JOURNAL OF RHEOLOGY

On the Free Energy and Stability of Nonlinear Fluids

J. Ernest Dunn

Citation: Journal of Rheology (1978-present) **26**, 43 (1982); doi: 10.1122/1.549659
View online: http://dx.doi.org/10.1122/1.549659
View Table of Contents: http://scitation.aip.org/content/sor/journal/jor2/26/1?ver=pdfcov
Published by the The Society of Rheology

On the Free Energy and Stability of Nonlinear Fluids

J. ERNEST DUNN, *Department of Engineering Science and Mechanics, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24060*

Synopsis

For any incompressible fluid whose stress is a frame indifferent function of the velocity gradient and the material time derivative of the velocity gradient, i.e., for any Rivlin–Ericksen fluid of complexity 2, we show that thermodynamics implies that the first normal stress difference of viscometric flows must be nonpositive for small enough shearings unless a certain very special degeneracy occurs. More precisely, we show that the Clausius–Duhem inequality, together with the postulate that the Helmholtz free energy has a minimum in equilibrium, suffices to ensure that, except for a very special subclass, every Rivlin–Ericksen fluid of complexity 2 has a *negative* first normal stress difference for all small enough shearings in any viscometric flow. Our results significantly extend a similar analysis given by Dunn and Fosdick in 1974 for those special Rivlin–Ericksen fluids of complexity 2 known as second grade fluids. In addition, they direct attention at a new class of complexity 2 fluids that have been little explored by theorists or experimenters. Furthermore, we study in detail the implications of our thermodynamic postulates for a certain subclass of these complexity 2 fluids that is more general than either second grade fluids or generalized Newtonian fluids. We find that for the fluids in this class the first normal stress difference may change sign as the shearing changes, and we find an interesting linkage between such sign alterations and potential local instabilities in the flow field. Finally, we examine the global stability of the rest state for our fluids and show that if the free energy has a strict, gobal minimum in equilibrium, then our fluids are better behaved than any Navier–Stokes fluid, since not only does the kinetic energy of any disturbance decay in mean but so too does a certain positive definite function of the stretching tensor.

INTRODUCTION

In the last 30 years many fluid models have been introduced in an effort to describe the response of liquids not adequately modeled by the Navier–Stokes theory of incompressible fluids. While we are interested here in a much broader class of materials, we begin by recalling that one of the most oft used of these non-Newtonian fluid

 Published by John Wiley & Sons, Inc.
Journal of Rheology, 26(1), 43–68 (1982) CCC 0148-6055/82/010043-26$02.60

models has been the incompressible fluid of second grade, for which the stress $\mathbf{T}$ is given by

$$\mathbf{T} = -p\mathbf{1} + \mu(\theta)\mathbf{A}_1 + \alpha_1(\theta)\mathbf{A}_2 + \alpha_2(\theta)\mathbf{A}_1^2 , \tag{1}$$

where the constitutively indeterminate spherical stress $-p\mathbf{1}$ is due to incompressibility, $\mathbf{A}_1$ and $\mathbf{A}_2$ are the first two Rivlin–Ericksen tensors, and, as indicated, the viscosity μ and the two normal stress moduli α_1 and α_2 may depend on the temperature θ. The form (1) was obtained for a special class of *flows* (now known as steady, viscometric flows) by Criminale, Ericksen, and Filbey[1] as the most general one possible for all Rivlin–Ericksen fluids of differential type (with μ, α_1, and α_2 depending possibly also on the trace of $\mathbf{A}_1^2$). Later, in work that is often taken as justifying the use of (1) in all flows for a special class of *materials*, Coleman and Noll[2] showed that for simple fluids with a certian type of "fading memory," (1) emerges for any flow after the truncation of terms of order greater than 2 in a flow retardation parameter—just as, they showed, the Navier–Stokes fluid* emerges after the truncation of terms of order greater than 1.

Over the last 20 years rheologists have collected a rather large body of experimental data frequently organized, in essence, on the assumption that the liquid within their devices satisfied Eq. (1) exactly, at least for the particular flow (almost always viscometric) they wish to study. Under this assumption they have inferred from their data that for the liquids they study

$$\alpha_1 < 0, \tag{2a}$$

$$\alpha_1 + \alpha_2 \neq 0. \tag{2b}$$

Dunn and Fosdick,[3] however, studied the thermodynamics and stability of fluids of second grade, i.e., of materials that satisfy Eq. (1) in all flows (as does, for instance, the Navier–Stokes fluid*), and found that for Eq. (1) to be compatible with commonly accepted thermodynamic principles the negation of Eqs. (2) must maintain; that is, one must have

$$\alpha_1(\theta) \geq 0, \tag{3a}$$

$$\alpha_1(\theta) + \alpha_2(\theta) = 0 \tag{3b}$$

at all temperatures θ. Moreover, Dunn and Fosdick showed that any second grade fluid satisfying Eq. (3) with constant μ, α_1, and α_2 had

* That is, the form (1) with $\alpha_1 \equiv 0 \equiv \alpha_2$.

pleasant stability properties analogous to those long familiar for Navier–Stokes fluids and that, further, when μ, α_1, and α_2 are constants, if Eq. (3a) is violated—that is, if Eq. (2a) holds—while Eq. (3b) continues to hold, then in quite arbitrary flows inside fixed, small enough, rigid containers Ω, the mean stretching in the fluid, $_\Omega\int |\mathbf{A}_1|^2 dv$, grows without bound. More recently, Fosdick and Rajagopal[4] have shown that for the above class of flows a similar physically unrealistic response still follows if $\alpha_1 < 0$ regardless of whether Eq. (3b) is satisfied or not; in particular, they show that whenever Eqs. (2) holds none of the above flows of the model (1) will ever decay to the rest state.

We take the above outlined mismatch between theory and experiment as demonstrating that the experimenters are not in fact dealing with a second grade fluid. The question then arises: To which mathematical class do the particular liquids of the experimenters belong? Or, less specifically: Which mathematical classes of materials admit of the data found by experimenters? What we show here is that unless a certain very interesting "degeneracy" occurs, thermodynamics seems to preclude *any* Rivlin–Ericksen fluid of complexity 2 (see Section 2) from being compatible with the usual data of rheologists. That is, barring a certain degeneracy, even if we replace (1) with the much more general hypothesis that

$$\mathbf{T} = -p\mathbf{1} + \tilde{\mathbf{T}}(\theta, \mathbf{g}, \mathbf{A}_1, \mathbf{A}_2), \tag{4}$$

where $\mathbf{g}$ is the temperature gradient and where $\tilde{\mathbf{T}}$ is an arbitrary, frame indifferent function, the experimental data that leads to Eqs. (2) will be incompatible with Eq. (4) if Eq. (4) satisfies the principles of thermodynamics. To describe this degeneracy and this incompatibility more precisely, recall that as a consequence of its frame indifference $\tilde{\mathbf{T}}$ in Eq. (4) admits at $\mathbf{g} = 0$ of the representation

$$\tilde{\mathbf{T}}(\theta, 0, \mathbf{A}_1, \mathbf{A}_2) = \alpha_0\mathbf{1} + \mu\mathbf{A}_1 + \alpha_1\mathbf{A}_2 + \alpha_2\mathbf{A}_1^2 + \alpha_3\mathbf{A}_2^2 + \alpha_4\{\mathbf{A}_1\mathbf{A}_2 + \mathbf{A}_2\mathbf{A}_1\} + \alpha_5\{\mathbf{A}_1^2\mathbf{A}_2 + \mathbf{A}_2\mathbf{A}_1^2\} + \alpha_6\{\mathbf{A}_1\mathbf{A}_2^2 + \mathbf{A}_2^2\mathbf{A}_1\} + \alpha_7\{\mathbf{A}_1^2\mathbf{A}_2^2 + \mathbf{A}_2^2\mathbf{A}_1^2\},$$

where $\mu = \tilde{\mu}(\theta, 0, \mathbf{A}_1, \mathbf{A}_2)$ and $\alpha_i = \tilde{\alpha}_i(\theta, 0, \mathbf{A}_1, \mathbf{A}_2)$, $i = 0, 1, \ldots, 7$, are isotropic functions of $\mathbf{A}_1$ and $\mathbf{A}_2$. It thus follows (see ref. 5 for details) that at $\mathbf{g} = 0$ the viscometric functions μ^v, σ_1^v, and σ_2^v for (4) are given by

$$\mu^v = \mu^v(\kappa) = \mu + 2\kappa^2\alpha_4 + 4\kappa^4\alpha_6,$$
$$\sigma_1^v = \sigma_1^v(\kappa) = \kappa^2[2\alpha_1 + \alpha_2 + 4\kappa^2(\alpha_3 + \alpha_5) + 8\kappa^4\alpha_7],$$
$$\sigma_2^v = \sigma_2^v(\kappa) = \kappa^2\alpha_2,$$

where κ is the shear rate or shearing and where $\mu = \tilde{\mu}(\theta, 0, \mathbf{A}_1, \mathbf{A}_2)$ and $\alpha_i = \tilde{\alpha}_i(\theta, 0, \mathbf{A}_1, \mathbf{A}_2)$, $i = 1, 2, \ldots, 7$, are evaluated on a viscometric flow so that $\mathbf{A}_1 = \kappa(\mathbf{N} + \mathbf{N}^T)$ and $\mathbf{A}_2 = 2\kappa^2\mathbf{N}^T\mathbf{N}$ with $\mathbf{N} = \mathbf{a} \otimes \mathbf{b}$ for perpendicular unit vectors $\mathbf{a}$ and $\mathbf{b}$. The combination $\sigma_2^v - \sigma_1^v$ is called the "first normal stress difference" and is commonly denoted by N_1*; since

$$N_1 = \sigma_2^v - \sigma_1^v = -\kappa^2[2\alpha_1 + 4\kappa^2(\alpha_3 + \alpha_5) + 8\kappa^4\alpha_7],$$

the fact that experimenters find $N_1 > 0$ for small shearings of their liquids is easily seen to imply, if their liquid is a complexity 2 fluid, that α_1 cannot be positive near $(\theta, \mathbf{g}, \mathbf{A}_1, \mathbf{A}_2) = (\theta, 0, 0, 0)$. In Section 2, however, we show that (see Theorem 1)

$$\tilde{\alpha}_1(\theta, 0, 0, \cdot) = \tilde{\alpha}_1(\theta, 0, 0, 0) \geq 0 \tag{5}$$

for any fluid of complexity 2 which both satisfies the "reduced dissipation inequality" (shown in ref. 3 to be a consequence of the Clausius–Duhem inequality) and has a local minimum for its Helmholtz free energy ψ at the rest state. Thus, thermodynamics tells us that only those complexity 2 fluids with the "degeneracy" $\tilde{\alpha}_1(\theta, 0, 0, \cdot) \equiv 0$† may be looked to model at all shearings κ those liquids possessing an everywhere non-negative first normal stress difference. This not only at once strikes down second grade fluids with their constant material moduli, but also directs our attention toward a very broad subclass of complexity 2 fluids that has been little looked at by experimenters or theorists.

Our results depend on a simple, explicit, and delicate linkage necessitated by thermodynamics between the response functions for stress and free energy in any complexity 2 fluid. This linkage, like its earlier, less general form found in ref. 3, seems to have extremely interesting physical and mathematical implications. Because of this and because of the historical interest in the form of (1), in Section 3 we take up in detail the thermodynamics of those complexity 2 fluids for which

$$\mathbf{T} = -p\mathbf{1} + \tilde{\tilde{\mu}}(\theta, \mathbf{A}_1)\mathbf{A}_1 + \tilde{\tilde{\alpha}}_1(\theta, \mathbf{A}_1)\mathbf{A}_2 + \tilde{\tilde{\alpha}}_2(\theta, \mathbf{A}_1)\mathbf{A}_1^2, \tag{6}$$

* The "second normal stress difference" N_2 is then just σ_1^v.

