fluids

MDPI

Article

On Objectivity, Irreversibility and Non-Newtonian Fluids

A. D. Kirwan, Jr.

School of Marine Science and Policy, University of Delaware, Robinson Hall, Newark, DE 19716, USA; adk@udel.edu

Academic Editor: Mehrdad Massoudi
Received: 18 December 2015; Accepted: 24 February 2016; Published: 1 March 2016

Abstract: Early progress in non-Newtonian fluid mechanics was facilitated by the emergence of two fundamental and complementary principles: objective constitutive characterizations and unambiguous identification of irreversible processes. Motivated by practical and economic concerns in recent years, this line of fluid research has expanded to include debris flows, slurries, biofluids and fluid-solid mixtures; *i.e.*, complex nonlinear fluids with disparate flow properties. Phenomenological descriptions of these fluids now necessarily include strong nonlinear coupling between the fluxes of mass, energy and momentum. Here, I review these principles, illustrate how they constrain the constitutive equations for non-Newtonian fluids and demonstrate how they have impacted other areas of fluid research.

Keywords: objectivity; material frame indifference; irreversibility; non-Newtonian fluids; turbulence; coherent Lagrangian structures

PACS: J0101

1. Introduction

Perhaps the original motivation for non-Newtonian fluid research was to characterize the viscoelastic properties of materials, such as paints and resins. In contrast to typical low Reynolds number viscous flow described by linear Newtonian type viscosity, it was found that constitutive equations for the stress required nonlinear terms. Walters [1] and Astarita [2] provide extensive reviews of early developments in non-Newtonian fluids.

Driven by economic concerns, interest in recent years has turned to even more complex flows. Examples are debris and slurries, biofluids and exotic mixtures, such as the huge surface slick resulting from the Deepwater Horizon accident, along with turbulent phenomena in these flows. Not only must phenomenological descriptions be characterized by nonlinearity, they usually require robust nonlinear coupling between fluxes of matter, momentum and energy; *i.e.*, processes not considered important in many early studies in non-Newtonian fluid mechanics. These processes also are now deemed important in many other areas of fluid mechanics not traditionally considered *non-Newtonian*.

Largely motivated by early research on non-Newtonian fluids, theorists developed two fundamental principles: the principle of material frame indifference (MFI, also called objectivity) and irreversibility. Considering the vast scope of fluid phenomena studied today and the inevitable push for progress, these principles sometimes are neglected, even though they are rigorously and well articulated in the theoretical mechanics literature. See [3] for a history and synopsis. They also have emerged as important constraints in other areas of fluid mechanics usually not considered to be non-Newtonian. Moreover, as noted by Hutter and Rajagopal [4], and Hutter and Schneider [5,6] both principles play complimentary roles in constraining constitutive equations.

The main goals here are to provide an overview of these two principles, demonstrate their applications to non-Newtonian fluid mechanics and illustrate how they have impacted other areas of fluid mechanics. It is hoped that this will contribute to a productive dialogue between disparate research groups. To further this, I have adopted an informal presentation style.

The balance of the paper is organized as follows. Section 2 reviews the foundations of MFI. It provides examples of objective and non-objective fluid mechanics quantities, develops objective rates and extends the analysis to mixtures. Section 3 considers irreversibility and develops a general formula that relates entropy production to scalar, vector and tensor processes. Section 4 briefly discusses applications of MFI to turbulence. The paper concludes with a brief synopsis and discussion of some areas of further research.

2. What is *Objectivity*?

2.1. Background

The notion of objectivity is found in early Greek and Chinese philosophies. This concept was often implied in solid mechanics research, particularly in the theoretical foundations of nonlinear elasticity early in the 20th century. Oldroyd [7] used the idea effectively in his work in rheology. However, to my knowledge, Noll [8–10] was the first to quantify this concept for broader use in physics. Malvern [11] and Gurtin [12] have lucid descriptions of the underlying mathematics. See also, Speziale [13], Murdoch [14], Frewer [15] and Pucci *et al.* [16] for recent discussions of some basic issues. As cogently explained by Truesdell and Toupin [3], *objectivity* encompasses two concepts. One is simply a coordinate transformation involving just rotation and transformation. The other is concerned with the philosophical matter of comparing measurements made by different observers attached to these coordinate systems. At a fundamental level, a change of observer is more than just a change of coordinate systems.

As noted by [3], Noll's formulation of MFI provided important restrictions to the construction of power law constitutive theories for viscoelastic materials. MFI also crystallizes the primitive concept that material responses to dynamic processes, such as stress or inter-constituent fluxes, are innate properties and thus insensitive to observer motions. I propose an additional reason. The most fundamental characteristic of non-Newtonian fluid behavior is irreversibility. Not only should constitutive equations that parameterize the intrinsic transport of mass, energy and momentum be insensitive to observer motions, they should unequivocally agree on irreversible behavior as posited by Grad [17].

Nevertheless, MFI is controversial. Müller [18] claimed that generally-accepted approximations for the momentum and heat fluxes arising from kinetic theory were incompatible with the principle of objectivity. Woods [19] further questioned the basic definitions. Murdoch [20] argued that Müller's results were in fact objective and that other studies, such as [21], could be readily rendered into frame-indifferent forms. The utility of MFI as a constraint on constitutive equations was the topic of an incisive discussion reported in *Physica A* [22]. Here, several investigators questioned the general validity of objectivity in material where centrifugal and Coriolis accelerations are dominate. In a later study [23], Evans and Heyes showed that ensemble averages arising from molecular dynamics simulations and group theoretic considerations are frame dependent.

What should be made of this? As noted recently by Liu and Sampio [24], much of the debate about MFI arises from confusion between the coordinate frame indifference and material frame indifference. The former is concerned with transformations between coordinate systems moving with respect to each other, while the latter concerns intrinsic properties of fluids, which are independent of observers. Perhaps the position of Bird [22] is appropriate here. He agreed that MFI was an approximation, but it has proven useful in many studies. To this, I would add that MFI also plays an important, but rarely appreciated, role in irreversibility.

2.2. Definition of Objectivity

The rationale for objectivity is that intrinsic properties of substances are not affected by the motions of observers. Measurements by different observers vary because they may be made at different times and because the observers may be moving and rotating with respect to each other. However, relative motion and time delay effects cancel for objective measurements. To quantify this, consider observers α and β embedded in two coordinate systems that are translating and rotating with respect to each other:

$$\mathbf{x}^{\alpha}(\mathbf{X}, t^{*}) = \mathbf{Q}(t) \cdot \mathbf{x}^{\beta}(\mathbf{X}, t) + \mathbf{b}(t) \tag{1}$$

Here, $\mathbf{Q}$ accounts for the rotation of β with respect to α. It satisfies $\mathbf{Q} \cdot \mathbf{Q}^{\dagger} = \mathbf{I}$, where $\mathbf{Q}^{\dagger}$ is the inverse of $\mathbf{Q}$ and $\mathbf{I}$ is the unit matrix. In the context used here, $\mathbf{Q}$ is the rotation matrix. The $\mathbf{X}$ are material coordinates embedded in the observed specimen and, thus, are unaffected by the motion of the observers. Furthermore, $\mathbf{b}$ is the translation of β relative to α. Finally, the observer times are simply shifted relative to each other as given by $t^{*} = t - a$, where a is an arbitrary time delay. I stress that objective transformations are more general than simple Galilean transformations in that they account for the instantaneous relative orientations of observers.

