

# The generalized engineering Bernoulli equation (GEBE) and the first and second laws of thermodynamics for viscoelastic fluids

Gianni Astarita<sup>a)</sup> and Michael E. Mackay<sup>b),c)</sup>

*Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716*

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## Synopsis

In this work we thoroughly explore the meanings of dissipation (sometimes referred to as viscous dissipation) and stress power. To do this we utilize the Cauchy momentum equations and the first and second laws of thermodynamics. First, the generalized engineering Bernoulli equation (GEBE) is derived from the Cauchy momentum equations and it is clearly shown to have nothing to do with a balance of energy. Next, the first law of thermodynamics or energy balance is discussed and a combined equation by subtracting the two is derived which we refer to as the mechanoenergy balance (sometimes referred to as the “equation of thermal energy”). The fact that a difference exists further reinforces that the GEBE is not related to a balance of energy. Finally, the second law of thermodynamics is presented and the concept of dissipation introduced. An example is presented to demonstrate the utility of these equations which will hopefully eliminate some confusion in the literature. © 1996 Society of Rheology.

## I. INTRODUCTION

One of us (M.E.M.) has recently coauthored a paper [Mackay *et al.* (1995)] where elongation stresses in stagnation flow were estimated by the application of what was called the first law of thermodynamics applied to a finite control volume within which steady flow of a viscoelastic fluid takes place. We have re-examined the Mackay *et al.* analysis from the viewpoint of (a) the classical fluid mechanics derivation of the Bernoulli equation, and (b) the thermodynamic theory as applicable to materials endowed with any conceivable rheological equation of state, including, in particular, viscoelastic liquids.

While doing that, we have realized that a macroscopic (i.e., applicable to a gross open system) formulation of either the equivalent of an engineering Bernoulli equation or the first law of thermodynamics as applicable to materials with arbitrary rheological properties are, rather surprisingly, misunderstood in the literature. Choplin and Carreau (1981) did present a form of the engineering Bernoulli equation; however, they have incorrectly interpreted one term as due to “dissipation” which is not true for all fluid types. Bird

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<sup>a)</sup>Permanent address: Department of Materials and Production Engineering, University of Naples Federico II, Piazzale Tecchio, 80125 Naples, Italy.

<sup>b)</sup>Permanent address: Department of Chemical Engineering, The University of Queensland, Brisbane 4072, Queensland, Australia.

<sup>c)</sup>Corresponding author.

(1957, 1993 and 1994) and Slattery (1972) have also either stated or strongly implied the same term is due to dissipation. For completeness we also cite the work of Joseph and Liao (1994) which is, however, restricted to potential flow. Thus, in this article we try to provide a correct formulation for this equation as well as the laws of thermodynamics for general flows and fluids.

We try to be as general as possible in developing our formulation by refraining from a specific constitutive assumption as long as possible. However, the analysis given in this article is based on two strong assumptions: (a) the material under consideration is incompressible, and (b) only steady state kinematics are considered. Relaxing these assumptions would not be difficult, yet, the resulting analysis would be so complex as to defy our main purpose: the clarification of the relative logical status of the generalized engineering Bernoulli equation (GEBE), and of the first and second laws of thermodynamics as applicable to viscoelastic liquids.

In writing down the GEBE, as well as the first and second laws, we adhere to the following approach. First, the local forms of the equations are written in what may be called their “unadulterated” form: the local Bernoulli equation as a direct consequence of the local momentum balance, the local energy balance, and the local entropy inequality. In this form, the three equations are entirely independent of each other, and each one would hold true by itself even if the other ones did not.

At this stage, one may proceed to integrate the local form of the equations over the whole volume of the flow field of interest, to obtain an unadulterated macroscopic form. One may also combine two of the local forms (the energy balance and the Bernoulli equation) to obtain what may be called a “combined local form” of the energy balance or the mechanoenergy balance; or one may combine all three local forms to obtain a combined local form of the second law. Clearly, the combined forms derive from more than one fundamental physical principle. The combined forms may in turn be integrated over the volume of interest to obtain macroscopic combined forms of the balance of energy and of the entropy inequality.