† As our Eq. (16) makes clear, the Helmholtz free energy ψ will have a strict minimum at the rest state if Eq. (5) is strict, while if $\tilde{\alpha}_1(\theta, 0, 0, \cdot)$ vanishes, then the necessary conditions for this minimum devolve onto higher-order derivatives of ψ with respect to $\mathbf{A}_1$. We do not examine these higher-order conditions in any generality here but it should be noted that the fluids of Sections 3 and 4 certainly admit the simultaneous vanishing of $\tilde{\alpha}_1(\theta, 0, 0, \cdot)$ and minimization of ψ at the rest state.

where $\tilde{\tilde{\mu}}(\cdot, \cdot)$, $\tilde{\tilde{\alpha}}_1(\cdot, \cdot)$, and $\tilde{\tilde{\alpha}}_2(\cdot, \cdot)$ may be arbitrary isotropic functions of θ and $\mathbf{A}_1$. Such fluids are easily seen to admit of arbitrary shear thinning and/or thickening of their viscosity and of normal stress moduli that, as experiments show, vary greatly with the shear rate κ. More particularly, the class of fluids (6) is broad enough to include "generalized Newtonian fluids"[6–8] (for which $\alpha_1 \equiv 0 \equiv \alpha_2$, while μ is a nonconstant function of $|\mathbf{A}_1|^2$) which have been used not only as a special model of non-Newtonian fluid behavior but have also been used to model dilute suspensions.[9,10] * Indeed, the data on suspensions reviewed by Jeffrey and Acrivos[10] constitutes a compelling case for a nontrivial dependence of μ on $\mathbf{A}_1$; additionally, while Jeffrey and Acrivos report data only for μ, they suggest that neither α_1 nor α_2 need be zero.

We show that for the model (6) thermodynamics requires $\tilde{\tilde{\alpha}}_1(\theta, \mathbf{A}_1)$ to depend on $\mathbf{A}_1$ only through the magnitude of $\mathbf{A}_1$ so that $\tilde{\tilde{\alpha}}_1(\theta, \mathbf{A}_1) = \bar{\alpha}_1(\theta, |\mathbf{A}_1|^2)$. Thus, the measurement of α_1 versus the single parameter $|\mathbf{A}_1|^2$ for any one set of flows suffices to determine the deformation dependence of α_1 in all flows. In particular, viscometric flows alone suffice to completely determine $\tilde{\tilde{\alpha}}_1(\theta, \mathbf{A}_1)$. Furthermore, we show that the global (local) minimization of the Helmholtz free energy at the rest state is equivalent to

$$\int_0^z \bar{\alpha}_1(\theta, \xi)\, d\xi \geq 0 \tag{7}$$

for $z \in [0, \infty)$ [for $z \in [0, \epsilon), \epsilon > 0$]. It is particularly noteworthy that Eq. (7) can be satisfied by functions $\bar{\alpha}_1(\theta, \cdot)$ that change sign on $[0, \infty)$ and/or have $\bar{\alpha}_1(\theta, 0) = 0$. In addition, while it is no longer true that $\alpha_1 + \alpha_2$ must vanish, we find that thermodynamics implies for certain subfamilies of (6) that

$$\tilde{\tilde{\alpha}}_1(\theta, \mathbf{A}_1) + \tilde{\tilde{\alpha}}_2(\theta, \mathbf{A}_1) \rightarrow 0$$

for certain classes of ever-increasing stretching paths $\mathbf{A}_1 = \mathbf{A}_1(\tau)$, $|\mathbf{A}_1(\tau)| \rightarrow \infty$ as $\tau \rightarrow \infty$.

In Section 4 we examine the dynamic mechanical stability of the rest state for the fluids described by Eq. (6) by considering the temporal evolution of flows inside a fixed, rigid container Ω to the walls of which the fluid adheres. Even though our problem is highly non-

* See ref. 10 also for a clear articulation of the point of view that "when we deal with suspensions, it is not always necessary to acknowledge that they are mixtures of particles and fluid; instead, it is often possible to regard them as homogeneous fluids . . . ."

linear, we are able to show that if the Helmholtz free energy has a weak global minimum at the rest state and if certain mild growth conditions are satisfied by the response functions for μ, α_1, and α_2, then the positive definite functional of the velocity field $\mathbf{v}$ given by

$$E(t) = \int_\Omega \left\{ |\mathbf{v}|^2 + \frac{1}{2\rho} \int_0^{|\mathbf{A}_1|^2} \overline{\alpha}_1(\theta, \xi) d\xi \right\} dv$$

decays to zero as $t \to \infty$. (Here ρ is the density of the fluid, a fixed positive number.) This, our Theorem 3, generalizes an analogous result in ref. 3 (see Theorem 9, Corollary 2) for second grade fluids and, like that result, suggests that those fluids of (6) for which (7) is not an identity are better behaved physically and analytically than Navier–Stokes fluids since for them not only does $|\mathbf{v}|$ decay in mean but so too does a certain non-negative function of $|\mathbf{A}_1|$.

Finally, we remark that although we do not examine here the thermal stability of the fluids (6), the general analysis in Section 4 of ref. 3 is easily particularized to these fluids.

SECTION 2

For a (homogeneous, incompressible) fluid of complexity 2 the *Helmholtz free energy* ψ, the (*symmetric*) *Cauchy stress tensor* $\mathbf{T}$, and the *heat flux vector* $\mathbf{q}$ are given by

$$\psi = \hat{\psi}(\theta, \mathbf{g}, \mathbf{L}, \dot{\mathbf{L}}), \tag{8a}$$

$$\mathbf{T} = -p\mathbf{1} + \hat{\mathbf{T}}(\theta, \mathbf{g}, \mathbf{L}, \dot{\mathbf{L}}), \tag{8b}$$

$$\mathbf{q} = \hat{\mathbf{q}}(\theta, \mathbf{g}, \mathbf{L}, \dot{\mathbf{L}}), \tag{8c}$$

where θ is the (positive) *temperature*, $\mathbf{g} \equiv \operatorname{grad} \theta(\mathbf{x}, t)$ is the (spatial) *temperature gradient*, $\mathbf{L} \equiv \operatorname{grad} \mathbf{v}(\mathbf{x}, t)$ is the (spatial) *gradient* of the divergence-free *velocity* $\mathbf{v}$, $\dot{\mathbf{L}} \equiv (d/dt)\,\mathbf{L}$ is the *material time derivative* of $\mathbf{L}$, and p is a constitutively indeterminate pressure reflecting the *a priori* constraint of incompressibility. If we let $\mathbb{R}^+$ denote the positive real numbers, V denote a three-dimensional inner product space, and T, T^0, and T^0_s denote, respectively, the set of tensors, traceless tensors, and traceless, symmetric tensors over V, then we have that $\theta \in \mathbb{R}^+$, $\mathbf{g} \in V$, $\mathbf{L} \in T^0$, and $\dot{\mathbf{L}} \in T^0$.* Thus, the domain of the response functions $\hat{\psi}$, $\hat{\mathbf{T}}$, and $\hat{\mathbf{q}}$ is $\mathbb{R}^+ \times V \times T^0 \times T^0$, on which we will initially suppose them to be continuously differentiable.

* That $\mathbf{L}$ and, hence, $\dot{\mathbf{L}}$ must be in T^0 is a consequence of incompressibility since the trace of $\mathbf{L}$ is just the divergence of $\mathbf{v}$.

It is a consequence (for details see ref. 3, especially Theorem 1) of the Clausius–Duhem inequality that $\hat{\psi}$, $\hat{\mathbf{T}}$, and $\hat{\mathbf{q}}$ may not be prescribed arbitrarily but, rather, must be such that (i) $\hat{\psi}$ is independent of $\mathbf{g}$ and $\dot{\mathbf{L}}$, and (ii) $\hat{\psi}$, $\hat{\mathbf{T}}$, and $\hat{\mathbf{q}}$ must jointly satisfy the reduced dissipation inequality; that is, first

$$\psi = \hat{\psi}(\theta, \mathbf{L}), \tag{9a}$$

and second

$$\rho\hat{\psi}_{\mathbf{L}}(\theta, \mathbf{L}) \cdot \dot{\mathbf{L}} - \hat{\mathbf{T}}(\theta, \mathbf{g}, \mathbf{L}, \dot{\mathbf{L}}) \cdot \mathbf{L} - \frac{\hat{\mathbf{q}}(\theta, \mathbf{g}, \mathbf{L}, \dot{\mathbf{L}}) \cdot \mathbf{g}}{\theta} \leq 0, \tag{9b}$$

for all $(\theta, \mathbf{g}, \mathbf{L}, \dot{\mathbf{L}}) \in \mathbb{R}^+ \times V \times T^0 \times T^0$, where ρ is the constant, uniform density of the fluid, "$\cdot$" denotes an inner product operation,* and $\hat{\psi}_{\mathbf{L}} \in \mathbf{T}^0$ denotes the partial derivative of $\hat{\psi}$ with respect to $\mathbf{L}$. Equations (8) and (9) are the starting point of the current work.

We see that if we set $\mathbf{g} = \mathbf{L} = 0$ in Eq. (9b) then $\rho\hat{\psi}_{\mathbf{L}}(\theta, 0) \cdot \dot{\mathbf{L}} \leq 0$ for all $\dot{\mathbf{L}} \in T^0$ and hence

$$\hat{\psi}_{\mathbf{L}}(\theta, 0) = 0. \tag{10}$$

If we now return to Eq. (9b), set $\mathbf{g} = 0$, and replace $\mathbf{L}$ with $x\mathbf{L}$, we find that

$$h(x) \equiv \rho\hat{\psi}_{\mathbf{L}}(\theta, x\mathbf{L}) \cdot \dot{\mathbf{L}} - \hat{\mathbf{T}}(\theta, 0, x\mathbf{L}, \dot{\mathbf{L}}) \cdot (x\mathbf{L}) \leq 0$$

for any real number x. But by Eq. (10) we see that $h(0) = 0$ so the function h has a local maximum at 0 and, therefore, $h'(0) = 0$ while $h''(0) \leq 0$, i.e.,

$$\rho\hat{\psi}_{\mathbf{LL}}(\theta, 0) \cdot (\dot{\mathbf{L}} \otimes \mathbf{L}) = \hat{\mathbf{T}}(\theta, 0, 0, \dot{\mathbf{L}}) \cdot \mathbf{L}, \tag{11a}$$

and

$$\tfrac{1}{2}\rho\hat{\psi}_{\mathbf{LLL}}(\theta, 0) \cdot (\dot{\mathbf{L}} \otimes \mathbf{L} \otimes \mathbf{L}) \leq \hat{\mathbf{T}}_{\mathbf{L}}(\theta, 0, 0, \dot{\mathbf{L}})[\mathbf{L}] \cdot \mathbf{L}, \tag{11b}$$

where we have supposed that $\hat{\psi}(\theta, \cdot)$ and $\hat{\mathbf{T}}(\theta, 0, \cdot, \dot{\mathbf{L}})$ are, respectively, three times and two times continuously differentiable† and where $\otimes$ denotes the tensor product operation.

When taken together Eqs. (10) and (11a) are particularly inter-

* If $\mathrm{tr}(\cdot)$ denotes the trace operator on T, then we have $\mathbf{A} \cdot \mathbf{B} \equiv \mathrm{tr}\mathbf{A}\mathbf{B}^T$ for all $\mathbf{A}$ and $\mathbf{B}$, where $\mathbf{B}^T$ is the transpose of $\mathbf{B}$. Also, we then set $|\mathbf{A}| \equiv (\mathbf{A} \cdot \mathbf{A})^{1/2}$ for the norm of any tensor $\mathbf{A}$.

† A more delicate analysis of Eqs. (9) reveals that Eqs. (11) in fact hold if $\hat{\mathbf{T}}(\theta, 0, \cdot, \dot{\mathbf{L}})$ is just continuously differentiable and if $\hat{\psi}_{\mathbf{L}}(\theta, \cdot)$ is twice differentiable at 0. See also Corollary 1 of Theorem 1 in ref. 3.

esting: Eq. (10) asserts that a state of local rest (i.e., $\mathbf{L} = 0$) provides a stationary point for the Helmholtz free energy $\hat{\psi}(\theta, \cdot)$, while Eq. (11a) shows that the character of this stationary point (maximum, minimum, or saddle) for the free energy is completely governed by the response function for the stress through the form

$$\mathbf{T}(\theta, 0, 0, \dot{\mathbf{L}}) \cdot \mathbf{L}, \tag{12}$$

assuming that this form does not vanish identically. Moreover, Eq. (11a) also tells us that the form (12) must be linear in $\dot{\mathbf{L}}$.