Obviously, relative motions of the observers will not affect measurements of scalar properties, such as temperature. It is not so simple with observations of vectors and tensors, as their components depend on observer coordinates. Objective vectors and tensors must depend only on the instantaneous orientations of the observers. That is, objective vectors $\mathbf{v}$ and tensors $\mathbf{T}$ must satisfy:

$$\begin{gathered} \mathbf{v}^{*} = \mathbf{Q} \cdot \mathbf{v} \\ \mathbf{T}^{*} = \mathbf{Q} \cdot \mathbf{T} \cdot \mathbf{Q}^{\dagger} \end{gathered} \tag{2}$$

Here, I have used * to denote the coordinates and objects of one of the coordinate systems. This is in distinction to Equation (1), where the superscripts denoted observers embedded in the coordinate systems. It is noted that in solid mechanics applications, certain tensors that are functions of both spatial and initial coordinates transform objectively as vectors in the spatial frame [11].

Is the velocity of $\mathbf{X}$ as observed by α and β objective? Differentiation of Equation (1) gives:

$$\frac{d\mathbf{x}^{\alpha}}{dt^{*}} = \mathbf{u}^{\alpha} = \frac{d\mathbf{Q}}{dt} \cdot \mathbf{x}^{\beta} + \mathbf{Q} \cdot \frac{d\mathbf{x}^{\beta}}{dt} + \frac{d\mathbf{b}}{dt} = \frac{d\mathbf{Q}}{dt} \cdot \mathbf{x}^{\beta} + \mathbf{Q} \cdot \mathbf{u}^{\beta} + \frac{d\mathbf{b}}{dt} \tag{3}$$

Clearly, velocity is not consistent with Equation (2), so such observations are not MFI. This is due to the relative rotation rate of the coordinate systems and any time dependence of the relative translation. A second differentiation of Equation (1) shows that acceleration observations also are not objective.

What about observations of gradients of objective vectors? The gradient of Equation (2) gives:

$$\nabla^{*}\mathbf{v}^{*} = \mathbf{Q} \cdot \nabla\mathbf{v} \cdot \nabla^{*}\mathbf{x} = \mathbf{Q} \cdot \nabla\mathbf{v} \cdot \mathbf{Q}^{\dagger} \tag{4}$$

Here, Equation (1) was solved for $\mathbf{x}^{\beta}$ to get $\nabla^{*}\mathbf{x}^{\beta} = \mathbf{Q}^{\dagger}$. Apparently, the gradient of an objective vector is objective. However, the gradient operation applied to Equation (3) gives:

$$\begin{gathered} \nabla^{*}\mathbf{u}^{\alpha} = \mathbf{L}^{\alpha} = \mathbf{Q} \cdot \mathbf{L}^{\beta} \cdot \mathbf{Q}^{\dagger} + \tfrac{d\mathbf{Q}}{dt} \cdot \mathbf{Q}^{\dagger} = \mathbf{Q} \cdot \mathbf{L}^{\beta} \cdot \mathbf{Q}^{\dagger} + \mathbf{\Omega} \\ (\nabla^{*}\mathbf{u}^{\alpha})^{\dagger} = (\mathbf{L}^{\alpha})^{\dagger} = \mathbf{Q}^{\dagger} \cdot \left(\mathbf{L}^{\beta}\right)^{\dagger} \cdot \mathbf{Q} + \mathbf{Q} \cdot \tfrac{d\mathbf{Q}^{\dagger}}{dt} = \mathbf{Q}^{\dagger} \cdot \left(\mathbf{L}^{\beta}\right)^{\dagger} \cdot \mathbf{Q} + \mathbf{\Omega}^{\dagger} \end{gathered} \tag{5}$$

The velocity gradient is not MFI, because of the difference in coordinate rotations Ω. Differentiation of $\mathbf{Q} \cdot \mathbf{Q}^{\dagger} = \mathbf{I}$ establishes that $\mathbf{\Omega} + \mathbf{\Omega}^{\dagger} = 0$; hence, the spin cancels for the symmetric part of the velocity gradient, as seen by adding the two equations of Equation (5). Thus:

$$\mathbf{L}^{\alpha} + (\mathbf{L}^{\alpha})^{\dagger} = 2\mathbf{D}^{\alpha} = \mathbf{Q} \cdot [\mathbf{L}^{\beta} + (\mathbf{L}^{\beta})^{\dagger}] \cdot \mathbf{Q}^{\dagger} = 2\mathbf{Q} \cdot \mathbf{D}^{\beta} \cdot \mathbf{Q}^{\dagger} \tag{6}$$

In contrast, the fluid spin or vorticity is not objective, as the difference gives:

$$\nabla^{*}\mathbf{u}^{\alpha} - (\nabla^{*}\mathbf{u}^{\alpha})^{\dagger} = 2\mathbf{W}^{\alpha} = \mathbf{Q}\cdot[\nabla\mathbf{u}^{\beta} - (\nabla\mathbf{u}^{\beta})^{\dagger}]\cdot\mathbf{Q}^{\dagger} + 2\boldsymbol{\Omega} = 2\mathbf{Q}\cdot\mathbf{W}^{\beta}\cdot\mathbf{Q}^{\dagger} + 2\boldsymbol{\Omega} \tag{7}$$

Expressions for $d\mathbf{Q}/dt$ and $d\mathbf{Q}^{\dagger}/dt$ are readily obtained from either Equation (5) or Equation (7). Two particularly useful in non-Newtonian fluid research are:

$$\begin{aligned} \tfrac{d\mathbf{Q}}{dt} &= \mathbf{W}^{\alpha}\cdot\mathbf{Q} - \mathbf{Q}\cdot\mathbf{W}^{\beta} = \mathbf{L}^{\alpha}\cdot\mathbf{Q} - \mathbf{Q}\cdot\mathbf{L}^{\beta} \\ \tfrac{d\mathbf{Q}^{\dagger}}{dt} &= \mathbf{W}^{\beta}\cdot\mathbf{Q}^{\dagger} - \mathbf{Q}^{\dagger}\cdot\mathbf{W}^{\alpha} = \mathbf{Q}^{\dagger}\cdot(\mathbf{L}^{\alpha})^{\dagger} - \left(\mathbf{L}^{\beta}\right)^{\dagger}\cdot\mathbf{Q}^{\dagger} \end{aligned} \tag{8}$$

Viscoelastic non-Newtonian models require rates of change of dynamic quantities, such as stress or the heat flux, and even kinematic quantities, such as deformation rate or vorticity. Of course, these derivatives must also be objective; hence the question: Are material derivatives of objective quantities objective? Start with the derivative of the first equation of Equation (2) to get:

$$\frac{d\mathbf{v}^{*}}{dt^{*}} = \mathbf{Q}\cdot\frac{d\mathbf{v}}{dt} + \frac{d\mathbf{Q}}{dt}\cdot\mathbf{v} = \mathbf{Q}\cdot\frac{d\mathbf{v}}{dt} + \left(\mathbf{W}^{\alpha}\cdot\mathbf{Q} - \mathbf{Q}\cdot\mathbf{W}^{\beta}\right)\cdot\mathbf{v} \tag{9}$$

Using Equation (8) and recognizing that $\mathbf{u}^{\alpha} = \mathbf{v}^{*}$ and $\mathbf{u}^{\beta} = \mathbf{v}$, this reduces to:

$$\frac{d\mathbf{v}^{*}}{dt^{*}} - \mathbf{W}^{\alpha}\cdot\mathbf{v}^{*} = \frac{d_j\mathbf{v}^{*}}{dt} = \mathbf{Q}\cdot\left(\frac{d\mathbf{v}}{dt} - \mathbf{W}^{\beta}\cdot\mathbf{v}\right) = \mathbf{Q}\cdot\frac{d_j\mathbf{v}}{dt} \tag{10}$$