This article is organized as follows. First, we discuss the Bernoulli equation in the context of ideal and Newtonian fluids. Next, we derive all useful forms of the equations without making any constitutive assumptions other than incompressibility (and steady state). Finally, we discuss an example where the key conceptual points are made concrete. Hopefully, this article will clarify the relative logical status of the GEBE and the two laws.

## II. THE GENERALIZED ENGINEERING BERNOULLI EQUATION (GEBE)

### A. The local engineering Bernoulli equation

First of all, it is important to point out that Bernoulli’s equation has nothing whatsoever to do with the balance of energy: at Bernoulli’s time (second half of the eighteenth century), the word “energy” had not even been coined yet. Bernoulli only knew about “ideal fluids” or fluids with zero viscosity: the stress is isotropic no matter what, just as it is at equilibrium. (The simplest constitutive assumption is of course that whatever holds at equilibrium holds always.) One starts with the balance of momentum, written for incompressible, ideal fluids as

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla p + \rho \mathbf{g}, \quad (1)$$

where  $\rho$  is the fluid’s density,  $\mathbf{v}$  the velocity vector,  $D/Dt$  the substantial derivative,  $\nabla$  the gradient operator, and  $\mathbf{g}$  the body-force field vector. One now makes the mild assumption

that the body-force field admits a potential. Thus,  $\mathbf{g}$  is equal to  $-g\nabla h$ , where  $g$  is a constant and  $h$  is the height above some arbitrary datum. One now takes the scalar product of this equation with the velocity vector to obtain

$$\rho \frac{D}{Dt} \left( \frac{1}{2} v^2 \right) = -\mathbf{v} \cdot \nabla (p + \rho gh), \quad (2)$$

so that the equation, under the assumption of steady flow, reduces to

$$\mathbf{v} \cdot \nabla \left( \frac{1}{2} \rho v^2 + p + \rho gh \right) = 0. \quad (3)$$

This implies that the quantity  $\rho v^2/2 + p + \rho gh$ , call this  $Y$ , is either constant over the whole flow field [so that  $\nabla Y = 0$ ], or that its gradient is everywhere orthogonal to the velocity vector, which implies that  $Y$  is constant along any streamline. So, in the classical case, the streamline form of the Bernoulli equation is simply  $Y$  is equal to a constant. Since  $Y$  can (perhaps) be interpreted as mechanical energy, i.e., the sum of kinetic, potential, and pressure energy (whatever the latter may be), the Bernoulli equation in its classical formulation acquires a strong, but entirely spurious flavor of having to do with some sort of energy balance. It is simply a consequence of the momentum balance, and energy has nothing to do with it.

Incidentally, of the three terms appearing in  $Y$ ,  $v^2/2$  is the kinetic energy per unit mass, call this  $K$ , and  $gh$  is the potential energy per unit mass (which can be defined if the body forces admit a potential). The concept of kinetic energy was available at Bernoulli's time, though it was called "living force" (*vis viva*), to contrast it with the "dead forces" appearing in statics. These mechanical preliminaries to the general concept of energy played a crucial role in the later development of thermodynamics [Astarita (1977a)].

The Bernoulli equation in its classical form only applies to ideal fluids. Indeed, Landau and Lifshitz (1960), Whitaker (1968), and Aris (1962) discuss the Bernoulli equation only for ideal fluids; they consider the general case of unsteady flow, but they never extend the Bernoulli equation "concept" to any fluids other than ideal ones. In contrast with this, the so-called "engineering Bernoulli equation" appears in fluid mechanics books of a more practical slant [this is not necessarily true; for instance, the eminently pragmatic book by Roberson and Crowe (1975) does not discuss the engineering Bernoulli equation]. The most interesting derivation is probably in Denn (1980), where in fact two derivations are offered: one is based essentially on the arguments given below (based solely on the momentum balance), while the other is based on using the laws of thermodynamics. The logic of the second derivation is discussed later.