In addition to the thermodynamic restrictions, Eqs. (10) and (11a), which were established in ref. 3, there are also certain restrictions placed upon the response functions $\hat{\psi}$, $\hat{\mathbf{T}}$, and $\hat{\mathbf{q}}$ by the principle of frame indifference.[5] In particular and as is well known,[5] the function $\hat{\mathbf{T}}(\theta, 0, \cdot, \cdot)$ must be of the form

$$\begin{aligned}\hat{\mathbf{T}}(\theta, 0, \mathbf{L}, \dot{\mathbf{L}}) = \tilde{\mathbf{T}}(\theta, 0, \mathbf{A}_1, \mathbf{A}_2) = \alpha_0 \mathbf{1} + \mu \mathbf{A}_1 \\ + \alpha_1 \mathbf{A}_2 + \alpha_2 \mathbf{A}_1^2 + \alpha_3 \mathbf{A}_2^2 + \alpha_4 \{\mathbf{A}_1 \mathbf{A}_2 + \mathbf{A}_2 \mathbf{A}_1\} \\ + \alpha_5 \{\mathbf{A}_1^2 \mathbf{A}_2 + \mathbf{A}_2 \mathbf{A}_1^2\} + \alpha_6 \{\mathbf{A}_1 \mathbf{A}_2^2 + \mathbf{A}_2^2 \mathbf{A}_1\} + \alpha_7 \{\mathbf{A}_1^2 \mathbf{A}_2^2 + \mathbf{A}_2^2 \mathbf{A}_1^2\},\end{aligned} \tag{13}$$

where $\mathbf{A}_1$ and $\mathbf{A}_2$ are, respectively, the first two Rivlin–Ericksen tensors and are given by

$$\mathbf{A}_1 = \mathbf{L} + \mathbf{L}^T, \tag{14a}$$

$$\mathbf{A}_2 = \dot{\mathbf{A}}_1 + \mathbf{A}_1 \mathbf{L} + \mathbf{L}^T \mathbf{A}_1 = \dot{\mathbf{L}} + \dot{\mathbf{L}}^T + \mathbf{A}_1 \mathbf{L} + \mathbf{L}^T \mathbf{A}_1, \tag{14b}$$

and where $\alpha_i = \tilde{\alpha}_i(\theta, 0, \mathbf{A}_1, \mathbf{A}_2)$, $i = 0, 1, \ldots, 7$, and $\mu = \tilde{\mu}(\theta, 0, \mathbf{A}_1, \mathbf{A}_2)$ are isotropic functions of the symmetric tensors $\mathbf{A}_1$ and $\mathbf{A}_2$.* Note that, by Eq. (14a), $\mathbf{A}_1$ is just twice the stretching tensor of classical hydrodynamics. Note also that since $\mathbf{L}$ and $\dot{\mathbf{L}}$ are traceless, it follows from Eqs. (14) that $\mathrm{tr}\mathbf{A}_2 = \mathrm{tr}\mathbf{A}_1^2$ and that, therefore, for each $\mathbf{A}_1 \in T_s^0$ the domain of $\tilde{\mathbf{T}}(\theta, 0, \mathbf{A}_1, \cdot)$ [and, hence, of $\tilde{\mu}(\theta, 0, \mathbf{A}_1, \cdot)$ and $\tilde{\alpha}_i(\theta, 0, \mathbf{A}_1, \cdot)$] is $T_s^0 + (1/3)(\mathrm{tr}\mathbf{A}_1^2)\mathbf{1}$. We further note that if we adopt the usual normalization that $\hat{\mathbf{T}}$ be traceless then, by Eq. (8b), the negative mean stress and the "hydrostatic" pressure p will coincide and moreover, by Eq. (13), $\tilde{\alpha}_0$ will then by uniquely determined by the $\tilde{\alpha}_i$, $i = 1, 2, \ldots, 7$.

* We remark that additional terms must be added to the right-hand side of Eq. (13) to obtain the general, frame indifferent representation of $\hat{\mathbf{T}}(\theta, \mathbf{g}, \mathbf{L}, \dot{\mathbf{L}})$ when $\mathbf{g} \neq 0$. See, in particular, the study by Wang.[11] We also note that the problem of determining the continuity and smoothness of the functions $\tilde{\mu}$ and $\tilde{\alpha}_i$ in terms of the continuity and smoothness of $\tilde{\mathbf{T}}$ (and so, of $\hat{\mathbf{T}}$) is currently unsolved. Here we adopt the usual practice of postulating whatever degree of smoothness we require of $\tilde{\mu}$ and the $\tilde{\alpha}_i$. In fact, with the exception of Eq. (11b), it suffices for our analyses that they be continuous.

If we now couple the thermodynamic restriction in Eq. (11a) with the consequence of Eq. (13) of frame indifference, we obtain

Theorem 1: *For any fluid of complexity* 2 *the response functions* $\tilde{\alpha}_1$ *and* $\tilde{\alpha}_3$ *of the representation* (13) *must satisfy*

$$\tilde{\alpha}_1(\theta, 0, 0, \mathbf{A}_2) = \tilde{\alpha}_1(\theta, 0, 0, 0), \tag{15a}$$

$$\tilde{\alpha}_3(\theta, 0, 0, \mathbf{A}_2) = 0, \tag{15b}$$

for all tensors $\mathbf{A}_2 \in T_s^0$, *the domain of* $\tilde{\alpha}_i(\theta, 0, 0, \cdot)$. *Furthermore, the Helmholtz free energy must satisfy*

$$\rho\hat{\psi}_{\mathbf{LL}}(\theta, 0) \cdot (\dot{\mathbf{L}} \otimes \mathbf{L}) = \tfrac{1}{2}\tilde{\alpha}_1(\theta, 0, 0, 0)(\dot{\mathbf{L}} + \dot{\mathbf{L}}^T) \cdot (\mathbf{L} + \mathbf{L}^T) \tag{16}$$

for any two tensors $\mathbf{L}$ *and* $\dot{\mathbf{L}}$ *in* T^0. A fortiori, *no saddle point behavior is possible for* $\hat{\psi}(\theta, \cdot)$ *at* 0 *unless* $\tilde{\alpha}_1(\theta, 0, 0, 0) = 0$, *while* $\hat{\psi}(\theta, \cdot)$ *a local minimum (maximum) at* 0 *implies that* $\tilde{\alpha}_1(\theta, 0, 0, 0) \geq 0(\leq 0)$*—this minimum (maximum) being strict on* T_s^0 *if* $\tilde{\alpha}_1(\theta, 0, 0, 0) > 0(<0)$.

If one adopts the standard thermodynamic belief that the Helmholtz free energy should be a minimum in equilibrium (i.e., when $\mathbf{L} = 0$), our theorem then tells us that it is impossible for $\tilde{\alpha}_1(\theta, 0, 0, \cdot) = \tilde{\alpha}_1(\theta, 0, 0, 0)$ to ever be negative for any realistic fluid of complexity 2. Furthermore, it is then clear from our discussion in the Introduction that if the first normal stress difference N_1 is to be positive for all small enough shearings then the only possible behavior for α_1 is $\tilde{\alpha}_1(\theta, 0, 0, \cdot) \equiv 0$. By Eq. (16), $\hat{\psi}(\theta, \cdot)$ will then be extremely flat at the stationary point $\mathbf{L} = 0$.

Proof: If we put $\mathbf{L} = 0$ in Eqs. (13) and (14) we find that

$$\hat{\mathbf{T}}(\theta, 0, 0, \dot{\mathbf{L}}) = \alpha_0 1 + \alpha_1(\dot{\mathbf{L}} + \dot{\mathbf{L}}^T) + \alpha_3(\dot{\mathbf{L}} + \dot{\mathbf{L}}^T)^2 \tag{17}$$

for any $\dot{\mathbf{L}} \in T^0$ and where now $\alpha_i = \tilde{\alpha}_i(\theta, 0, 0, \dot{\mathbf{L}} + \dot{\mathbf{L}}^T)$ for $i = 0, 1$, and 3. It thus follows that the form (12) is given by

$$\begin{aligned}\hat{\mathbf{T}}(\theta, 0, 0, \dot{\mathbf{L}}) \cdot \mathbf{L} = {} & \tfrac{1}{2}\tilde{\alpha}_1(\theta, 0, 0, \dot{\mathbf{L}} + \dot{\mathbf{L}}^T)(\dot{\mathbf{L}} + \dot{\mathbf{L}}^T) \cdot (\mathbf{L} + \mathbf{L}^T) \\ & + \tfrac{1}{2}\tilde{\alpha}_3(\theta, 0, 0, \dot{\mathbf{L}} + \dot{\mathbf{L}}^T)(\dot{\mathbf{L}} + \dot{\mathbf{L}}^T)^2 \cdot (\mathbf{L} + \mathbf{L}^T)\end{aligned} \tag{18}$$

for any $\mathbf{L}$ and $\dot{\mathbf{L}}$ in T^0, and, as we have seen, this expression must be linear in $\dot{\mathbf{L}}$. In particular then we must have $\hat{\mathbf{T}}(\theta, 0, 0, x\dot{\mathbf{L}})\cdot\mathbf{L} = x\hat{\mathbf{T}}(\theta, 0, 0, \dot{\mathbf{L}})\cdot\mathbf{L}$ for any number x, i.e.,

$$\tilde{\alpha}_1(\theta, 0, 0, x\mathbf{N})x\mathbf{N}\cdot\mathbf{M} + \tilde{\alpha}_3(\theta, 0, 0, x\mathbf{N})x^2\mathbf{N}^2\cdot\mathbf{M} = x\{\tilde{\alpha}_1(\theta, 0, 0, \mathbf{N})\mathbf{N}\cdot\mathbf{M} + \tilde{\alpha}_3(\theta, 0, 0, \mathbf{N})\mathbf{N}^2\cdot\mathbf{M}\}$$

for any number x and any two tensors $\mathbf{M}$ and $\mathbf{N}$ in T_s^0. Equivalently, we see that

$$\tilde{\alpha}_1(\theta, 0, 0, x\mathbf{N})\mathbf{N}\cdot\mathbf{M} + \tilde{\alpha}_3(\theta, 0, 0, x\mathbf{N})x\mathbf{P}\cdot\mathbf{M} = \tilde{\alpha}_1(\theta, 0, 0, \mathbf{N})\mathbf{N}\cdot\mathbf{M} + \tilde{\alpha}_3(\theta, 0, 0, \mathbf{N})\mathbf{P}\cdot\mathbf{M} \quad (19)$$

for any number $x \neq 0$, for any two tensors $\mathbf{N}$ and $\mathbf{M}$ in T_s^0, and where $\mathbf{P} = \mathbf{P}(\mathbf{N}^2) \equiv \mathbf{N}^2 - \frac{1}{3}(\mathrm{tr}\mathbf{N}^2)\mathbf{1}$ is the projection of $\mathbf{N}^2 \in T_s$ onto T_s^0.

Now select any $\mathbf{N} \in T_s^0$ for which $\mathbf{N}$ is not parallel to $\mathbf{P}(\mathbf{N}^2)$; that is, by the lemma below, select any $\mathbf{N} \in T_s^0$, with three distinct eigenvalues and let

$$\mathbf{M} = |\mathbf{P}(\mathbf{N}^2)|^2\mathbf{N} - [\mathbf{N}\cdot\mathbf{P}(\mathbf{N}^2)]\mathbf{P}(\mathbf{N}^2).$$

We see that

$$\mathbf{P}(\mathbf{N}^2)\cdot\mathbf{M} = |\mathbf{P}|^2\mathbf{N}\cdot\mathbf{P} - (\mathbf{N}\cdot\mathbf{P})\mathbf{P}\cdot\mathbf{P} = 0$$

and

$$\mathbf{N}\cdot\mathbf{M} = |\mathbf{P}|^2|\mathbf{N}|^2 - (\mathbf{N}\cdot\mathbf{P})^2 > 0,$$

where the inequality is just the Cauchy–Schwarz inequality for the nonparallel tensors $\mathbf{N}$ and $\mathbf{P}$. If we enter these choices for $\mathbf{N}$ and $\mathbf{M}$ into Eq. (19) we thus find that

$$\tilde{\alpha}_1(\theta, 0, 0, x\mathbf{N}) = \tilde{\alpha}_1(\theta, 0, 0, \mathbf{N})$$

for any number $x \neq 0$ and for any $\mathbf{N} \in T_s^0$ with three distinct eigenvalues. But any element $\mathbf{N} \in T_s^0$ may be reached as a limit of a sequence in T_s^0, each term of which has three distinct eigenvalues and so, by the continuity of $\tilde{\alpha}_1(\theta, 0, 0, \cdot)$, we have shown that

$$\tilde{\alpha}_1(\theta, 0, 0, x\mathbf{N}) = \tilde{\alpha}_1(\theta, 0, 0, \mathbf{N}) \quad (20)$$

for any number $x \neq 0$ and any tensor $\mathbf{N} \in T_s^0$. Upon letting $x \to 0$ and again invoking continuity, we see that Eq. (15a) holds.