The material derivative is not objective, but the operator denoted by the subscript j is. This is the Jaumann derivative [25]. An analogous calculation for an objective tensor leads to:

$$\frac{d_j\mathbf{T}^{*}}{dt^{*}} = \frac{d\mathbf{T}^{*}}{dt^{*}} - \mathbf{W}^{\alpha}\cdot\mathbf{T}^{*} + \mathbf{T}^{*}\cdot\mathbf{W}^{\alpha} = \mathbf{Q}\cdot\left(\frac{d\mathbf{T}}{dt} - \mathbf{W}^{\beta}\cdot\mathbf{T} + \mathbf{T}\cdot\mathbf{W}^{\beta}\right)\cdot\mathbf{Q}^{\dagger} \tag{11}$$

Obviously, Equations (10) and (11) are not unique, as other combinations of terms in Equation (8) could be used. For example, straightforward calculations give:

$$\begin{aligned} \tfrac{d_o\mathbf{v}^{*}}{dt^{*}} &= \tfrac{d\mathbf{v}^{*}}{dt^{*}} - \mathbf{L}^{\alpha}\cdot\mathbf{v}^{*} = \mathbf{Q}\cdot\left(\tfrac{d\mathbf{v}}{dt} - \mathbf{L}^{\beta}\cdot\mathbf{v}\right) \\ \tfrac{d_o\mathbf{T}^{*}}{dt^{*}} &= \tfrac{d\mathbf{T}^{*}}{dt^{*}} + (\mathbf{L}^{\alpha})^{\dagger}\cdot\mathbf{T}^{*} + \mathbf{T}^{*}\cdot\mathbf{L}^{\alpha} = \mathbf{Q}\cdot\left(\tfrac{d\mathbf{T}}{dt} + \left(\mathbf{L}^{\beta}\right)^{\dagger}\cdot\mathbf{T} + \mathbf{T}\cdot\mathbf{L}^{\beta}\right)\cdot\mathbf{Q}^{\dagger} \end{aligned} \tag{12}$$

This last operator is known as the convective or Oldroyd derivative [7].

It is stressed that although these and other co-rotation rate measures are objective, they are not equal. Hence, predictions of non-Newtonian fluid responses depend on which MFI derivative operator is used. Appendix D of [25] summarizes these derivatives and includes tables that compare notations.

There is considerable empirical evidence suggesting that the constitutive behavior of non-Newtonian fluids should include some measure of fluid vorticity. Consequently, considerable effort has been spent to develop objective measures using MFI operators, such as the above. See, for example, [26] for an application to Rivlin–Ericksen fluids, [27] for an application to a general polymeric fluid, [28] for a straightforward application to viscoelastic flows and [29,30] for applications to objective measures of vortices in geophysical fluid settings. Useful theoretical templates for constructing objective measures of skew-symmetric tensors are given by [31–34].

Typically, these measures depend on a “co-rotation rate” of the principle axes of the deformation tensor. In this case, care should be exercised in applying these measures whenever two or more of the axes are the same. Moreover, delineating these axes from experimental or computational experiments is not always straightforward. Nevertheless, as the cited studies show, inclusion of an objective spin in constitutive models has produced some remarkable successes.

2.3. Objectivity in Mixtures and Multiphase Materials

Application of MFI to multiphase materials and mixtures raises additional issues. Massoudi [35] has discussed these in the context of an application to lift forces in multiphase flows. His approach is followed here.

Instead of a single test specimen with material coordinates $\mathbf{X}$, consider two specimens with material coordinates $\mathbf{X}_1$ and $\mathbf{X}_2$. The specimens may be different constituents or different phases of the same constituent. A fundamental tenant of mixture theory is that the two specimens occupy the same geometric point, *i.e.*, $\mathbf{x}_1 = \mathbf{x}_2$. See [36,37] for thorough discussions of the tenants of mixture theory. Whether a mixture or multiphase material, Equation (1) is generalized to:

$$\begin{aligned} \mathbf{x}_1^{\alpha}(\mathbf{X}_1, t^{\dagger}) &= \mathbf{Q}(t) \cdot \mathbf{x}_1^{\beta}(\mathbf{X}_1, t) + \mathbf{b}(t) \\ \mathbf{x}_2^{\alpha}(\mathbf{X}_2, t^{\dagger}) &= \mathbf{Q}(t) \cdot \mathbf{x}_2^{\beta}(\mathbf{X}_2, t) + \mathbf{b}(t) \end{aligned} \tag{13}$$

The velocities of the specimens are:

$$\begin{aligned} \frac{d\mathbf{x}_1^{\alpha}}{d\tau} &= \mathbf{u}_1^{\alpha} = \frac{d\mathbf{Q}}{dt} \cdot \mathbf{x}_1^{\beta} + \mathbf{Q} \cdot \mathbf{u}_1^{\beta} + \frac{d\mathbf{b}}{dt} \\ \frac{d\mathbf{x}_2^{\alpha}}{d\tau} &= \mathbf{u}_2^{\alpha} = \frac{d\mathbf{Q}}{dt} \cdot \mathbf{x}_2^{\beta} + \mathbf{Q} \cdot \mathbf{u}_2^{\beta} + \frac{d\mathbf{b}}{dt} \end{aligned} \tag{14}$$

Then:

$$\mathbf{u}_1^{\alpha} - \mathbf{u}_2^{\alpha} = \mathbf{u}_{12} = \mathbf{Q} \cdot (\mathbf{u}_1^{\beta} - \mathbf{u}_2^{\beta}) \tag{15}$$

Here, $\mathbf{u}_{12} = -\mathbf{u}_{21}$ is the "diffusion" velocity. For those not familiar with mixture theory, it is noted that the material derivatives of the two substances are not the same, since their velocities are different (see Massoudi [35] and Rajagopal and Tao [37] for a careful analysis and discussion of this matter). Nevertheless, the constituent velocity differences are objective! Moreover, as shown by [35], the relative acceleration and spin differences are also objective. This is a key result for developing constitutive equations for mixtures of solids and fluids.

3. What Does *Irreversibility* Mean?

It is widely accepted that all natural processes are irreversible. Entropy production is the standard gauge of irreversibility. However, as astutely noted by Denbigh [38], many processes are irreversible that apparently do not result in significant entropy production. In this regard, Pavelka *et al.* [39] showed that it is possible to make a distinction between entropy production and irreversibility in nonequilibrium thermodynamics. Thermodynamic analyses of Newtonian fluids and linear heat flow establish that the appropriate phenomenological coefficients are constrained so as to produce positive entropy production. However, as noted in [26], some objective constitutive models of non-Newtonian fluids may have phenomenological coefficients that do not appear in the entropy production inequality. In the case of viscous fluids with deformable microstructure [40], such unconstrained coefficients can produce solutions that grow rather than decay in time. I conclude that objective characterizations of dissipative fluxes alone do not guarantee realistic solutions.

As widely noted (see [3,36,37,41]), entropy is produced by heat flux, mass flux in the case of mixtures, mechanical dissipation from viscous processes, chemical reactions and electro-magnetic processes. This is described by the Clausius–Duhem inequality, a generic form of which is:

$$\rho \frac{ds}{dt} + \nabla \cdot \left(\frac{\mathbf{q}}{\theta} \right) - \rho \left(\frac{r}{\theta} \right) = \sigma \geq 0 \tag{16}$$

The symbols are standard: ρ is density; s is entropy; $\mathbf{q}$ is heat flux; θ is temperature; and r is radiation. σ is the rate of entropy production and for irreversible processes is > 0. Now, chemical reactions are characterized by scalar affinities, heat and mass fluxes and electro-magnetic processes by vectors and mechanical dissipation by second order tensors. See Klika [41] for an extension that includes biochemical reactions. For fluids with microstructure, one must also include higher order tensors [42], but this is not considered here. The disparate processes involved in entropy production of non-Newtonian fluids, along with the requirement that the flux characterizations obey MFI, may require tedious analysis and, hence, are not often attempted.

