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Second Gradient Viscoelastic Fluids: Dissipation Principle and Free Energies

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Keywords	Non-simple fluid – Viscoelasticity – Free energy – Thermodynamic constraints – Mechanical power
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Footnotes

Second gradient viscoelastic fluids: dissipation principle and free energies

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the minimal state are proposed. Derivations of various formulae are abbreviated if closely analogous proofs already exist in the literature.

Keywords Non-simple fluid · Viscoelasticity · Free energy · Thermodynamic constraints · Mechanical power

1 Introduction

In this work we consider new constitutive equations for incompressible second order fluids, which include memory effects. These are materials for which the stress tensor is a function of the history of $\mathbf{D}$ and $\nabla \cdot \nabla \mathbf{D}$, where $\mathbf{D} = \frac{\nabla \mathbf{v} + (\nabla \mathbf{v})^T}{2}$ is the strain rate tensor and $\mathbf{v}$ the velocity. It is the presence of the quantity $\nabla \cdot \nabla \mathbf{D}$ ($= \Delta \mathbf{D}$, where Δ is the Laplacian) which renders the material non-local or non-simple. The classical laws of thermodynamics must be modified for such materials either by introducing suitable extra fluxes, or directly, by expressing these laws in terms of internal powers, characteristic of the material under consideration [13]. For the first method, there is the problem that the vector fluxes are introduced *a posteriori*, in order that compatibility with the laws of thermodynamics is maintained. The second formulation, in terms of internal powers, is more general than the first, since it is defined *a priori* by means of the constitutive equations, taking into account the power balance laws. In this article we use the second method.

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The assumed constitutive equation includes thermal and viscoelastic effects in the expression for the stress tensor. We firstly discuss the laws of thermodynamics and use the equations of motion of the fluid to determine an expression for the internal mechanical power. Also, thermodynamic constraints on the constitutive equation are derived. Then, some free energy functionals are generalized to apply to this new material. This includes a functional of the minimal state introduced in [7, 10] and an explicit formula for the minimum free energy.

The layout of the paper is as follows. In Sect. 2, the constitutive equation with memory effects is presented and an expression for the internal mechanical power is derived. Moreover, the concepts of a free energy and of the corresponding internal dissipation rate are introduced. Thermodynamic constraints on the constitutive equation are also given. In Sect. 3, some free energies, already introduced for simple viscoelastic materials, are adapted to our non-simple fluid and their related internal dissipation rates are also deduced. The required properties of free energies in this new context are discussed.

Various steps in the derivations are omitted or abbreviated when they are closely analogous to developments in [3] (also [4]) for non-simple heat conductors.

2 Basic equations

For an incompressible second order fluid without memory, the stress tensor $\mathbf{T}$ is given by [14]

$$\mathbf{T} = -p\mathbf{I} + 2\mu\mathbf{D} - \kappa\nabla \cdot \nabla\mathbf{D} \quad (2.1)$$

where p is the scalar function known as the reaction pressure, μ and κ are two positive constants, while $\mathbf{I}$ is the identity second order tensor.

In this work we generalize (2.1), by assuming that the incompressible fluid, which is isotropic and homogeneous, exhibits both viscoelastic and thermal effects. The following constitutive equation is adopted:

$$\begin{aligned} \mathbf{T}(t) = & -p(t)\mathbf{I} + 2 \int_0^{+\infty} \mu(s)\mathbf{D}^t(s) ds \\ & - \int_0^{+\infty} \kappa(s)[\nabla \cdot \nabla\mathbf{D}^t(s)] ds \\ & + \alpha[\vartheta(t) - \vartheta_0]\mathbf{I}, \end{aligned} \quad (2.2)$$

where ϑ denotes the absolute temperature and ϑ_0 is a fixed ambient absolute temperature, while μ and κ are

smooth functions which belong to $L^1(\mathbf{R}^+) \cap H^1(\mathbf{R}^+)$. It is assumed that the motions are infinitesimal so that second order terms in $\mathbf{v}$ or $\mathbf{D}$ are neglected.

We consider this relation at a specific point $\mathbf{x} \in \Omega$, which is the domain occupied by the fluid. For brevity, however, the space dependence of the fields is henceforth generally omitted.

Let

$$\mathbf{E}(t) = \frac{\nabla\mathbf{u}(t) + [\nabla\mathbf{u}(t)]^\top}{2} \quad (2.3)$$

be the infinitesimal strain tensor at time t , where $\mathbf{u}$ is the displacement vector. Then

$$\mathbf{D}(t) = \frac{d}{dt}\mathbf{E}(t) = \dot{\mathbf{E}}(t). \quad (2.4)$$

Also, let $\mathbf{E}^t(s) = \frac{\nabla\mathbf{u}^t(s) + [\nabla\mathbf{u}^t(s)]^\top}{2}$ be the infinitesimal strain history where

$$\begin{aligned} \frac{d}{dt}\mathbf{E}^t(s) &= \dot{\mathbf{E}}^t(s) = \mathbf{D}^t(s), \\ \frac{d}{ds}\mathbf{E}^t(s) &= -\frac{d}{dt}\mathbf{E}^t(s) = -\mathbf{D}^t(s). \end{aligned} \quad (2.5)$$

We define the relative history as

$$\mathbf{E}_r^t(s) = \mathbf{E}^t(s) - \mathbf{E}(t). \quad (2.6)$$

The dependence of the stress tensor on $\mathbf{D}^t$ and $\nabla \cdot \nabla\mathbf{D}^t$ in (2.2) can be expressed in terms of $\mathbf{E}_r^t(s)$ and $\nabla \cdot \nabla\mathbf{E}_r^t(s)$, since we have

$$\begin{aligned} \int_0^{+\infty} \mu(s)\mathbf{D}^t(s) ds &= - \int_0^{+\infty} \mu(s) \frac{d}{ds}\mathbf{E}^t(s) ds \\ &= - \int_0^{+\infty} \mu(s) \frac{d}{ds}\mathbf{E}_r^t(s) ds \\ &= \int_0^{+\infty} \mu'(s)\mathbf{E}_r^t(s) ds \end{aligned} \quad (2.7)$$

and, analogously,

$$\begin{aligned} \int_0^{+\infty} \kappa(s)\nabla \cdot \nabla\mathbf{D}^t(s) ds \\ = \int_0^{+\infty} \kappa'(s)\nabla \cdot \nabla\mathbf{E}_r^t(s) ds. \end{aligned} \quad (2.8)$$