If we now return to Eq. (19) and use Eq. (20) and take $\mathbf{M} = \mathbf{P}(\mathbf{N}^2)(\neq 0$ if $\mathbf{N} \neq 0)$ we find that

$$x\tilde{\alpha}_3(\theta, 0, 0, x\mathbf{N}) = \tilde{\alpha}_3(\theta, 0, 0, \mathbf{N})$$

for all $x \neq 0$ and for all $\mathbf{N} \in T_s^0 - \{0\}$ which, since $\tilde{\alpha}_3(\theta, 0, 0, \cdot)$ is continuous at 0, can only hold if Eq. (15b) holds.

To finish the proof we merely note that Eq. (18) has now become $\hat{\mathbf{T}}(\theta, 0, 0, \dot{\mathbf{L}})\cdot\mathbf{L} = (1/2)\tilde{\alpha}_1(\theta, 0, 0, 0)(\dot{\mathbf{L}} + \dot{\mathbf{L}}^T)\cdot(\mathbf{L} + \mathbf{L}^T)$ which, by Eq. (11a), means Eq. (16) holds. ■

Lemma: *Let* $\mathbf{N}$ *be any tensor in* T_s^0 *and let* $\mathbf{P} = \mathbf{P}(\mathbf{N}^2) \equiv \mathbf{N}^2 - (1/3)(\mathrm{tr}\mathbf{N}^2)\mathbf{1}$ *be the projection of* $\mathbf{N}^2$ *onto* T_s^0*; then* $\mathbf{N}$ *and* $\mathbf{P}(\mathbf{N}^2)$ *are parallel if and only if at least two eigenvalues of* $\mathbf{N}$ *are equal.*

Proof: The result is trivial for $\mathbf{N} = 0$ so we first suppose that $\mathbf{N} \neq 0$ and is parallel to $\mathbf{P}(\mathbf{N}^2)$. In this case $\mathbf{P}(\mathbf{N}^2) = \lambda\mathbf{N}$ for some number λ and thus $\mathbf{N}^2 - (1/3)(\mathrm{tr}\mathbf{N}^2)\mathbf{1} = \lambda\mathbf{N}$ or, in terms of the eigenvalues n_i, $i = 1, 2, 3$, of $\mathbf{N}$,

$$n_i^2 - \tfrac{1}{3}\mathrm{tr}\mathbf{N}^2 = \lambda n_i.$$

We thus find that $n_i^2 - n_j^2 = \lambda(n_i - n_j)$ for any i and j and that, therefore,

$$n_i + n_j = \lambda$$

for any i and j with $n_i \neq n_j$. Now suppose that, say, $n_1 \neq n_3$ and $n_1 \neq n_2$, then $n_1 + n_3 = \lambda = n_1 + n_2$ so $n_3 = n_2$ and two eigenvalues of $\mathbf{N}$ are equal.

If, on the other hand, $\mathbf{N} \in T_s^0$ has two equal eigenvalues, then $\mathbf{N}$ must be of the form

$$\mathbf{N} = n\{\mathbf{a} \otimes \mathbf{a} + \mathbf{b} \otimes \mathbf{b}\} - 2n\mathbf{c} \otimes \mathbf{c},$$

for three orthonormal eigenvectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ and for some number n. Thus,

$$\mathbf{N}^2 = n^2\{\mathbf{a} \otimes \mathbf{a} + \mathbf{b} \otimes \mathbf{b}\} + 4n^2\mathbf{c} \otimes \mathbf{c}$$

and

$$\begin{aligned} P(\mathbf{N}^2) &= \mathbf{N}^2 - \tfrac{1}{3}(\mathrm{tr}\mathbf{N}^2)\mathbf{1} \\ &= n^2\{\mathbf{a} \otimes \mathbf{a} + \mathbf{b} \otimes \mathbf{b}\} + 4n^2\mathbf{c} \otimes \mathbf{c} - 2n^2\mathbf{1} \\ &= -n^2\{\mathbf{a} \otimes \mathbf{a} + \mathbf{b} \otimes \mathbf{b}\} + 2n^2\mathbf{c} \otimes \mathbf{c} \\ &= -n\mathbf{N}, \end{aligned}$$

and $\mathbf{P}(\mathbf{N}^2)$ and $\mathbf{N}$ are parallel as claimed. ■

In Section 3 we shall see that the reduced dissipation inequality, Eq. (9b), implies further restrictions on the forms of $\hat{\psi}$ and $\hat{\mathbf{T}}$ for a certain subclass of complexity 2 fluids. Before turning to these additional restrictions we collect some simple observations that follow from our general analysis above.

First, we recall that in addition to the representation formula (13) for the stress, the principle of frame indifference also implies[5] that the response function $\hat{\psi}(\theta, \cdot)$ is of the form

$$\hat{\psi}(\theta, \mathbf{L}) = \tilde{\psi}(\theta, \mathbf{A}_1) \ \forall \ \mathbf{L} \in T^0, \tag{21}$$

where $\mathbf{A}_1$ is as in Eq. (14a) and where $\tilde{\psi}(\theta, \cdot)$ is an isotropic tensor function on T^0_s. As a consequence of Eqs. (13), (16), and (21), Eqs. (10) and (11) become the assertions that

$$\tilde{\psi}_{\mathbf{A}_1}(\theta, 0) = 0,$$

$$\begin{aligned}\rho\tilde{\psi}_{\mathbf{A}_1\mathbf{A}_1}(\theta, 0) \cdot (\dot{\mathbf{A}}_1 \otimes \mathbf{A}_1) &= \tfrac{1}{2}\tilde{\mathbf{T}}(\theta, 0, 0, \dot{\mathbf{A}}_1) \cdot \mathbf{A}_1 \\ &= \tfrac{1}{2}\tilde{\alpha}_1(\theta, 0, 0, 0)\dot{\mathbf{A}}_1 \cdot \mathbf{A}_1,\end{aligned}$$

$$\rho\tilde{\psi}_{\mathbf{A}_1\mathbf{A}_1\mathbf{A}_1}(\theta, 0) \cdot (\dot{\mathbf{A}}_1 \otimes \mathbf{A}_1 \otimes \mathbf{A}_1) \leq \tilde{\mathbf{T}}_{\mathbf{A}_1}(\theta, 0, 0, \dot{\mathbf{A}}_1)[\mathbf{A}_1] \cdot \mathbf{A}_1,$$

for all $\mathbf{A}_1$ and $\dot{\mathbf{A}}_1$ in T^0_s.

Second, if we apply the identity $h(1) - h(0) = \int_0^1 h'(\xi)d\xi$ to the function $h(\xi) = \hat{\mathbf{T}}(\theta, 0, \xi\mathbf{L}, \dot{\mathbf{L}}) \cdot \mathbf{L}$, we find that the stress power at $\mathbf{g} = 0$, $\hat{\mathbf{T}}(\theta, 0, \mathbf{L}, \dot{\mathbf{L}}) \cdot \mathbf{L}$, satisfies

$$\begin{aligned}\hat{\mathbf{T}}(\theta, 0, \mathbf{L}, \dot{\mathbf{L}}) \cdot \mathbf{L} &= \hat{\mathbf{T}}(\theta, 0, 0, \dot{\mathbf{L}}) \cdot \mathbf{L} + \int_0^1 \hat{\mathbf{T}}_{\mathbf{L}}(\theta, 0, \xi\mathbf{L}, \dot{\mathbf{L}})[\mathbf{L}] \cdot \mathbf{L}d\xi \\ &= \rho\hat{\psi}_{\mathbf{LL}}(\theta, 0) \cdot (\dot{\mathbf{L}} \otimes \mathbf{L}) + \hat{\boldsymbol{\mu}}(\theta, 0, \mathbf{L}, \dot{\mathbf{L}})[\mathbf{L} \otimes \mathbf{L}],\end{aligned}$$

where we have used Eq. (11a) and where we have defined the "viscosity tensor"

$$\hat{\boldsymbol{\mu}}(\theta, 0, \mathbf{L}, \dot{\mathbf{L}})[\mathbf{A} \otimes \mathbf{B}] \equiv \int_0^1 \hat{\mathbf{T}}_{\mathbf{L}}(\theta, 0, \xi\mathbf{L}, \dot{\mathbf{L}})[\mathbf{A}] \cdot \mathbf{B}d\xi$$

for $\mathbf{A}$ and $\mathbf{B}$ in T^0. We note that by Eq. (11b)

$$\hat{\boldsymbol{\mu}}(\theta, 0, 0, 0,)[\mathbf{L} \otimes \mathbf{L}] \geq 0 \ \forall \ \mathbf{L} \in T^0.$$

SECTION 3

In terms of the representation (13), we now consider fluids of complexity 2 for which, at $\mathbf{g} = 0$, $\tilde{\alpha}_i \equiv 0$ for $i \geq 3$ and $\tilde{\mu}$, $\tilde{\alpha}_0$, $\tilde{\alpha}_1$, and $\tilde{\alpha}_2$ depend only on θ and $\mathbf{A}_1$, i.e.,

$$\hat{\mathbf{T}}(\theta, 0, \mathbf{L}, \dot{\mathbf{L}}) = \tilde{\mathbf{T}}(\theta, 0, \mathbf{A}_1, \mathbf{A}_2) = \alpha_0\mathbf{1} + \mu\mathbf{A}_1 + \alpha_1\mathbf{A}_2 + \alpha_2\mathbf{A}_1^2, \tag{22}$$

where $\mu = \tilde{\mu}(\theta, 0, \mathbf{A}_1, \mathbf{A}_2) = \tilde{\tilde{\mu}}(\theta, \mathbf{A}_1)$ and $\alpha_i = \tilde{\alpha}_i(\theta, 0, \mathbf{A}_1, \mathbf{A}_2) = \tilde{\tilde{\alpha}}_i(\theta, \mathbf{A}_1)$, $i = 0, 1, 2$ [note that $\mathrm{tr}\hat{\mathbf{T}} = 0 \Rightarrow \tilde{\tilde{\alpha}}_0 = -(1/3)(\tilde{\tilde{\alpha}}_1 + \tilde{\tilde{\alpha}}_2)\mathrm{tr}\mathbf{A}_1^2$]. Furthermore, in addition to the continuity of $\tilde{\tilde{\mu}}$ and $\tilde{\tilde{\alpha}}_i$, $i = 0, 1, 2$, we now only require that the Helmholtz free energy $\tilde{\psi}$ be once continuously differentiable. This subclass of complexity 2 fluids thus admits of the arbitrary dependence of μ, α_1, and α_2 on the stretching $(1/2)\mathbf{A}_1$, and so clearly contains all "generalized Newtonian fluids" as well as all fluids of second grade. Moreover, as was found in ref. 3 for second grade fluids, we will shortly find that all those complexity 2 fluids satisfying Eq. (22) have the property that $\tilde{\tilde{\alpha}}_1(\theta, \mathbf{A}_1)$ determines $\tilde{\psi}(\theta, \mathbf{A}_1)$ up to a function of temperature alone.

If we substitute Eq. (22) into the reduced dissipation inequality Eq. (9b) and use Eq. (14) we find that

$$\rho\tilde{\psi}_{\mathbf{A}_1}(\theta, \mathbf{A}_1) \cdot \dot{\mathbf{A}}_1 - \tfrac{1}{2}\{\tilde{\tilde{\mu}}(\theta, \mathbf{A}_1)\mathrm{tr}\mathbf{A}_1^2 + \tilde{\tilde{\alpha}}_1(\theta, \mathbf{A}_1)\mathbf{A}_1 \cdot \dot{\mathbf{A}}_1 + [\tilde{\tilde{\alpha}}_1(\theta, \mathbf{A}_1) + \tilde{\tilde{\alpha}}_2(\theta, \mathbf{A}_1)]\mathrm{tr}\mathbf{A}_1^3\} \leq 0$$

for all $\mathbf{A}_1$ and $\dot{\mathbf{A}}_1$ in T_s^0 and where we have used Eq. (21). Since this inequality is linear in $\dot{\mathbf{A}}_1$ we conclude that it can hold if and only if both

$$\rho\tilde{\psi}_{\mathbf{A}_1}(\theta, \mathbf{A}_1) \cdot \dot{\mathbf{A}}_1 = \tfrac{1}{2}\tilde{\tilde{\alpha}}_1(\theta, \mathbf{A}_1)\mathbf{A}_1 \cdot \dot{\mathbf{A}}_1 \tag{23a}$$

for any $\mathbf{A}_1$ and $\dot{\mathbf{A}}_1$ in T_s^0 and

$$\tilde{\tilde{\mu}}(\theta, \mathbf{A}_1)\mathrm{tr}\mathbf{A}_1^2 + \{\tilde{\tilde{\alpha}}_1(\theta, \mathbf{A}_1) + \tilde{\tilde{\alpha}}_2(\theta, \mathbf{A}_1)\}\mathrm{tr}\mathbf{A}_1^3 \geq 0 \tag{23b}$$

for any $\mathbf{A}_1$ in T_s^0. The implications of Eq. (23a) form the content of

Theorem 2: *The response functions $\tilde{\psi}$ and $\tilde{\tilde{\alpha}}_1$ satisfy* Eq. (23a) *if and only if for all $\mathbf{A}_1 \in T_s^0$*

$$\tilde{\tilde{\alpha}}_1(\theta, \mathbf{A}_1) = \bar{\alpha}_1(\theta, |\mathbf{A}_1|^2), \tag{24a}$$

and

$$\tilde{\psi}(\theta, \mathbf{A}_1) = \bar{\psi}(\theta, |\mathbf{A}_1|^2) = \tilde{\psi}(\theta, 0) + \frac{1}{4\rho}\int_0^{|\mathbf{A}_1|^2} \bar{\alpha}_1(\theta, \xi)d\xi.^* \tag{24b}$$

A fortiori, $\tilde{\psi}(\theta, \cdot)$ *has a local (global) minimum at* $\mathbf{A}_1 = 0$ *if and only if*

$$\int_0^z \bar{\alpha}_1(\theta, \xi)d\xi \geq 0 \tag{24c}$$

for all $z \in [0, \delta)$, $\delta > 0 (\delta = \infty)$. This minimum is strict if Eq. (24c) *is strict for $z \neq 0$.*

* Cf. Eq. (5.13) of ref. 3.