The processes that make up σ are intrinsic and so are quantified by "conjugate forces" through constitutive relations, which vanish under equilibrium conditions. Elementary examples are Fourier's law, which characterizes heat flux, Ohm's law, which specifies the electrical current, and the Navier–Stokes law, which relates deformation rate to viscous stress for Newtonian fluids. Generally, one expects nonlinear constitutive relations.

Kuiken [43] has outlined an elegant approach that simplifies the analysis. Standard manipulation of the evolution equations for mass, momentum and energy renders $\sigma \geq 0$ as:

$$\sigma = S^s G^s + \mathbf{V}^v \cdot \mathbf{G}^v + \mathbf{T}^t : \mathbf{G}^t \tag{17}$$

Here, S^s, $\mathbf{V}^v$ and $\mathbf{T}^t$ account for the scalar, vector and tensor fluxes of mass, momentum and energy. The G's are the appropriate scalar, vector and tensor functions of the dependent variables of the evolution equations. The superscripts remind us that the particular terms refer to scalars, vectors and tensors.

It is emphasized that the fluxes are generally nonlinear functions of the G's. There is no restriction on the functional forms, other than Equation (17). As shown shortly, non-Newtonian fluids may require several scalar, vector and tensor processes, so each term in Equation (17) may itself be a sum. It also will be convenient to use the canonical decomposition of $\mathbf{T}^t$ given by:

$$\mathbf{T}^t = \left(\frac{T}{3}\right)\mathbf{I} + \mathbf{T}^t_d + \mathbf{T}^t_a \tag{18}$$

In Equation (18), T is the trace of $\mathbf{T}^t$; $\mathbf{T}^t_d$ is its traceless deviator; and $\mathbf{T}^t_a$ is its skew symmetric component. $\mathbf{T}^t$ is taken as objective, so $\mathbf{T}^t_a$ is, as well. An analogous decomposition for $\mathbf{G}^t$ can be made.

In the theoretical development of constitutive equations, the principle of *equipresence* is evoked. This states that S^s, $\mathbf{V}^v$ and $\mathbf{T}^t$ must all depend on G^s, $\mathbf{G}^v$ and $\mathbf{G}^t$. I have never seen this principle rigorously used in any application. The simplest approach is to evoke Curie's principle that fluxes depend only on like forces. That is, a scalar flux can only depend on scalar forces. A somewhat more general, yet commonly-applied approach is to postulate a symmetry center for the material. As shown by [43], this produces:

$$\begin{aligned} S^s &= L^{ss} G^s + \mathbf{L}^{st} : \mathbf{G}^t \\ \mathbf{V}^v &= \mathbf{L}^{vv} \cdot \mathbf{G}^v \\ \mathbf{T}^t &= \mathbf{L}^{ts} G^s + \mathbf{L}^{tt} \cdot \mathbf{G}^t \end{aligned} \tag{19}$$

Here, the L are phenomenological coefficients usually evaluated from controlled experiments. They are functions of invariant properties of the forces, as well as other thermodynamic functions.

This model allows the scaler fluxes to depend on a tensor process, and *vice versa*, while vector fluxes only depend on vector processes. The L^{ss} are scalars; $\mathbf{L}^{st}$, $\mathbf{L}^{ts}$ and $\mathbf{L}^{vv}$ are second order tensors; and $\mathbf{L}^{tt}$ is fourth order. If Curie's principle is applied to Equation (19), then $\mathbf{L}^{st} = \mathbf{L}^{ts} = 0$.

It is instructive to consider the special case where the constitutive equations are linear and the coefficients are all isotropic. Then, Equation (19) reduces to:

$$\begin{aligned} S^s &= L_{ss} G^s + L_{st} G \\ \mathbf{V}^v &= L_{vv} \mathbf{G}^v \\ \mathbf{T}^t &= (L_{ts} G^s + L_{tt} G)\,\mathbf{I} + L_{td} \mathbf{G}^t_d + L_{ta} \mathbf{G}^t_a. \end{aligned} \tag{20}$$

The isotropic assumption reduces the number of phenomenological coefficients to just seven: L_{ss}, L_{st}, L_{vv}, L_{ts}, L_{tt}, L_{td} and L_{ta}. Inserting Equation (20) into Equation (17) gives:

$$\sigma = \left[L_{ss}\left(G^s\right)^2 + \left(L_{st} + L_{ts}\right)G^sG + L_{tt}G^2\right] + L_{vv}(\mathbf{G}^v \cdot \mathbf{G}^v) + L_{td}(\mathbf{G}_d^t : \mathbf{G}_d^t) + L_{ta}(\mathbf{G}_a^t : \mathbf{G}_a^t) \geq 0 \quad (21)$$

This is a quadratic form, and the inequality constrains the phenomenological coefficients to:

$$\begin{gathered} L_{ss}, L_{tt}, L_{vv}, L_{td}, L_{ta} \geq 0 \\ 4L_{ss}L_{tt} - \left(L_{st} + L_{ts}\right)^2 \geq 0 \end{gathered} \quad (22)$$

The requirement of nonnegative entropy production provides six constraints on the seven phenomenological coefficients. However, all seven coefficients appear in Equation (22). The irreversibility constraints should be useful in experiments to determine the coefficients; however, I am unaware of a case where this was done.

4. Parsing Constitutive Equations

4.1. Introduction

The purpose of this section is to use two recent results in non-Newtonian fluid mechanics to show how MFI impacts irreversibility. The following subsection focuses on a constitutive model for a mixture of two viscous fluids at different temperatures. Although the constitutive equations are linear, there is considerable interaction between the temperature and velocity fields of the two fluids. Subsection 4.3 deals with a nonlinear constitutive model for a granular substance. Here, the nonlinear cross-coupling between the vector and tensor processes is fundamentally nonlinear. In both cases, objective specification of the vector and tensor processes is a key aspect to demonstrating irreversibility.

4.2. Linear Two-Fluid Mixture at Different Temperatures

A distinctive characteristic of many non-Newtonian fluids is the robust interaction between different dynamic fields, such as stress and heat flux. An illustration of the interaction of these fields and the consequent impact on irreversibility was reported by [44]. The vector processes are restricted to just sensible heat flux associated with two temperature gradients and heat generated by the friction of the fluids moving past each other. Vectorial mechanisms, such as Dufour and Soret processes, are certainly important in many applications, but are not considered here. Tensor processes include the viscous stresses of each of the constituents in addition to viscous interactions between the constituents. Consequently, the constitutive equations for the stresses include the asymmetric effects depicted in Equation (21). Characterization of asymmetric stresses uses the spin differences of the two fluids in accordance with [35].

The appropriate vector objective variables are the two temperature gradients, $\nabla\theta_1$ and $\nabla\theta_2$, along with the diffusion velocity $\mathbf{u}_{12}$. Applying the restricted principle of equipresence noted earlier, the constitutive equations are given as:

$$\begin{gathered} \mathbf{q}_i = -\phi_i\left[k_{ii}\nabla\theta_i + \sum_{j=1}^{2}\phi_j\left(k_{ij}\nabla\theta_j + h_{ij}\mathbf{u}_{ij}\right)\right] \\ \mathbf{m}_i = -\sum_{j=1}^{2}\phi_i\phi_j\left(l_{ij}\mathbf{u}_{ij} + \sum_{\gamma=1}^{2}r_{ij\gamma}\nabla\theta_\gamma\right) \end{gathered} \quad (23)$$

Here, $\mathbf{q}_i$ and $\mathbf{m}_i$ are the heat flux and internal momentum source of substance/phase i, respectively; ϕ_i is the volume fraction of that constituent; and k_{ij}, h_{ij}, l_{ij} and $r_{ij\gamma}$ are phenomenological coefficients. These equations were formulated so that if one of the constituents vanishes, the system reduces to just Fourier's law of heat conduction for a single constituent.