Consider the case of Newtonian fluids, and proceed along exactly the same line of reasoning as for the classical case. One ends up, under the same assumptions, with

$$\mathbf{v} \cdot \nabla Y = \mathbf{v} \cdot \mu \nabla^2 \mathbf{v}. \quad (4)$$

One is tempted (particularly if one takes the word "engineering" in a slightly derogatory sense) to make a handwaving argument which runs something like this:  $Y$  is not quite constant along a streamline, but perhaps it is approximately constant, and perhaps the right-hand side is a sort of loss term; mechanical energy is not quite conserved along a streamline, but perhaps it is almost conserved. Well, it is not. At this stage (where we have not yet discussed the first law, let alone the second one) we should not dare to talk about dissipation; however, for the case of Newtonian fluids we may follow Bird *et al.* (1960) and recall that the "dissipation function" is

$$\phi = \mu \nabla \mathbf{v} : \nabla \mathbf{v}, \quad (5)$$

and this is not the right-hand side of Eq. (4).

### B. The streamline GEBE

First consider a Newtonian fluid and what one can do is to integrate Eq. (4) along a streamline. Let  $s$  be the curvilinear coordinate along the streamline, and let  $\lambda$  be the curvilinear length of the streamline over which we integrate. One observes that, since the velocity vector is everywhere tangent to the streamline,  $dt$  is equal to  $ds/v$ , where  $v$  is the modulus of the velocity vector (which may well depend on  $s$ , unless the flow is without translational acceleration). At steady state, the left-hand side of Eq. (4) is equal to  $v dY/ds$ , and one obtains

$$\int_0^\lambda v \frac{dY}{ds} ds = \int_0^\lambda \mu \mathbf{v} \cdot \nabla^2 \mathbf{v} ds. \quad (6)$$

The left-hand side can be integrated by parts to obtain (stations 1 and 2 indicate the beginning and end of the streamline, respectively)

$$\int_0^\lambda v \frac{dY}{ds} ds = [vY]_{@2} - [vY]_{@1} - \int_0^\lambda Y \frac{dv}{ds} ds, \quad (7)$$

where the @ symbol is employed to denote evaluation at that station. So one obtains the following form of the engineering Bernoulli equation or GEBE integrated along a streamline:

$$[vY]_{@2} - [vY]_{@1} = \int_0^\lambda \left[ \mu \mathbf{v} \cdot \nabla^2 \mathbf{v} + Y \frac{dv}{ds} \right] ds. \quad (8)$$

It is useful at this stage to consider a simple example, which may clarify some conceptual issues: Poiseuille flow between two infinitely wide, horizontal, parallel plates,  $2H$  apart from each other with fluid flowing at an average velocity  $V$ . Let  $x$  be the flow direction, and  $y$  the transverse direction, with the origin at the centerline. One has

$$v_x = \frac{3}{2} V \left\{ 1 - \left[ \frac{y}{H} \right]^2 \right\}. \quad (9)$$

Now the dissipation function is

$$\phi = \frac{9\mu V^2 y^2}{H^4}, \quad (10)$$

but the right-hand side of Eq. (4) or the first term in the integral of Eq. (8) is

$$\mu \mathbf{v} \cdot \nabla^2 \mathbf{v} = -3\mu \frac{V^2}{H^2} \left\{ 1 - \left[ \frac{y}{H} \right]^2 \right\}. \quad (11)$$

In Eq. (8), the only term of  $Y$  which changes along the streamline is  $p$ ; furthermore,  $dv/ds$  is equal to zero. Hence the equation reduces to (taking the curvilinear length  $\lambda$  equal to that of the parallel plates  $L$  between the stations 1 and 2):

$$p_{@2} - p_{@1} = -2\mu L \frac{V}{H^2}. \quad (12)$$

There is a lot to be learned from Eq. (12). First of all, it tells us that the pressure drop is proportional to the length  $L$ , which of course we know to be right. Second, it tells us

that the pressure gradient is not a function of  $y$ , which again we know to be right. The expression for the pressure drop is correct. So everything is fine, but notice what follows:

The pressure drop along any streamline is the same. It is correctly given by the GEBE. However, in no sense is it a result of dissipation along that streamline: the dissipation function is zero on the center streamline, and yet the quantity  $Y$  decreases along the flow direction. A negative  $[vY]_{@2} - [vY]_{@1}$  does not in any way imply that there is dissipation along the streamline. In its streamline form, the right-hand side of the GEBE cannot be interpreted as a loss term, not even for Newtonian fluids.