We see then that thermodynamics permits $\tilde{\bar{\alpha}}_1$ and $\tilde{\psi}$ to depend on only the magnitude of $\mathbf{A}_1$ and that, moreover, the dependence of $\tilde{\psi}$ on $|\mathbf{A}_1|$ is completely determined by that of $\tilde{\bar{\alpha}}_1$. The result of (24c) is particularly interesting since it tells us that for the fluids considered here α_1 may indeed take on negative values and still have a free energy which is a minimum in equilibrium—it is not necessary that α_1 itself always be positive, only the integral of $\bar{\alpha}_1(\theta, \cdot)$ need be positive. We also note that (24c) implies that

$$\bar{\alpha}_1(\theta, 0) \geq 0; \tag{25}$$

while if (25) is strict, then (24c) is also strict on some interval $(0, \epsilon)$, $\epsilon > 0$.

So little is known about the deformation response of the free energy for nonclassical fluids, it is perhaps of interest to note yet another simple consequence of Eq. (24b). Let $\mathbf{M} \in T_s^0 - \{0\}$ be a point where $\tilde{\psi}(\theta, \cdot)$ has a local minimum (maximum); thus $\tilde{\psi}(\theta, \mathbf{M}) \leq (\geq)\, \tilde{\psi}(\theta, \mathbf{A}_1)$ for all $\mathbf{A}_1$ near $\mathbf{M}$ and, by Eq. (24b), this means that $\int_0^m \bar{\alpha}(\theta, \xi)d\xi \leq (\geq) \int_0^z \bar{\alpha}_1(\theta, \xi)d\xi$ for all z in some neighborhood of $m = |\mathbf{M}|^2 \neq 0$.

Equivalently,

$$h(z) \equiv \int_0^z \bar{\alpha}_1(\theta, \xi)d\xi - \int_0^m \bar{\alpha}_1(\theta, \xi)d\xi \geq (\leq)\ 0$$

for all z near to m, while $h(m) = 0$; therefore $h'(m) = 0$ and $h''(m) \geq (\leq)\ 0$, i.e.,

$$\bar{\alpha}_1(\theta, m) = 0 \quad \text{and} \quad \partial_\xi \bar{\alpha}_1(\theta, m) \geq (\leq)\ 0. \tag{$\dagger$}$$

Furthermore, if ($\dagger$) holds with a strict inequality then $\tilde{\psi}(\theta, \cdot)$ will indeed have a strict local minimum (maximum) at any tensor $\mathbf{M} \in T_s^0$ with $|\mathbf{M}|^2 = m \neq 0$. Thus, for each fixed θ, *the places where the graph of* $\bar{\alpha}_1(\theta, \xi)$ *crosses the* ξ *axis determine the nonzero tensors for which* $\tilde{\psi}(\theta, \cdot)$ *is stationary and if* $\partial_\xi \bar{\alpha}_1 \neq 0$ *at such a crossing then the stationary value of* $\tilde{\psi}(\theta, \cdot)$ *is a minimum (maximum) for an increasing (decreasing) crossing.* This suggests that the fluids examined here admit of a mechanism for the successive interlacing of locally stable and locally unstable classes of stretchings (1/2) $\mathbf{A}_1$ and, if Eq. (24c) holds for all $z \in [0, \infty)$, the first such class on nonzero stretchings will necessarily be locally unstable, i.e., will render $\tilde{\psi}(\theta, \cdot)$ a local maximum. Interesting possible connections with the problem of turbulence are thus brought to mind but we do not pursue these matters here.

Proof: We begin the proof of Theorem 2 by showing that $\tilde{\psi}(\theta, \mathbf{A}_1)$ can depend on $\mathbf{A}_1$ only through $|\mathbf{A}_1|$. To do this let $\mathbf{M}_0$ and $\mathbf{M}_1$ be any two tensors in T_s^0 with $|\mathbf{M}_0| = |\mathbf{M}_1|$; we will show that $\tilde{\psi}(\theta, \mathbf{M}_0) = \tilde{\psi}(\theta, \mathbf{M}_1)$. Indeed, since $\mathbf{M}_0$ and $\mathbf{M}_1$ lie on the same sphere in T_s^0 (of radius

$|\mathbf{M}_0|$ and centered at 0) and since this sphere is pathwise connected,* there exists a continuously differentiable path $\mathbf{M}(\tau)$ in T_s^0 such that $\mathbf{M}(0) = \mathbf{M}_0$, $\mathbf{M}(1) = \mathbf{M}_1$, and $|\mathbf{M}(\tau)| = |\mathbf{M}_0|$ for all $\tau \in [0, 1]$.* For such a path we see, by Eq. (23a), that

$$\begin{aligned}\frac{d}{d\tau}\tilde{\psi}[\theta, \mathbf{M}(\tau)] &= \tilde{\psi}_{\mathbf{A}_1}[\theta, \mathbf{M}(\tau)] \cdot \dot{\mathbf{M}}(\tau)\\ &= \tfrac{1}{2}\tilde{\tilde{\alpha}}_1[\theta, \mathbf{M}(\tau)]\mathbf{M}(\tau) \cdot \dot{\mathbf{M}}(\tau)\\ &= \frac{1}{4}\tilde{\tilde{\alpha}}_1[\theta, \mathbf{M}(\tau)]\frac{d}{d\tau}|\mathbf{M}(\tau)|^2\\ &= 0,\end{aligned}$$

since $|\mathbf{M}(\tau)|$ is constant and where $\dot{\mathbf{M}}(\tau) \equiv (d/d\tau)\mathbf{M}(\tau)$. We conclude then that $\tilde{\psi}[\theta, \mathbf{M}(\tau)]$ is constant so, as claimed,

$$\tilde{\psi}(\theta, \mathbf{M}_0) = \tilde{\psi}(\theta, \mathbf{M}_1) \tag{26}$$

for any two tensors $\mathbf{M}_0$ and $\mathbf{M}_1$ in T_s^0 with $|\mathbf{M}_0| = |\mathbf{M}_1|$.

It follows from Eq. (26) that if we select any tensor $\mathbf{G}$ in T_s^0 with $|\mathbf{G}| = 1$ and if we define

$$\bar{\psi}(\theta, m) \equiv \tilde{\psi}(\theta, m^{1/2}\mathbf{G}) \tag{27a}$$

for $m \in [0, \infty)$, then

$$\tilde{\psi}(\theta, \mathbf{M}) = \tilde{\psi}(\theta, |\mathbf{M}|\mathbf{G}) = \bar{\psi}(\theta, |\mathbf{M}|^2) \tag{27b}$$

for all $\mathbf{M} \in T_s^0$. Furthermore, it is clear that the function $\bar{\psi}(\theta, \cdot)$ is continuously differentiable everywhere with the possible exception of 0 and, indeed,

$$\partial_m\bar{\psi}(\theta, m) = \tfrac{1}{2}m^{-1/2}\tilde{\psi}_{\mathbf{A}_1}(\theta, m^{1/2}\mathbf{G}) \cdot \mathbf{G}$$

for all $m > 0$. Thus, by Eq. (23a) we have that for $m > 0$

* Let $m_i^\gamma \mathbf{e}_i^\gamma \otimes \mathbf{e}_i^\gamma$, γ-no sum, be the spectral representation of $\mathbf{M}_\gamma$, $\gamma = 0, 1$, where both the orthonormal bases $\{\mathbf{e}_1^\gamma, \mathbf{e}_2^\gamma, \mathbf{e}_3^\gamma\}$ are right-handed. Let $\mathbf{Q}(\tau)$ be an orthogonal tensor function that rotates $\{\mathbf{e}_1^0, \mathbf{e}_2^0, \mathbf{e}_3^0\}$ into $\{\mathbf{e}_1^1, \mathbf{e}_2^1, \mathbf{e}_3^1\}$, i.e., $\mathbf{Q}(\cdot)$ is smooth on $[0, 1]$ with $\mathbf{Q}(0) = \mathbf{1}$ and $\mathbf{Q}(1)\mathbf{e}_i^0 = \mathbf{e}_i^1$, $i = 1, 2, 3$. Thus, $\mathbf{e}_i(\tau) \equiv \mathbf{Q}(\tau)\mathbf{e}_i^0$, $i = 1, 2, 3$, will define an orthonormal basis. Since $\mathbf{M}_0$ and $\mathbf{M}_1$ are traceless we see that $\sum_{i=1}^3 m_i^\gamma = 0$, $\gamma = 0, 1$, and hence each eigentriad $\{m_1^\gamma, m_2^\gamma, m_3^\gamma\}$ lies in the plane $\Pi = \{(x, y, z) | x + y + z = 0\}$ in $\mathbb{R}^3$. Furthermore, since $|\mathbf{M}_0| = |\mathbf{M}_1|$, we also see that

$$\sum_{i=1}^3 (m_i^0)^2 = \sum_{i=1}^3 (m_i^1)^2,$$

i.e., the triads $\{m_1^\gamma, m_2^\gamma, m_3^\gamma\}$ also lie on the same circle $\mathcal{C}$ in the plane Π. Since this circle is certainly pathwise connected, there are smooth functions $m_i(\tau)$ on $[0, 1]$, $i = 1, 2, 3$, such that $m_i(0) = m_i^0$, $m_i(1) = m_i^1$, and $\{m_1(\tau), m_2(\tau), m_3(\tau)\} \in \mathcal{C} \cap \Pi$. The desired path $\mathbf{M}(\tau)$ connecting $\mathbf{M}_0$ to $\mathbf{M}_1$ may now be taken to be $\mathbf{M}(\tau) = m_i(\tau)\mathbf{e}_i(\tau) \otimes \mathbf{e}_i(\tau)$.

$$2m^{1/2}\partial_m\bar{\psi}(\theta, m) = \tilde{\psi}_{\mathbf{A}_1}(\theta, m^{1/2}\mathbf{G}) \cdot \mathbf{G} = \frac{1}{2\rho}\,\tilde{\tilde{\alpha}}_1(\theta, m^{1/2}\mathbf{G})(m^{1/2}\mathbf{G}) \cdot \mathbf{G}$$

or, equivalently,

$$\partial_m\bar{\psi}(\theta, m) = \frac{1}{4\rho}\,\tilde{\tilde{\alpha}}_1(\theta, m^{1/2}\mathbf{G}) \;\forall\; m \in (0, \infty).$$

Therefore, by the continuity of $\tilde{\tilde{\alpha}}_1(\theta, \cdot)$, we see that $\lim_{m\to 0}\partial_m\bar{\psi}(\theta, m)$ exists [and equals $(1/4\rho)\tilde{\tilde{\alpha}}_1(\theta, 0)$] and so, by a standard mean value type of argument, we know that $\bar{\psi}(\theta, \cdot)$ is differentiable from the right at 0 [with $\partial_m\bar{\psi}(\theta, 0) = (1/4\rho)\tilde{\tilde{\alpha}}_1(\theta, 0)$].*