Tensor processes are simply generalizations of the Navier–Stokes law to include all objective tensor quantities. These are the deformation of each phase $\mathbf{D}_i$ and the spin difference $\mathbf{W}_i$. Consistent with Equation (18), deformation is divided into trace and deviator components.

The tensor constitutive equation is:

$$\mathbf{T}_i = \phi_i \left[\left(\lambda_{ii} D_i + \sum_{j=1}^{2} \phi_j \lambda_{ij} D_j \right) \mathbf{I} + 2 \left(\mu_{ii} \mathbf{D}_{di} + \sum_{j=1}^{2} \phi_j \mu_{ij} \mathbf{D}_{dj} \right) + \sum_{j=1}^{2} \nu_{ij} \phi_j \left(\mathbf{W}_i - \mathbf{W}_j \right) \right] \tag{24}$$

Note that if one of the volume fractions vanishes, then Equation (24) reduces to the Navier–Stokes equations for a single constituent.

The irreversibility condition is given by:

$$\sigma = - \sum_{i=1}^{2} \mathcal{C}_i \left(\mathcal{C}_i \mathbf{q}_i \cdot \nabla \theta_i + \mathbf{m}_i \cdot \mathbf{v}_i - \mathbf{T}_i : \nabla \mathbf{v}_i \right) \geq 0 \tag{25}$$

Here, $\mathcal{C}_i = \theta_i^{-1}$. This is sometimes called the *coldness* of constituent i. Examination of Equation (25) indicates a dilemma: all of the dependent variables are objective, except $\mathbf{v}_i$. This obstacle was overcome in [44] by imposing the following constraints on l_{ij} and $r_{ij\gamma}$:

$$\begin{aligned} \mathcal{C}_1 l_{12} &= -\mathcal{C}_2 l_{21} = L \\ \mathcal{C}_1 r_{121} &= -\mathcal{C}_2 r_{211} = R_1 \\ \mathcal{C}_1 r_{122} &= -\mathcal{C}_2 r_{212} = R_2 \end{aligned} \tag{26}$$

Then, Equation (25) reduces to:

$$\begin{aligned} &\mathcal{C}_1^2 \phi_1 k_{11} \nabla \theta_1 \cdot \nabla \theta_1 + \mathcal{C}_2^2 \phi_2 k_{22} \nabla \theta_2 \cdot \nabla \theta_2 + \phi_1 \phi_2 \left(\mathcal{C}_1^2 k_{12} + \mathcal{C}_2^2 k_{21} \right) \nabla \theta_1 \cdot \nabla \theta_2 \\ &+ \phi_1 \phi_2 \mathbf{u}_d \cdot \left(\mathcal{C}_1^2 h_{12} \nabla \theta_1 - \mathcal{C}_2^2 h_{21} \nabla \theta_2 \right) + \phi_1 \phi_2 \mathbf{u}_d \cdot \left[L \mathbf{u}_d + R_1 \nabla \theta_1 + R_2 \nabla \theta_2 \right] \\ &+ \phi_1 \lambda_{11} \mathcal{C}_1 D_1^2 + \phi_2 \lambda_{22} \mathcal{C}_2 D_2^2 + \phi_1 \phi_2 D_1 D_2 \left(\mathcal{C}_1 \lambda_{12} + \mathcal{C}_2 \lambda_{21} \right) \\ &+ 2 \left(\phi_1 \mu_{11} \mathcal{C}_1 \mathbf{D}_{d1}^2 + \phi_2 \mu_{22} \mathcal{C}_2 \mathbf{D}_{d2}^2 \right) + 2 \phi_1 \phi_2 \mathbf{D}_{d1} : \mathbf{D}_{d2} \left(\mathcal{C}_1 \mu_{12} + \mathcal{C}_2 \mu_{21} \right) \\ &+ \phi_1 \phi_2 \left[\nu_{12} \mathcal{C}_1 \mathbf{W}_1^2 + \nu_{21} \mathcal{C}_2 \mathbf{W}_2^2 - \left(\mathcal{C}_1 \nu_{12} + \mathcal{C}_2 \nu_{21} \right) \mathbf{W}_1 : \mathbf{W}_2 \right] \geq 0 \end{aligned} \tag{27}$$

The irreversibility constraints arising from Equation (27) can be divided into two groups. The first are essentially those that would arise from single fluid analysis:

$$k_{ii}, \ \lambda_{ii}, \ \mu_{ii}, \geq 0 \tag{28}$$

The second group are Onsager-type constraints involving the magnitudes of the interaction coefficients. These are:

$$\begin{aligned} 4 \, \lambda_{11} \, \lambda_{22} \, \mathcal{C}_1 \, \mathcal{C}_2 &\geq \phi_1 \, \phi_2 \left(\mathcal{C}_1 \lambda_{21} + \mathcal{C}_1 \lambda_{22} \right)^2 \\ 4 \, \mu_{11} \, \mu_{22} \, \mathcal{C}_1 \, \mathcal{C}_1 &\geq \phi_1 \, \phi_2 \left(\mathcal{C}_1 \mu_{12} + \mathcal{C}_2 \lambda_{21} \right)^2 \\ \nu_{12} \, \mathcal{C}_1 &= \nu_{21} \, \mathcal{C}_2 \end{aligned} \tag{29}$$

and that the roots of the matrix:

$$\begin{bmatrix} \mathcal{C}_1^2 \phi_1 k_{11} & \phi_1 \phi_2 (\mathcal{C}_1^2 k_{12} + \mathcal{C}_2^2 k_{21})/2 & \phi_1 \phi_2 (R_1 + \mathcal{C}_1^2 h_{12})/2 \\ \phi_1 \phi_2 (\mathcal{C}_1^2 k_{12} + \mathcal{C}_2^2 k_{21})/2 & \mathcal{C}_2^2 \phi_1 k_{22} & \phi_1 \phi_2 (R_2 - \mathcal{C}_2^2 h_{21})/2 \\ \phi_1 \phi_2 (R_1 + \mathcal{C}_1^2 h_{12})/2 & \phi_1 \phi_2 (R_2 - \mathcal{C}_2^2 h_{21})/2 & \phi_1 \phi_2 L \end{bmatrix}$$

be nonnegative. A special case of the latter condition is when the diffusion velocity $\mathbf{u}_{12} = 0$. Then:

$$4\mathcal{C}_1^2\mathcal{C}_2^2 k_{11}k_{22} \geq \phi_1\phi_2(\mathcal{C}_1^2 k_{12} + \mathcal{C}_2^2 k_{21})^2 \tag{30}$$

Note that the interaction irreversibility constraints impose both temperature and volume fraction dependences on the phenomenological coefficients. Both functions are obtained from solutions to the dynamic equations. That they also appear in the irreversibility constraint indicates a coupling between the solution and the irreversibility condition. This connection is rarely, if ever, explored.

