Bracket Formulation of Nonequilibrium Thermodynamics for Interacting Systems

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Abstract

In this work we show how to naturally modify the expressions for the total time derivatives of functionals of the field variables in complex systems, expressed originally using generalized brackets in the bracket formulation of nonequilibrium thermodynamics for non-interacting systems, in order to account for the interactions of the systems with the environment. After a short description of the problem, the approach is illustrated in a simple example involving the flow of a non-isothermal incompressible viscous fluid in a fixed domain. The resulting surface terms in the final expression can then be used to fully identify the fluxes describing the surface interactions of the system with the environment. In this way, it is shown that the generalized bracket formalism as described before, i.e. in terms of bracket equations applicable only for non-interacting (isolated) systems, is nevertheless complete. Although those original bracket equations cannot be directly used to describe the evolution equations for functionals defined for complex interacting systems, those can be derived in a straightforward fashion from the governing dynamic equations of the field variables that have themselves been derived from the original generalized bracket equations. The final equations are then automatically compatible with thermodynamics and duly comply with both the first and the second law of thermodynamics. Additional long range interactions can also be taken into account naturally though a modification of the system's Hamiltonian. This work parallels and extends to open systems involving constrained variables recent work [Öttinger, Phys. Rev. E 73:036126 (2006)] that also addresses the treatment of surface excess variables.

Introduction

During the last 20 years considerable effort has been placed in developing a systematic framework for the generation of the equations governing the dynamics of continuum media---see [1-11] and references therein. This entails the consistent extension of equilibrium thermodynamics under nonequilibrium conditions. Following the pioneering work by Truesdell and coworkers in the axiomatic foundation of continuum mechanics

[12], the new approaches emphasize more the physical content (namely, thermodynamics) and the existing interconnections between various formalisms applied at different scales of length and time, thus offering a systematic way for multiscale analysis [10-11].

The use of thermodynamics enters at different levels. First of all, equilibrium thermodynamics suggests the minimum variables for an adequate description of the continuum system: those are the ones that are required for the description of the equilibrium thermodynamic system, like the density, entropy, etc. Of course, in addition of those, one needs more variables in order to describe departures from equilibrium, at a minimum, the velocity (or, equivalently, the momentum density) and on many occasions, other variables necessary to describe the nonequilibrium structure of the system, like the conformation tensor, **c**, for polymer dynamics.

Second, thermodynamics imposes strict relations for the evolution of key extensive thermodynamic quantities, like the total energy of the system, H, (which is customarily called the Hamiltonian) and the total entropy of the system, S. Namely, the first law of thermodynamics can be written for an open system as

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \dot{Q} - \dot{W} \,, \tag{1}$$

where $\dot{Q}$ is the rate of heat transfer from the environment to the system, and $\dot{W}$ the rate of work performed by the system to the environment. On the other hand, the second law of thermodynamics can be described by the inequality

$$\dot{S} \geq 0 \,, \tag{2}$$

where $\dot{S}$ is the total rate of entropy production within the system and its environment; this automatically also implies that the local rate of entropy production also has to be a non-negative quantity. Eqs. (1-2) impose stringent conditions on the dynamics that need to be satisfied in any models.

The bracket formulation

To achieve further contributions, it is necessary to make additional assumptions regarding the structure of the dynamic equations. Various nonequilibrium thermodynamic extensions have been developed over the last twenty years. The very first one, originating from the pioneering work of Morrison [2] and Grmela [3], is based on an extension of the Poisson bracket to accommodate dissipation and irreversibility. The Poisson bracket is a mathematical quantity that it is alternatively used for the expression of conservative, Hamiltonian dynamics [7]. It is defined for both discrete and continuum systems. For example, for a particle moving within a given potential field, $V(\mathbf{x})$, the Poisson bracket $\{F,G\}$ corresponding to two arbitrary functions of the particle's position, $\mathbf{x}$, and the particle's momentum, $\mathbf{p}$, $F(\mathbf{x},\mathbf{p})$ and $G(\mathbf{x},\mathbf{p})$, is given as [7,8]

$$\{F,G\} \equiv \frac{\partial F}{\partial \mathbf{x}} \cdot \frac{\partial G}{\partial \mathbf{p}} - \frac{\partial G}{\partial \mathbf{x}} \cdot \frac{\partial F}{\partial \mathbf{p}} \,. \tag{3}$$

This definition of the Poisson bracket exhibits all its generic properties: namely that is is bilinear and antisymmetric with respect to F and G, and that is satisfies the Jacobi equality

$$\{F,\{G,H\}\}+\{G,\{H,F\}\}+\{H,\{F,G\}\}=0, \tag{4}$$

for any three arbitrary functions F, G and H. The key property of the Poisson bracket is that it can be used in an alternative formulation of the particle dynamics. This is generated by the following general equation, valid for any arbitrary function F:

$$\frac{\mathrm{d}F}{\mathrm{dt}}=\{F,H\}, \tag{5}$$

where H is the total energy, Hamiltonian, of the system, which for a particle in a potential field is simply the sum of its kinetic and potential energies:

$$H=\frac{1}{(2m)}\mathbf{p}^2+V(\mathbf{x}), \tag{6}$$

where m is the mass of the particle. Indeed, it can be easily shown that the traditional Hamiltonian equations for particle dynamics can be recovered simply by substituting into the master equation, Eq. (5) , the expression for the particle's Hamiltonian provided by Eq. (6), and by requiring that the final result is, for all functions $F=F(\mathbf{x},\mathbf{p})$, the same as that obtained by evaluating the left hand side of Eq. (5) using differentiation by parts:

$$\frac{\mathrm{d}F}{\mathrm{d}t}=\frac{\partial F}{\partial \mathbf{x}}\cdot\frac{\partial \mathbf{x}}{\partial \mathrm{t}}+\frac{\partial F}{\partial \mathbf{p}}\cdot\frac{\partial \mathbf{p}}{\partial \mathrm{t}}. \tag{7}$$

The very interesting fact is that the Poisson structure can also be extended to describe the conservative Hamiltonian dynamics of continua. This extension is accomplished simply by switching from a set of low dimensionality vectors (for example, $\mathbf{x}$, and $\mathbf{p}$ in the example above) to a set of continuum field variables (such as the mass density $\rho(\mathbf{x})$) in describing the state of the system. Correspondingly, the arbitrary functions, F, G and H are replaced by functionals of those field variables whereas the partial derivatives of the functions, entering the definition of the Poisson bracket---see Eq. (7)---are to be replaced by Volterra (or functional) derivatives [8](for functionals represented as simple integrals involving functions of unconstrained variables these are simply the partial derivatives of these functions). It is possible to show then that suitable expressions for the Poisson bracket exist (which now is expressed as a bilinear functional) so that the dynamics can still be described using the master equation, Eq. (5) and the corresponding Hamiltonian (also a functional!) of the system. Examples include the Euler equations for ideal fluids [8], the Maxwell-Vlasov equations in plasma dynamics [13] etc.