Incidentally, the even simpler example of drag driven flow between two parallel plates (where the velocity profile is triangular and the pressure gradient zero) results in the streamline GEBE being satisfied trivially as zero equals zero; yet the dissipation is not zero! This again shows that in no sense can the right-hand side of Eq. (4) be regarded as a loss term.

At this point we consider a general fluid and write the momentum balance in the general form

$$\rho \frac{D\mathbf{v}}{Dt} = \nabla \cdot \mathbf{T} - \nabla[\rho gh], \quad (13)$$

where  $\mathbf{T}$  represents the stress tensor. One can now go through exactly the same derivation to obtain the general form of the streamline GEBE:

$$[vZ]_{@2} - [vZ]_{@1} = \int_0^\lambda \left[ [\nabla \cdot \mathbf{T}] \cdot \mathbf{v} + Z \frac{dv}{ds} \right] ds, \quad (14)$$

where  $Z$  is equal to  $\rho v^2/2 + \rho gh$ . This result, however, turns out not to be very useful.

### C. The macroscopic GEBE

A more useful approach is to obtain the GEBE applicable to a finite volume for the flow field of interest. We approach this problem directly for the general case, say we begin with Eq. (13). Taking the scalar product of every term with the velocity vector, we obtain

$$\rho \mathbf{v} \cdot \frac{D\mathbf{v}}{Dt} = \mathbf{v} \cdot [\nabla \cdot \mathbf{T}] - \mathbf{v} \cdot \nabla[\rho gh]. \quad (15)$$

This is called the **local GEBE** by us.

One wants to integrate Eq. (15) over the system volume of interest,  $V_{\text{sys}}$ , and one wants to have as many terms as possible appearing as volume integrals of either the gradient of a scalar or the divergence of a vector or tensor, since then the three classical divergence theorems can be used to reduce such integrals to surface integrals. Assuming incompressibility, steady state and a symmetric stress tensor we arrive at

$$\mathbf{v} \cdot [\nabla \cdot \mathbf{T}] = \nabla \cdot [\mathbf{T} \cdot \mathbf{v}] - w, \quad (16)$$

where  $w$  is the “stress power” (a physical interpretation of the stress power is given later—it would be misleading at this stage):

$$w = \mathbf{T} : \nabla \mathbf{v}. \quad (17)$$

Integrating the above equations over  $V_{\text{sys}}$  one can now apply the Gauss–Ostrogradskii theorem to transform all volume integrals (except that of  $w$ ) to surface integrals over the system surface  $S_{\text{sys}}$ , to obtain

$$\int_{S_{\text{sys}}} [\mathbf{T} \cdot \mathbf{v}] \cdot d\mathbf{S} - \int_{S_{\text{sys}}} Z \mathbf{v} \cdot d\mathbf{S} = W, \quad (18)$$

where  $\mathbf{S}$  denotes the orientation of the surface with respect to the velocity vector  $\mathbf{v}$ , and  $W$  is the volume integral of the stress power

$$W = \int_{V_{\text{sys}}} w dV. \quad (19)$$

We denote Eq. (18) as the **macroscopic GEBE**. A form similar to Eq. (18) was derived by Choplin and Carreau (1981), however, they interpreted  $W$  (denoted as  $E_v$  by them) as due to “viscous dissipation.” This is incorrect, which we will clarify below, and represents a major motivation to our presenting this work.

It is perhaps evident that the first term on the left-hand side of Eq. (18) yields, under appropriate simplifying assumptions, the left-hand side of the macroscopic engineering Bernoulli equation. (Should the total stress within the second integral on the left-hand side be decomposed as  $\mathbf{T} = -\hat{p}\mathbf{I} + \boldsymbol{\tau}$ , where  $\hat{p}$  is an isotropic term and  $\boldsymbol{\tau}$  the deviatoric stress. The isotropic part, when added to the first term, would produce  $Y$  instead of  $Z$ .) The first term on the left-hand side accounts (under the same assumptions) for the fact the flow work term is not given simply by a pressure term unless  $\boldsymbol{\tau}$  is zero. This term also accounts for any shaft work. Here it is important to point out the physical significance of the  $W$  term.