Thus, we can write (2.2) as follows:

$$\begin{aligned} \mathbf{T}(t) = & \{-p(t) + \alpha[\vartheta(t) - \vartheta_0]\}\mathbf{I} \\ & + 2 \int_0^{+\infty} \mu'(s)\mathbf{E}_r^t(s) ds \\ & - \int_0^{+\infty} \kappa'(s)\nabla \cdot \nabla\mathbf{E}_r^t(s) ds. \end{aligned} \quad (2.9)$$

The extra stress tensor has the form

$$\tilde{\mathbf{T}}(t) = 2 \int_0^{+\infty} \mu'(s) \mathbf{E}_r^t(s) ds - \int_0^{+\infty} \kappa'(s) \nabla \cdot \nabla \mathbf{E}_r^t(s) ds. \quad (2.10)$$

2.1 Thermodynamics

For a mechanical system, we have in general that

$$\frac{d}{dt} T(t) + \mathcal{P}_m^i(t) = \mathcal{P}_m^e(t), \quad (2.11)$$

where $T(t)$ is the kinetic energy, while $\mathcal{P}_m^i(t)$ and $\mathcal{P}_m^e(t)$ denote the internal and external mechanical power per unit volume of the system, respectively. In the case of a simple fluid, $\mathcal{P}_m^i(t) = \mathbf{T}(t) \cdot \mathbf{D}(t)$. Equation (2.11) is an expression of the balance of power.

For non-simple materials the first law assumes the form

$$\rho \dot{e}(t) = \rho h(t) + \mathcal{P}_m^i(t), \quad (2.12)$$

where e is the internal energy and h is the specific internal heat power, defined as the rate at which heat is absorbed per unit mass. *The heat balance law*

$$\rho h = -\nabla \cdot \mathbf{q} + \rho r, \quad (2.13)$$

relates h to the heat supply r and the heat flux $\mathbf{q}$. The Fourier relation,

$$\mathbf{q} = -k_0 \nabla \vartheta, \quad k_0 > 0, \quad (2.14)$$

will be adopted. The second law yields the existence of the entropy function η with the property that

$$\rho \dot{\eta} \geq -\nabla \cdot \left(\frac{\mathbf{q}}{\vartheta} \right) + \rho \frac{r}{\vartheta}, \quad (2.15)$$

whence it follows that

$$\rho \dot{\eta} \geq \rho \frac{h}{\vartheta} - \frac{k_0}{\vartheta^2} |\nabla \vartheta|^2. \quad (2.16)$$

Introducing the free energy $\psi = e - \vartheta \eta$, we can write this as

$$\dot{\psi} \leq -\eta \dot{\vartheta} + \frac{1}{\rho} \mathcal{P}_m^i + \frac{k_0}{\rho \vartheta} |\nabla \vartheta|^2, \quad (2.17)$$

where (2.12) has been used.

The equation of motion for the material has the form

$$\rho \dot{\mathbf{v}} = \nabla \cdot \mathbf{T} + \rho \mathbf{f}, \quad (2.18)$$

where $\mathbf{f}$ denotes the body forces. In order to derive an expression for $\mathcal{P}_m^i$, we multiply this relation by $\mathbf{v}$ to obtain

$$\rho \frac{d}{dt} \left(\frac{1}{2} \mathbf{v}^2 \right) = (\nabla \cdot \mathbf{T}) \cdot \mathbf{v} + \rho \mathbf{f} \cdot \mathbf{v}, \quad (2.19)$$

where, taking into account (2.9) and the incompressibility condition $\nabla \cdot \mathbf{v} = 0$,

$$\begin{aligned} (\nabla \cdot \mathbf{T}) \cdot \mathbf{v} &= -\mathbf{T} \cdot \nabla \mathbf{v} + \nabla \cdot (\mathbf{T} \mathbf{v}) \\ &= -2 \int_0^{+\infty} \mu'(s) \mathbf{E}_r^t(s) \cdot \nabla \mathbf{v}(t) ds \\ &\quad - \int_0^{+\infty} \kappa'(s) \nabla \mathbf{E}_r^t(s) \cdot \nabla \nabla \mathbf{v}(t) ds \\ &\quad + \nabla \cdot \left(\left[-p + \alpha(\vartheta(t) - \vartheta_0) \right] \mathbf{I} \right. \\ &\quad \left. + 2 \int_0^{+\infty} \mu'(s) \mathbf{E}_r^t(s) ds \right. \\ &\quad \left. - \int_0^{+\infty} \kappa'(s) \nabla \cdot \nabla \mathbf{E}_r^t(s) ds \right) \mathbf{v} \\ &\quad + \int_0^{+\infty} \kappa'(s) \nabla \mathbf{E}_r^t(s) ds \nabla \mathbf{v}(t). \end{aligned}$$

Therefore, the equation of power balance is given by

$$\begin{aligned} \rho \frac{d}{dt} \left(\frac{1}{2} \mathbf{v}^2 \right) &+ 2 \int_0^{+\infty} \mu'(s) \mathbf{E}_r^t(s) \cdot \nabla \mathbf{v}(t) ds \\ &+ \int_0^{+\infty} \kappa'(s) \nabla \mathbf{E}_r^t(s) \cdot \nabla \nabla \mathbf{v}(t) ds \\ &= \nabla \cdot \left(\left[-p + \alpha(\vartheta(t) - \vartheta_0) \right] \mathbf{I} \right. \\ &\quad \left. + 2 \int_0^{+\infty} \mu'(s) \mathbf{E}_r^t(s) ds \right. \\ &\quad \left. - \int_0^{+\infty} \kappa'(s) \nabla \cdot \nabla \mathbf{E}_r^t(s) ds \right) \mathbf{v}(t) \\ &\quad + \int_0^{+\infty} \kappa'(s) \nabla \mathbf{E}_r^t(s) ds \nabla \mathbf{v}(t) + \rho \mathbf{f} \cdot \mathbf{v}. \quad (2.20) \end{aligned}$$