The Poisson bracket for an ideal (Euler) incompressible fluid in the absence of any interactions with the environment has first been developed by Arnold [14]---see also [8] for a history of its development and a detailed analysis:

$$
\begin{aligned}
\{F,H\} &= \int_\Omega \left[\nabla\cdot\left(\frac{\delta F}{\delta \mathbf{M}}\mathbf{M}\right)\cdot\frac{\delta H}{\delta \mathbf{M}} - \nabla\cdot\left(\frac{\delta H}{\delta \mathbf{M}}\mathbf{M}\right)\cdot\frac{\delta F}{\delta \mathbf{M}}\right] \mathrm{dV} \\
&+ \int_\Omega \left[\nabla\cdot\left(\frac{\delta F}{\delta \mathbf{M}}s\right)\frac{\delta H}{\delta s} - \nabla\cdot\left(\frac{\delta H}{\delta \mathbf{M}}s\right)\frac{\delta F}{\delta s}\right] \mathrm{dV} \\
&= \int_\Omega \mathbf{M}\cdot\left[\frac{\delta H}{\delta \mathbf{M}}\cdot\nabla\left(\frac{\delta F}{\delta \mathbf{M}}\right) - \frac{\delta F}{\delta \mathbf{M}}\cdot\nabla\left(\frac{\delta H}{\delta \mathbf{M}}\right)\right] \mathrm{dV} \\
&+ \int_\Omega s\left[\frac{\delta H}{\delta \mathbf{M}}\cdot\nabla\left(\frac{\delta F}{\delta s}\right) - \frac{\delta F}{\delta \mathbf{M}}\cdot\nabla\left(\frac{\delta H}{\delta s}\right)\right] \mathrm{dV}
\end{aligned}
\tag{8}
$$

Note that albeit both expressions above are formally equivalent for a non-interacting system (being different by a surface integral which is identically zero) it is the second one that can be shown to be consistent with Jacobi identity without the need of any leftover boundary terms [15].

The main limitation of the original Poisson bracket formalism is its restriction to conservative systems. What Kaufman [1], Morrison [2] and Grmela [3] did was to add an extra term to the Poisson bracket so that one can apply the extended equations to describe dissipative dynamics as well. Following that original work, several reformulations have been made [5,8-11]. The one that we will use here is the one generator bracket formalism [8], basically because of its inherent simplicity.

According to the single generator generalized bracket formalism, the extended master equation involves in addition to the Poisson bracket, another bracket, (written as $[F,G]$ for two arbitrary functionals F and G), called the dissipation bracket:

$$
\frac{\mathrm{d}F}{\mathrm{d}t} = \{F,H\} + [F,H], \tag{9}
$$

where H is again the Hamiltonian. The dissipation bracket is also a functional of F and H , but, with different properties. It is linear only with respect to the first argument (F) but, in general, non-linear in the second (H). Moreover, its linearization with respect to H exhibits upon exchange of F and H the same symmetry/anti-symmetry as shown by the corresponding field variables in terms of their dependence on time (this follows the Onsager/Casimir relations based on the concept of microscopic reversibility and represents the consequence of incorporating linear irreversible thermodynamics as a subcase of the much more general generalized bracket formalism [8]). Finally, in order to preserve the first and second laws of thermodynamics, Eqs. (1) and (2), the dissipation bracket for a non-interacting with the environment system is required to have the following properties:

$$
[H,H] = 0; \quad [S,H] \geq 0. \tag{10}
$$

The dissipation bracket corresponding to an incompressible viscous (Newtonian) homogeneous and isotropic fluid can be shown to be [8]:

$$
\begin{aligned}
[F,H] = &-\int_\Omega \frac{\mu}{2}\left[\nabla\left(\frac{\delta F}{\delta \mathbf{M}}\right)+\left(\nabla\left(\frac{\delta F}{\delta \mathbf{M}}\right)\right)^T\right]:\left[\nabla\left(\frac{\delta H}{\delta \mathbf{M}}\right)+\left(\nabla\left(\frac{\delta H}{\delta \mathbf{M}}\right)\right)^T\right]\mathrm{dV} \\
&-\int_\Omega \frac{k}{T}\left[\nabla\left(\frac{\delta F}{\delta s}\right)\right]\cdot\left[\nabla\left(\frac{\delta H}{\delta s}\right)\right]\mathrm{dV} \\
&+\int_\Omega \frac{1}{T}\frac{\delta F}{\delta s}\left[\begin{array}{l}\dfrac{\mu}{2}\left[\nabla\left(\dfrac{\delta H}{\delta \mathbf{M}}\right)+\left(\nabla\left(\dfrac{\delta H}{\delta \mathbf{M}}\right)\right)^T\right]:\left[\nabla\left(\dfrac{\delta H}{\delta \mathbf{M}}\right)+\left(\nabla\left(\dfrac{\delta H}{\delta \mathbf{M}}\right)\right)^T\right] \\ +\dfrac{k}{T}\left[\nabla\left(\dfrac{\delta H}{\delta s}\right)\right]\cdot\left[\nabla\left(\dfrac{\delta H}{\delta s}\right)\right]\end{array}\right]\mathrm{dV}
\end{aligned}
\qquad ,(11)
$$

where μ and k are the system's Newtonian shear viscosity and thermal conductivity, respectively.

The major usefulness in practical applications of the generalized Poisson bracket formalism has been so far its usage as a guidance for the development of thermodynamically consistent models for the governing equations of the dynamics of complex systems [8,16]. To perform that role, after the selection of the proper expressions for the Poisson and dissipation brackets, (and in parallel to the procedure illustrated for the particle dynamics example above) one simply compares the result of the application of the generalized master equation, Eq. (9) above, to that obtained after a direct time differentiation of the functional expression. For that purpose, one uses the standard expressions for the bracket and dissipation functionals, defined for non-interacting systems [8,16].

The evolution equations for functionals

However, recently new applications have emerged where a more direct usage of the generalized bracket equations as the governing equations for arbitrary functionals is shown [17]. For that to be possible, more general expressions for the governing equations are necessary to be used, also applicable for interacting systems. It is the purpose of this work to show how these expressions can be systematically derived. We do that in an illustrative example albeit the approach used here can also apply to more general settings in a similar fashion.