First of all, the derivation sketched above is based only on the momentum balance: thermodynamics has nothing to do with it, and in no sense can an energetic significance be given to Eq. (18). However, in the case of Newtonian fluids the stress power is indeed equal to the dissipation function, and so  $W$  does coincide with the total rate of energy dissipation in the case of a Newtonian fluid. As will be discussed in more detail later, this is a special feature of Newtonian fluids which does not carry over to viscoelastic fluids, for which  $W$  is not the total rate of energy dissipation. There are other instances [Astarita (1977b, 1983)] where, for sufficiently simple constitutive equations, purely mechanical results acquire a spurious thermodynamic flavor which is lost in the general case. In spite of that, Eq. (18), under the stated assumptions, does hold for viscoelastic fluids, thus showing in general, even in its macroscopic form, the right-hand side of the GEBE is not to be interpreted as a loss term.

### III. THE FIRST LAW

The balance of energy written for the neighborhood of a material point is

$$\rho \frac{D[U+K]}{Dt} = Q - \nabla \cdot \mathbf{q} + \nabla \cdot [\mathbf{T} \cdot \mathbf{v}] + \rho \mathbf{g} \cdot \mathbf{v}, \quad (20)$$

where  $U$  is internal energy per unit mass, so that the left-hand side represents the local rate of accumulation of internal and kinetic energy.  $Q$  is the local influx of radiant energy per unit volume. The second term on the right-hand side represents the local influx of heat due to conduction; the third term is the rate at which internal stresses are doing work on the element considered; and the last term is the rate of work done by body forces. As

it stands, Eq. (20) is the unadulterated local form of the energy balance: the momentum balance is not invoked in writing it down, and we call this the **local energy balance**.

Under the assumptions of steady state and incompressibility, this equation can be integrated over the whole volume of interest and all volume integrals, except that containing  $Q$ , can be transformed to surface integrals to yield the **macroscopic energy balance**:

$$\int_{S_{\text{sys}}} [U + K + gh] \mathbf{v} \cdot d\mathbf{S} - \int_{S_{\text{sys}}} [\mathbf{T} \cdot \mathbf{v}] \cdot d\mathbf{S} = - \int_{S_{\text{sys}}} \mathbf{q} \cdot d\mathbf{S} + \int_{V_{\text{sys}}} Q dV. \quad (21)$$

The first term on the left-hand side represents the net difference between the influx and efflux of internal, kinetic, and potential energy. The second term on the left-hand side represents the total rate of work done through the surfaces which bound the volume considered, including both the so-called “flow work” done at surfaces through which matter flows, and any additional work done at surfaces through which there is no flow. No term having to do with the total work done by body forces appears, because that is nothing else but the change in potential energy which is accounted for in the first term. The two terms on the right-hand side represent the heat input by conduction through the bounding surfaces, and the heat input by radiation.

So far, so good—one has only considered the balance of energy, and Eqs. (20) and (21) would hold even if we knew nothing about the Bernoulli equation. After all, the balance of energy is a fundamental law of physics which is totally independent of the momentum balance (from which the Bernoulli equation is derived). However, we do know that Bernoulli’s equation holds true, and hence we can subtract its local formulation, Eq. (15), from the local formulation of the balance of energy, to obtain (under the assumptions of steady state and incompressibility as well as a symmetric stress tensor)