If we now combine Eq. (23a) with Eq. (27b) we find that

$$\tfrac{1}{2}\tilde{\tilde{\alpha}}_1(\theta, \mathbf{M})\mathbf{M} \cdot \dot{\mathbf{M}} = \rho\tilde{\psi}_{\mathbf{A}_1}(\theta, \mathbf{M}) \cdot \dot{\mathbf{M}} = \rho\partial_m\bar{\psi}(\theta, |\mathbf{M}|^2)2\mathbf{M} \cdot \dot{\mathbf{M}}$$

for any two tensors $\mathbf{M}$ and $\dot{\mathbf{M}}$ in T_s^0. Clearly then $\tilde{\tilde{\alpha}}_1(\theta, \mathbf{M}) = 4\rho\partial_m\bar{\psi}(\theta, |\mathbf{M}|^2)$ for every $\mathbf{M} \in T_s^0$ and so $\tilde{\alpha}_1(\theta, \mathbf{M})$ depends on $\mathbf{M}$ only through $|\mathbf{M}|$. Thus, with

$$\bar{\alpha}_1(\theta, m) \equiv \tilde{\tilde{\alpha}}_1(\theta, m^{1/2}\mathbf{G}), \quad m \in [0, \infty),$$

we have shown that

$$\frac{1}{4\rho}\,\bar{\alpha}_1(\theta, |\mathbf{M}|^2) = \partial_m\bar{\psi}(\theta, |\mathbf{M}|^2) = \frac{1}{4\rho}\,\tilde{\tilde{\alpha}}_1(\theta, \mathbf{M}) \;\forall\; \mathbf{M} \in T_s^0$$

which, with Eq. (27b), establishes Eq. (24). ■

By Theorem 2 all that remains of the reduced dissipation inequality is the restriction in Eq. (23b), i.e., that for every $\mathbf{A}_1 \in T_s^0$

$$\tilde{\tilde{\mu}}(\theta, \mathbf{A}_1)\mathrm{tr}\mathbf{A}_1^2 + \{\bar{\alpha}_1(\theta, |\mathbf{A}_1|^2) + \tilde{\tilde{\alpha}}_2(\theta, \mathbf{A}_1)\}\mathrm{tr}\mathbf{A}_1^3 \geq 0, \tag{28}$$

where we have used Eq. (24a). Now $\tilde{\tilde{\mu}}(\theta, \mathbf{A}_1)$ and $\tilde{\tilde{\alpha}}_2(\theta, \mathbf{A}_1)$ are isotropic functions of $\mathbf{A}_1$ and therefore we may use standard representation theorems[5] to write $\tilde{\tilde{\mu}}(\theta, \mathbf{A}_1) = \bar{\mu}(\theta, |\mathbf{A}_1|^2, \mathrm{tr}\mathbf{A}_1^3)$ and $\tilde{\tilde{\alpha}}_2(\theta, \mathbf{A}_1) = \bar{\alpha}_2(\theta, |\mathbf{A}_1|^2, \mathrm{tr}\mathbf{A}_1^3)$. Thus, the inequality (28) takes the form

$$\bar{\mu}(\theta, |\mathbf{A}_1|^2, \mathrm{tr}\mathbf{A}_1^3)|\mathbf{A}_1|^2 + \{\bar{\alpha}_1(\theta, |\mathbf{A}_1|^2) + \bar{\alpha}_2(\theta, |\mathbf{A}_1|^2, \mathrm{tr}\mathbf{A}_1^3)\}\mathrm{tr}\mathbf{A}_1^3 \geq 0 \tag{29}$$

for $\mathbf{A}_1 \in T_s^0$.

* One can show that differentiability of $\bar{\psi}(\theta, \cdot)$ at 0 is equivalent to the existence of $\psi_{\mathbf{A}_1\mathbf{A}_1}(\theta, 0)$ and that, indeed, $\partial_m\bar{\psi}(\theta, 0) = (1/2)\tilde{\psi}_{\mathbf{A}_1\mathbf{A}_1}(\theta, 0) \cdot (\mathbf{G} \otimes \mathbf{G})$. This is a special case of a more general result obtained in ref. 3 that a continuity assumption on the stress (here, on α_1) yields a differentiability condition on a derivative of the free energy [here, on $\tilde{\psi}_{\mathbf{A}_1}(\theta, \cdot)$].

To analyze (29) we need a result of Fosdick and Rajagopal[4] who showed that

$$-\frac{1}{\sqrt{6}}\,|\mathbf{A}_1|^3 \le \mathrm{tr}\mathbf{A}_1^3 \le \frac{1}{\sqrt{6}}\,|\mathbf{A}_1|^3$$

for any tensor $\mathbf{A}_1$ in T_s^0.* Moreover, since $\mathrm{tr}\mathbf{A}_1^3$ is a continuous function of $\mathbf{A}_1$, it follows* that on each sphere $|\mathbf{A}_1| = \text{const}$, $\mathrm{tr}\mathbf{A}_1^3$ ranges over the entire interval $[-(1/\sqrt{6})|\mathbf{A}_1|^3, (1/\sqrt{6})|\mathbf{A}_1|^3]$. We see then that the domain of $\bar{\mu}(\theta, \cdot, \cdot)$ and $\bar{\alpha}_2(\theta, \cdot, \cdot)$ is the closed wedge in $\mathbb{R}^2$ given by

$$W = \left\{(x, y)\,\middle|\, x \ge 0, -\frac{1}{\sqrt{6}}\,x^{3/2} \le y \le \frac{1}{\sqrt{6}}\,x^{3/2}\right\},$$

and that now the inequality (29) may be put in the form

$$\bar{\mu}(\theta, x, y)x + \{\bar{\alpha}_1(\theta, x) + \bar{\alpha}_2(\theta, x, y)\}y \ge 0 \tag{30}$$

for all $(x, y) \in W$.

If we set $y = 0$ in (30) we find straightaway that $\bar{\mu}(\theta, x, 0) \ge 0$ for all $x \ge 0$, i.e., since $\mathrm{tr}\mathbf{A}_1^3 = 3 \det \mathbf{A}_1$ (by the Cayley–Hamilton theorem for $\mathbf{A}_1 \in T_s^0$), we have that

$$\tilde{\bar{\mu}}(\theta, \mathbf{A}_1) = \bar{\mu}(\theta, |\mathbf{A}_1|^2, 0) \ge 0$$

for every $\mathbf{A}_1$ in T_s^0 with at least one eigenvalue equal to zero. Next, replace y in (30) with $-y$ to find

$$\{\bar{\alpha}_1(\theta, x) + \bar{\alpha}_2(\theta, x, -y)\}y \le \bar{\mu}(\theta, x, -y)x \tag{31}$$

for all $(x, y) \in W$. Thus, if $\bar{\alpha}_2(\theta, x, y)y \le \bar{\alpha}_2(\theta, x, -y)y$ on W (see below), then the inequalities (30) and (31) together imply that

$$-\bar{\mu}(\theta, x, y)x \le \{\bar{\alpha}_1(\theta, x) + \bar{\alpha}_2(\theta, x, y)\}y \le \bar{\mu}(\theta, x, -y)x$$

on W and so, in particular,

$$\frac{-\bar{\mu}(\theta, x, |y|)}{|y|/x} \le \bar{\alpha}_1(\theta, x) + \bar{\alpha}_2(\theta, x, y) \le \frac{\bar{\mu}(\theta, x, -|y|)}{|y|/x} \tag{32}$$

for all (x, y) in W with $x \neq 0 \neq y$. Thus, if $(x, y) = [x(\tau), y(\tau)]$ is any

* The estimate is sharp since equality results if $\mathbf{A}_1 = 1/\sqrt{6}\,(3\mathbf{e} \otimes \mathbf{e} - 1)$, $|\mathbf{e}| = 1$.

curve in W for which

$$\frac{|y(\tau)|}{x(\tau)} \to \infty \text{ as } \tau \to \infty,^*$$

and if $\bar{\mu}[\theta, x(\tau), \pm |y(\tau)|]$ stays bounded on such curves, then $\bar{\alpha}_1[\theta, x(\tau)] + \bar{\alpha}_2[\theta, x(\tau), y(\tau)] \to 0$ as $\tau \to \infty$, i.e.,

$$\tilde{\tilde{\alpha}}_1[\theta, \mathbf{A}_1(\tau)] + \tilde{\tilde{\alpha}}_2[\theta, \mathbf{A}_1(\tau)] = \bar{\alpha}_1[\theta, |\mathbf{A}_1(\tau)|^2] + \bar{\alpha}_2[\theta, |\mathbf{A}_1(\tau)|^2, \mathrm{tr}\mathbf{A}_1^3(\tau)] \to 0$$

as $\tau \to \infty$ for all stretching paths $\mathbf{A}_1(\cdot)$: $[0, \infty) \to T_s^0$ for which

$$\frac{|\mathrm{tr}\mathbf{A}_1^3(\tau)|}{\mathrm{tr}\mathbf{A}_1^2(\tau)} \to \infty \text{ as } \tau \to \infty.^\dagger$$

Lastly, we observe that in the special case when $\bar{\mu}(\theta, x, y)$ and $\bar{\alpha}_2(\theta, x, y)$ are independent of y the estimate (32) automatically holds and we may take $|y| = (1/\sqrt{6})x^{3/2}$ to find that

$$-\sqrt{6}\,\frac{\bar{\mu}(\theta, |\mathbf{A}_1|^2)}{|\mathbf{A}_1|} \le \bar{\alpha}_1(\theta, |\mathbf{A}_1|^2) + \bar{\alpha}_2(\theta, |\mathbf{A}_1|^2) \le \sqrt{6}\,\frac{\bar{\mu}(\theta, |\mathbf{A}_1|^2)}{|\mathbf{A}_1|},^\ddagger$$

for all $|\mathbf{A}_1| \neq 0$ and where now $\mu = \bar{\mu}(\theta, |\mathbf{A}_1|^2)$ is always non-negative. In particular, we see that if the viscosity μ is bounded then $\alpha_1 + \alpha_2 \to 0$ as $|\mathbf{A}_1| \to \infty$.

The condition that $\bar{\alpha}_2(\theta, x, y)y \le \bar{\alpha}_2(\theta, x, -y)y$ on W is equivalent to $\bar{\alpha}_2(\theta, x, y) \le \bar{\alpha}_2(\theta, x, -y)$ on W for $y \ge 0$. To interpret this let $x = |\mathbf{A}_1|^2$ and $y = \mathrm{tr}\mathbf{A}_1^3 = 3 \det \mathbf{A}_1$ for $\mathbf{A}_1 \in T_s^0$ so that $y \geqslant 0$ if and only if exactly two eigenvalues of $\mathbf{A}_1$ are nonpositive. Since $\tilde{\tilde{\alpha}}_2(\theta, \mathbf{A}_1) = \bar{\alpha}_2(\theta, |\mathbf{A}_1|^2, \mathrm{tr}\mathbf{A}_1^3)$, we see that we are requiring that $\tilde{\tilde{\alpha}}_2(\theta, \mathbf{A}_1) \le \tilde{\tilde{\alpha}}_2(\theta, -\mathbf{A}_1)$ for every $\mathbf{A}_1 \in T_s^0$ with exactly two nonpositive eigenvalues, i.e., each uniaxial elongation $\mathbf{A}_1$ is to yield a value of α_2 no larger than that yielded by the uniaxial contraction $-\mathbf{A}_1$.

SECTION 4: ASYMPTOTIC MECHANICAL STABILITY

Suppose we now enclose one of the fluids of Section 3 in a rigid container Ω which, up to time $t = 0$, we shake in an arbitrary fashion and then hold fixed for all $t \ge 0$. Assuming that the Helmholtz free

* Note that since $|y|/x \le (1/\sqrt{6})\, x^{1/2}$ for $(x, y) \in W$, $x \neq 0$, this limit condition means that $x(\tau) \to \infty$ with τ and that $|y(\tau)|$ must grow with τ at a rate larger than $x(\tau)$ and less than or equal to $(1/\sqrt{6})x^{3/2}(\tau)$.

† Note that this is satisfied by all nonconstant straight line paths $\mathbf{A}_1(\tau) = \mathbf{A} + \tau\mathbf{B}$, $\mathbf{A}$ and $\mathbf{B}$ in T_s^0.