The general idea is simple. The main advantage of the original expressions proposed for the brackets is their symmetry, made possible through the use of integration by parts, allowed (in the sense of not giving rise of any additional surface contributions) given the constraint of no interactions of the system with the environment. This results in an evaluation (by comparison to the direct differentiation result) of the field dynamics [8,16]. In the general case, in the presence of interactions, it is the field dynamics (but not necessarily the symmetries of the bracket equations) that it is preserved. Therefore, the starting point for the master equation for the dynamics of an arbitrary functional needs to be the expression that one gets upon substitution of the field dynamics in the general

dynamic equation that one gets upon straightforward time differentiation of the functional expression. This is illustrated in a simple but comprehensive example below.

To illustrate how to adapt the generalized bracket formalism to accommodate the system's interactions with the environment we examine here a simple example application, the flow of a homogeneous viscous Newtonian incompressible fluid in a fixed domain, of volume Ω and surface boundary $\partial\Omega$. Both temperature and velocity effects are taken into account, as well as those of an external, constant, gravitational field, $\mathbf{g}$, but no other non-local effects are taken into account---for a more general, compressible case, please see the Appendix. The starting point are the governing equations for the two nontrivial field variables needed to describe the state of that system (the other trivial one is the mass density, ρ, which for an incompressible system is constant) namely the velocity $\mathbf{v}$ (or, equivalently, momentum density, $\mathbf{M} = \rho\mathbf{v}$) and the entropy density s. The corresponding Hamiltonian is

$$H = \int_{\Omega} \left(\frac{M^2}{2\rho} - \rho \mathbf{g} \cdot \mathbf{R} + e(s) \right) \mathrm{dV} , \tag{12}$$

i.e., the sum of kinetic, potential (gravitational here) and internal energies, where **g** is the gravitational acceleration, **R** the position vector and $e(s)$ the internal energy density which for an ideal incompressible fluid is only a function of the entropy density, *s*.

Following the standard practices (i.e, developing the functional evolution equation using the Poisson and dissipation brackets indicated by Eqs. (8) and (11) above, respectively and equating the result against the straightforward answer obtained through the chain rule of differentiation, as outlined in [8]) the following governing equations are obtained

$$\frac{\partial \mathbf{M}}{\partial t} = \rho \frac{\partial \mathbf{v}}{\partial t} = \Pi\left(-\rho \mathbf{v} \cdot \nabla \mathbf{v} + \mu \Delta \mathbf{v} \right) = \Pi\left(\nabla \cdot \left(-\rho \mathbf{v}\mathbf{v} + \mu \mathbf{A} \right) \right), \tag{13}$$

where $\mathbf{A}$ is the rate of strain tensor

$$\mathbf{A} = \nabla \mathbf{v} + \nabla \mathbf{v}^T , \tag{14}$$

and

$$\frac{\mathrm{d}s}{\mathrm{d}t} = -\mathbf{v} \cdot \nabla s + \frac{\mu}{2T} \mathbf{A} : \mathbf{A} + \frac{1}{T} \nabla \cdot (k \nabla T) , \tag{15}$$

where by $\Pi(\mathbf{w})$ we denote the projection operator of any vector field $\mathbf{w}$ to a divergence-free field, defined in terms of a scalar field *r* (which coincides with the effective pressure $p_{eff} \equiv p - \rho \mathbf{g} \cdot \mathbf{R}$, where *p* is the hydrodynamic pressure, as far as its application to Eq. (13) is concerned when the appropriate boundary conditions are used for *r*) as

$$\Pi(\mathbf{w}) \equiv \mathbf{w} - \nabla r ; \quad \Delta r = \nabla \cdot \mathbf{w} ; \quad \mathbf{n} \cdot (\mathbf{w} - \nabla r) \text{ or } r \text{ specified on } \partial\Omega , \tag{16}$$

and $T \equiv \dfrac{\delta H}{\delta s}$ is the system's equilibrium temperature.

In this case, the bracket formalism simply confirms these standard equations in transport processes [18] for the particular case of fixed boundaries with fixed zero velocity

boundary conditions, in which case the appropriate boundary conditions for the scalar pressure are

$$\mathbf{n}\cdot\Pi(-\rho\mathbf{v}\cdot\nabla\mathbf{v}+\mu\Delta\mathbf{v})\equiv\mathbf{n}\cdot\left(-\rho\mathbf{v}\cdot\nabla\mathbf{v}+\mu\Delta\mathbf{v}+\rho\mathbf{g}-\nabla p\right)=\mathbf{n}\cdot\frac{\partial\mathbf{M}}{\partial t}=0 \text{ on } \partial\Omega\,. \qquad (17)$$

When we allow for general momentum boundary conditions at the boundary, the same equations apply with the only difference that now in the boundary conditions for the pressure one has to suitably modify the normal pressure gradient boundary value to reflect the local value of $\mathbf{n}\cdot\frac{\partial\mathbf{M}}{\partial t}\equiv\frac{\partial M_n}{\partial t}$ which can now be, in general, different from zero.

Formally, for a general functional $F\equiv\int_\Omega f(\mathbf{M},\nabla\mathbf{M},\nabla\nabla\mathbf{M},...,s,\nabla s,\nabla\nabla s,...)\mathrm{dV}$, the following general governing evolution equation is obtained for an Eulerian (stationary control volume Ω) frame of reference:

$$\left(\frac{\mathrm{d}F}{\mathrm{d}t}\right)_{Eulerian}=\int_\Omega\left(\begin{array}{l}\left(\frac{\partial f}{\partial\mathbf{M}}\cdot\frac{\partial\mathbf{M}}{\partial t}+\frac{\partial f}{\partial\nabla\mathbf{M}}:\frac{\partial\nabla\mathbf{M}}{\partial t}+\frac{\partial f}{\partial\nabla\nabla\mathbf{M}}:\frac{\partial\nabla\nabla\mathbf{M}}{\partial t}+...\right)+\\ \left(\frac{\partial f}{\partial s}\frac{\partial s}{\partial t}+\frac{\partial f}{\partial\nabla s}\cdot\frac{\partial\nabla s}{\partial t}+\frac{\partial f}{\partial\nabla\nabla s}:\frac{\partial\nabla\nabla s}{\partial t}+...\right)\end{array}\right)\mathrm{dV}\,. \qquad (18)$$

