

A Phenomenological Gradient Approach to Generalized Constitutive Equations for Isotropic Fluids

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Abstract

An extension of the linear irreversible thermodynamics is proposed through the inclusion of the first gradients of velocity and of the classical local state parameters as additional independent variables in the fundamental energy state equation of a fluid system. We show that consistency of this hypothesis with the energy balance equation leads to generalized nonlinear constitutive equations, which we discuss in terms of an isotropic non-Newtonian viscous fluid.

Keywords

Non-Local Thermodynamics, Non-Newtonian Viscous Fluids, Generalized Constitutive Equations

1. Introduction

Non-Newtonian fluid mechanics is an area of active and intense research. Most of the materials that are of interest in a variety of manufacturing processes, exhibit non-Newtonian behaviors, which implies that the shear stress is not proportional to the shear rate [1]. Apart from some common fluids such as air and water, virtually no fluid is actually Newtonian. The non-Newtonian fluids arise everywhere. Examples are the blood and mucus within our own bodies, toothpaste, tomato ketchup, paints, molten rubber, and emulsions. Other examples are the geophysical flows that involve rapid gravity-driven mass movements of solid particles within a fluid, such as snow avalanches, debris flows, lava flows, and submarine avalanches. In general, engineers are faced with the practical difficulties of modeling a variety of industrial processes involving the flow of some of these materials.

Basic principles of continuum mechanics, namely, the balances of mass, momentum, energy, and entropy, lead to the following fundamental equations [1]:

$$D\rho = 0, \quad (1)$$

$$D(\rho\mathbf{v}) = \rho\mathbf{f} + \nabla \cdot \mathbf{T}, \quad (2)$$

$$D(\rho\varepsilon) = \mathbf{T}^T : \mathbf{G} - \nabla \cdot \mathbf{q}, \quad (3)$$

$$D(\rho\eta) = \sigma - \nabla \cdot \mathbf{j}, \quad (4)$$

where, for any function F , operator D is defined by

$$DF \equiv dF/dt + F\nabla \cdot \mathbf{v} \equiv \dot{F} + F\nabla \cdot \mathbf{v}. \quad (5)$$

In total, Equations (1)-(4) constitute 6 independent equations for 22 unknown field variables, namely, mass density ρ , velocity \mathbf{v} , specific internal energy ε , specific entropy η , stress tensor \mathbf{T} , heat flux \mathbf{q} , entropy flux \mathbf{j} , and the entropy production σ (per unit volume and time). No distribution of heat sources is being considered, and the specific body force \mathbf{f} is assumed to be known. Clearly, the foregoing basic equations are not adequate for the determination of these unknowns except for some trivial situations (for example, rigid body motions in the absence of heat conduction). Hence, 16 additional equations must be supplied in order to make the problem well-posed. Restriction to non-polar materials (*i.e.* when there are no assigned traction couples or body couples and no couple stresses), the moment of momentum principle establishes the symmetry of the stress tensor in general without any assumption of equilibrium or of uniformity of the stress distribution [1, pp. 215-216]. Then, in the case of non-polar materials, the number of unknown variables is reduced to 19.

In the derivation of the Equations (1) to (4), no specification has been required about any particular material. Therefore, the foregoing equations are not sufficient to explain fully the motions of materials having various types of physical properties. The character of the material is brought into the formulation through the constitutive equations, which specify the mechanical and thermal properties of particular materials based upon their internal constitution. These equations describe the relationships among the kinematic, mechanical, and thermal field variables, allowing the formulations of well-posed problems of continuum mechanics. Constitutive equations, from the physical standpoint, define various idealized materials that serve as models for the behavior of real materials.

In Gibbsian linear irreversible thermodynamics (LIT), the local equilibrium hypothesis (LEH) postulates the existence of a fundamental state equation for energy (or entropy), and the state equations of pressure and temperature are derived from it. However, the constitutive equations for the stress tensor and the heat flux remain as an open problem to be solved by the constitutive theory, which strives to find the form or at least restricts the generality of the constitutive functions [2].