We deduce from (2.11) that the internal power is expressed by

$$\begin{aligned} \mathcal{P}_m^i(t) &= 2 \int_0^{+\infty} \mu'(s) \mathbf{E}_r^t(s) \cdot \nabla \mathbf{v}(t) ds \\ &\quad + \int_0^{+\infty} \kappa'(s) \nabla \mathbf{E}_r^t(s) \cdot \nabla \nabla \mathbf{v}(t) ds \\ &= 2 \int_0^{+\infty} \mu(s) \dot{\mathbf{E}}^t(s) \cdot \dot{\mathbf{E}}(t) ds \\ &\quad + \int_0^{+\infty} \kappa(s) \nabla \dot{\mathbf{E}}^t(s) \cdot \nabla \dot{\mathbf{E}}(t) ds. \quad (2.21) \end{aligned}$$

The last form follows from (2.4), (2.5)₁, (2.7) and (2.8). The external power is given by the quantity at the right-hand side of (2.20), since the divergence term can be expressed as a surface contribution and the body force is clearly external.

To characterize the behaviour of our fluid, we introduce the state

$$\sigma^T(t) = (\vartheta, \sigma(t)) = (\vartheta, \mathbf{E}_r^t(s), \nabla \mathbf{E}_r^t(s)), \quad (2.22)$$

and the process P^T given by a piecewise continuous map defined as

$$P^T(\tau) = (\dot{\vartheta}_P, P) \\ = (\dot{\vartheta}_P, \dot{\mathbf{E}}_P(\tau), \nabla \dot{\mathbf{E}}_P(\tau)) \quad \forall \tau \in [0, d], \quad (2.23)$$

where d , which generally has a finite value, denotes the duration of the process.

More details on this abstract terminology, which is used below to a limited extent, may be found in [13], for example.

Now, we seek a free energy ψ having the form

$$\psi(\sigma^T(t)) = \psi_1(\vartheta) + \psi_2(\mathbf{E}_r^t(s), \nabla \mathbf{E}_r^t(s)), \quad (2.24)$$

expressed as the sum of $\psi_1(\vartheta)$, a temperature dependent function, and $\psi_2(\mathbf{E}_r^t(s), \nabla \mathbf{E}_r^t(s))$, a functional of $(\mathbf{E}_r^t(s), \nabla \mathbf{E}_r^t(s))$.

Substituting into (2.17), we obtain

$$\left[\frac{\partial \psi_1(\vartheta)}{\partial \vartheta} + \eta \right] \dot{\vartheta} + \dot{\psi}_2(\mathbf{E}_r^t(s), \nabla \mathbf{E}_r^t(s)) \\ \leq \frac{1}{\rho} \mathcal{P}_m^i + \frac{k_0}{\rho \vartheta} |\nabla \vartheta|^2. \quad (2.25)$$

The final term on the right is non-negative. This inequality, taking account of (2.21), is satisfied if

$$\eta = -\frac{\partial \psi_1(\vartheta)}{\partial \vartheta}, \\ \dot{\psi}_2(\mathbf{E}_r^t(s), \nabla \mathbf{E}_r^t(s)) \\ \leq \frac{1}{\rho} \left[2 \int_0^{+\infty} \mu'(s) \mathbf{E}_r^t(s) \cdot \dot{\mathbf{E}}(t) ds \right. \\ \left. + \int_0^{+\infty} \kappa'(s) \nabla \mathbf{E}_r^t(s) \cdot \nabla \dot{\mathbf{E}}(t) ds \right]. \quad (2.26)$$

The inequality (2.26)₂ is an expression of the second law for the mechanical aspect of the problem. Taking account of the incompressibility of the fluid, we can absorb the density into the kernels and write this relation as

$$\dot{\psi}_2(\mathbf{E}_r^t(s), \nabla \mathbf{E}_r^t(s)) \leq \mathcal{A}(\sigma, P), \quad (2.27)$$

where

$$\mathcal{A}(t) = \mathcal{A}(\sigma, P) = \frac{1}{\rho} \mathcal{P}_m^i(t) \\ = 2 \int_0^{+\infty} \mu'(s) \mathbf{E}_r^t(s) ds \cdot \dot{\mathbf{E}}(t) \\ + \int_0^{+\infty} \kappa'(s) \nabla \mathbf{E}_r^t(s) ds \cdot \nabla \dot{\mathbf{E}}(t) \\ = 2 \int_0^{+\infty} \mu(s) \dot{\mathbf{E}}^t(s) \cdot \dot{\mathbf{E}}(t) ds \\ + \int_0^{+\infty} \kappa(s) \nabla \dot{\mathbf{E}}^t(s) \cdot \nabla \dot{\mathbf{E}}(t) ds \\ = 2 \int_{-\infty}^t \mu(t-u) \dot{\mathbf{E}}(u) du \cdot \dot{\mathbf{E}}(t) \\ + \int_{-\infty}^t \kappa(t-u) \nabla \dot{\mathbf{E}}(u) du \cdot \nabla \dot{\mathbf{E}}(t), \quad (2.28)$$

with the aid of (2.5)–(2.8) and a change of integration variables. This quantity, which is the internal mechanical power per unit mass, is analogous to what was termed the entropy action in [3] and generalizes the work function which is central to the discussion of simple materials.

By introducing $D_2(\mathbf{x}, t)$, a non-negative function referred to as the *internal dissipation rate*, we can transform the inequality (2.27) into an equality

$$\dot{\psi}_2(t) + D_2(t) = \mathcal{A}(t). \quad (2.29)$$

The non-negativity of D_2 in (2.29) is in effect a statement of the second law for the mechanical aspect of the problem.

Recalling (2.6), we see that $\mathbf{E}_r^t(s)$ and $\nabla \mathbf{E}_r^t(s)$ depend on the histories $\mathbf{E}^t(s)$, $\nabla \mathbf{E}^t(s)$ and current values $\mathbf{E}(t)$ and $\nabla \mathbf{E}(t)$. Thus,

$$\psi_2(t) = \tilde{\psi}(\mathbf{E}^t(s), \nabla \mathbf{E}^t(s), \mathbf{E}(t), \nabla \mathbf{E}(t)) \quad (2.30)$$

which is a functional of the histories and a function of the current values.