4.3. Nonlinear Granular Fluid

Yang *et al.* [45] proposed a general nonlinear constitutive model for granular materials that includes both dissipation and heat conduction. Furthermore, see Massoudi and Kirwan [46] for additional analysis and discussion of this model. For an incompressible fluid, the constitutive equations reduce to:

$$\begin{aligned} \mathbf{T}_d &= \beta_3\mathbf{D}_d + \beta_4(\nabla\phi\otimes\nabla\phi)_d \\ \mathbf{q} &= [a_1\mathbf{I} + a_3\mathbf{D}_d + a_5\mathbf{D}_d\cdot\mathbf{D}_d]\cdot\nabla\theta + [a_2\mathbf{I} + a_4\mathbf{D}_d + a_6\mathbf{D}_d\cdot\mathbf{D}_d]\cdot\nabla\phi \end{aligned} \tag{31}$$

Here, ϕ is the volume fraction; θ is the temperature; $\mathbf{D}_d$ is the deviator of the velocity gradient; and the subscript on $(\nabla\phi\otimes\nabla\phi)_d$ indicates the deviator of the tensor product. I imposed this restriction so that this model only applies to the deviator component of $\mathbf{T}$. Furthermore, the phenomenological coefficients β_j and a_j are functions of ϕ and perhaps geometric invariants of $\mathbf{D}_d$. Note also that $\mathbf{D}_d : \mathbf{D}_d$ was neglected in the equation for $\mathbf{T}$ in Equation (31). As detailed by [45], the variables $\nabla\theta$, $\nabla\phi$ and $\mathbf{D}_d$ are objective. Note also that Equation (31) reduces to the Navier–Stokes equation for viscous stress when only $\beta_3 \neq 0$ and Fourier's heat conduction law when only $a_1 \neq 0$.

Application of the Clausius–Duhem inequality, Equation (16), to Equation (31) requires:

$$\mathbf{q}\cdot\nabla\theta + \mathbf{T}_d : \mathbf{D}_d = \sigma \geq 0 \tag{32}$$

Using Equation (31) in Equation (32) produces the inequality:

$$\begin{aligned} &\beta_3(\mathbf{D}_d)^2 + \beta_4(\nabla\phi\otimes\nabla\phi)_d : \mathbf{D}_d + a_1(\nabla\theta)^2 + a_2\nabla\rho\cdot\nabla\theta + a_3(\mathbf{D}_d\cdot\nabla\theta)\cdot\nabla\theta \\ &+ a_5\mathbf{D}_d\cdot(\mathbf{D}_d\cdot\nabla\theta) + a_4(\mathbf{D}_d\cdot\nabla\phi)\cdot\nabla\theta + a_6(\mathbf{D}_d\cdot\mathbf{D}_d\cdot\nabla\phi)\cdot\nabla\theta \geq 0. \end{aligned} \tag{33}$$

The constraints that arise from Equation (33) are:

$$\begin{aligned} &\beta_3,\ a_1 \geq 0 \\ &\beta_3(\mathbf{D}_d)^2 + a_1(\nabla\theta)^2 \geq -[\beta_4(\nabla\phi\otimes\nabla\phi)_d : \mathbf{D}_d + a_2\nabla\rho\cdot\nabla\theta + a_3(\mathbf{D}_d\cdot\nabla\theta)\cdot\nabla\theta \\ &+a_5\mathbf{D}_d\cdot(\mathbf{D}_d\cdot\nabla\theta) + a_4(\mathbf{D}_d\cdot\nabla\phi)\cdot\nabla\theta + a_6(\mathbf{D}_d\cdot\mathbf{D}_d\cdot\nabla\phi)]\cdot\nabla\theta. \end{aligned} \tag{34}$$

The first two conditions are recognized as the irreversibility conditions for Navier–Stokes fluids and Fourier's law for heat conduction. As in the previous example, the second condition restricts the interaction coefficients and the solution properties. In view of Equation (29) and the fundamental nonlinearity of the constitutive model, it is not surprising that the dependent dynamic variables appear in the irreversibility constraint. I am unaware of any study that evokes this condition on solutions for the dynamic variables.

5. Turbulence

As reviewed by Luca and Hutter [47], turbulence is emerging as an important process in non-Newtonian fluids. Moreover, there are many similarities between constitutive modeling of non-Newtonian fluids and the closure problem in turbulence. It seems appropriate then to review relevant aspects of turbulent theory that are applicable to non-Newtonian fluids.

Classical turbulence theory is based on an elementary application of statistical mechanics to the Navier–Stokes equations and related balance equations for density and any added constituents.

The basic assumption is that any field quantity, such as the velocity, can be partitioned into mean and turbulent components. For the velocity $\mathbf{u}$, this produces:

$$\mathbf{u} = \bar{\mathbf{u}} + \mathbf{w} \tag{35}$$

where $\bar{\mathbf{u}}$ and $\mathbf{w}$ are the mean and turbulent velocities, respectively. Ideally the statistics are based on an ensemble of experiments; in practice, experimenters often rely on temporal statistics and the assumption of stationarity in the flow.

Recall now the Navier–Stokes equations for an incompressible fluid:

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = -\rho^{-1} \nabla p + \mu \nabla^2 \mathbf{u} \tag{36}$$

Here, p is pressure and μ is the molecular viscosity. For the present purpose, it is sufficient to neglect external forces and take density ρ constant, as the theory readily generalizes to include these effects. Following, for example, [48,49], substitute Equation (35) into Equation (36) and average to produce:

$$\frac{\partial \bar{\mathbf{u}}}{\partial t} + \bar{\mathbf{u}} \cdot \nabla \bar{\mathbf{u}} + \nabla \cdot \mathbf{R} = -\rho^{-1} \nabla \bar{p} + \mu \nabla^2 \bar{\mathbf{u}} \tag{37}$$

Here, $\mathbf{R} = \overline{\mathbf{w} \otimes \mathbf{w}}$ is the Reynolds stress. Two aspects of this last equation are noteworthy. First, nonlinear advection is still present in the mean field. In many studies, mean fields are prescribed, so nonlinearity issues in these fields rarely arise. Second, there is a second order statistic, the divergence of the Reynolds stress. This term resembles the viscous stress term in Equation (36), except that here, it arises purely from the nonlinearity of the Navier–Stokes equations and not from intrinsic mechanisms. Much of classical turbulence theory is concerned with developing models for $\mathbf{R}$.

An evolution equation can be obtained for the Reynolds stress by subtracting Equation (37) from Equation (36), multiplying by $\mathbf{w}$ and averaging. Details are given in [48,49], for example. This gives:

$$\frac{\partial \mathbf{R}}{\partial t} + \bar{\mathbf{u}} \cdot \nabla \mathbf{R} = -\mathbf{R} \cdot \nabla \bar{\mathbf{u}} - (\nabla \bar{\mathbf{u}})^{\dagger} \cdot \mathbf{R} + \mathbf{\Pi} - 2\mu \overline{\nabla \mathbf{w} \cdot (\nabla \mathbf{w})^{\dagger})} - \nabla \cdot \mathcal{C} - \nabla \mathbf{P} + \mu \nabla^2 \mathbf{R} \tag{38}$$

Here:

$$\begin{aligned} \mathbf{\Pi} &= \rho^{-1} \overline{p' [\nabla \mathbf{w} + (\nabla \mathbf{w})^{\dagger}]} \\ \mathcal{C} &= \overline{\mathbf{w} \otimes \mathbf{w} \otimes \mathbf{w}} \\ \mathbf{P} &= \rho^{-1} 2 \overline{p' \mathbf{w}} \end{aligned} \tag{39}$$

Note that Equation (38) can also be written in terms of Oldroyd or Jaumann derivatives. Here, $\mathcal{C}$ is the triple turbulent velocity correlation and is a third order tensor. Of course, evolution equations could be derived for it, as well, but it is clear that unknown higher order correlations will arise, hence the need to close the hierarchy of equations that arise from this procedure by parameterizations. Most turbulence theories are based on models for $\mathbf{R}$. It appears then that the approach to closing the turbulent hierarchy is similar to that used for early non-Newtonian fluid models. See [49–51] for examples of the formulations of these equations.