For Newtonian fluids, the constitutive equation for the stress tensor is partic-

ularly simple: the deviatoric stress is linearly proportional to the rate of strain and the coefficient of proportionality is the viscosity. For non-Newtonian fluids, the constitutive equations can be much more complicated, implying, in general, a non-linear dependence of the stress tensor on the rate of strain. These constitutive relations must be built to reflect the macroscopic properties engendered by the fluid microstructure. One can go about this construction in several different ways.

In extended irreversible thermodynamics (EIT), for example, the LEH of LIT is replaced by an extension of the state variables space, accomplished by rising the thermodynamic fluxes (such as stress tensor and heat flux vector) to the status of additional independent variables. Then, the constitutive equations in this theory are intended to be recovered as solutions of the evolution equations of the new independent variables [3] [4] [5]. A different approach to derive the constitutive equations for non-uniform complex fluids was proposed in [6], an extension of which we present in this work.

Our main objective in this paper is the development of a phenomenological gradient approach that consents to obtain generalized expressions for the constitutive equations of non-equilibrium fluid systems. To do it, we presumed that the local values of the ordinary state variables (mass density and specific entropy or energy) provide only a first approximation to the complete definition of the local state of a non-equilibrium fluid. In consequence, we also assumed that the specific internal energy of an isotropic, viscous and heat conducting fluid might depend not only on the ordinary state variables (mass density and specific entropy) but also on the first gradients of the mass density, specific entropy, and velocity fields. Our main hypothesis implies a fundamental state equation of energy that contains new information about the local behavior of the ordinary state variables and endows the fluid with a non-local character. Notwithstanding, the LEH is not relaxed completely in the theoretical framework of this approach, and the mass, momentum, energy and entropy balance equations, Equations (1)-(4), are still accepted as the complete set of fundamental physical laws that govern the fluid behavior.

We showed that consistence of our hypothesis with the energy balance equation brings out generalized non-linear expressions for the pressure and temperature state equations and for the constitutive equation of the stress tensor. We discussed this method for isotropic generalized viscous and heat conducting fluids. As simple examples, we applied this method to obtain the explicit forms of the constitutive equations for a second-order fluid [7], for the square density gradient approximation of fluid energy [8] [9], and for a power law viscous fluid [10] [11] [12]. We finish this work with a brief comparison against the results reported for a Lennard-Jones fluid from non-equilibrium molecular dynamics simulations [13] [14] [15] [16] [17].

The paper is organized as follows. In Section 2, the theoretical framework that supports the method we are proposing to derive constitutive equations for com-

plex fluids is presented, and the method is developed. In particular, the generalized equations that consent the derivation of pressure, temperature, and stress tensor from the derivatives of the internal energy are drawn. In Section 3, we discussed the proposed method in terms of an isotropic fluid. Here, by considering the frame-indifferent and isotropic scalar character of the energy function, and with the base on the representation theorems for isotropic scalar functions of tensor arguments, the generalized expressions for pressure, temperature, and stress tensor are obtained. In Section 4, we applied the method to three cases of non-Newtonian viscous fluids for which an expression of the internal energy can be written explicitly as a function of the extended state variables such as the gradient of mass density and the shear rate, and the corresponding generalized constitutive equations were obtained. Finally, a brief paragraph of conclusions is presented in Section 5.

2. Thermodynamic Formalism

The LIT description of a system presupposes that one can find a partition of a non-uniform and non-equilibrium system with the property that each subsystem can be considered uniform and be locally described by exactly the same fundamental state equation of entropy that is valid under equilibrium conditions. This statement is the local equilibrium hypothesis and it implies that the Gibbs fundamental relation, which combines the first and second laws of thermodynamics, remains valid as a first approximation in the LIT description of a non-equilibrium system. The LEH restricts the applicability of LIT to systems close to equilibrium and presupposes that the gradients of the intensive properties are small enough that can be ignored locally. In case of fluid systems, LIT is only applicable to describe the Newtonian fluid behavior not far from equilibrium.