The quantity $\mathcal{A}(t)$ allows us to derive the *total mechanical work per unit mass* $\mathcal{B}(\sigma, P)$ done on the material during the application of a process P of duration d ,

$$\mathcal{B}(\sigma, P) = \int_t^{t+d} \mathcal{A}(\xi) d\xi. \quad (2.31)$$

A consequence of the second law is expressed by the following principle.

Referring to (2.22), we define the state $\sigma(t)$ for the mechanical aspect as

$$\sigma(t) = (\mathbf{E}_r^t(s), \nabla \mathbf{E}_r^t(s)), \quad (2.32)$$

while $P(\tau) = (\dot{\mathbf{E}}_P(\tau), \nabla \dot{\mathbf{E}}_P(\tau))$. Let us denote by Σ and Π the sets of states and processes, which are admissible for the body. For any initial state $\sigma_i \in \Sigma$ and any process $P \in \Pi$, the state transition function $\hat{\rho}$ provides the final state $\sigma_f = \hat{\rho}(\sigma_i, P) \in \Sigma$. Moreover, let $P_\tau \in \Pi$ be any restriction of P to a subset $[0, \tau) \subset [0, d)$, with duration $\tau < d$. So, we have $\sigma(t) = \hat{\rho}(\sigma_0, P_t)$. A *cycle* is defined as any pair (σ, P) for which $\hat{\rho}(\sigma, P) = \sigma$.

Dissipation principle. On any cycle (σ, P) we have

$$\mathcal{B}(\sigma, P) \geq 0, \quad (2.33)$$

in which the equality sign occurs if and only if the cycle is reversible.

We define the total mechanical work per unit mass done on the material up to time t as

$$\mathcal{B}(t) = \int_{-\infty}^t \mathcal{A}(u) du, \quad (2.34)$$

where it is assumed that the infinite integral exists. Substituting the last form of $\mathcal{A}$, given by (2.28), into (2.34), we obtain, after integrations by parts, change of variables and other standard manipulations,

$$\begin{aligned} \mathcal{B}(t) = & \int_0^{+\infty} \int_0^{+\infty} \mu_{12}(|u-s|) \mathbf{E}_r^t(s) \cdot \mathbf{E}_r^t(u) ds du \\ & + \frac{1}{2} \int_0^{+\infty} \int_0^{+\infty} \kappa_{12}(|u-s|) \nabla \mathbf{E}_r^t(s) \\ & \cdot \nabla \mathbf{E}_r^t(u) ds du, \end{aligned} \quad (2.35)$$

where

$$\begin{aligned} \mu_{12}(|u-s|) &= \frac{\partial^2}{\partial u \partial s} \mu(|u-s|), \\ \kappa_{12}(|u-s|) &= \frac{\partial^2}{\partial u \partial s} \kappa(|u-s|). \end{aligned} \quad (2.36)$$

2.2 Thermodynamic restrictions

The dissipation principle imposes thermodynamic restrictions on the constitutive equation (2.2). This can be demonstrated by combining (2.28)₃ and (2.31) with periodic histories of period $d = 2\pi/|\omega|$, for $\dot{\mathbf{E}}$ and $\nabla \dot{\mathbf{E}}$ given by

$$\begin{aligned} \dot{\mathbf{E}}(s) &= \cos \omega s \mathbf{c}_1 + \sin \omega s \mathbf{c}_2, \\ \nabla \dot{\mathbf{E}}(s) &= \cos \omega s \mathbf{C}_1 + \sin \omega s \mathbf{C}_2 \end{aligned} \quad (2.37)$$

where $\omega \in \mathbf{R} \setminus \{0\}$ and $\mathbf{c}_i, \mathbf{C}_i$ ($i = 1, 2$) are arbitrary non-zero second and third order tensors, respectively, depending only of $\mathbf{x}$. Following the steps outlined in [3], we deduce that

$$\mu_c(\omega) > 0, \quad \kappa_c(\omega) > 0 \quad \forall \omega \in \mathbf{R}. \quad (2.38)$$

These in fact require the extra assumptions

$$\begin{aligned} \mu_c(0) &= \int_0^{+\infty} \mu(s) ds \neq 0, \\ \kappa_c(0) &= \int_0^{+\infty} \kappa(s) ds \neq 0. \end{aligned} \quad (2.39)$$

Let

$$\mathbf{D}^t(s) = \dot{\mathbf{E}} \quad \forall s \in \mathbf{R}^+,$$

be a constant (in time) history. Then (2.2) yields

$$\begin{aligned} \tilde{\mathbf{T}}(t) &= \mathbf{T}(t) + \{p - \alpha[\vartheta(t) - \vartheta_0]\} \mathbf{I} \\ &= 2\mu_\infty^{(1)} \dot{\mathbf{E}} - \kappa_\infty^{(1)} \nabla \cdot \nabla \dot{\mathbf{E}}, \end{aligned}$$

where $\tilde{\mathbf{T}}$ is the extra stress tensor for constant histories and

$$\mu_\infty^{(1)} = \mu_c(0) > 0, \quad \kappa_\infty^{(1)} = \kappa_c(0) > 0 \quad (2.40)$$

by virtue of (2.38) and (2.39).

3 Free energies

We now consider some possible expressions for the part of the free energy $\psi_2(t) = \psi_2(\mathbf{E}_r^t, \nabla \mathbf{E}_r^t)$ introduced in (2.24). Our aim here is to adapt to non-simple fluids several classical functionals already introduced for simple linear viscoelastic solids and later modified to apply to simple fluids [1, 2].

For a simple fluid, any free energy has the well-known property that

$$\frac{\partial}{\partial \mathbf{E}(t)} \psi_2(t) = \tilde{\mathbf{T}}(t) \quad (3.1)$$

where $\tilde{\mathbf{T}}(t)$ is the extra stress defined by the first term on the right of (2.10). We will see that this does not hold for non-simple materials. Instead, a generalized version of this relation holds, which will be determined below.

