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PREAMBLE TO THE ANALYSIS OF THERMODYNAMIC PROCESSES IN SPARSE PHASES

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ABSTRACT. We propose an interpretation of heat in a multi-scale continuum representation of sparse media dynamics. We attribute the emergence of heat processes to residual fluctuations beyond average and meso-scale affine dynamics.

1. Introduction

In an inaugural address delivered at the *Accademia Peloritana dei Pericolanti* as a contribution to the proceedings of the same Academy, Capriz (2019) stressed attention on a number of conceptual implications of his multi-scale proposal to explore the dynamics of ephemeral continua. That fully Eulerian view, presented first by Capriz (2003) and refined later (see Capriz 2007a,b, 2008; Brocato and Capriz 2011; Capriz and Mariano 2014; Capriz and Giovine 2016, 2018; Capriz and Mariano 2018, 2019; Mariano 2020), rests on the choice of spatial windows, each a cube with side size sufficiently larger than the molecular mean free path, a cube called *loculus* in short. The essential trait of such loculus is that it is reckoned to contain a cluster of molecules so populous as to allow its continuum modeling to make sense. Such approach excludes acceptance of the tacit ground axiom of everlasting identity permanence of material elements (and related properties of one-to-one correspondence between places occupied by the cluster of constituent atoms) sustaining traditional continuum mechanics.

The key difference from views pursued in molecular dynamics is a decomposition of fluctuations into affine and residual components. The former appear already in the representation of mechanics at a continuum scale. Associated bulk and contact interactions define a tensor moment of momentum balance, which is additional to the standard one for forces. Since each loculus is a grand canonical ensemble from a statistical viewpoint, being open to mass and energy exchanges, a Lie time derivative referring to the relative motion between average and fluctuations accounting for mass variation appears necessary. Capriz (2008) defined one such as an extension of one proposed by Oldroyd for tensor entities but specified here also for some of scalar or vector nature.

In that already mentioned multi-scale view on the dynamics of sparse media, beyond the (standard) balance of forces, a tensor moment of momentum appears; it accounts for the (mesoscopic) affine component of fluctuations beyond average. It is well-known that such extension stumbles against a chaining of increasing order moments (as regards this aspect we can look at extended thermodynamics (Mueller and Ruggeri 1998)), so that some trick is called for to avoid impasse. In the proffering recalled in references listed above, the resolve is introduction of a tensor H, defined by an integral over the loculus of a dyad composed by residual fluctuations; a resolve which calls for an evolution equation for H with no precedent in the context. Resulting balances offer challenging analytical problems even in constrained cases, the one tackled by Bisconti *et al.* (2020).

We now offer a *different view* by noting that the time rate of moments has the same physical dimension of an energy; then the quantity under discussion might be absconded into an amount of heat, as always done in a case prone to a loss of energy. We presume that the reader is familiar with the address delivered by Capriz (2019) and, in particular, with the key definitions and balance equations reported in it. We explore consequences of such a view, by adopting a simplified version of the scheme mentioned above, namely we assume H to be of the form χI, with $\chi = \tilde{\chi}(x,\tau)$ a real-valued function and I the second-rank identity. Itself, χ summarizes the effects of velocity distribution moments higher than those involved in B and collects their cumulative effects into heat. We then have an evolution equation for χ, which plays here the role of a *first principle of thermodynamics*. We restrict here our attention to it.

2. A summary of a multi-scale continuum view on sparse phases

2.1. Basic fields and derivatives. As already mentioned in the introduction we consider the elements of a sparse phase as mass points, all with the same mass μ. A cube $\mathfrak{e}(x)$, centered at x and with edge δ, represents the control volume we call a *loculus*. We imagine it as suggested by a magnified view of a point x in the Euclidean space $\mathscr{E}$. For this reason, we imagine $\mathfrak{e}(x)$ embedded in a copy, called $\mathscr{E}_x$, of $\mathscr{E}$ and identify its mass center with x itself so that a vector y, issued form x indicates a generic place in $\mathfrak{e}(x)$, through which a grain with velocity w may transit. In this way, the geometric setting we refer to a fiber bundle with basis is the $\mathscr{E}$ and typical fiber $\mathscr{E}_x$, where the subscript x indicates that $\mathscr{E}_x$ contains $\mathfrak{e}(x)$, so that we consider distinct and non-overlapping loculi. The geometrical picture formalizes the naive idea of considering two scales in $\mathscr{E}$, one larger than δ, the other smaller.

A distribution $\Theta(\tau,x;y,w)$ counts the number of molecules per unit volume, $\Theta\,\mathrm{d}w$, with $\mathrm{d}w$ the vector measure in $\mathscr{V}$, having velocities within the infinitesimal ball $(w+\mathrm{d}w)$ around w. Such a phase-space picture of the mesoscopic scale (sub-loculus level) agrees with Gibbs' suggestions (see Morrey Jr. 1955, for analytical consequences) for describing families of particles. In other words, we presume at y to know the velocity distribution in a small (sub-loculus) neighborhood of y. Θ represents, in fact, a joint distribution at each x and τ. We consider $\Theta(\tau,x;y,w)$ to be regular enough to justify the pertinent analyses so that we express the local averaged velocity w_* at y within the loculus by