It is interesting to underline, however, that LIT definition of the entropy fundamental equation is the simplest among all possibilities because the second law requires merely that the entropy of an adiabatically isolated system should not decrease when a transition occurs between equilibrium states. Therefore, acceptable definitions may render an entropy function dependent on the values of the intensive variables at a point in the system, but also on their gradients, in such a way that one recovers the equilibrium entropy when the gradients go to zero [18].

Consequently, we postulate, within the framework of the energy representation, that the specific internal energy (ε) depends on the specific entropy (η) and mass density (ρ), but also on its first gradients $\nabla\eta$, $\nabla\rho$, and on the gradient of velocity, $\mathbf{G}(=\nabla\mathbf{v})$:

$$\varepsilon = \varepsilon(\rho, \nabla\rho, \eta, \nabla\eta, \mathbf{G}) \quad (6)$$

Under this hypothesis, we presume that a better description of the thermodynamic behavior of a non-equilibrium and non-uniform fluid system can be obtained.

The specific energy given by Equation (6), however, must be a frame-indifferent scalar function that reduces itself to the local equilibrium specific internal energy of the fluid, $\varepsilon_0(\rho, \eta)$, when the gradients become negligible small:

$$\varepsilon(\rho, \nabla \rho, \eta, \nabla \eta, \mathbf{G}) \xrightarrow{\nabla \rho, \nabla \eta, \mathbf{G} \rightarrow 0} \varepsilon_0(\rho, \eta) \quad (7)$$

Then, our main hypothesis in this work comprises the assumptions expressed by the Equation (6) and Equation (7), and the acceptance of the Equations (1) to (4) as the complete set of fundamental physical laws that will govern the fluid behavior.

2.1. Generalized Pressure and Temperature State Equations

Equation (6) allows writing the following generalized Gibbs equation,

$$D(\rho\varepsilon) = \theta D(\rho\eta) + (p/\rho)\dot{\rho} - [A + B + D(\rho\mathbf{H})] : \mathbf{G} + \nabla \cdot \mathbf{h} + D(\rho\mathbf{H} : \mathbf{G}) \quad (8)$$

where

$$\rho\theta = \rho(\partial\varepsilon/\partial\eta) - \nabla \cdot [\rho(\partial\varepsilon/\partial\nabla\eta)] \quad (9)$$

$$p/\rho = \rho(\partial\varepsilon/\partial\rho) - \nabla \cdot [\rho(\partial\varepsilon/\partial\nabla\rho)] \quad (10)$$

$$A = \rho[(\partial\varepsilon/\partial\nabla\rho)\nabla\rho + (\partial\varepsilon/\partial\nabla\eta)\nabla\eta] \quad (11)$$

$$\mathbf{B} = \rho(\mathbf{G}^T \cdot \mathbf{H} - \mathbf{H} \cdot \mathbf{G}^T) \quad (12)$$

$$\mathbf{H} = \partial\varepsilon/\partial\mathbf{G} \quad (13)$$

$$\mathbf{h} = \rho[(\partial\varepsilon/\partial\nabla\rho)\dot{\rho} + (\partial\varepsilon/\partial\nabla\eta)\dot{\eta}] \quad (14)$$

Equation (9) and Equation (10) are generalized state equations for temperature θ and pressure p , respectively. When the specific energy does not depend on the gradients of specific entropy and mass density, these equations give the local equilibrium temperature and pressure.