3.1 The Gaffi–Volterra free energy

We firstly consider the important functional, frequently used in applications, known as the Gaffi–Volterra free energy [19, 20, 22]. A generalization of this functional to our non-simple fluid is given by

$$\begin{aligned} \psi_{\mathcal{G}}(t) = & - \int_0^{+\infty} \mu'(s) \mathbf{E}_r^t(s) \cdot \mathbf{E}_r^t(s) ds \\ & - \frac{1}{2} \int_0^{+\infty} \kappa'(s) \nabla \mathbf{E}_r^t(s) \cdot \nabla \mathbf{E}_r^t(s) ds. \end{aligned} \quad (3.2)$$

This is a free energy if the conditions

$$\begin{aligned} \mu'(s) &< 0, & \kappa'(s) &< 0, \\ \mu''(s) &\geq 0, & \kappa''(s) &\geq 0 \quad \forall s \in \mathbf{R}^+, \end{aligned} \quad (3.3)$$

are satisfied. The first two relations yield that $\psi_{\mathcal{G}}$ is positive, while the remaining relations are required to ensure a non-negative rate of dissipation related to this quantity. Indeed, differentiating $\psi_{\mathcal{G}}$ and integrating by parts, we can show, with the aid of (2.28)₂ and (2.29) that

$$\begin{aligned} D_{\mathcal{G}}(t) = & \int_0^{+\infty} \mu''(s) [\mathbf{E}_r^t(s)]^2 ds \\ & + \frac{1}{2} \int_0^{+\infty} \kappa''(s) [\nabla \mathbf{E}_r^t(s)]^2 ds \geq 0 \end{aligned} \quad (3.4)$$

can be identified as the internal dissipation rate.

Note that, by virtue of (2.6),

$$\frac{\partial}{\partial \mathbf{E}(t)} \psi_{\mathcal{G}}(t) = 2 \int_0^{+\infty} \mu'(s) \mathbf{E}_r^t(s) ds \quad (3.5)$$

and (3.1) does not hold. Instead, we have

$$\frac{\partial}{\partial \nabla \mathbf{E}(t)} \psi_{\mathcal{G}}(t) = \int_0^{+\infty} \kappa'(s) \nabla \mathbf{E}_r^t(s) ds \quad (3.6)$$

and the extra stress tensor (2.10) obeys the relation

$$\begin{aligned} \tilde{\mathbf{T}}(t) = & \frac{\partial}{\partial \mathbf{E}(t)} \psi_{\mathcal{G}}(t) - \nabla \cdot \frac{\partial}{\partial \nabla \mathbf{E}(t)} \psi_{\mathcal{G}}(t) \\ = & \frac{\delta}{\delta \mathbf{E}(t)} \psi_{\mathcal{G}}(t), \end{aligned} \quad (3.7)$$

which is a variational derivative, in the sense of the Calculus of Variations, for a function of $(\mathbf{E}(t), \nabla \mathbf{E}(t))$.

A relation exactly analogous to this form applies to all the free energy functionals considered in this work, and indeed to any free energy for any second order material.

3.2 Conditions for a free energy

We can generalize the Gaffi conditions [11, 19, 20] for a free energy in the light of (3.7). The properties listed below will apply to all free energies for all second gradient materials, not just those discussed here.

P1 The first condition will be taken to be (3.7), replacing (3.1), or for a general free energy,

$$\begin{aligned} \tilde{\mathbf{T}}(t) = & \frac{\partial}{\partial \mathbf{E}(t)} \psi(t) - \nabla \cdot \frac{\partial}{\partial \nabla \mathbf{E}(t)} \psi(t) \\ = & \frac{\delta}{\delta \mathbf{E}(t)} \psi(t), \end{aligned} \quad (3.8)$$

which is a variational derivative with respect to the dependence of ψ on the fields $(\mathbf{E}(t), \nabla \mathbf{E}(t))$ at the current time. For linear constitutive relations such as (2.10), conditions analogous to (3.5) and (3.6) hold, which yield (3.8).

P2 Let $\mathbf{E}^\dagger$ be a static history equal to $\mathbf{E}(t)$ at the current and all past times. Then

$$\psi(\mathbf{E}^\dagger, \nabla \mathbf{E}^\dagger, \mathbf{E}(t), \nabla \mathbf{E}(t)) = \phi(\mathbf{E}(t), \nabla \mathbf{E}(t)), \quad (3.9)$$

where $\phi(\mathbf{E}(t), \nabla \mathbf{E}(t))$ is the equilibrium free energy. This is in fact a definition of ϕ , included here for completeness. It vanishes for the free energies relating to the material under discussion.

P3 For any history and current value $(\mathbf{E}^\dagger, \nabla \mathbf{E}^\dagger, \mathbf{E}(t), \nabla \mathbf{E}(t))$,

$$\psi(\mathbf{E}^\dagger, \nabla \mathbf{E}^\dagger, \mathbf{E}(t), \nabla \mathbf{E}(t)) \geq \phi(\mathbf{E}(t), \nabla \mathbf{E}(t)). \quad (3.10)$$

P4 Condition (2.29) holds or, omitting subscripts,

$$\dot{\psi}(t) + D(t) = \mathcal{A}(t), \quad D(t) \geq 0, \quad (3.11)$$

where $D(t)$ is the rate of internal dissipation. The form of $\mathcal{A}(t)$ will depend on the material. The first relation is a statement of the first law, while the non-negativity of $D(t)$ is in effect the second law.

3.3 Dill's free energy

The Dill functional [9] can be generalized to the form

$$\begin{aligned} \psi_{Dill}(t) = & \int_0^{+\infty} \int_0^{+\infty} \mu''(\xi_1 + \xi_2) \mathbf{E}_r^t(\xi_1) \\ & \cdot \mathbf{E}_r^t(\xi_2) d\xi_1 d\xi_2 \\ & + \frac{1}{2} \int_0^{+\infty} \int_0^{+\infty} \kappa''(\xi_1 + \xi_2) \nabla \mathbf{E}_r^t(\xi_1) \\ & \cdot \nabla \mathbf{E}_r^t(\xi_2) d\xi_1 d\xi_2. \end{aligned} \quad (3.12)$$

Differentiating this with respect to time, as for the Graffi-Volterra case, we find, after standard manipulations ([3], for example) and using (3.11), that the associated rate of dissipation is given by

$$\begin{aligned} D_{Dill}(t) = & - \int_0^{+\infty} \int_0^{+\infty} \mu'(\xi_1 + \xi_2) \dot{\mathbf{E}}^t(\xi_1) \\ & \cdot \dot{\mathbf{E}}^t(\xi_2) d\xi_1 d\xi_2 \\ & - \int_0^{+\infty} \int_0^{+\infty} \kappa'(\xi_1 + \xi_2) \nabla \dot{\mathbf{E}}^t(\xi_1) \\ & \cdot \nabla \dot{\mathbf{E}}^t(\xi_2) d\xi_1 d\xi_2. \end{aligned} \quad (3.13)$$

Both of these functionals are non-negative for all histories if μ' and κ' are strictly monotonic, as defined in [6].