The above expression can be recast into a volume and surface integral, through a straight forward integration by parts and application of the Gauss (divergence) theorem, leading to the following result

$$\left(\frac{\mathrm{d}F}{\mathrm{d}t}\right)_{Eulerian}=\int_\Omega\left(\begin{array}{l}\left(\frac{\partial f}{\partial\mathbf{M}}-\nabla\cdot\frac{\partial f}{\partial(\nabla\mathbf{M})}+\nabla\nabla:\frac{\partial f}{\partial(\nabla\nabla\mathbf{M})}-...\right)\cdot\frac{\partial\mathbf{M}}{\partial t}+\\ \left(\frac{\partial f}{\partial s}-\nabla\cdot\frac{\partial f}{\partial(\nabla s)}+\nabla\nabla:\frac{\partial f}{\partial(\nabla\nabla s)}-...\right)\frac{\partial s}{\partial t}\end{array}\right)\mathrm{dV}+$$

$$\int_{\partial\Omega}\mathbf{n}\cdot\left(\begin{array}{l}\left(\left(\frac{\partial f}{\partial\nabla\mathbf{M}}-\nabla\cdot\frac{\partial f}{\partial(\nabla\nabla\mathbf{M})}+...\right)\cdot\frac{\partial\mathbf{M}}{\partial t}+\left(\frac{\partial f}{\partial\nabla\nabla\mathbf{M}}-...\right):\frac{\partial\nabla\mathbf{M}}{\partial t}+...\right)+\\ \left(\left(\frac{\partial f}{\partial\nabla s}-\nabla\cdot\frac{\partial f}{\partial(\nabla\nabla s)}+...\right)\cdot\frac{\partial s}{\partial t}+\left(\frac{\partial f}{\partial\nabla\nabla s}-...\right):\frac{\partial\nabla s}{\partial t}+...\right)\end{array}\right)\mathrm{dA}$$

. (19)

It is useful to recast Eq. (19) in a form that also takes into account the allowed variable variability, namely the divergence-free condition for the momentum. In that case, we need to analyze all volume terms weighting $\partial\mathbf{M}/\partial t$ in the above expression. Then, in terms of a "formal pressure", p_f and a divergence-free projection, both characteristic to the functional density *f*

$$\frac{\partial f}{\partial \mathbf{M}} - \nabla \cdot \frac{\partial f}{\partial (\nabla \mathbf{M})} + \nabla\nabla : \frac{\partial f}{\partial (\nabla\nabla \mathbf{M})} - \ldots = \Pi \left(\frac{\partial f}{\partial \mathbf{M}} - \nabla \cdot \frac{\partial f}{\partial (\nabla \mathbf{M})} + \nabla\nabla : \frac{\partial f}{\partial (\nabla\nabla \mathbf{M})} - \ldots \right) + \nabla p_f$$

,(20)

we arrive formally to the following expression:

$$\left(\frac{\mathrm{d}F}{\mathrm{d}t} \right)_{Eulerian} = \int_\Omega \left(\begin{array}{l} \Pi \left(\frac{\partial f}{\partial \mathbf{M}} - \nabla \cdot \frac{\partial f}{\partial (\nabla \mathbf{M})} + \nabla\nabla : \frac{\partial f}{\partial (\nabla\nabla \mathbf{M})} - \ldots \right) \cdot \frac{\partial \mathbf{M}}{\partial t} + \\ \left(\frac{\partial f}{\partial s} - \nabla \cdot \frac{\partial f}{\partial (\nabla s)} + \nabla\nabla : \frac{\partial f}{\partial (\nabla\nabla s)} - \ldots \right) \frac{\partial s}{\partial t} \end{array} \right) \mathrm{dV} +$$

$$\int_{\partial\Omega} \mathbf{n} \cdot \left(\begin{array}{l} \left(\left(p_f \mathbf{I} + \frac{\partial f}{\partial \nabla \mathbf{M}} - \nabla \cdot \frac{\partial f}{\partial (\nabla\nabla \mathbf{M})} + \ldots \right) \cdot \frac{\partial \mathbf{M}}{\partial t} + \left(\frac{\partial f}{\partial \nabla\nabla \mathbf{M}} - \ldots \right) : \frac{\partial \nabla \mathbf{M}}{\partial t} + \ldots \right) + \\ \left(\left(\frac{\partial f}{\partial \nabla s} - \nabla \cdot \frac{\partial f}{\partial (\nabla\nabla s)} + \ldots \right) \cdot \frac{\partial s}{\partial t} + \left(\frac{\partial f}{\partial \nabla\nabla s} - \ldots \right) : \frac{\partial \nabla s}{\partial t} + \ldots \right) \end{array} \right) \mathrm{dA}$$

, (21)

where now we can consistently identify the bulk (volume) contributions with the standard expressions using the functional (Volterra) derivatives:

$$\left(\frac{\mathrm{d}F}{\mathrm{d}t} \right)_{Eulerian} = \int_\Omega \left(\frac{\delta F}{\delta \mathbf{M}} \cdot \frac{\partial \mathbf{M}}{\partial t} + \frac{\delta F}{\delta s} \frac{\partial s}{\partial t} \right) \mathrm{dV} +$$

$$\int_{\partial\Omega} \mathbf{n} \cdot \left(\begin{array}{l} \left(\left(p_f \mathbf{I} + \frac{\partial f}{\partial \nabla \mathbf{M}} - \nabla \cdot \frac{\partial f}{\partial (\nabla\nabla \mathbf{M})} + \ldots \right) \cdot \frac{\partial \mathbf{M}}{\partial t} + \left(\frac{\partial f}{\partial \nabla\nabla \mathbf{M}} - \ldots \right) : \frac{\partial \nabla \mathbf{M}}{\partial t} + \ldots \right) + \\ \left(\left(\frac{\partial f}{\partial \nabla s} - \nabla \cdot \frac{\partial f}{\partial (\nabla\nabla s)} + \ldots \right) \cdot \frac{\partial s}{\partial t} + \left(\frac{\partial f}{\partial \nabla\nabla s} - \ldots \right) : \frac{\partial \nabla s}{\partial t} + \ldots \right) \end{array} \right) \mathrm{dA}$$

. (22)

This last expression can also be written in a more concise form as

$$\left(\frac{\mathrm{d}F}{\mathrm{d}t} \right)_{Eulerian} = \int_\Omega \left(\frac{\delta F}{\delta \mathbf{M}} \cdot \frac{\partial \mathbf{M}}{\partial t} + \frac{\delta F}{\delta s} \frac{\partial s}{\partial t} \right) \mathrm{dV} +$$

$$\int_{\partial\Omega} \mathbf{n} \cdot \left(\begin{array}{l} \left(\frac{\delta F}{\delta \nabla \mathbf{M}} \cdot \frac{\partial \mathbf{M}}{\partial t} + \frac{\delta F}{\delta \nabla\nabla \mathbf{M}} : \frac{\partial \nabla \mathbf{M}}{\partial t} + \ldots \right) + \\ \left(\frac{\delta F}{\delta \nabla s} \cdot \frac{\partial s}{\partial t} + \frac{\delta F}{\delta \nabla\nabla s} : \frac{\partial \nabla s}{\partial t} + \ldots \right) \end{array} \right) \mathrm{dA} \quad . \qquad (23)$$