2.2. Generalized Stress Tensor, Entropy Flux, and Entropy Production

Now, with the help of the mass and entropy balance equations (Equation (1) and Equation (4), respectively), Equation (8) can be written as

$$D(\rho\varepsilon) = -[p\mathbf{I} + A + B + D(\rho\mathbf{H})] : \mathbf{G} - \nabla \cdot (\theta\mathbf{j} - \mathbf{h}) + [\theta\sigma + \mathbf{j} \cdot \nabla\theta + D(\rho\mathbf{H} : \mathbf{G})] \quad (15)$$

where \mathbf{I} denotes the unit tensor.

Then, from the comparison of Equation (15) with Equation (3), we obtain the following expressions for the stress tensor \mathbf{T} , the entropy flux \mathbf{j} , and the entropy production σ :

$$\mathbf{T} = -[p\mathbf{I} + A + B + D(\rho\mathbf{H})]^T \quad (16)$$

$$\mathbf{j} = (\mathbf{q} + \mathbf{h})/\theta \quad (17)$$

$$\sigma = -[\mathbf{j} \cdot \nabla\theta + D(\rho\mathbf{H} : \mathbf{G})]/\theta \quad (18)$$

In principle, the Equations (9), (10) and (16) allow to calculate the temperature (θ), pressure (p), and the stress tensor (\mathbf{T}) of the fluid from the derivatives of the generalized specific internal energy with respect the classical state variables, its gradients, and the gradient of velocity. Equation (17) and Equation (18), however, provide expressions for the entropy flux (\mathbf{j}) and entropy production (σ) which also involve the derivatives of the generalized internal energy, but these properties are not completely determined by these energy derivatives because the heat flux (\mathbf{q}) remains as an unknown within this formalism.

3. Generalized Constitutive Equations for an Isotropic Fluid

Within the framework of a phenomenological theory, the internal energy function must be determined by experiment for each particular fluid. However, it is possible to obtain important information about the constitutive equations for an isotropic fluid if we consider the frame-indifferent and isotropic scalar character of the energy function¹.

Therefore, in the case of an isotropic fluid, the specific internal energy can be a function of the velocity gradient, \mathbf{G} , only through the strain tensor

$$\mathbf{D} = \frac{1}{2}(\mathbf{G} + \mathbf{G}^T), \quad (19)$$

because \mathbf{G} itself is non-indifferent [19]. So

$$\varepsilon(\rho, \nabla\rho, \eta, \nabla\eta, \mathbf{G}) = \varepsilon(\rho, \nabla\rho, \eta, \nabla\eta, \mathbf{D}). \quad (20)$$

Now, according to the representation theorems for isotropic scalar functions of tensor arguments, the specific internal energy of an isotropic fluid can be expressed as a function of the scalar invariants I_α of $\nabla\rho$, $\nabla\eta$ and \mathbf{D} , that is,

$$\varepsilon(\rho, \nabla\rho, \eta, \nabla\eta, \mathbf{D}) = \varepsilon(\rho, \eta, I_\alpha). \quad (21)$$

Therefore, the partial derivatives of the energy function with respect to the variables $\nabla\rho$, $\nabla\eta$ and \mathbf{D} can be expressed in the form

$$(\partial\varepsilon/\partial\nabla u) = \sum A_\alpha (\partial I_\alpha / \partial \nabla u) \equiv \sum (\partial\varepsilon/\partial I_\alpha) (\partial I_\alpha / \partial \nabla u) \quad (22)$$

where the sums run over the number of the independent scalar invariants. In general, the coefficients A_α depend on the same variables as the internal energy.