‡ This is bound on $\alpha_1 + \alpha_2$, should be compared with the bound (4.15c) of ref. 12 for *third* grade fluids.

energy has a weak global minimum at the rest state, we now formulate rather mild hypotheses on the response functions for μ, α_1, and α_2 sufficient to ensure the decay to zero as $t \to \infty$ of the positive definite functional of the velocity field $\mathbf{v}(\cdot, \cdot)$ given by

$$E(t) \equiv \int_\Omega \left\{ |\mathbf{v}(\mathbf{x}, t)|^2 + \frac{1}{2\rho} \int_0^{|\mathbf{A}_1(\mathbf{x},t)|^2} \bar{\alpha}_1(\theta, \xi) d\xi \right\} dv, \tag{33}$$

where, by Eq. (14a), $\mathbf{A}_1(\mathbf{x}, t) \equiv \text{grad } \mathbf{v}(\mathbf{x}, t) + \text{grad } \mathbf{v}(\mathbf{x}, t)^T$. Thus, even though the stress-deformaton response of our fluid is highly nonlinear, we see that its rest state is strongly stable in that any initial disturbance necessarily evolves over time in such a way that both

$$|\mathbf{v}(\mathbf{x}, t)|^2 \quad \text{and} \quad \int_0^{|\mathbf{A}_1(\mathbf{x},t)|^2} \bar{\alpha}_1(\theta, \xi) d\xi$$

tend in mean to zero. Like the less involved analyses presented in ref. 3 for second grade fluids, the results here suggest that those fluids of Section 3 for which the free energy has a strict global minimum in equilibrium are much better behaved physically and analytically than Navier–Stokes fluids since not only does $|\mathbf{v}|^2$ decay in mean but so also does the function of grad $\mathbf{v}$, $\int_0^{|\mathbf{A}_1|^2} \bar{\alpha}_1(\theta, \xi) d\xi$. However, unlike Corollary 2 of Theorem 9 of ref. 3, our results do not yield the exponential decay of the functional $E(t)$ as $t \to \infty$.

Before starting the analysis we eliminate the temperature θ from our considerations—it will then appear as essentially a parameter—by either supposing that the temperature field is uniform over Ω and constant in time for all $t \geq 0$, or by supposing that for all θ, $\mathbf{L}$, $\dot{\mathbf{L}}$, and $\mathbf{g}$,

$$\hat{\mathbf{T}}(\theta, \mathbf{g}, \mathbf{L}, \dot{\mathbf{L}}) = \alpha_0 \mathbf{1} + \mu \mathbf{A}_1 + \alpha_1 \mathbf{A}_2 + \alpha_2 \mathbf{A}_1^2,$$

where $\tilde{\mu} = \tilde{\tilde{\mu}}(\theta, \mathbf{A}_1)$ and $\alpha_i = \tilde{\tilde{\alpha}}_i(\theta, \mathbf{A}_1)$, $i = 0, 1, 2$, with $\partial_\theta \tilde{\tilde{\alpha}}_1(\theta, \mathbf{A}_1) \equiv 0$. In either case all of the results and restrictions of Section 3 will then apply to the response functions of the fluid throughout its motion in Ω on $[0, \infty)$ and (see below) we will have that $(d/dt) \int_0^{|\mathbf{A}_1|^2} \bar{\alpha}_1(\theta, \xi) d\xi = \bar{\alpha}_1(\theta, |\mathbf{A}_1|^2) \overline{|\mathbf{A}_1|^2}^{\cdot}$ for all $t \geq 0$.

Now, throughout its motion in the rigid container Ω, the fluid must satisfy the balance of linear momentum, i.e.,

$$\text{div } \mathbf{T} + \rho \mathbf{b} = \rho \dot{\mathbf{v}}, \tag{34}$$

where $\mathbf{b} = \mathbf{b}(\mathbf{x}, t)$ is the specific body force per unit mass acting throughout the fluid. So, if we form the scalar product of Eq. (34)

with $\mathbf{v}$, integrate over Ω, use the divergence theorem and conservation of mass, we find the familiar power theorem:

$$\frac{d}{dt}\int_\Omega \frac{1}{2}\rho|\mathbf{v}|^2\,dv + \int_\Omega \mathbf{T}\cdot\mathbf{L}\,dv = \int_{\partial\Omega}\mathbf{v}\cdot\mathbf{T}\,\mathbf{n}\,da + \int_\Omega \rho\mathbf{v}\cdot\mathbf{b}\,dv.$$

Therefore, if for $t \geq 0$ we suppose that the fluid adheres to the stationary walls of the container Ω and that $\mathbf{b}$ is derivable from a potential, then we have that

$$\frac{d}{dt}\int_\Omega \frac{1}{2}\rho|\mathbf{v}|^2\,dv + \int_\Omega \mathbf{T}\cdot\mathbf{L}\,dv = 0 \;\forall\; t \geq 0. \tag{35}$$

We see next that, by Eqs. (22) and (14) the stress power is given by $\mathbf{T}\cdot\mathbf{L} = (1/2)\,\mathbf{T}\cdot\mathbf{A}_1 = (1/2)\{\mu|\mathbf{A}_1|^2 + \alpha_1\mathbf{A}_1\cdot\dot{\mathbf{A}}_1 + (\alpha_1+\alpha_2)\mathrm{tr}\mathbf{A}_1^3\}$. Therefore, since here $\alpha_1 = \alpha_1(\theta, \mathbf{A}_1)$, we may apply Eq. (24a) of Theorem 2 to write

$$\begin{aligned}\mathbf{T}\cdot\mathbf{L} &= \frac{1}{2}\left\{\mu|\mathbf{A}_1|^2 + \frac{1}{2}\,\bar{\alpha}_1(\theta, |\mathbf{A}_1|^2)\dot{\overline{|\mathbf{A}_1|^2}} + (\alpha_1+\alpha_2)\mathrm{tr}\mathbf{A}_1^3\right\}\\ &= \frac{1}{2}\left\{\mu|\mathbf{A}_1|^2 + \frac{1}{2}\frac{d}{dt}\int_0^{|\mathbf{A}_1|^2}\bar{\alpha}_1(\theta,\xi)d\xi + (\alpha_1+\alpha_2)\mathrm{tr}\mathbf{A}_1^3\right\},\end{aligned} \tag{36}$$

since, as discussed above, $\partial_\theta\bar{\alpha}_1\dot{\theta} \equiv 0$ for the process we are considering. If we substitute Eq. (36) into Eq. (35) and use conservation of mass and the fact that ρ is constant we see that

$$\begin{aligned}\frac{d}{dt}\int_\Omega &\left\{|\mathbf{v}|^2 + \frac{1}{2\rho}\int_0^{|\mathbf{A}_1|^2}\bar{\alpha}_1(\theta,\xi)d\xi\right\}dv\\ &+ \int_\Omega \frac{1}{\rho}\{\mu|\mathbf{A}_1|^2 + (\alpha_1+\alpha_2)\mathrm{tr}\mathbf{A}_1^3\}dv = 0\end{aligned} \tag{37a}$$

for all $t \geq 0$, i.e.,

$$\frac{d}{dt}E(t) = -\int_\Omega \frac{1}{\rho}\{\mu|\mathbf{A}_1|^2 + (\alpha_1+\alpha_2)\mathrm{tr}\mathbf{A}_1^3\}dv \leq 0, \tag{37b}$$

where we have used the definition Eq. (33) and the thermodynamic inequality (23b) and where, by (24c) of Theorem 2, $E(t)$ is a positive definite functional of the velocity field if the Helmholtz free energy as a weak global minimum at equilibrium.

By (37b) we see that the functional $E(t)$ is nonincreasing on $[0, \infty)$ and indeed, by Eq. (23b), can only cease decreasing if the non-negative form $\mu|\mathbf{A}_1|^2 + (\alpha_1+\alpha_2)\mathrm{tr}\mathbf{A}_1^3$ vanishes throughout Ω. This suggests that if we can bound $\mu|\mathbf{A}_1|^2 + (\alpha_1 + \alpha_2)\mathrm{tr}\mathbf{A}_1^3$ away from zero in an appropriate fashion then we will ensure that the energy dissipation throughout the fluid is extensive enough for $E(t) \to 0$ as $t \to \infty$. In fact, for our fluids we have

Theorem 3: *Let $\mathbf{v}(\cdot, \cdot)$ be the velocity field of any flow which takes place inside a stationary rigid container Ω under the action of a conservative body force field with $\mathbf{v}(\mathbf{x}, t)|_{\mathbf{x}\in\partial\Omega} = 0$ for all $t \geq 0$. Suppose that the Helmholtz free energy has a global minimum in equilibrium, that the response functions $\tilde{\tilde{\mu}}$, $\tilde{\tilde{\alpha}}_1$, and $\tilde{\tilde{\alpha}}_2$ are such that*

$$0 \leq \phi(|\mathbf{A}_1|^2) \leq \tilde{\tilde{\mu}}(\theta, \mathbf{A}_1)|\mathbf{A}_1|^2 + \{\tilde{\tilde{\alpha}}_1(\theta, \mathbf{A}_1) + \tilde{\tilde{\alpha}}_2(\theta, \mathbf{A}_1)\}\mathrm{tr}\mathbf{A}_1^3 \;\forall\; \mathbf{A}_1 \in T_s^0 \tag{38}$$

for some continuous, convex function $\phi(\cdot)$: $[0, \infty) \to [0, \infty)$ which vanishes only at 0 and, lastly, suppose that $\tilde{\tilde{\alpha}}_1[\theta, \mathbf{A}_1(\cdot, \cdot)] = \bar{\alpha}_1[\theta, |\mathbf{A}_1(\cdot, \cdot)|^2]$ is bounded above on $\Omega \times [0, \infty)$, where $\mathbf{A}_1(\cdot, \cdot) \equiv \mathrm{grad}\, \mathbf{v}(\cdot, \cdot) + \mathrm{grad}\, \mathbf{v}(\cdot, \cdot)^T$. *Then, with $E(t)$ as in* Eq. (33), *we have*

$$E(t) \to 0 \text{ as } t \to \infty.$$

The condition that $\bar{\alpha}_1[\theta, |\mathbf{A}_1(\cdot, \cdot)|^2]$ be bounded above on $\Omega \times [0, \infty)$ will be satisifed if either $\bar{\alpha}_1(\theta, x)$, $x \geq 0$, is bounded above (a material restriction) or if $|\mathbf{A}_1(\mathbf{x}, t)|^2$, $(\mathbf{x}, t) \in \Omega \times [0, \infty)$, is bounded (a flow restriction). To analyze the restriction (38), consider the function

$$\delta(\theta, x) \equiv \inf_{y \in I(x)} \{\bar{\mu}(\theta, x, y)x + [\bar{\alpha}_1(\theta, x) + \bar{\alpha}_2(\theta, x, y)]y\},$$

where $I(x) = \{y \,|\, |y| \leq (1/\sqrt{6})\; x^{3/2}\}$ and $\bar{\mu}(\theta, \cdot, \cdot)$, $\bar{\alpha}_1(\theta, \cdot, \cdot)$, and $\bar{\alpha}_2(\theta, \cdot, \cdot)$, defined on the wedge $W = \cup_{x \geq 0}\{x\} \times I(x)$, are as in (29) and (30). It may be shown that $\delta(\theta, \cdot)$ is continuous as well as, by (30), non-negative and it is easily seen that (38) is equivalent to the requirement that

$$0 \leq \phi(x) \leq \delta(\theta, x) \;\forall\; x \in [0, \infty) \tag{39}$$

for some continuous, convex function $\phi(\cdot)$ which vanishes only at 0. Setting aside the dependence of $\delta(\theta, x)$ on the value(s) of θ taken on in the process—and to do this is essentially to impose a uniformity requirement—what (39) asserts is that the non-negative function $\delta(\cdot) \equiv \delta(\theta, \cdot)$ is minorizable by a continuous, non-negative, convex function that vanishes only at 0. This is a fairly mild requirement on $\delta(\cdot)$; indeed, (39) necessitates that (i) $\delta(x) = 0$ only if $x = 0$, and that (ii) for

$N \in (0, \infty)$ there exists $a_N > 0$ such that $a_N x \leq \delta(x)$ for all $x \in [N, \infty)$ (see lemma A.1 of the Appendix). The first of these conditions is just a strengthening of the thermodynamic requirement (30) while the second condition is, in essence, a growth requirement at ∞ on $\delta(\cdot)$, i.e., $\delta(x)$ must go to infinity with x at least as fast as some straight line $a_N x$, $a_N > 0$. Moreover, it may be shown that the above two conditions also suffice for $\delta(\cdot)$ to satisfy (39). For Theorem 3 we now have the following:

Proof: By Eqs. (37b) and (38), we see that

$$\begin{aligned} -\frac{d}{dt}E(t) &= \frac{1}{\rho}\int_\Omega \{\mu|\mathbf{A}_1|^2 + (\alpha_1+\alpha_2)\mathrm{tr}\mathbf{A}_1^3\}dv \\ &\geq \frac{1}{\rho}\int_\Omega \phi(|\mathbf{A}_1|^2)dv \\ &\geq \frac{V}{\rho}\phi\left(\frac{1}{V}\int_\Omega |\mathbf{A}_1|^2\,dv\right), \end{aligned} \tag{40}$$

where the final inequality follows from Jensen's inequality[13] for the convex function $\phi(\cdot)$ and V denotes the volume of Ω.

