiant heating.

Finally, we document the second law of thermodynamics in a slightly unconventional form. The second law is a statement to the effect that the rate of entropy production of a body is non-negative. We follow Green and Naghdi [9] and Rajagopal and Srinivasa [27] and express the second law as

$$\rho_{\kappa t} \frac{d \eta_{\kappa t}}{dt} + \nabla \left( \frac{q_{\kappa t}}{\theta_{\kappa t}} \right) - \rho_{\kappa t} r_{\kappa t} := \rho_{\kappa t} \xi_{\kappa t} \geq 0,$$ (27)

where $\eta_{\kappa t}$ is the specific entropy, $\theta_{\kappa t}$ the temperature, and $\xi_{\kappa t}$ is the rate of entropy production. One of the main points of departure as to how the second law is usually interpreted in continuum thermodynamics, namely an identification with the Clausius-Duhem inequality, is our providing a constitutive relation for the rate of entropy production $\xi_{\kappa t}$ in a form that is automatically non-negative.

3. Reduced Dissipation Equation. We shall now proceed to document the reduced dissipation equation. Before doing so, we shall make the following observation concerning the second law stated in equation (27). The terms on the left hand side of equation (27) denote the rate at which entropy is produced in various ways and we express this as the product of the density and the specific rate of entropy production $\xi_{\kappa t}$, which has to be non-negative.

On combining the above form for the second law and the energy equation, we arrive at the reduced entropy equation

$$T_{\kappa i} \cdot L - \rho_{\kappa t} \frac{d \varepsilon_{\kappa t}}{dt} - \rho_{\kappa t} \theta_{\kappa t} \frac{d \eta_{\kappa t}}{dt} - \frac{q_{\kappa t}}{\theta_{\kappa t}} \cdot \nabla \theta_{\kappa t} = \rho_{\kappa t} \theta_{\kappa t} \xi_{\kappa t} := \zeta_{\kappa t} \geq 0.$$ (28)

Since we shall be interested in purely mechanical issues, the temperature being assumed to be uniform in the body, the reduced dissipation equation is further reduced to

$$T_{\kappa t} \cdot L - \rho_{\kappa t} \frac{d \psi_{\kappa t}}{dt} = \zeta_{\kappa t} \geq 0,$$ (29)

where $\psi_{\kappa t}$ is the Helmholtz potential given by

$$\psi_{\kappa t} = \varepsilon_{\kappa t} - \theta_{\kappa t} \eta_{\kappa t}.$$ (30)

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6 Within a purely mechanical context, the only manner in which entropy is produced is due to conversion of mechanical working into heat, i.e., dissipation. In general entropy can be produced due to conduction, mixing, phase change, growth, chemical reactions, etc.
4. Helmholtz Potential approach to obtain rate type models. We shall now discuss the general thermodynamic framework that appeals to the maximization of the rate of entropy production wherein, amongst other quantities, an assumption is made for the constitutive relations for the rate of entropy production and the specific Helmholtz potential. As observed in the introduction, this procedure will not deliver many of the useful models that are currently used. For instance, this procedure is not the natural methodology to develop constitutive relations wherein the material moduli depend on the stress. In order to illustrate the procedure, we shall discuss the work of Rajagopal and Srinivasa [27] wherein they developed models for describing the viscoelastic response of fluids.

A key notion in the development of the thermodynamic framework is the notion of natural configuration and its evolution during the process. The evolution of the natural configuration is intimately related to the manner in which entropy is produced. We can view the natural configuration as the configuration that the body would attain on the removal of the external stimuli that the body is subject to (see Rajagopal [22] for a detailed discussion of the notion of natural configuration). Many entropy producing processes such as those exhibited by inelastic and viscoelastic bodies can be viewed as a class of responses from an evolving set of natural configurations. However, it is possible to have entropy producing processes without the natural configuration changing. Also, one can associate a single natural configuration, as in the case of elasticity, or a finite number of natural configurations such as in bodies that twin or undergo solid-to-solid phase transition, or infinite number of natural configurations as in the case of the classical Navier-Stokes fluid or many viscoelastic fluids, etc. (see Rajagopal and Srinivasa [29, 30] for a detailed discussion of the same).

We shall illustrate our ideas by discussing the response of rate type viscoelastic fluids (see Rajagopal and Srinivasa [27]). We shall consider the class of fluids that possess the ability of instantaneous elastic response, and which are usually described by implicit constitutive relations. Models due to Maxwell [17], Burgers [4], and Oldroyd [19] belong to the class of such bodies. We shall interpret such bodies within the context of bodies that exhibit elastic response from a class of evolving natural configurations. Thus, such fluid bodies are not described by the single constitutive response function but by defining a family of response functions. That one needs a family of response functions to describe such bodies becomes clear when one recognizes that such bodies are defined through constitutive relations that are differential equations; depending on what initial condition is to be enforced, one would have a different constitutive relation. Within the context of bodies with evolving natural configurations, different initial conditions are associated with the response starting from different natural configurations.