One can show that the equivalent of (3.5) and (3.6) are true for ψ_{Dill} , from which it follows that relation (3.8) holds.

3.4 A free energy in terms of the minimal state

A free energy $\psi_{\mathcal{F}}$, recently introduced and considered, in particular, in [10] and [7] for viscoelastic solids, can be adapted to our fluid.

Two different histories $(\mathbf{E}_{1r}^0, \nabla \mathbf{E}_{1r}^0)$ and $(\mathbf{E}_{2r}^0, \nabla \mathbf{E}_{2r}^0)$ up to time $t = 0$, which coincide after this time, are in the same minimal state if they produce the same stress function for $t \geq 0$. This terminology was introduced in [11] where references to the earlier development of the underlying ideas are given. The categories of materials for which non-trivial examples of such states can arise are discussed in [7]. A simple generalization of arguments in these and other references (*e.g.* [1, 2]) yields that the quantities

$$\begin{aligned} \mathbf{I}^t(\tau, \mathbf{E}_r^t) &= 2 \int_0^{+\infty} \mu'(\tau + \eta) \mathbf{E}_r^t(\eta) d\eta, \\ \mathcal{J}^t(\tau, \nabla \mathbf{E}_r^t) &= \int_0^{+\infty} \kappa'(\tau + \eta) \nabla \mathbf{E}_r^t(\eta) d\eta, \end{aligned} \quad (3.14)$$

have the same values for different histories in the same minimal state, in other words are functionals of the minimal state. Consider the following functional

$$\begin{aligned} \psi_{\mathcal{F}}(t) = & -\frac{1}{4} \int_0^{+\infty} \frac{1}{\mu'(\tau)} |\mathbf{I}_{(1)}^t(\tau, \mathbf{E}_r^t)|^2 d\tau \\ & - \frac{1}{2} \int_0^{+\infty} \frac{1}{\kappa'(\tau)} |\mathcal{J}_{(1)}^t(\tau, \nabla \mathbf{E}_r^t)|^2 d\tau, \end{aligned} \quad (3.15)$$

where $\mathbf{I}_{(1)}^t$ and $\mathcal{J}_{(1)}^t$ are the derivatives with respect to τ of $\mathbf{I}^t$ and $\mathcal{J}^t$, giving

$$\begin{aligned} \mathbf{I}_{(1)}^t(\tau, \mathbf{E}_r^t) &= \frac{d}{d\tau} \mathbf{I}^t(\tau, \mathbf{E}_r^t) \\ &= 2 \int_0^{+\infty} \mu''(\tau + \eta) \mathbf{E}_r^t(\eta) d\eta, \\ \mathcal{J}_{(1)}^t(\tau, \nabla \mathbf{E}_r^t) &= \frac{d}{d\tau} \mathcal{J}^t(\tau, \nabla \mathbf{E}_r^t) \\ &= \int_0^{+\infty} \kappa''(\tau + \eta) \nabla \mathbf{E}_r^t(\eta) d\eta. \end{aligned} \quad (3.16)$$

The absolute value squared notation in (3.15) indicates scalar products of $\mathbf{I}_{(1)}^t$ and $\mathcal{J}_{(1)}^t$ with themselves in the appropriate vector spaces. Under the hypotheses (3.3), this functional is a free energy. Note that

$$\begin{aligned} \mathbf{I}^t(0, \mathbf{E}_r^t) &= 2 \int_0^{+\infty} \mu'(\eta) \mathbf{E}_r^t(\eta) d\eta, \\ \mathcal{J}^t(0, \nabla \mathbf{E}_r^t) &= \int_0^{+\infty} \kappa'(\eta) \nabla \mathbf{E}_r^t(\eta) d\eta \end{aligned} \quad (3.17)$$

and

$$\begin{aligned} \mathbf{I}_{(1)}^t(0, \mathbf{E}_r^t) &= 2 \int_0^{+\infty} \mu''(\eta) \mathbf{E}_r^t(\eta) d\eta, \\ \mathcal{J}_{(1)}^t(0, \nabla \mathbf{E}_r^t) &= \int_0^{+\infty} \kappa''(\eta) \nabla \mathbf{E}_r^t(\eta) d\eta. \end{aligned} \quad (3.18)$$

Use of (3.17) and (2.28)₂ gives that $\psi_{\mathcal{F}}(t)$ obeys (3.11) where the associated rate of dissipation has the form

$$\begin{aligned} D_{\mathcal{F}}(t) = & \frac{1}{4} \int_0^{+\infty} \frac{\mu''(\tau)}{[\mu'(\tau)]^2} |\mathbf{I}_{(1)}^t(\tau, \mathbf{E}_r^t)|^2 d\tau \\ & - \frac{1}{4\mu'(0)} |\mathbf{I}_{(1)}^t(0, \mathbf{E}_r^t)|^2 \\ & + \frac{1}{2} \int_0^{+\infty} \frac{\kappa''(\tau)}{[\kappa'(\tau)]^2} |\mathcal{J}_{(1)}^t(\tau, \nabla \mathbf{E}_r^t)|^2 d\tau \\ & - \frac{1}{2\kappa'(0)} |\mathcal{J}_{(1)}^t(0, \nabla \mathbf{E}_r^t)|^2 \geq 0, \end{aligned} \quad (3.19)$$

because of the hypotheses (3.3).