Hereafter, we will be considering a specific internal energy dependent only on the first nine independent scalar invariants of $\nabla\rho$, $\nabla\eta$ and \mathbf{D} . These scalar invariants involve the variables $\nabla\rho$, $\nabla\eta$ and \mathbf{D} up to third order:

$$\begin{aligned} I_1 &= \nabla\eta \cdot \nabla\eta, \quad I_2 = \nabla\eta \cdot \nabla\rho, \quad I_3 = \nabla\rho \cdot \nabla\rho, \\ I_4 &= \text{Tr}(\mathbf{D}), \quad I_5 = \text{Tr}(\mathbf{D}^2), \quad I_6 = \text{Tr}(\mathbf{D}^3), \\ I_7 &= \nabla\eta \cdot \mathbf{D} \cdot \nabla\eta, \quad I_8 = \nabla\eta \cdot \mathbf{D} \cdot \nabla\rho, \quad I_9 = \nabla\rho \cdot \mathbf{D} \cdot \nabla\rho. \end{aligned} \quad (23)$$

¹A scalar function F of a tensor argument \mathbf{X} is said to be indifferent if it remains unchanged after a change of frame, so that $F(\mathbf{X}') = F(\mathbf{X})$, where \mathbf{X}' is the image of \mathbf{X} under the change of frame. In addition, the function F is an isotropic scalar function of the tensor argument \mathbf{X} , if it satisfies $\mathbf{X}' = \mathbf{Q} \cdot \mathbf{X} \cdot \mathbf{Q}^T$, for any orthogonal tensor \mathbf{Q} [19].

In this case, Equation (16) leads to the following expression for the generalized stress tensor:

$$\begin{aligned}
 \mathbf{T} = & -(p + \pi)\mathbf{I} + 2\mu\left\{\mathbf{D} + \alpha_1\left[\dot{\mathbf{D}} + (\mathbf{D} \cdot \boldsymbol{\Omega} - \boldsymbol{\Omega} \cdot \mathbf{D})\right] + \alpha_2\mathbf{D}^2 + \alpha_3(\mathbf{D} \cdot \dot{\mathbf{D}} + \dot{\mathbf{D}} \cdot \mathbf{D})\right\} \\
 & - 2\rho\left(A_1\nabla\eta\nabla\eta + A_2\nabla\eta\nabla\rho + A_3\nabla\rho\nabla\rho\right) \\
 & - D\left[\rho\left(A_7\nabla\eta\nabla\eta + A_8\nabla\eta\nabla\rho + A_9\nabla\rho\nabla\rho\right)\right]
 \end{aligned} \tag{24}$$

where only the terms up to second order in $\nabla\rho$, $\nabla\eta$ and \mathbf{D} have been retained. In this equation, we have introduced the vorticity tensor

$$\boldsymbol{\Omega} = \frac{1}{2}(\mathbf{G} - \mathbf{G}^T), \tag{25}$$

and the following definitions

$$\pi = \rho\dot{A}_4, \quad \mu = -\rho\dot{A}_5, \quad \overline{\nabla\eta\nabla\rho} = \frac{1}{2}(\nabla\eta\nabla\rho + \nabla\rho\nabla\eta), \tag{26}$$

$$\alpha_1 = A_5/\dot{A}_5, \quad \alpha_2 = \frac{3}{2}(\dot{A}_6/\dot{A}_5), \quad \alpha_3 = \frac{3}{2}(A_6/\dot{A}_5). \tag{27}$$

The generalized state equations for temperature and pressure are obtained in a similar way starting from Equation (9) and Equation (10), respectively. The results are

$$\begin{aligned}
 \theta = & (\partial\varepsilon/\partial\eta) - \left(B_1|\nabla\eta|^2 + B_2\nabla\eta \cdot \nabla\rho + B_3|\nabla\rho|^2\right) \\
 & - \left[2(A_1\mathbf{I} + A_7\mathbf{D}) : \mathbf{N} + (A_2\mathbf{I} + A_8\mathbf{D}) : \mathbf{M}\right] \\
 & - \left[2A_7(\nabla \cdot \mathbf{D}) \cdot \nabla\eta + A_8(\nabla \cdot \mathbf{D}) \cdot \nabla\rho\right]
 \end{aligned} \tag{28}$$