Where the following definitions apply:

$$\left(\begin{array}{l} \dfrac{\delta F}{\delta \mathbf{M}} \equiv \Pi\left(\dfrac{\partial f}{\partial \mathbf{M}} - \nabla \cdot \dfrac{\partial f}{\partial (\nabla \mathbf{M})} + \nabla\nabla : \dfrac{\partial f}{\partial (\nabla\nabla \mathbf{M})} - \ldots \right) \\ \dfrac{\delta F}{\delta s} \equiv \left(\dfrac{\partial f}{\partial s} - \nabla \cdot \dfrac{\partial f}{\partial (\nabla s)} + \nabla\nabla : \dfrac{\partial f}{\partial (\nabla\nabla s)} - \ldots \right) \\ \dfrac{\delta F}{\delta \nabla \mathbf{M}} \equiv \left(p_f \mathbf{I} + \dfrac{\partial f}{\partial \nabla \mathbf{M}} - \nabla \cdot \dfrac{\partial f}{\partial (\nabla\nabla \mathbf{M})} + \ldots \right) \\ \dfrac{\delta F}{\delta \nabla\nabla \mathbf{M}} \equiv \left(\dfrac{\partial f}{\partial \nabla\nabla \mathbf{M}} - \nabla \cdot \dfrac{\partial f}{\partial (\nabla\nabla\nabla \mathbf{M})} + \ldots \right) \\ \ldots \\ \dfrac{\delta F}{\delta \nabla s} \equiv \left(\dfrac{\partial f}{\partial \nabla s} - \nabla \cdot \dfrac{\partial f}{\partial (\nabla\nabla s)} + \ldots \right) \\ \dfrac{\delta F}{\delta \nabla\nabla s} \equiv \left(\dfrac{\partial f}{\partial \nabla\nabla s} - \nabla \cdot \dfrac{\partial f}{\partial (\nabla\nabla\nabla s)} + \ldots \right) \\ \ldots \end{array} \right). \qquad (24)$$

Now, the governing equations, Eqs. (13) and (15) need to be used in replacing the time derivatives for the corresponding field variables within the volume integral in Eq. (24). When this happens and use of the Gauss theorem is made to replace all volume integral contributions containing complete divergence terms with the corresponding surface integral terms, one obtains the following form:

$$\left(\frac{\mathrm{d}F}{\mathrm{d}t}\right)_{Eulerian} = \int_\Omega \left(\begin{array}{l} \frac{\delta F}{\delta \mathbf{M}} \cdot \left(\nabla \cdot \left(\boldsymbol{\pi}_e \right) + \rho \mathbf{g} \right) + \\ \frac{\delta F}{\delta s} \left(-\nabla \cdot \left(s\mathbf{v} \right) + \frac{\mu}{2T} \mathbf{A} : \mathbf{A} + \frac{\left(\kappa - \frac{2}{3}\mu \right)}{T} \left(\nabla \cdot \mathbf{v} \right)^2 + \frac{1}{T} \nabla \cdot (k \nabla T) \right) \end{array} \right) \mathrm{dV} +$$

$$\int_{\partial\Omega} \mathbf{n} \cdot \left(\begin{array}{l} \left(\frac{\delta F}{\delta \nabla \mathbf{M}} \cdot \frac{\partial \mathbf{M}}{\partial t} + \frac{\delta F}{\delta \nabla \nabla \mathbf{M}} : \frac{\partial \nabla \mathbf{M}}{\partial t} + \ldots \right) + \\ \left(\frac{\delta F}{\delta \nabla s} \cdot \frac{\partial s}{\partial t} + \frac{\delta F}{\delta \nabla \nabla s} : \frac{\partial \nabla s}{\partial t} + \ldots \right) \end{array} \right) \mathrm{dA}$$

$$= \int_\Omega \left[\left(-\boldsymbol{\pi}_e \right) : \nabla \frac{\delta F}{\delta \mathbf{M}} + \left(\frac{\mathbf{q}_e}{T} \right) \cdot \nabla \frac{\delta F}{\delta s} + \frac{\delta F}{\delta \mathbf{M}} \cdot \left(\rho \mathbf{g} \right) + \frac{1}{T} \left(\frac{\mu}{2} \mathbf{A} : \mathbf{A} + \frac{k}{T} \nabla T \cdot \nabla T \right) \frac{\delta F}{\delta s} \right] \mathrm{dV} +$$

$$\int_{\partial\Omega} \mathbf{n} \cdot \left[\boldsymbol{\pi}_e \cdot \frac{\delta F}{\delta \mathbf{M}} + \left(-\frac{\mathbf{q}_e}{T} \right) \frac{\delta F}{\delta s} \right] \mathrm{dA} +$$

$$\int_{\partial\Omega} \mathbf{n} \cdot \left(\begin{array}{l} \left(\frac{\delta F}{\delta \nabla \mathbf{M}} \cdot \frac{\partial \mathbf{M}}{\partial t} + \frac{\delta F}{\delta \nabla \nabla \mathbf{M}} : \frac{\partial \nabla \mathbf{M}}{\partial t} + \ldots \right) + \\ \left(\frac{\delta F}{\delta \nabla s} \cdot \frac{\partial s}{\partial t} + \frac{\delta F}{\delta \nabla \nabla s} : \frac{\partial \nabla s}{\partial t} + \ldots \right) \end{array} \right) \mathrm{dA}$$

, (25)

where $\boldsymbol{\pi}_e$ represents the effective stress tensor, defined for an incompressible Newtonian fluid as

$$\boldsymbol{\pi}_e \equiv -\rho \mathbf{v}\mathbf{v} - p\mathbf{I} + \mu \mathbf{A} \,, \tag{26}$$

$\mathbf{I}$ is the unit tensor, and $\mathbf{q}_e$ is the effective heat flux for which a Fourier law is assumed to be applicable:

$$\mathbf{q}_e \equiv Ts\mathbf{v} - k\nabla T \,. \tag{27}$$

Comparing Eq. (25) against the Poisson and dissipative bracket contributions postulated for a non-interacting system, Eqs. (8) and (11), respectively, we can make the following important observations. First, one sees that the bulk terms correspond to the full Poisson bracket as given by the second one of the two expressions provided in Eq. (8), except for the pressure term that requires use of the Gauss theorem to transfer its contribution from the surface to the bulk. However, notice that in addition to those bulk terms we also have very specific surface contributions that are needed in order for the Poisson bracket to be applicable for interacting systems. Similarly, regarding the dissipation bracket contributions, one sees that in addition to the bulk terms appearing in the original bracket provided in Eq. (11), there are now also corresponding surface terms hidden within the first one of the two surface integrals appearing in the right hand side of Eq. (25). In fact, in the first integral we have all the new terms that now we explicitly need to include for interacting systems in order to restore their consistency to the bulk equations even for the simplest functionals. Moreover, there are additional surface terms, represented by the second surface integral in Eq. (25), which contribute only when there are "formal

pressure" and/or gradient contributions to the functional F, in addition to time variations for the boundary values of the system variables, **M**, s. Those terms also provide naturally hints for proper additional boundary conditions should the functionals depend on their corresponding gradient terms. Of course, for a non-interacting system, all surface terms are identically zero and the expression for the time derivative of the functional F provided by Eq. (25) reduces to the previous one established for a non-interacting system.