The viscoelastic fluid models that are developed within the framework of evolving natural configurations lends itself most aptly to interpretation of energy storage and energy dissipation (entropy production) mechanisms. Such a viewpoint, within the context of one-dimensional response, is amenable to interpretation as mechanical-spring-dashpot systems (see Bland [3], Ferry (1980) [6], Wineman and Rajagopal [35]) that are very popular.

We shall consider the modeling within a purely mechanical context. The mechanism for the storage of energy is captured by the specific Helmholtz free energy
of the body and as we are within a purely mechanical framework, the entropy production is purely due to dissipation, that is, the conversion of working into energy in thermal form, i.e., heat.

As we mentioned earlier, the manner in which the natural configuration of the body evolves and how the thermodynamic process proceeds is determined by the nature of the rate of entropy production; in the case under consideration the rate of dissipation. We assume that from amongst the class of admissible constitutive relations, that which is selected is that in which the rate of dissipation is maximized. Of course, it is necessary that any constraint such as incompressibility or inextensibility has to be met in addition, and we shall also require that the second law stated in the form (29) is also met. Thus, we need to maximize the auxiliary function

\[ \Phi := \zeta_{\kappa_t} + \lambda_1 \left( \zeta_{\kappa_t} - T_{\kappa_t} \cdot D + \rho_{\kappa_t} \frac{d\psi_{\kappa_t}}{dt} \right) + \lambda_2 (\text{tr } D) \]  

as we are interested in modeling incompressible fluids that are only capable of isochoric motions, i.e.,

\[ \text{tr } D = 0. \]  

We shall assume that the Helmholtz potential for the fluid is given by

\[ \psi_{\kappa_t} = \psi_{\kappa_t}(F_{\kappa_p(t)}), \]  

that is, it is that for an elastic body whose reference configuration is the natural configuration \( \kappa_p(t)(\mathcal{B}) \). Frame-indifference\(^7\) and isotropy then imply that

\[ \psi_{\kappa_t} = \hat{\psi}_{\kappa_t}(I_1, I_2, I_3), \]  

where

\[ I_1 = \text{tr } B_{\kappa_p(t)}, \quad I_2 = \text{tr } (B_{\kappa_p(t)}^2), \quad I_3 = \det B_{\kappa_p(t)}. \]  

As we are interested in incompressible bodies, (34) reduces to

\[ \psi_{\kappa_t} = \hat{\psi}_{\kappa_t}(I_1, I_2). \]

We shall assume that the rate of dissipation \( \zeta \) is given by

\[ \zeta_{\kappa_t} = \zeta_{\kappa_t}(B_{\kappa_p(t)}, D_{\kappa_p(t)}). \]  

To illustrate our ideas, we make the following specific choices for \( \psi_{\kappa_t} \) and \( \zeta_{\kappa_t} \):

\[ \rho_{\kappa_t} \psi_{\kappa_t} = \frac{\mu}{2} (I_1 - 3), \]  

\[ \zeta_{\kappa_t} = \eta D_{\kappa_p(t)} \cdot B_{\kappa_p(t)} D_{\kappa_p(t)}, \]  

where \( \mu \) and \( \eta \) are positive constants.

On maximizing the auxiliary function, with the above special choices for the Helmholtz potential and the rate of dissipation, one obtains (see Rajagopal and Srinivasa [27])

\[ T_{\kappa_t} = -p I + \mu B_{\kappa_p(t)}, \]  

\[ -\frac{1}{2} B_{\kappa_p(t)} = \frac{\mu}{\eta} \left[ B_{\kappa_p(t)} - \frac{3}{\text{tr } (B_{\kappa_p(t)}^{-1})} I \right]. \]

\(^7\)In the case of purely elastic response, the result which follows does not need the requirement of frame-indifference; merely requiring Galilean invariance suffices. Even in the case of viscous fluids and viscoelastic fluids capable of instantaneous elasticity, the balance of angular momentum and Galilean invariance suffice (see Rajagopal and Srinivasa [34]).
The equation (41) describes how the natural configuration evolves, and the equation (38) tells us that the elastic response from the natural configuration is that of a neo-Hookean material. The above is in keeping with a spring-dashpot analog wherein one has a non-linear neo-Hookean spring to which a viscous dashpot is attached.

A straightforward calculation yields (see Rajagopal and Srinivasa [27])

$$T_{\kappa t} = -pI + M_{\kappa t}, \quad (42)$$

$$M_{\kappa t} + \lambda \nabla M_{\kappa t} = 2\hat{\mu}D, \quad (43)$$

where

$$\hat{\mu} = \frac{3\lambda}{\text{tr}(M_{\kappa t})}, \quad \lambda = \frac{\eta}{2\mu}. \quad (44)$$

The system (42) – (44) represents a generalization of the classical Maxwell model.