$$\begin{aligned}
 p = & \rho^2(\partial\varepsilon/\partial\rho) - \left(C_1|\nabla\eta|^2 + C_2\nabla\eta \cdot \nabla\rho + C_3|\nabla\rho|^2\right) \\
 & - \rho^2\left[(A_2\mathbf{I} + A_8\mathbf{D}) : \mathbf{N} + 2(A_3\mathbf{I} + A_9\mathbf{D}) : \mathbf{M}\right] \\
 & - \rho^2\left[A_8(\nabla \cdot \mathbf{D}) \cdot \nabla\eta + 2A_9(\nabla \cdot \mathbf{D}) \cdot \nabla\rho\right]
 \end{aligned} \tag{29}$$

where

$$\begin{aligned}
 B_1 = & 2(\partial A_1/\partial\eta), \quad B_2 = (1/\rho)\left[2A_1 + 2(\partial A_1/\partial\rho) + (\partial A_2/\partial\eta)\right], \\
 B_3 = & (1/\rho)\left[A_2 + \rho(\partial A_2/\partial\rho)\right],
 \end{aligned} \tag{30}$$

$$\begin{aligned}
 C_1 = & \rho^2(\partial A_2/\partial\eta), \quad C_2 = \rho\left[A_2 + \rho(\partial A_2/\partial\rho) + 2\rho(\partial A_3/\partial\eta)\right], \\
 C_3 = & 2\rho\left[A_3 + (\partial A_3/\partial\rho)\right],
 \end{aligned} \tag{31}$$

$$\mathbf{M} = \nabla(\nabla\rho), \quad \mathbf{N} = \nabla(\nabla\eta). \tag{32}$$

Equation (24), Equation (28) and Equation (29) reduce themselves to the corresponding linear expressions of LIT when the time rate terms are negligible and the gradients are small enough to neglect the quadratic and higher order terms involving them. When this is not the case, the additional terms in these equations represent nonlinear corrections that become relevant when gradients are not locally negligible. In particular, the expression for the stress tensor contains some additional terms that one can find in rheological constitutive equations [20]

[21]. For example, in the classical models of second-order fluids [7], the stress tensor \mathbf{T} is represented in terms of the first and second Rivlin-Ericksen tensors, $2\mathbf{D}$ and $2[\dot{\mathbf{D}} + (\mathbf{D} \cdot \boldsymbol{\Omega} - \boldsymbol{\Omega} \cdot \mathbf{D})]$ [22], respectively, according to

$$\mathbf{T} = -p\mathbf{I} + 2\mu_0\mathbf{D} + 4\mu_1\mathbf{D}^2 + 2\mu_2[\dot{\mathbf{D}} + (\mathbf{D} \cdot \boldsymbol{\Omega} - \boldsymbol{\Omega} \cdot \mathbf{D})]. \quad (33)$$

4. Simple Examples

In this section, as simple applications of the proposed method, we used the generalized equations for pressure, temperature, and the stress tensor that we found in the previous section, in order to obtain explicit forms of these properties for three cases already reported in literature. In the first case, we started with the square gradient approximation for the specific internal energy, and the corresponding constitutive equations were obtained. In the second case, we proposed an expression for the internal energy of a power law viscous fluid, and then the known constitutive equations were derived. Finally, we carry out a comparison with results reported from non-equilibrium molecular dynamics simulations.

4.1. The Square Gradient Approximation

From the standpoint of the square gradient approximation [9] [23], the specific internal energy for a fluid can be written as

$$\varepsilon(\eta, \rho, \nabla\rho) = \varepsilon_0(\eta, \rho) + (b/2\rho)|\nabla\rho|^2, \quad (34)$$

where ε_0 is the local equilibrium energy and b is a constant. Application of Equation (24) to the energy given by Equation (34), leads to the following stress tensor

$$\mathbf{T} = -\left[p_0 - b\left(\frac{1}{2}|\nabla\rho|^2 + \rho\nabla^2\rho\right) \right] \mathbf{I} - b\nabla\rho\nabla\rho, \quad (35)$$

with p_0 being the local equilibrium pressure given by

$$p_0 = \rho^2(\partial\varepsilon_0/\partial\rho). \quad (36)$$

The pressure p is defined by

$$p = -\frac{1}{3}\text{Tr}(\mathbf{T}) = p_0 - \frac{1}{6}b|\nabla\rho|^2 - b\rho\nabla^2\rho. \quad (37)$$