By rewriting Equation (35) to express $\mathbf{w}$ as a velocity difference, Speziale [48] constructed a clever argument reminiscent of that used by [35] for mixtures to show that $\mathbf{w}$ was objective. Using this, he was able to show that all of the terms in Equation (38) were objective. He then argued that closure models for the terms in Equation (38) should also be objective. This initiated a major direction of research in turbulence. Among many others, this includes a generalized $K - \epsilon$ model for turbulent dissipation [52]; an objective model for $\mathbf{\Pi}$ [53]; objective models for $\mathbf{R}$ as detailed in [13,54,55]; and a special objective rotation tensor for non-Newtonian fluids [28].

The parallel of MFI in turbulence and non-Newtonian fluids is striking. In fact, Speziale's original motivation for objective stresses was drawn from this area. As with non-Newtonian fluids, the concept of MFI was controversial. Shortly before his untimely death in 1999, Speziale reversed his view on the role of MFI in turbulence [56]. Nevertheless, it is still widely employed in turbulence modeling. See Dafalias [57] for a recent discussion about the impact of MFI in this field.

6. Envoi

The huge breadth of phenomenology now classified as non-Newtonian demonstrates that this is the dominant branch of fluid mechanics research. Two concepts proposed here unify this research: objective characterizations of the intrinsic processes and the inevitable tendency to irreversibility. Two examples were given that showed how objectivity plays a role in the thermodynamic face of irreversibility. In these examples, all phenomenological parameters appear in the irreversibility inequality, as do some of the solution variables. This is in contrast to some non-Newtonian fluid models, such as reported by [26].

Constitutive equations that involve space and/or time integrals of objective variables were, by omission, indirectly identified as another topic worthy of further study. Two prominent examples are the theory of fading memory developed by Coleman [58] and the theory of nonlocal fluid mechanics as proposed by Eringen [59]. Since the integral kernels used in these theories are objective, so too are the consequent constitutive equations. However, the irreversibility requirement used here is based on thermodynamics and, thus, is differential. This constraint applies instantaneously to point values of the field variables. In contrast, memoric and nonlocal theories use information from surrounding regions of space and time. Consequently, the inequality given by Equation (17) would use integral convolutions of objective functions to characterize $\mathbf{q}$ and $\mathbf{T}$. Then, Equation (17) would involve products of these integrals with instantaneous point values of the temperature gradient and velocity gradient. It is not clear, at least to me, how the irreversibility requirement establishes constraints on the integral kernels.

A reviewer appropriately noted that the thermodynamic irreversibility conditions considered here are restricted to centrosymmetric fluids. Certainly, other symmetry classes along with non-isotropic constitutive properties are important for many non-Newtonian fluid applications.

It should be noted that MFI, a concept originally developed in non-Newtonian fluid mechanics, has migrated to another area of fluid mechanics, namely the identification of long-lasting coherent structures in turbulent fluids identified by Lagrangian analysis [60,61]. These features are typically referred to as Lagrangian coherent structures (LCS). As reviewed by Peacock [62], numerous methods have been developed to identify these structures. Consequently, there is some confusion as to what constitutes LCS. Haller [29] first raised the possibility of using objectivity as a criterion for assessing the methodologies. See the papers in the Special Issue *Chaos* 15, 2015, for recent developments.

This last development raises another issue worthy of further research. Here, I used entropy production as the sole gauge of irreversibility. However, in turbulence, this is problematic, since there can be several routes to dissipation. See [63–66] for lucid discussions of routes to viscous dissipation in large-scale turbulent flow. The evolution of large turbulent structures, like LCS, shows irreversible behavior with negligible generation of heat. Similarly, other non-Newtonian fluids exhibit irreversible behavior over large time and space scales, and not all aspects are amenable to thermodynamic analysis. Perhaps, other gauges of irreversibility should be explored.

Acknowledgments: Karal Gregory provided valuable technical and editorial assistance with this manuscript. A critique by Henry Chang was most illuminating. Finally, I thank the reviewers for perceptive and constructive criticisms.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Walters, K. Developments in non-Newtonian fluid mechanics — A personal view. *J. Non-Newtonian Fluid Mech.* **1979**, *5*, 113–124.

2. Astarita, G. Three alternative approaches to the development of constitutive equations. *J. Non-Newtonian Fluid Mech.* **1979**, *5*, 125–140.
3. Truesdell, C.; Toupin, R. The classical field theories. In *Handbuch der Physik*; Flügge, S., Ed.; Springer Verlag: Berlin, Germany, 1960; Volume 3, pp. 226–793.
4. Hutter, K.; Rajagopal, K.R. On flows of granular materials. *Continuum Mech. Thermodyn.* **1994**, *6*, 81–139.
5. Hutter, K.; Schneider, L. Important aspects in the formulation of solid-fluid debris-flow models. Part I. Thermodynamic implications. *Continuum Mech. Thermodyn.* **2010**, *22*, 363–390.
6. Hutter, K.; Schneider, L. Important aspects in the formulation of solid-fluid debris-flow models. Part II. Constitutive modelling. *Continuum Mech. Thermodyn.* **2010**, *22*, 391–411.
7. Oldroyd, J.G. On the formulation of rheological equations of state. *Proc. Roy. Soc.* **1950**, *A200*, 523–541.
8. Noll, W. On the continuity of solid and fluid states. *J. Math. Mech.* **1955**, *4*, 3–81.
9. Noll, W. A mathematical theory of the mechanical behavior of continuous media. *Arch. Ration. Mech. Anal.* **1958**, *2*, 197–226.
10. Noll, W. The foundations of classical mechanics in the light of recent advances in continuum mechanics. In *The Axiomatic Method: With Special Reference to Geometry and Physics*; Henkin, L.; Suppes, P.; Tarski, A., Eds.; North-Holland: Pennsylvania, PA, USA, 1959; pp. 266–281.
11. Malvern, L.E. *Introduction to the Mechanics of a Continuous Medium*; Prentice Hall: Englewood Cliffs, NJ, USA, 1969.
12. Gurtin, M.E. *An Introduction to Continuum Mechanics*, 1st ed.; Academic Press: New York, NY, USA, 1981.
13. Speziale, C.G.; Younis, B.A.; Rubinstein, R.; Zhou, Y. On consistency conditions for rotating turbulent flows. *Phys. Fluids* **1998**, *10*, 2108–2110.
14. Murdoch, A.I. On criticism of the nature of objectivity in classical continuum physics. *Continuum Mech. Thermodyn.* **2005**, *17*, 135–148.
15. Frewer, M. More clarity on the concept of material frame-indifference in classical continuum mechanics. *Acta Mech.* **2009**, *202*, 213–246.
16. Pucci, E.; Saccomandi, G.; Vitolo, R. Bogus transformations in mechanics of continua. *Int. J. Eng. Sci.* **2016**, *99*, 13–21.
17. Grad, H. The many faces of entropy. *Commun. Pure Appl. Math.* **1961**, *14*, 323–354.
18. Müller, I.A. On the frame dependence of stress and heat flux. *Arch. Ration. Mech. Anal.* **1972**, *45*, 241–250.
19. Woods, L.C. The bogus axioms of continuum mechanics. *Bull. IMA* **1981**, *17*, 98–102.
20. Murdoch, A.I. On material frame-indifference, intrinsic spin, and certain constitutive relations motivated by the kinetic theory of gases. *Arch. Ration. Mech. Anal.* **1983**, *83*, 185–194.
21. Edelen, D.G.B.; McLennan, J.A. Material indifference: a principle or a convenience. *Int. J. Eng. Sci.* **1973**, *11*, 813–817.
22. Bird, R.B.; de Gennes, P.G. Discussion about the principle of objectivity. *Physica A* **1983**, *118*, 43–47.
23. Evans, M.W.; Heyes, D.M. On the material frame indifference controversy: Some results from group theory and computer simulation. *J. Mol. Liquid* **1989**, *40*, 297–304.
24. Liu, I.S.; Sampaio, R. Remarks on material frame-indifference controversy. *Acta Mech.* **2014**, *225*, 331 – 348.
25. Fredrickson, A.G. *Principles and Applications of Rheology*; Prentice Hall: Englewood Cliffs, NJ, USA, 1964.
26. VanArsdale, W.E. Objective spin and the Rivlin-Ericksen model. *Acta Mech.* **2003**, *162*, 111–124.
27. Yao, D. A non-Newtonian fluid model with an objective vorticity. *J. Non-Newtonian Fluid Mech.* **2015**, *218*, 99–105.
28. Wedgewood, L.E. An objective rotation tensor applied to non-Newtonian fluid mechanics. *Rheol. Acta* **1999**, *38*, 91–99.
29. Haller, G. An objective definition of a vortex. *J. Fluid Mech.* **2005**, *525*, 1–26.
30. Haller, G. Dynamic rotation and stretch tensors from a dynamic polar decomposition. *J. Mech. Phys. Solids* **2016**, *86*, 70–93.
31. Xiao, H.; Bruhns, O.T.; Meyers, A.T.M. Strain rates and material spins. *J. Elast.* **1998**, *52*, 1–41.
32. Xiao, H.; Bruhns, O.T.; Meyers, A.T.M. On objective corotational rates and their defining spin tensors. *Int. J. Eng. Sci.* **1998**, *35*, 4001–4014.
33. MacMillan, E.H. On the spin of tensors. *J. Elast.* **1992**, *27*, 69–84.
34. Guansuo, D. Some new representations of spin tensors. *Mech. Res. Commun.* **1999**, *26*, 1–6.