The functional $\psi_{\mathcal{F}}$ is manifestly a functional of the minimal state. This is not a necessary requirement for a free energy (and in particular is not true for $\psi_{\mathcal{G}}$ given by (3.2)) though it is an attractive property from a theoretical viewpoint. The Dill free energy and the minimum free energy, derived in the next section, both have this property.

The equivalent of (3.5) and (3.6) for $\psi_{\mathcal{F}}$ can be obtained within the manipulations leading to (3.19). These then imply that relation (3.8) holds.

3.5 The minimum free energy

The form of the minimum free energy for second gradient incompressible viscoelastic fluids of the kind under discussion can be derived by generalizing one of the direct methods outlined in [8, 11, 16] or [1, 2, 15], which was done in [3]. However, we shall adopt a simpler approach here, namely by using a precise analogy between the present theory and that for a simple material.

The core observation is that an explicit formula for the minimum free energy can be derived by exactly the same formalism for materials described on different vector spaces, provided that the work function has the same general structure in each case. Thus, we have the theory developed in [8] for a simple material with independent and dependent field variables in Sym and relaxation tensors in $Lin(Sym)$, while in [12, 18], non-isothermal theories were developed on more general vector spaces. However, the procedures and results are precisely analogous for these materials. In particular they all depend on the factorization of a positive definite tensor which arises in the work function. The level of practical difficulty associated with carrying out this factorization will of course depend on the details of the material.

For a second gradient incompressible viscoelastic fluid, the underlying vector space is $\Gamma = Sym \times (Sym \times \mathbf{R})$ associated with states $\sigma(t) = (\mathbf{E}_r^t, \nabla \mathbf{E}_r^t)$. Referring to (2.6), we introduce the compact notation

$$\begin{aligned} \mathbb{C}(t) &= (\mathbf{E}(t), \nabla \mathbf{E}(t)) \in \Gamma, \\ \mathbb{C}_r^t(s) &= (\mathbf{E}_r^t(s), \nabla \mathbf{E}_r^t(s)) = \mathbb{C}^t(s) - \mathbb{C}(t) \in \Gamma. \end{aligned} \quad (3.20)$$

The quantity $\mathcal{B}(t)$, given by (2.35), can be written in the form

$$\mathcal{B}(t) = \frac{1}{2} \int_0^\infty \int_0^\infty \mathbb{L}_{12}(|u-s|) \mathbb{C}_r^t(s) \cdot \mathbb{C}_r^t(u) du ds, \quad (3.21)$$

where $\mathbb{L} \in Lin(\Gamma)$ is the diagonal tensor

$$\mathbb{L}(s) = 2\mu(s)\mathbb{P}_S + \kappa(s)\mathbb{P}_{SR}, \quad (3.22)$$

where the quantities $\mathbb{P}_S, \mathbb{P}_{SR} \in Lin(\Gamma)$ are real orthogonal projectors on Sym and $Sym \times \mathbf{R}$, respectively. The quantity $\mathcal{B}(t)$ corresponds to the work function for simple materials and crucially for our purposes, has exactly the same general form. Using the convolution theorem and Parseval's formula, we can write it in terms of the frequency domain quantities, as follows:

$$\mathcal{B}(t) = \frac{1}{2\pi} \int_{-\infty}^\infty \mathbb{H}(\omega) \mathbb{C}_{r+}^t(\omega) \cdot \overline{\mathbb{C}_{r+}^t(\omega)} d\omega, \quad (3.23)$$

where $\mathbb{C}_{r+}^t(\omega)$ is the Fourier transform of $\mathbb{C}_r^t(s)$, defined by (4.2)₂, while $\overline{\mathbb{C}_{r+}^t(\omega)}$ is its complex conjugate. The tensor $\mathbb{H} \in Lin(\Gamma)$ is given by

$$\begin{aligned} \mathbb{H}(\omega) &= -\omega \mathbb{L}'_s(\omega) \\ &= 2\omega^2 \mu_c(\omega) \mathbb{P}_S + \omega^2 \kappa_c(\omega) \mathbb{P}_{SR} \geq 0, \end{aligned} \quad (3.24)$$

where (4.4) has been used.

Therefore, for purposes of deriving the form of the minimum free energy, the only difference relating to non-simple materials is that they are described on a larger vector space. Indeed, the same is true for any other free energy. Such a formulation is being developed in the context of a general theory of non-simple materials and the free energies associated with them [5]. It emerges from this work that the free energies discussed here are special (diagonal) cases of more general formulae.

Because of the thermodynamic constraints (2.38), the scalar functions $\mu_c(\omega)$ and $\kappa_c(\omega)$ in (3.24) can be factorized [16] to give

$$\begin{aligned} \mu_c(\omega) &= \mu_+(\omega) \mu_-(\omega), \\ \kappa_c(\omega) &= \kappa_+(\omega) \kappa_-(\omega), \end{aligned} \quad (3.25)$$

where $\mu_+(\omega)$ and $\kappa_+(\omega)$ are analytic in $\mathbf{C}^-$ while $\mu_-(\omega)$ and $\kappa_-(\omega)$ are analytic in $\mathbf{C}^+$. Therefore

$$\begin{aligned} \mathbb{H}(\omega) &= \mathbb{H}_+(\omega) \mathbb{H}_-(\omega) \\ &= [H_{\mu+}(\omega) \mathbb{P}_S + H_{\kappa+}(\omega) \mathbb{P}_{SR}] \\ &\quad \times [(H_{\mu-}(\omega) \mathbb{P}_S + H_{\kappa-}(\omega) \mathbb{P}_{SR})], \end{aligned} \quad (3.26)$$

$$H_{\mu\pm}(\omega) = \sqrt{2}\omega\mu_{\pm}(\omega), \quad H_{\kappa\pm}(\omega) = \omega\kappa_{\pm}(\omega),$$

which gives the required factorization of $\mathbb{H}$ for the present diagonal case. The general non-diagonal case is discussed in [5].