Next, note that for any positive number N

$$\begin{aligned} \int_\Omega |\mathbf{A}_1|^2\,dv &= N\int_\Omega |\mathbf{A}_1|^2\,dv + (1-N)\int_\Omega |\mathbf{A}_1|^2\,dv \\ &\geq \frac{2N}{c}\int_\Omega |\mathbf{v}|^2\,dv + (1-N)\int_\Omega |\mathbf{A}_1|^2\,dv, \end{aligned}$$

since $\int_\Omega|\mathrm{grad}\,\mathbf{v}|^2\,dv = (1/2)\int_\Omega|\mathrm{grad}\,\mathbf{v} + \mathrm{grad}\,\mathbf{v}^{\mathbf{T}}|^2\,dv$ for any smooth vector field $\mathbf{v}$ vanishing on $\partial\Omega$ with $\mathrm{div}\,\mathbf{v} = 0$ throughout Ω and since, by Poincaré's inequality, $\int_\Omega|\mathbf{v}|^2\,dv \leq c\int_\Omega|\mathrm{grad}\,\mathbf{v}|^2\,dv$ for any smooth vector field $\mathbf{v}$ vanishing on $\partial\Omega$, where $c = c(\Omega)$ is a positive constant depending only on the domain Ω. Thus, we see that

$$\begin{aligned} \int_\Omega |\mathbf{A}_1|^2\,dv &\geq \frac{2N}{c}\int_\Omega \left\{|\mathbf{v}|^2 + \frac{1-N}{2N}c|\mathbf{A}_1|^2\right\}dv \\ &\geq \frac{2N}{\mathrm{c}}E(t), \end{aligned} \tag{41}$$

where for the final inequality we require, since $E(t)$ is as in Eq. (33), that

$$\frac{1-N}{2N}c\int_\Omega |\mathbf{A}_1|^2\,dv \geq \frac{1}{2\rho}\int_\Omega\int_0^{|\mathbf{A}_1|^2}\bar{\alpha}_1(\theta,\xi)\mathrm{d}\xi\,dv,$$

which will surely hold if

$$\int_0^{|\mathbf{A}_1|^2} \bar{\alpha}(\theta, \xi) d\xi \leq \frac{1-N}{N} \rho c |\mathbf{A}_1|^2 = \int_0^{|\mathbf{A}_1|^2} \frac{1-N}{N} \rho c \, d\xi.$$

In particular then, the estimate (41) will hold if

$$\bar{\alpha}_1(\theta, \xi) \leq \frac{1-N}{N} \rho c \ \forall \ \xi \in [0, \sup|\mathbf{A}_1|^2 (\cdot, \cdot)$$

which, since $[(1/N) - 1] \nearrow \infty$ as $N \searrow 0$, will surely be the case for an appropriate choice of $N = N^\dagger > 0$ given our hypothesis that $\bar{\alpha}_1[\theta, |\mathbf{A}_1|^2(\cdot, \cdot)]$ is bounded on $\Omega \times [0, \infty)$.

Now $\phi(\cdot)$ is convex, non-negative, and vanishes at 0; it thus follows (see lemma A.1 of the Appendix) that $\phi(\cdot)$ is monotone nondecreasing and therefore, by the estimate (41),

$$\phi\left(\frac{1}{V}\int_\Omega |\mathbf{A}_1|^2 \, dv\right) \geq \phi\left[\frac{2N^\dagger}{Vc} E(t)\right] \ \forall \ t \geq 0, \tag{42}$$

where we have used the fact that $E(t) \in [0, \infty)$ for all times t, since the Helmholtz free energy has a weak global minimum in equilibrium. If we combine the estimates (40) and (42) we reach the differential inequality

$$\frac{d}{dt} E(t) + \frac{V}{\rho} \phi\left[\frac{2N^\dagger}{Vc} E(t)\right] \leq 0 \ \forall \ t \geq 0,$$

which governs the evolution of the functional $E(t)$ throughout the flow. The theorem now follows at once if we set $f(\cdot) = (V/\rho)\phi[(2N^\dagger/Vc)(\cdot)]$ and apply lemma A.2 of the Appendix. ∎

The support of the Research Initiation Fund of the Engineering Science and Mechanics Department, Virginia Polytechnic Institute and State University, is gratefully acknowledged.

APPENDIX

For completeness we include here the following two useful lemmas. The first consists of some simple and well-known observations about convex functions; the second concerns the behavior at infinity enforced on any non-negative function $E(t)$ satisfying a rather simple and common differential inequality.

Lemma A.1: *Let $f(\cdot):[0, \infty) \to \mathbb{R}$ be convex with $f(0) = 0$. Then $z^{-1} f(z)$ is a monotone nondecreasing function of z on $(0, \infty)$.*

If, in addition, $f(\cdot)$ is non-negative then $f(\cdot)$ is also monotone non-decreasing on $[0, \infty)$.

Proof: The convexity of $f(\cdot)$ means that $f[\alpha p + (1-\alpha)q] \le \alpha f(p) + (1-\alpha)f(q)$ for all $\alpha \in [0, 1]$ and for all p and q in $[0, \infty)$. If we take $q = 0$ we find that $f(\alpha p) \le \alpha f(p)$ since $f(0) = 0$. Thus, for $0 \le z_1 < z_2 < \infty$, we may take $p = z_2$ and $\alpha = z_1/z_2$ to find that

$$f(z_1) \le \frac{z_1}{z_2} f(z_2),$$

which gives the first half of the lemma and also gives, if $f(\cdot)$ is non-negative, the second half since then $(z_1/z_2)f(z_2) \le f(z_2)$. ■

As a consequence of lemma A.1 we see that for any $\epsilon > 0$, $f(z)/z \le f(\epsilon)/\epsilon$ for all z in $(0, \epsilon]$, i.e., $f(z) \le kz$, $k \equiv f(\epsilon)/\epsilon$, for all $z \in [0, \epsilon)$. This means that continuous, non-negative, convex functions $f(\cdot)$ on $[0, \infty)$ which vanish only at 0 satisfy the hypotheses of

Lemma A.2: *Let $E(\cdot){:}[0, \infty) \to [0, \infty)$ be smooth and satisfy the differential inequality*

$$\frac{d}{dt}E(t) + f[E(t)] \le 0 \ \forall\ t \ge 0,$$

where $f(\cdot){:}[0, \infty) \to [0, \infty)$ is continuous, vanishes only at 0, and meets $f(z) \le kz^p$ on some interval $[0, \epsilon)$, $\epsilon > 0$, with $k > 0$ and $p \ge 1$. Then,

$$E(t) \to 0 \quad \text{as} \quad t \to \infty.$$

Proof: Since $(d/dt)E(t) \le -f[E(t)] \le 0$, the non-negative function $E(t)$ is monotone nonincreasing and possesses a limit as $t \to \infty$. Furthermore, it is thus clear that if $E(t^\dagger) = 0$ for any finite $t^\dagger$, then $E(\cdot)$ will vanish for all later times and the lemma holds trivially. We thus suppose that $E(t) > 0$ for all $t \in [0, \infty)$ and therefore our differential inequality takes the form

$$\frac{(d/dt)E(t)}{f[E(t)]} \le -1.$$

Equivalently,

$$\frac{d}{dt}F[E(t)] \le -1,$$

and therefore, for all $t \geqslant 0$,

$$F[E(t)] \le F[E(0)] - t, \tag{A1}$$

where $F(\cdot):(0, \infty) \to \mathbb{R}$ is defined by

$$F(z) \equiv \int_{z_0}^{z} \frac{d\xi}{f(\xi)}$$

for z_0 any fixed value in $(0, \infty)$.

Since $f(\cdot)$ is continuous and positive on $(0, \infty)$, we see that $F(z_0) = 0$, $F(z) > 0$ if $z > z_0$, and $F(z) < 0$ if $z < z_0$; moreover, $F(\cdot)$ is smooth and strictly monotone increasing on $(0, \infty)$. Furthermore, it also happens that $F(z) \downarrow -\infty$ as $z \downarrow 0$; indeed, since $f(z) \le kz^p$ on $[0, \epsilon)$, we see that

$$\int_{z}^{\epsilon} \frac{d\xi}{k\xi^p} \le \int_{z}^{\epsilon} \frac{d\xi}{f(\xi)} \;\forall\; z \in (0, \epsilon),$$

and therefore, for $z \in (0, \epsilon)$, we have the estimate

$$\begin{aligned} F(z) = \int_{z_0}^{z} \frac{d\xi}{f(\xi)} &= \int_{z_0}^{\epsilon} \frac{d\xi}{f(\xi)} + \int_{\epsilon}^{z} \frac{d\xi}{f(\xi)} \\ &\le F(\epsilon) + \int_{\epsilon}^{z} \frac{d\xi}{k\xi^p} \\ &= \begin{cases} \dfrac{z^{1-p}}{k(1-p)} + F(\epsilon) - \dfrac{\epsilon^{1-p}}{k(1-p)} & \text{if } p > 1 \\ \dfrac{\ln z}{k} + F(\epsilon) - \dfrac{\ln \epsilon}{k} & \text{if } p = 1. \end{cases} \end{aligned}$$

Clearly then for $p \ge 1$ we have that $F(z) \downarrow -\infty$ as $z \downarrow 0$. It follows then that the range of $F(\cdot)$ is of the form $(-\infty, \hat{a})$, where $\hat{a} \in (0, \infty]$.

Since $F(\cdot)$ is continuous and strictly increasing on $(0, \infty)$, it possesses a continuous and strictly increasing inverse $F^{-1}(\cdot)$ whose domain is, of course, the range of $F(\cdot)$, $(-\infty, \hat{a})$. Thus, the functional inequality (A1) yields

$$0 \le E(t) \le F^{-1}[F(E(0) - t)] \;\forall\; t \ge \hat{t}, \tag{A2}$$

where $\hat{t} \in [0, \infty)$ is the unique time t when $F[E(0)] - t = 0$, since from this time onward $F[E(t)]$ and $F[E(0)] - t$ are, by (A1), surely in the domain of $F^{-1}(\cdot)$. The lemma now follows upon letting $t \to \infty$ in (A2) since $F^{-1}(x) \to 0$ as $x \to -\infty$. ■

As the proof of lemma A.2 makes clear the hypothesis that $f(z) \le kz^p$ on $[0, \epsilon)$ for some $k > 0$ and $p \ge 1$ may be replaced with any condition on $f(\cdot)$ that ensures

$$\int_{z_0}^{z} \frac{d\xi}{f(\xi)} \downarrow -\infty \quad \text{as} \quad z \downarrow 0.$$

References

1. W. O. Criminale, J. L. Ericksen, and G. L. Filbey, Jr., *Arch. Rational Mech. Anal.*, **1**, 410 (1958).
2. B. D. Coleman and W. Noll, *Arch. Rational Mech. Anal.*, **6**, 355 (1960).
3. J. E. Dunn and R. L. Fosdick, *Arch. Rational Mech. Anal.*, **56**, 191 (1974).
4. R. L. Fosdick and K. R. Rajagopal, *Arch. Rational Mech. Anal.*, **70**, 145 (1979).
5. C. Truesdell and W. Noll, "The Non-Linear Field Theories of Mechanics," *Flügge's Handbuch der Physik, III/3*, Springer, Berlin, 1965.
6. R. B. Bird, *Phys. Fluids*, **3**, 539 (1960).
7. J. M. Dealy, *Trans. Soc. Rheol.*, **14**, 461 (1970).
8. J. L. Duda, *Trans. Soc. Rheol.*, **17**, 89 (1973).
9. V. J. Kremesec and J. C. Slattery, *Trans. Soc. Rheol.*, **21**, 469 (1977).
10. D. J. Jeffrey and A. Acrivos, *AIChE J.*, **22**, 417 (1976).
11. C.-C. Wang, *Arch. Rational Mech. Anal.*, **33**, 249 (1969).
12. R. L. Fosdick and K. R. Rajagopal, *Proc. R. Soc. London Ser. A*, **339**, 351 (1980).
13. W. Rudin, *Real and Complex Analysis*, McGraw-Hill, New York, 1974.

Received November 24, 1980
Accepted as revised September 1, 1981