35. Massoudi, M. On the importance of material frame-indifference and lift forces in multiphase flows. *Chem. Eng. Sci.* **2002**, *57*, 3687–3701.
36. Müller, I.A. A thermodynamic theory of mixtures of fluids. *Arch. Ration. Mech. Anal.* **1968**, *28*, 1–39.
37. Rajagopal, K.R.; Tao, L. *Mechanics of Mixtures*; World Scientific: Singapore, 1995.
38. Denbigh, K.G. The many faces of irreversibility. *Brit. J. Phil. Sci* **1989**, *40*, 501–518.
39. Pavelka, M.; Klika, V.; Grmela, M. Time reversal in nonequilibrium thermodynamics. *Phys. Rev. E* **2014**, *90*, 062131:1–062131:19.
40. Kirwan, A.D., Jr.; Neuman, N. Simple flow of a fluid containing deformable structures. *Int. J. Eng. Sci.* **1969**, *7*, 1067–1078.
41. Klika, V. A guide through available mixture theories for applications. *Crit. Rev. Solid State Mater. Sci.* **2014**, *39*, 154–174.
42. Kirwan, A.D., Jr.; Neuman, N.; Chang, M.S. On microdeformable fluids: A special case of microfluids. *Int. J. Eng. Sci.* **1976**, *14*, 673–684.
43. Kuiken, G.D.C. *Thermodynamics of Irreversible Processes*; Wiley: New York, NY, USA, 1994.
44. Kirwan, A.D., Jr. Second law constraints on the dynamics of a mixture of two fluids at different temperatures. *Entropy* **2012**, *14*, 880–891.
45. Yang, H.; Aubry, N.; Massoudi, M. Heat transfer in granular materials: Effects of nonlinear heat conduction and viscous dissipation. *Math. Methods Appl. Sci.* **2013**, *36*, 1947–1964.
46. Massoudi, M.; Kirwan, A.D., Jr. On Thermomechanics of a Nonlinear Heat Conducting Suspension. *Fluids*, **2016**, submitted for publication.
47. Luca, I.; Fang, C.; Hutter, K. A thermodynamic model of turbulent motions in a granular material. *Continuum Mech. Thermodyn.* **2004**, *16*, 363–390.
48. Speziale, C.G. Invariance of turbulent closure models. *Phys. Fluids* **1979**, *22*, 1033–1037.
49. Gatski, T. Constitutive equations for turbulent flows. *Theor. Comput. Fluid Dyn.* **2004**, *18*, 345–369.
50. Speziale, C.G. On turbulence Reynolds stress closure and modern continuum mechanics. *Int. J. Non-Linear Mech.* **1981**, *16*, 387–393.
51. Speziale, C.G. Analytic methods for the development of Reynolds-stress closures in turbulence. *Annu. Rev. Fluid Mech.* **1991**, *23*, 107–157.
52. Speziale, C.G. On a generalized nonlinear $K - \epsilon$ model and the use of extended thermodynamics in turbulence. *Theor. Comput. Fluid Dyn.* **1991**, *13*, 161–166.
53. Speziale, C.G.; Sarkar, S.; Gatski, T.B. Modelling the pressure strain correlation of turbulence: An invariant dynamical systems approach. *J. Fluid Mech.* **1991**, *227*, 245–272.
54. Speziale, C.G. On the consistency of Reynolds stress turbulence closures with hydrodynamic stability theory. *Phys. Fluids* **1996**, *8*, 781–788.
55. Speziale, C.G. A consistency condition for non-linear algebraic Reynolds stress models in turbulence. *Int. J. Non-Linear Mech.* **1998**, *33*, 579–584.
56. Spalart, P.R.; Speziale, C.G. A note on constraints in turbulence modelling. *J. Fluid Mech.* **1999**, *391*, 373–376.
57. Dafalias, Y.F. Objectivity in turbulence under change of reference frame and superposed rigid body motion. *J. Eng. Mech.* **2011**, *137*, 699–707.
58. Coleman, B.D. Thermodynamics of materials with memory. *Arch. Ration. Mech. Anal.* **1964**, *17*, 1–46.
59. Eringen, A.C. On non-local fluid mechanics. *Int. J. Eng. Sci.* **1972**, *10*, 561–575.
60. Wiggins, S. The dynamical systems approach to Lagrangian transport in oceanic flows. *Annu. Rev. Fluid Mech.* **2005**, *37*, 295–328.
61. Haller, G. Lagrangian coherent structures. *Annu. Rev. Fluid Mech.* **2015**, *47*, 137–162.
62. Peacock, T.; Froyland, G.; Haller, G. Introduction to Focus Issue: Objective detection of coherent structures. *Chaos* **2015**, *25*, 1–3.
63. Molemaker, J.; McWilliams, J.; Capet, X. Balanced and unbalanced routes to dissipation in an equilibrated Eady flow. *J. Fluid Mech.* **2010**, *654*, 35–63.
64. McWilliams, J. A Perspective on Submesoscale Geophysical Turbulence. In *IUTAM Symposium on Turbulence in the Atmosphere and Oceans: Proceedings of the IUTAM Symposium on Turbulence in the Atmosphere and Oceans, Cambridge, UK, December 8-12, 2008*; Dritschel, D., Ed.; IUTAM Bookseries, Springer: Dordrecht, The Netherlands, 2010; pp. 131–141.

65. McWilliams, J. A note on a uniformly valid model spanning the regimes of geostrophic and isotropic, stratified turbulence: Balanced turbulence. *J. Atmos. Sci.* **1985**, *42*, 1773–1774.
66. Charney, J. Geostrophic turbulence. *J. Atmos. Sci.* **1971**, *28*, 1087–1095.