The derivation of the form of the minimum free energy proceeds exactly as described in earlier papers, for example [8, 11, 16]. We simply present the results here. The Plemelj formulae [21] give that

$$\begin{aligned} \mathbb{H}_-(\omega) \mathbb{C}_{r+}^t(\omega) &= \mathbf{p}_-^t(\omega) - \mathbf{p}_+^t(\omega), \\ \mathbf{p}_\pm^t(\omega) &= \frac{1}{2\pi i} \int_{-\infty}^\infty \frac{\mathbb{H}_-(\omega') \mathbb{C}_{r+}^t(\omega')}{\omega' - \omega^\mp} d\omega', \end{aligned} \quad (3.27)$$

where $\omega^\mp = \lim_{\alpha \rightarrow 0^+} (\omega + i\alpha)$ and the limit is understood to take place after the integration has been carried out. The form of the minimum free energy is

$$\begin{aligned}\psi_m(t) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} |\mathbf{p}_{\mu-}^t(\omega)|^2 d\omega \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} |p_{\mu-}^t(\omega)|^2 d\omega \\ &\quad + \frac{1}{2\pi} \int_{-\infty}^{\infty} |p_{\kappa-}^t(\omega)|^2 d\omega,\end{aligned}\quad (3.28)$$

$$\begin{aligned}p_{\mu-}^t(\omega) &= \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{H_{\mu-}(\omega') \mathbf{E}_{\mu+}^t(\omega')}{\omega' - \omega^+} d\omega', \\ p_{\kappa-}^t(\omega) &= \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{H_{\kappa-}(\omega') \nabla \mathbf{E}_{\mu+}^t(\omega')}{\omega' - \omega^+} d\omega' .\end{aligned}$$

The second form of $\psi_m(t)$ follows from the properties of the projectors. Using the method outlined in [17] for example, one can show that results corresponding to (3.5), (3.6) and (3.8) hold. These may be written in the compact notation

$$\begin{aligned}\frac{\partial}{\partial \mathbb{C}(t)} \psi_m(t) &= \mathbb{D}(t) = (\mathbb{D}_1(t), \mathbb{D}_2(t)) \in \Gamma, \\ \mathbb{D}_1(t) &= 2 \int_0^{+\infty} \mu'(s) \mathbf{E}_r^t(s) ds \in \text{Sym}, \\ \mathbb{D}_2(t) &= \int_0^{+\infty} \kappa'(s) \nabla \mathbf{E}_r^t(s) ds \in \text{Sym} \times \mathbf{R}, \\ \tilde{\mathbf{T}}(t) &= \mathbb{D}_1(t) - \nabla \cdot \mathbb{D}_2(t) = \frac{\delta \psi_m(t)}{\delta \mathbf{E}(t)} .\end{aligned}\quad (3.29)$$

From (2.28)₂, we have the relation $\mathcal{A}(t) = \mathbb{D}(t) \cdot \dot{\mathbb{C}}(t)$, and (3.11) can be written as

$$\dot{\psi}_m(t) + D_m(t) = \mathbb{D}(t) \cdot \dot{\mathbb{C}}(t), \quad (3.30)$$

where D_m is the rate of dissipation corresponding to the minimum free energy and must be non-negative by the second law. Referring to the formulae developed in [8, 11, 16] for example, we see that it is given by

$$\begin{aligned}D_m(t) &= |\mathbf{K}_{\mu}(t)|^2 + |\mathbf{K}_{\kappa}(t)|^2, \\ \mathbf{K}_{\mu}(t) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} H_{\mu-}(\omega) \mathbf{E}_{\mu+}^t(\omega) d\omega, \\ \mathbf{K}_{\kappa}(t) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} H_{\kappa-}(\omega) \nabla \mathbf{E}_{\mu+}^t(\omega) d\omega,\end{aligned}\quad (3.31)$$

again with the use of the properties of projectors.

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Appendix

Various notations used in the main paper are defined here.

The real axis is denoted by $\mathbf{R}$, while $\mathbf{R}^+ = [0, +\infty)$ and $\mathbf{R}^- = (-\infty, 0]$. Also, $\mathbf{R}^{--} = (-\infty, 0)$ and $\mathbf{R}^{++} = (0, +\infty)$.

The Fourier transform of any function $f: \mathbf{R} \rightarrow \mathbf{R}^n$ is defined by

$$\begin{aligned}f_F(\omega) &= \int_{-\infty}^{+\infty} f(s) e^{-i\omega s} ds \\ &= f_{-}(\omega) + f_{+}(\omega) \quad \forall \omega \in \mathbf{R},\end{aligned}\quad (4.1)$$

where

$$\begin{aligned}f_{-}(\omega) &= \int_{-\infty}^0 f(s) e^{-i\omega s} ds, \\ f_{+}(\omega) &= \int_0^{+\infty} f(s) e^{-i\omega s} ds.\end{aligned}\quad (4.2)$$

The half-range Fourier cosine and sine transforms are given by

$$\begin{aligned}f_c(\omega) &= \int_0^{+\infty} f(s) \cos \omega s ds, \\ f_s(\omega) &= \int_0^{+\infty} f(s) \sin \omega s ds.\end{aligned}\quad (4.3)$$

If $f(u)$ vanishes as $u \rightarrow +\infty$, we have

$$f_s'(\omega) = -\omega f_c(\omega). \quad (4.4)$$

If $f'(0)$ is non-zero, then

$$\begin{aligned}\lim_{\omega \rightarrow \infty} i\omega f_{+}'(\omega) &= f'(0) = \lim_{\omega \rightarrow \infty} \omega f_s'(\omega) \\ &= -\lim_{\omega \rightarrow \infty} \omega^2 f_c(\omega),\end{aligned}\quad (4.5)$$

by virtue of (4.4).

Finally, we define the following subsets of the complex z -plane $\mathbf{C}$:

$$\begin{aligned}\mathbf{C}^{(-)} &= \{z \in \mathbf{C}; \text{Im } z \in \mathbf{R}^{--}\}, \\ \mathbf{C}^{(+)} &= \{z \in \mathbf{C}; \text{Im } z \in \mathbf{R}^{++}\}, \\ \mathbf{C}^{-} &= \{z \in \mathbf{C}; \text{Im } z \in \mathbf{R}^{-}\}, \\ \mathbf{C}^{+} &= \{z \in \mathbf{C}; \text{Im } z \in \mathbf{R}^{+}\}.\end{aligned}\quad (4.6)$$

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