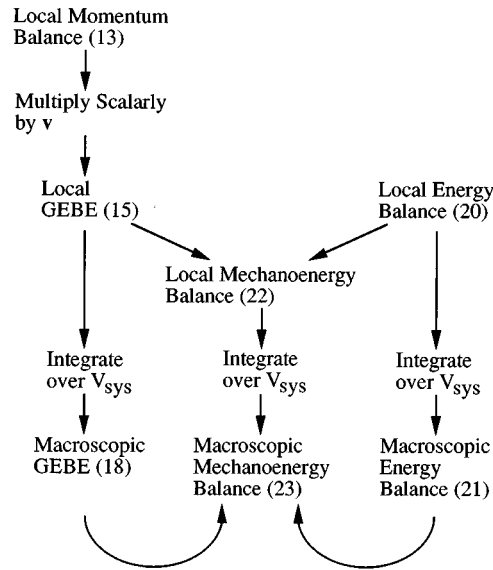
$$\rho \frac{DU}{Dt} = w + Q - \nabla \cdot \mathbf{q}. \quad (22)$$

Equation (22) may be regarded as the combined local formulation of the energy balance which we call the **local mechanoenergy balance**, since the Bernoulli equation (which is obtained from the momentum balance) has been invoked in deriving it. This equation is also called the “equation of thermal energy” by Bird *et al.* (1960, p. 314). The stress power  $w$  appears in Eq. (22), but again there is no reason to regard it as a dissipation term—dissipation is a second law concept. A simple example may clarify the issue.

Consider adiabatic stretching of a rubber network and note that internal energy is a unique function of temperature for incompressible rubber networks. Equation (22) shows that stretching the rubber network will result in an increase of internal energy, and hence in heating. Thus, the stress power  $w$  manifests itself in heating the rubber sample—it is an easy experiment to quickly stretch a piece of rubber and observe its temperature rise. While this may at first sight appear as “viscous heating,” it is far from being so. Ideal rubber networks are elastic solids, and hence no energy can be dissipated by stretching. This is confirmed by the fact that, as the piece of rubber is unstretched, it will cool down: the effect is totally reversible. Viscous heating cannot be switched to cooling by reversing the flow!

If Eq. (22) is integrated over the control volume one obtains the following combined macroscopic energy balance or **macroscopic mechanoenergy balance**:

$$\int_{S_{\text{sys}}} \rho U \mathbf{v} \cdot d\mathbf{S} + \int_{S_{\text{sys}}} \mathbf{q} \cdot d\mathbf{S} = \int_{V_{\text{sys}}} Q dV + W. \quad (23)$$



**FIG. 1.** Logical relation between the generalized engineering Bernoulli, mechanoenergy, and energy balances. Numbers in parentheses represent equations in the text.

While it may appear a bit funny that there are two macroscopic formulations of the energy balance [Eqs. (21) and (23)], which bear little if any resemblance to each other [where has the difference between the influx and the efflux of kinetic and potential energy ended up in Eq. (23)?], the fact is in reality quite simple. If one subtracts the macroscopic GEBE [Eq. (18)] from the “unadulterated” macroscopic formulation of the first law [Eq. (21)], one obtains again Eq. (23). It is of interest to note that, while Eq. (21) could perhaps be written down as a direct application of the principle of energy conservation to a macroscopic flow system, no such shortcut seems possible for Eq. (23).

This is, indeed, the root of some confusion existing in the literature. The GEBE is a purely mechanical result, but, it so happens that some terms appearing in it also appear in the energy balance, and hence the GEBE looks like some sort of energy equation. It is of course the fact that some terms appear in both the GEBE and the energy balance that makes it possible (and significant) to subtract the former from the latter. The logical status in obtaining the GEBE, energy balance and mechanoenergy balance is given in Fig. 1.

#### IV. THE SECOND LAW

So far, temperature has never appeared explicitly in any of the equations considered: in their general formulation, neither the GEBE nor the energy balance contain temperature. Of course, the local value of temperature influences, say, the stresses for any given kinematics, but as long as no constitutive equations are written down, temperature does not play any role.