For the general case, the boundary normal momentum flux has a locally non-zero time derivative; however we still have (from macroscopic continuity) the restriction that

$$\int_{\partial\Omega} \mathbf{n} \cdot \frac{\partial \mathbf{M}}{\partial t} \mathrm{d\,A} \equiv \int_{\partial\Omega} \frac{\partial M_n}{\partial t} \mathrm{d\,A} = 0 . \tag{28}$$

Therefore, in general, the surface integral in Eq. (22)may give a nonzero correction even for functionals for which there is no dependence on gradients, unless the corresponding value of the correcting "formal pressure" field p_f is specified to be constant at the open flow boundary. In fact, it is in this way that one can show what this value has to be to regain consistency between the abstract (i.e. in terms of the Volterra derivatives) and analytical (i.e. in terms of the partial derivatives) expressions for the time derivative of the functional $\frac{dF}{dt}$. By continuity, we propose that this constant boundary value condition is the appropriate one to use in order to remove the indeterminacy even when the time derivative of the normal momentum surface flux is everywhere zero. Thus, we fully defined the corresponding projection operator (with the only remaining trivial indeterminacy, that of the constant p_f surface value, paralleling that of the pressure in an incompressible flow field).

Another expression that directly follows from Eq. (25) is the one obtained through the application of Reynolds theorem [18] for the Lagrangian time derivative of the functional defined on a, generally variable, material volume

$$\begin{aligned}
\left(\frac{\mathrm{d}F}{\mathrm{d}t}\right)_{Lagrangian} &= \left(\frac{\mathrm{d}F}{\mathrm{d}t}\right)_{Eulerian} + \int_{\partial\Omega} \mathbf{n} \cdot [\mathbf{v}f]\, \mathrm{dA} \\
&= \int_{\Omega} \left[(-\boldsymbol{\pi}_e) : \nabla \frac{\delta F}{\delta \mathbf{M}} + \left(\frac{\mathbf{q}_e}{T}\right) \cdot \nabla \frac{\delta F}{\delta s} + \frac{\delta F}{\delta \mathbf{M}} \cdot (\rho \mathbf{g}) + \frac{1}{T}\left(\frac{\mu}{2}\mathbf{A} : \mathbf{A} + \frac{k}{T}\nabla T \cdot \nabla T\right)\frac{\delta F}{\delta s} \right] \mathrm{dV} + \\
&\int_{\partial\Omega} \mathbf{n} \cdot \left[\mathbf{v}f + \boldsymbol{\pi}_e \cdot \frac{\delta F}{\delta \mathbf{M}} + \left(-\frac{\mathbf{q}_e}{T}\right)\frac{\delta F}{\delta s} \right] \mathrm{dA} + \\
&\int_{\partial\Omega} \mathbf{n} \cdot \left(\begin{array}{l} \left(\frac{\delta F}{\delta \nabla \mathbf{M}} \cdot \frac{\partial \mathbf{M}}{\partial t} + \frac{\delta F}{\delta \nabla\nabla \mathbf{M}} : \frac{\partial \nabla \mathbf{M}}{\partial t} + \ldots \right) + \\ \left(\frac{\delta F}{\delta \nabla s} \cdot \frac{\partial s}{\partial t} + \frac{\delta F}{\delta \nabla\nabla s} : \frac{\partial \nabla s}{\partial t} + \ldots \right) \end{array} \right) \mathrm{dA}
\end{aligned}$$

, (29)

Eq. (29) has an aesthetically pleasing form involving clear contributions to the time changes of a functional from both bulk and surface terms. Those can be easily shown to be fully compatible will all standard macroscopic equations for a fully interacting system which can be easily derived from it through appropriate selections of the functional F corresponding to a homogeneous system and at zero velocity field (no gradients). For example, when $F = H$, we get the first law of thermodynamics for a closed but interacting with the environment system, with the only bulk terms surviving that corresponding to the action of the gravity and the two surface terms corresponding clearly to the rate of surface work and the heat flux, respectively:

$$\left(\frac{\mathrm{dH}}{\mathrm{d}t}\right)_{Lagrangian} = \int_{\Omega}\left[\mathbf{v}\cdot\left(\rho\mathbf{g}\right)\right]\mathrm{dV} + \int_{\partial\Omega}\mathbf{n}\cdot\left[\boldsymbol{\pi}_e\cdot\mathbf{v} + \left(-\mathbf{q}_e\right)\right]\mathrm{dA} \quad . \tag{30}$$

Similarly, when we take $F = \int_{\Omega} M_i \mathrm{dV}$, and at the end we combine the information from all components, i=1,3, we can get the expression of Newton's second law of motion for a closed but interacting with the environment system, with the only bulk term surviving that corresponding to the action of the gravity and two surface terms corresponding to the action of surface forces at the flow boundary by the pressure and viscous stress, respectively:

$$\begin{aligned}\left(\frac{\mathrm{d}\left(\int_{\Omega}\rho\mathbf{v}\mathrm{dV}\right)}{\mathrm{d}t}\right)_{Lagrangian} &= \int_{\Omega}\left[\left(\rho\mathbf{g}\right)\right]\mathrm{dV} + \int_{\partial\Omega}\mathbf{n}\cdot\left[\boldsymbol{\pi}_e + \rho\mathbf{v}\mathbf{v}\right]\mathrm{dA} \\ &= \int_{\Omega}\left[\left(\rho\mathbf{g}\right)\right]\mathrm{dV} + \int_{\partial\Omega}\mathbf{n}\cdot\left[\left(-p\mathbf{I} + \mu\mathbf{A}\right)\right]\mathrm{dA}\end{aligned} \quad . \tag{31}$$