By making appropriate choices for the specific Helmholtz potential and the rate of dissipation one can obtain numerous rate type non-Newtonian fluid models such as the Oldroyd-B model, Burgers model, etc. It is worth noting that if one identifies the tensor $B_{\kappa p(t)}$ with the conformation tensor $c$ (see Beris and Edwards [2]), then one can obtain all the models obtained using the conformation tensor approach (see Rajagopal and Srinivasa [28] for a more detailed discussion of the same). In fact, the approach presented here has clear physical underpinnings as $B_{\kappa p(t)}$ is clearly a identifiable kinematical quantity. On the other hand the conformation tensor $c$ is not a kinematical quantity and in the case of the constraint of incompressibility there is no clear indication how this is to be enforced within the context of the conformation tensor approach.

It is also worth observing that one can model the response of anisotropic fluids within the context of the above framework (see Rajagopal and Srinivasa [28] for details).

5. Gibbs potential approach for obtaining rate type models. We now turn our attention to a discussion of the development of rate type fluid models by making an assumption for the Gibbs’ potential, the rate of entropy production, and other relevant quantities. As we shall see, this approach allows us to develop models wherein the material parameters in the constitutive relation depend on the stress and also models that have a threshold with respect to their response, like that of an yield condition, that depends on the stress.

As indicated in the introduction, not all models that are currently in use, that have proved helpful in describing the response of viscoelastic fluids, can be cast within the framework using a Helmholtz potential approach outlined earlier. For describing the response of fluids whose material properties depend on the invariants of the stress, say the mean value of the stress (for instance mechanical pressure in an incompressible fluid), it would be natural to start with a Gibbs potential. Rate type models due to Giesekus, Phan-Thien and Tanner, White and Metzner, and others can be developed within such a construct.

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8 According to the theory of Simple Fluids (Noll [18]), a simple fluid cannot be anisotropic. Thus, materials such as liquid crystals cannot be described by models belonging to the class of simple fluids.

9 As mentioned earlier, one can not always obtain models based on the Gibbs potential approach by starting with a Helmholtz potential and using a Legendre transformation. An example of the same is provided by the system shown in Fig. 1.
An important advantage to the Gibbs potential approach is that it is fully Eulerian and thus very well suited to numerical and computational methods. The use of stress as a primitive rather than kinematics is also more in keeping with causality.

In this section, as we shall be working with terms only referred to in the current configuration, we shall for the ease of notation omit the suffix $\kappa$. We now start by assuming a constitutive relation for the Gibbs potential $G$ as a function of stress through

$$G = G(S), \quad S = \frac{T}{\rho},$$

and the rate of dissipation $\zeta$ through

$$\zeta = \zeta(S, \rho, D).$$

The equation for the rate of entropy production takes the form

$$\rho \theta \frac{d}{dt} \left( \frac{\partial G}{\partial \theta} \right) = \rho r - \text{div} \ q + \zeta.$$

In the case of isotropic materials, it can be shown that (see Rajagopal and Srinivasa [33] for details)

$$D = -\frac{\partial^2 G}{\partial S^2} \left[ \dot{S} - WS + SW \right] + \lambda \frac{\partial \zeta}{\partial S}, \quad \lambda := \frac{\zeta}{S}, \frac{\partial \zeta}{\partial S},$$

where $D$ and $W$ are the symmetric and skew-symmetric parts of velocity gradient.

It turns out the constraints such as incompressibility can be handled very easily within the context of this approach. Let $\tau$ denote the deviatoric part of $S$. Then, for isotropic incompressible viscoelastic fluids, one can show that the constitutive relations take the form (see Rajagopal and Srinivasa [33] for the details)

$$D = -\frac{\partial^2 G}{\partial \tau^2} \left[ \dot{\tau} - W\tau + \tau W \right] + \lambda \frac{\partial \zeta}{\partial \tau}, \quad \lambda := \frac{\zeta}{\tau}, \frac{\partial \zeta}{\partial \tau},$$

where $G$ and $\zeta$ are now expressed as functions of $\tau$.

One can also handle the modeling of anisotropic viscoelastic fluids in a straightforward manner within the context of the Gibbs potential approach In the case of compressible anisotropic viscoelastic bodies, $G$ and $\zeta$ are assumed to depend on $\dot{S} := RSR^T$, where $R$ is the rotation tensor, instead of $S$. It can be shown (see Rajagopal and Srinivasa [33] for details) that the constitutive relations take the form

$$D = -C \left[ \dot{S} - \Omega S + S\Omega \right] + \lambda R \frac{\partial \zeta}{\partial S} R^T, \quad \lambda := \frac{\zeta}{S}, \frac{\partial \zeta}{\partial S},$$

where $G$ and $\zeta$ are now expressed as functions of $\tau$.

Rajagopal and Srinivasa [33] show that the models due to Phan-Thien, Metzner, White and Denn and Giesekus can be obtained in a very straightforward manner using the above approach by making very simple choices for $G$ and $\zeta$. We shall not get into a detailed discussion of the methodology of generating specific models, suffice it is to say that by making appropriate choices for $G$ and $\zeta$ one can develop a whole host of new models that could prove to be useful.
Final Remarks. Since the two approaches, assuming the Helmholtz potential and the rate of entropy production, and assuming the Gibbs potential and the rate of entropy production, are not equivalent, the two approaches can be used together to generate new and useful models to describe the response of both isotropic and anisotropic viscoelastic fluids.

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