In contrast with this, temperature appears explicitly in the general formulation of the second law. We choose to follow the Clausius–Duhem inequality formulation of the second law [Truesdell (1984)]. Thus, we identify a conductive entropy flux as  $\mathbf{q}/T$ , and a radiative entropy influx per unit volume  $Q/T$ . The local form of the second law now requires entropy to accumulate at least as fast as entropy is supplied to the element considered, say

$$\rho \frac{DS}{Dt} \geq \frac{Q}{T} - \nabla \cdot \left( \frac{\mathbf{q}}{T} \right) = \frac{Q - \nabla \cdot \mathbf{q}}{T} + \frac{\mathbf{q} \cdot \nabla T}{T^2}. \quad (24)$$

Consider a very simple case: steady heat conduction with no radiation. All terms in Eq. (24) go to zero except the last one, and hence one obtains

$$\mathbf{q} \cdot \nabla T \leq 0, \quad (25)$$

which mathematically states that heat cannot flow in the direction of increasing temperature during steady heat conduction. Thus one may define  $D_T$  as the local rate of “thermal dissipation,” in other words the dissipation per unit volume due to heat conduction:

$$D_T \equiv - \frac{\mathbf{q} \cdot \nabla T}{T}. \quad (26)$$

Multiplying Eq. (24) throughout by  $T$  (which is legitimate since  $T$  is positive), one obtains

$$\rho T \frac{DS}{Dt} \geq Q - \nabla \cdot \mathbf{q} + D_T. \quad (27)$$

This is the “unadulterated” **local formulation of the second law**, and it can be integrated over the system volume to obtain the unadulterated **macroscopic formulation of the second law**. Restricting attention to the isothermal case (where  $D_T = 0$ ), this produces

$$\int_{S_{\text{sys}}} \rho T S \mathbf{v} \cdot d\mathbf{S} \geq \int_{V_{\text{sys}}} Q dV - \int_{S_{\text{sys}}} \mathbf{q} \cdot d\mathbf{S}. \quad (28)$$

Equation (28) simply states that the difference between the rates of efflux and of influx of entropy cannot be less than the total rate of heat supply divided by temperature. This, while obviously true for the stated conditions, is not a very useful result. It is more useful to combine Eq. (27) with Eq. (22), so as to obtain the following combined local formulation

$$0 \geq \rho \frac{DA}{Dt} + S \frac{DT}{Dt} - w + D_T, \quad (29)$$

where  $A$  is the Helmholtz free energy ( $A \equiv U - TS$ , all thermodynamic quantities are defined on a per mass basis). This equation, by the way it is obtained, is a combined form of the second and first laws and of the Bernoulli equation. We now define a local “mechanical” rate of dissipation,  $D_M$

$$D_M \equiv w - \rho \frac{DA}{Dt} - S \frac{DT}{Dt}, \quad (30)$$

which reduces the local form of the second law to the following deceptively simple form

$$D_M + D_T \geq 0, \quad (31)$$

which we call the local combined second law expression (we resist calling this equation something like the mechanoentropy balance because the second law is not a balance, it is an inequality). What Eq. (31) implies is that, while the sum of the thermal and mechanical dissipation rates is necessarily non-negative, either one of the two individual terms could in principle be negative. However, if the constitutive equations are not strongly

coupled (say, e.g., the heat flux does not depend on the kinematics of motion), then indeed the two terms have to be individually non-negative.

Be that as it may, we now first restrict attention to spatially isothermal systems [ $D_T = 0$ ], and then also to temporally isothermal systems [ $DT/Dt = 0$ ]. With this, the local form of the second law becomes

$$w \geq \rho \frac{DA}{Dt}, \quad (32)$$

that we define as the local isothermal combined second law expression.

The above equation clearly shows that the stress power  $w$  is not, in general, equal to the local rate of dissipation. In the isothermal flow of an incompressible, Newtonian fluid, the Helmholtz free energy, by virtue of being a unique function of density and temperature, is necessarily constant, and then indeed the stress power equals the mechanical dissipation rate. But in a flowing polymer  $A$  is certainly not a unique function of density and temperature: individual macromolecules can be stretched, without any change in temperature or density, and so the conformational entropy decreases and  $A$  increases. In such a case, the stress power has to be larger than the rate of increase of free energy, and since the latter may well be negative (macromolecules coiling back), the stress power itself could be negative (as indeed it is in all instances of recoil, and very probably in die swell as well).