Finally, in the case when $F = S$, we can easily see the non-negative coefficient multiplying the last term in Eq. (25), $\delta F / \delta S$, to be only bulk term surviving providing us the local rate of entropy production, consistent therefore with the second law of thermodynamics. This term together with a surface integral accounting for the contribution of the entropy from the heat received from the boundary:

$$\begin{aligned}\left(\frac{\mathrm{dS}}{\mathrm{d}t}\right)_{Lagrangian} &= \int_{\Omega}\left[\frac{1}{T}\left(\frac{\mu}{2}\mathbf{A}:\mathbf{A} + \frac{k}{T}\nabla T\cdot\nabla T\right)\right]\mathrm{dV} + \int_{\partial\Omega}\mathbf{n}\cdot\left[\mathbf{v}s + \left(-\frac{\mathbf{q}_e}{T}\right)\right]\mathrm{dA} \\ &= \int_{\Omega}\left[\frac{1}{T}\left(\frac{\mu}{2}\mathbf{A}:\mathbf{A} + \frac{k}{T}\nabla T\cdot\nabla T\right)\right]\mathrm{dV} + \int_{\partial\Omega}\mathbf{n}\cdot\left[\left(\frac{k\nabla T}{T}\right)\right]\mathrm{dA}\end{aligned} \quad . \tag{32}$$

In fact, this consistency automatically arises when the governing field equations are obtained using the generalized bracket approach, thus demonstrating its usefulness, and completeness, in the description of the dynamics (and its interactions with the environment) for complex systems with internal microstructures. This analysis therefore nicely complements the extensive analyses for non-interacting systems, as is to be found in [8] and [11] as well as the very recent analysis for open systems [15] where the presence of surface excess variables is also taken into account. In fact, in relation to

those systems (i.e. with surface excess variables), suffice to say that the present work fully elucidates and identifies the mixed terms surface integrals appearing in the brackets in these cases with the first surface integrals, coupling the Volterra derivatives with the corresponding boundary fluxes, appearing in the right hand side of Eq. (25).

Conclusions

We have shown that the information content within the governing equations for the field variables, like equations (13) and (15) for this example, are complete, i.e., contain all necessary information to construct the corresponding evolution equations for any arbitrary functional of the field variables, interacting or non interacting with the environment. When we have a non-interacting system, those equations are exactly equivalent to the original bracket equations. When there are however interactions, the bracket equations are considerably different as specific flux terms need also to be taken into account in surface integral expressions in addition to bulk integral contributions. The surface integral terms allow for the proper interpretation of more complex bracket expressions existing, for example, in the case where surface excess variables are present.

Correct usage of the full interacting system functional evolution equation also requires the proper definition of the Volterra derivatives, which need special care when constraints are to be taken into account, as for example is the case in the presence of the incompressibility assumption. Special care needs also to be exercised whenever the functional depends explicitly on gradients of the variables. Finally, for suitable choices for the functional, the corresponding functional evolution equations can directly provide us with all the thermodynamic and mechanical information for the system, including the first law of thermodynamics for open systems (when $F = H$) while the selection $F = S$ duly confirms consistency with the second law.

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APPENDIX

Compressible Flow of a Newtonian viscous fluid with non-local interactions.

The Poisson bracket for an ideal (Euler) compressible fluid in the absence of any interactions with the environment is given, similar to the expression for an incompressible fluid, Eq. (8), as:

$$\begin{aligned}\{F,H\} = &\int_\Omega \rho\left[\frac{\delta H}{\delta \mathbf{M}}\cdot\nabla\left(\frac{\delta F}{\delta \rho}\right)-\frac{\delta F}{\delta \mathbf{M}}\cdot\nabla\left(\frac{\delta H}{\delta \rho}\right)\right]\mathrm{dV}\\ &+\int_\Omega \mathbf{M}\cdot\left[\frac{\delta H}{\delta \mathbf{M}}\cdot\nabla\left(\frac{\delta F}{\delta \mathbf{M}}\right)-\frac{\delta F}{\delta \mathbf{M}}\cdot\nabla\left(\frac{\delta H}{\delta \mathbf{M}}\right)\right]\mathrm{dV}\\ &+\int_\Omega s\left[\frac{\delta H}{\delta \mathbf{M}}\cdot\nabla\left(\frac{\delta F}{\delta s}\right)-\frac{\delta F}{\delta \mathbf{M}}\cdot\nabla\left(\frac{\delta H}{\delta s}\right)\right]\mathrm{dV}\end{aligned}. \tag{33}$$

Similarly, the dissipation bracket for a viscous compressible fluid is provided through a generalization of the expression for an incompressible one, given by Eq. (11), as:

$$\begin{aligned}[F,H] = &-\int_\Omega \frac{\mu}{2}\left[\nabla\left(\frac{\delta F}{\delta \mathbf{M}}\right)+\left(\nabla\left(\frac{\delta F}{\delta \mathbf{M}}\right)\right)^T\right]:\left[\nabla\left(\frac{\delta H}{\delta \mathbf{M}}\right)+\left(\nabla\left(\frac{\delta H}{\delta \mathbf{M}}\right)\right)^T\right]\mathrm{dV}\\ &-\int_\Omega \left(\kappa-\tfrac{2}{3}\mu\right)\left[\nabla\cdot\left(\frac{\delta F}{\delta \mathbf{M}}\right)\right]:\left[\nabla\cdot\left(\frac{\delta H}{\delta \mathbf{M}}\right)\right]\mathrm{dV}\\ &-\int_\Omega \frac{k}{T}\left[\nabla\left(\frac{\delta F}{\delta s}\right)\right]\cdot\left[\nabla\left(\frac{\delta H}{\delta s}\right)\right]\mathrm{dV}\\ &+\int_\Omega \frac{1}{T}\frac{\delta F}{\delta s}\left[\begin{array}{l}\frac{\mu}{2}\left[\nabla\left(\frac{\delta H}{\delta \mathbf{M}}\right)+\left(\nabla\left(\frac{\delta H}{\delta \mathbf{M}}\right)\right)^T\right]:\left[\nabla\left(\frac{\delta H}{\delta \mathbf{M}}\right)+\left(\nabla\left(\frac{\delta H}{\delta \mathbf{M}}\right)\right)^T\right]\\ +\left(\kappa-\tfrac{2}{3}\mu\right)\left[\nabla\cdot\left(\frac{\delta H}{\delta \mathbf{M}}\right)\right]:\left[\nabla\cdot\left(\frac{\delta H}{\delta \mathbf{M}}\right)\right]\\ +\frac{k}{T}\left[\nabla\left(\frac{\delta H}{\delta s}\right)\right]\cdot\left[\nabla\left(\frac{\delta H}{\delta s}\right)\right]\end{array}\right]\mathrm{dV}\end{aligned}, \tag{34}$$

where κ is the system's Newtonian bulk (or dilatational) viscosity [18]. Finally, the expression for the Hamiltonian is assumed to be provided by a generalization of the one given before, in Eq. (12), as:

$$H = \int_\Omega \left(\frac{M^2}{2\rho}-\rho\mathbf{g}\cdot\mathbf{R}+e\left(\rho,s;\mathbf{R}\right)\right)\mathrm{dV}, \tag{35}$$

where, for the sake of generality, in addition to introducing a dependence on the mass density into the internal energy, *e*, of the system, we also assume here the possibility of non-local effects denoted through an explicit special dependence of the expression for the free energy density. Such cases can arise, for example, at the adjacency of a fluid with a surface, as shown in [19-20].