Equation (35) is the Lovett expression [24] for the stress tensor of a non-uniform fluid. L. Mistura [8] deduced also this stress tensor and the pressure given by equation (37) using a generalization of a device introduced independently by Bogoliubov [25] and Green [26] to calculate the scalar pressure in a homogeneous fluid. He also used these results to show that pressure exhibits the same singularity as the specific heat in the critical point.

4.2. The Power Law Fluid Model

A simple generalization of the Newtonian fluid is a phenomenological model that assumes that the flow regime changes the fluid viscosity (the rate of dissipa-

tion), but the tensorial structure of the Newtonian constitutive equation remains unchanged. The constitutive equation for this class of fluid models has the following form

$$\mathbf{T} = -p\mathbf{I} + 2\mu(\mathbf{D})\mathbf{D}, \quad (37)$$

where $\mu(\mathbf{D})$ is the viscosity, which is different from the Newtonian viscosity due to its possible dependence upon the fluid flow [10]. In this model, viscosity $\mu(\mathbf{D})$ can only depend on the invariants of the tensor \mathbf{D} , otherwise a change of coordinate system could be reflected on the value of the viscosity, which has no any physical meaning. The simplest possible deviation from the Newtonian fluid behavior occurs when the viscosity $\mu(\mathbf{D})$ is a function that only depends on the shear rate,

$$\gamma = \sqrt{\mathbf{D} : \mathbf{D}} = \sqrt{\text{Tr}(\mathbf{D}^2)},$$

(*i.e.*, on the square root of the second scalar invariant of the tensor \mathbf{D}). Then

$$\mu(\mathbf{D}) = \mu(\gamma).$$

The material properties of a generalized Newtonian fluid are determined entirely by the behavior of the function $\mu(\gamma)$. Often, over an interval of shear rate, a straight line can approximate the relationship between the apparent viscosity and the shear rate, when plotted in log-log coordinates, *i.e.*,

$$\mu(\gamma) = K\gamma^{n-1}. \quad (38)$$

This expression for the viscosity is called the Ostwald de Weale model or the power law model [12] [27]. It is valid at intermediate values of strain rate. In these equations, K and n are empirical curve-fitting parameters. They are known as the fluid consistency coefficient and the power law index (or flow behavior index), respectively [11]. The power law index is an important parameter in rheological measurements, because it gives some idea of how fast the viscosity decreases with strain rate. This also has an effect on the fluid functionality: for $n < 1$, the fluid exhibits shear-thinning properties; for $n = 1$, the fluid shows Newtonian viscous behavior; and for $n > 1$, the fluid shows shear-thickening behavior [10] [11] [12]. Under this model, the deviatoric stress tensor of a power law fluid is written as follows:

$$\tilde{\mathbf{T}} = 2K\gamma^{n-1}\mathbf{D}. \quad (39)$$

Now, for the power law fluid, let us assume a specific internal energy with the form

$$\varepsilon(\rho, \eta, \gamma) = \varepsilon_0(\rho, \eta) + \varepsilon_1(\rho, \eta)\gamma^{n+1}, \quad (40)$$

where ε_0 denote the local equilibrium value of energy, ε_1 denote a non-equilibrium coefficient, and n is the power law index.