Indeed, since no constitutive equation has been invoked in deriving Eq. (32), it applies to all materials. In the special case of elastic solids, which are incapable of any dissipation, Eq. (32) holds as an equality: the stress power results invariably in accumulation of elastic energy—which, for isothermal systems, coincides with the Helmholtz free energy.

Equation (32) can be integrated over the whole volume of interest to obtain the following macroscopic form:

$$W \geq \int_{S_{\text{sys}}} \rho A \mathbf{v} \cdot d\mathbf{S}, \quad (33)$$

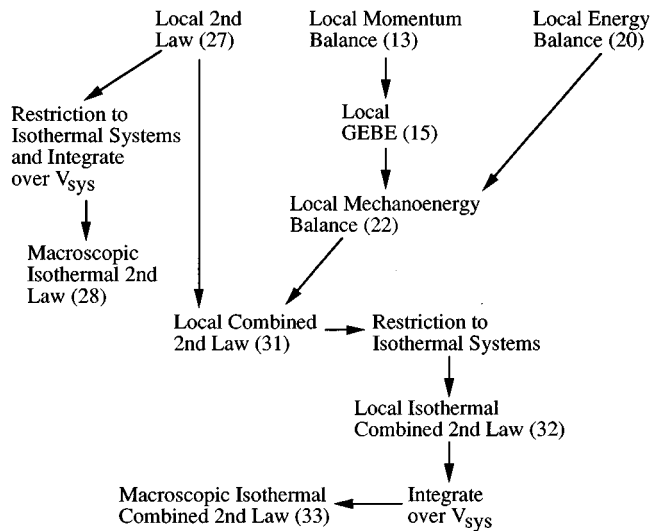
which simply states that the integral of the stress power has to exceed the difference between the efflux and the influx of free energy and may thus well be negative. This equation is referred to as the macroscopic isothermal combined second law expression.

The logical status of the different local and macroscopic formulations utilizing the second law is sketched in Fig. 2.

## V. EXAMPLE—UNSTEADY SHEARING OF A POLYMER

An example is given to demonstrate the principles discussed above. Consider the following experiments. A slab of a polymeric material between two parallel plates is subjected to a constant rate of shear by tangential motion of the upper plate. Shearing is started at time zero and stopped at time  $t^*$ . In experiment (a), no tangential force is exerted on the upper plate after time  $t^*$ ; the result will be partial recoil of the slab towards its initial shape. In experiment (b), the upper plate is held in position after time  $t^*$  and stress relaxation will occur.

This is an unsteady state process, but the kinematics of motion are the same throughout the sample at any given time during the deformation process. The total work done by the upper plate from time zero to  $t^*$  equals the integral of  $w$  over that time. The recoil observed in experiment (a) clearly shows that some elastic energy has been accumulated, since during recoil the sample is doing work on its surroundings. Thus the total work done up to  $t^*$  has not been entirely dissipated: some of it is stored in the sample at time



**FIG. 2.** Logical progression in deriving inequalities including the second law of thermodynamics. Numbers in parentheses represent equations in the text.

$t^*$  as accumulated elastic energy. In the period up to  $t^*$ , the dissipation is less than it would be in a Newtonian fluid at an equal level of stress power.

In experiment (a), at times larger than  $t^*$ ,  $w$  is in fact negative: stored elastic energy is decreasing, and hence Eq. (32) allows the possibility of a negative  $w$ . In experiment (b),  $w$  is zero at times larger than  $t^*$ , and yet the rate of dissipation is positive, since stress relaxation implies a decrease of stored elastic energy. So in this case the rate of dissipation is larger than it would be in a Newtonian fluid at the same level of stress power.

## VI. CONCLUSION

We have presented a quite general and thorough derivation of several microscopic and macroscopic balances and inequalities in order to understand the complicated flow behavior of non-Newtonian fluids. The generalized engineering Bernoulli equation or GEBE is discussed and clearly demonstrated to be independent of the first law of thermodynamics. The difference between dissipation and stress power is discussed. It is shown these two are different except for certain fluid types; one example being the ideal Newtonian fluid.

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