Corresponding to Eqs. (33), (34) and (35), one can then get the governing PDE's for a compressible fluid using the standard procedure of equating the right hand sides of the time evolution for a general functional as they arise a) from a straightforward application of the chain rule of differentiation and b) the use of Eq. (9), as explained in [8], as:

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\nabla\cdot\left(\rho\mathbf{v}\right), \tag{36}$$

$$\frac{\partial\mathbf{M}}{\partial t} \equiv \frac{\partial\left(\rho\mathbf{v}\right)}{\partial t} = -\nabla\cdot\left(\rho\mathbf{v}\mathbf{v}\right) - \nabla p + \nabla\cdot\boldsymbol{\sigma}_v + \rho\mathbf{g} - \left.\frac{\partial e}{\partial\mathbf{R}}\right|_{\rho,s} = \nabla\cdot\left(\boldsymbol{\pi}_e\right) + \rho\mathbf{g} - \left.\frac{\partial e}{\partial\mathbf{R}}\right|_{\rho,s}, \tag{37}$$

and

$$\frac{\mathrm{d}s}{\mathrm{d}t} = -\nabla\cdot\left(s\mathbf{v}\right) + \frac{\mu}{2T}\mathbf{A}:\mathbf{A} + \frac{\left(\kappa - \tfrac{2}{3}\mu\right)}{T}\left(\nabla\cdot\mathbf{v}\right)^2 + \frac{1}{T}\nabla\cdot\left(k\nabla T\right), \tag{38}$$

where $\boldsymbol{\sigma}_v$ is the viscous stress tensor

$$\boldsymbol{\sigma}_v \equiv \mu\mathbf{A} + \left(\kappa - \tfrac{2}{3}\mu\right)\nabla\cdot\mathbf{v}, \tag{39}$$

and $\boldsymbol{\pi}_e$ represents the total effective stress tensor, defined here for a compressible Newtonian fluid as

$$\boldsymbol{\pi}_e \equiv -\rho\mathbf{v}\mathbf{v} - p\mathbf{I} + \boldsymbol{\sigma}_v, \tag{40}$$

with p is the hydrodynamic pressure defined as

$$p \equiv \rho\frac{\partial e}{\partial\rho} + s\frac{\partial e}{\partial\rho} - e\left(\rho, s; \mathbf{R}\right). \tag{41}$$

These are exactly the same as the equations found in a standard reference, for example, [18], adapted for non-local interactions.

In this case, the formal expression for the time derivative (Eulerian) of any arbitrary functional F, $F \equiv \int_\Omega f\left(\rho, s, \mathbf{M}; \mathbf{R}\right)\mathrm{dV}$, which includes possibly non-local effects but not any dependence on higher derivatives, is given, through an adaptation of Eq. (23) as:

$$\left(\frac{\mathrm{d}F}{\mathrm{d}t}\right)_{Eulerian} = \int_\Omega \left(\frac{\delta F}{\delta \rho}\frac{\partial \rho}{\partial t} + \frac{\delta F}{\delta \mathbf{M}}\cdot\frac{\partial \mathbf{M}}{\partial t} + \frac{\delta F}{\delta s}\frac{\partial s}{\partial t}\right)\mathrm{dV}$$

$$= \int_\Omega \left(\begin{array}{l} \frac{\delta F}{\delta \rho}\left(-\nabla\cdot(\rho\mathbf{v})\right) + \\ \frac{\delta F}{\delta \mathbf{M}}\cdot\left(\nabla\cdot(\boldsymbol{\pi}_e) + \rho\mathbf{g} - \left.\frac{\partial e}{\partial \mathbf{R}}\right|_{\rho,s}\right) + \\ \frac{\delta F}{\delta s}\left(-\nabla\cdot(s\mathbf{v}) + \frac{\mu}{2T}\mathbf{A}:\mathbf{A} + \frac{\left(\kappa - \frac{2}{3}\mu\right)}{T}\left(\nabla\cdot\mathbf{v}\right)^2 + \frac{1}{T}\nabla\cdot(k\nabla T)\right) \end{array}\right)\mathrm{dV}$$

$$= \int_\Omega \left(\begin{array}{l} \left(\mathbf{j}_e\right)\cdot\nabla\frac{\delta F}{\delta \rho} - \left(\boldsymbol{\pi}_e\right)^T\cdot\nabla\frac{\delta F}{\delta \mathbf{M}} + \left(\frac{\mathbf{q}_e}{T}\right)\cdot\nabla\frac{\delta F}{\delta s} + \\ \frac{\delta F}{\delta \mathbf{M}}\cdot\left(\rho\mathbf{g} - \left.\frac{\partial e}{\partial \mathbf{R}}\right|_{\rho,s}\right) + \\ \frac{\delta F}{\delta s}\left(\frac{\mu}{2T}\mathbf{A}:\mathbf{A} + \frac{\left(\kappa - \frac{2}{3}\mu\right)}{T}\left(\nabla\cdot\mathbf{v}\right)^2 + \frac{k}{T}\nabla T\cdot\nabla T\right) \end{array}\right)\mathrm{dV} +$$

$$\int_{\partial\Omega}\mathbf{n}\cdot\left[\left(-\mathbf{j}_e\right)\cdot\nabla\frac{\delta F}{\delta \rho} + \left(\boldsymbol{\pi}_e\right)\cdot\frac{\delta F}{\delta \mathbf{M}} + \left(-\frac{\mathbf{q}_e}{T}\right)\frac{\delta F}{\delta s}\right]\mathrm{dA} \qquad ,(42)$$

where $\mathbf{j}_e$ is the effective mass flux:

$$\mathbf{j}_e \equiv \rho\mathbf{v}\,. \qquad (43)$$

Again, straightforward application of this equation for various functionals (i.e. $F = H, M_\alpha, S$, etc.), can give us well known equations pertaining to Thermodynamics and Mechanics, in parallel to the ones described above for an incompressible flow system.