This expression for energy constitutes a particular case of the more general expression given by the Equation (21) because it depends on the gradients of the velocity field through the shear rate. Then, for the power law fluid with an ener-

gy given by Equation (40), the Equation (28), Equation (29) and Equation (24) can be used to obtain the temperature and pressure generalized state equations and the stress tensor. Respectively, the results were

$$\theta(\rho, \eta, \gamma) = \theta_0(\rho, \eta) + \theta_1(\rho, \eta)\gamma^{n+1}, \quad (41)$$

$$p(\rho, \eta, \gamma) = p_0(\rho, \eta) + p_1(\rho, \eta)\gamma^{n+1}, \quad (42)$$

$$\mathbf{T} = -p(\rho, \eta, \gamma)\mathbf{I} + 2[\beta(\rho, \eta)\gamma^{n-1}]\mathbf{D}. \quad (43)$$

Here, the terms involving time derivatives of shear rate were ignored, and the following symbols were introduced

$$\theta_i = (\partial \varepsilon_i / \partial \eta), \quad i = 0, 1, \quad (44)$$

$$p_i = \rho^2 (\partial \varepsilon_i / \partial \rho), \quad i = 0, 1, \quad (45)$$

$$\beta(\rho, \eta) = -\frac{1}{2}(n+1)\rho\dot{\varepsilon}_1. \quad (46)$$

Equation (43) gives the deviatoric stress tensor with an apparent viscosity with the same dependence on shear rate as in Equation (38) of the power law model by Ostwald de Weale [12] [27].

4.3. Comparison with Non-Equilibrium Molecular Dynamics Simulations

The properties of a fluid under a shear have been investigated with non-equilibrium molecular dynamics (NEMD) simulations [13] [14] [15] [28] [29]. For a Lennard-Jones fluid, the strain rate dependent shear viscosity, hydrostatic pressure, and configurational internal energy were predicted (originally by Kawasaki and Gunton in 1973 [30]) by mode-mode coupling theory to follow the asymptotic expressions:

$$\mu = \mu_0 - \mu_1\gamma^{\frac{1}{2}}, \quad (47)$$

$$p = p_0 + p_1\gamma^{\frac{3}{2}}, \quad (48)$$

$$\varepsilon = \varepsilon_0 + \varepsilon_1\gamma^{\frac{3}{2}}, \quad (49)$$

where the quantities with zero subscript are the zero strain rate quantities, so that, in particular, μ_0 is the Newtonian viscosity. At temperatures at or near the triple point of a Lennard-Jones Fluid, the Equation (47) for viscosity is in good agreement with the simulation results. However, better overall agreement for other temperatures and densities has been obtained using other values of the exponent of the shear rate [16] [17].

For $n = 1/2$, Equation (40) and Equation (42) give the specific energy and the pressure with the same dependence on shear rate γ as in Equation (49) and Equation (48). For $n = 1/2$, however, Equation (43) gives a deviatoric stress tensor with an apparent viscosity with dependence on shear rate to the power minus one-half ($\gamma^{-1/2}$) which is different from that predicted by mode-coupling theory

in the NEMD simulations.

It is worth to mention, however, that the power law model, Equation (39), is perhaps the most widely used model in literature dealing with process engineering applications, and that there exist a variety of substances whose viscosity presents a dependence on $\dot{\gamma}^{-1/2}$ (power law index $n = 1/2$), such as chocolate, guava puree, papaya puree, and tomato paste, among others [11].

5. Conclusion

A slight generalization of the local equilibrium energy equation carried out with the inclusion of the first gradients of mass density, specific entropy, and velocity as additional state variables allowed developing a method to derive non-linear expressions for pressure, temperature, and the stress tensor for complex fluids. The proposed method was discussed in terms of an isotropic viscous fluid. As simple examples, it was shown that the generalized stress tensor could be reduced, under specific constraints, to the stress tensor of second-order fluids, to the Lovett expression for the stress tensor of a non-uniform fluid, and to stress tensor of a power law fluid. We also compared the results of the proposed method with results of NEMD simulations reported in the literature, and we could reproduce the pressure expression obtained for a Lennard-Jones fluid under shear.

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