$$w_*(\tau,x;y) := \int_{\mathscr{V}} \Theta\,(\tau,x;y,w)\,w\,\mathrm{d}w$$

We define the average of $\Theta(\tau,x;y,w)$ over the space of velocities as

$$\theta(x,\tau;y) := \int_{\mathscr{V}} \Theta(\tau,x;y,w)\,\mathrm{d}w,$$

so that

$$\omega(\tau,x) := \int_{\mathfrak{e}(x)} \theta(\tau,x;y)\,\mathrm{d}y$$

is the number of sparse phase elements (molecules, grains ...) in the loculus pertaining to x at the instant τ, and the continuum-scale *mass density* ρ is given by

$$\rho(\tau,x) := \mu\delta^{-3}\int_{\mathfrak{e}} \theta\,\mathrm{d}y.$$

The **averaged velocity** v over the loculus is then

$$v(\tau,x) := \int_{\mathfrak{e}(x)} \theta(\tau,x;y)\,w_*(\tau,x;y)\,\mathrm{d}y$$

Other pertinent ingredients to the present scenario are the instantaneous **inertia binor** of the cluster in $\mathfrak{e}(x)$, given by

$$Y(\tau,x) := \omega^{-1}\int_{\mathfrak{e}(x)} \theta y\otimes y\,\mathrm{d}y,$$

and the instantaneous **tensor moment of momentum per unit mass**, K, of all molecules in $\mathfrak{e}(x)$, namely

$$K(\tau,x) := \omega^{-1}\int_{\mathfrak{e}(x)} \theta y\otimes(w_*-v)\,\mathrm{d}y.$$

A *key choice* in what we discuss here is the decomposition

$$w_*(\tau,x;y) = v(\tau,x)+B(\tau,x)y+c(\tau,x;y)$$

with B a second-rank tensor depending on τ and x only, c a *residual fluctuation*, a vector depending on y besides τ and x. We choose B, in the decomposition of w_*, to be such that

$$K = YB^T,$$

i.e., $B := K^TY^{-T} = K^TY^{-1}$, a relation accounting for symmetry and non-singularity of Y. The superscript T indicates standard transposition.

For A arbitrarily one of the second-rank tensors Y, K, and H, we indicate by a superposed circle, namely $\mathring{A}$, a derivative (what we call *Capriz's derivative*) defined by

$$\mathring{A} := \dot{A} - BA - AB^T + \sigma A,$$

where

$$\dot{A} := \frac{\partial A}{\partial\tau} + (\nabla A)v,$$

and

$$\sigma := \mathrm{tr}\nabla v - \mathrm{tr}B,$$

so that, when $\sigma = 0$, $\mathring{A}$ reduces to the Oldroyd derivative $\mathring{A} = \dot{A} - BA - AB^T$, with A taken as second-rank tensor. Specifically, σ is the rate of mass variation in $\mathfrak{e}(x)$, along the relative

motion between average and affine fluctuations. For a double-vector G, *i.e.*, a linear operator with just one component in the physical (current) space, we define

$$\mathring{G} = \dot{G} - BG + \frac{\sigma}{2}G,$$

while for a vector we have

$$\mathring{v} = \dot{v} + \frac{\sigma}{2}v.$$

The geometric origins of the derivatives above are given by Capriz and Mariano (2014, 2018).

2.2. Balance equations. Pertinent balance equations are as follows, they substitute those proposed - and derived by invariance - for sparse phases in references already quoted in the introduction (Capriz 2003, 2008; Capriz and Giovine 2016, 2018; Capriz and Mariano 2018, 2019; Mariano 2020):

- Balance of mass:
$$\frac{\partial \rho}{\partial \tau} + \operatorname{div}(\rho v) - \sigma\rho = 0,$$
- Binor conservation law:
$$\dot{Y} - BY - YB^T + \sigma Y = 0,$$
- Balance of standard forces:
$$\rho\left(\frac{\partial v}{\partial \tau} + (\nabla v)v + \frac{1}{2}\sigma v\right) = \rho b + \operatorname{div} T,$$
- *Tensor* moment of momentum balance:
$$\rho\mathring{K} - \rho\chi I = O - A + \operatorname{div}\mathbf{m}.$$

Such equations have their precursors in the model of so-called pseudo-rigid bodies proposed by Cohen and Muncaster (1988).

2.3. Tensor kinetic energy and related balance. We define a *tensor kinetic energy* $\mathscr{W}_*$ as

$$\mathscr{W}_* = \frac{1}{2}(v \otimes v + BYB^T).$$

Previous balance equations imply the following identity:

$$\begin{aligned}\int_{\mathfrak{b}_\tau} \rho\mathring{\mathscr{W}}_* \,\mathrm{d}x \;=\; & \int_{\mathfrak{b}_\tau} \rho \operatorname{sym}(v \otimes b + BO)\,\mathrm{d}x \\ & + \int_{\partial\mathfrak{b}_\tau} \operatorname{sym}(v \otimes Tn + \mathbf{m}(Bn))\,\mathrm{d}\mathscr{H}^2(x) \\ & - \int_{\mathfrak{b}_\tau} \operatorname{sym}\left(LT^T + BA + \mathbf{b}\mathbf{m}^t\right)\,\mathrm{d}x,\end{aligned}$$

where $\mathbf{b} := \nabla B$ and the superscript t indicates minor right transposition for the third-rank tensor $\mathbf{m}$. We indicate by $\mathscr{P}^{inn}$ the term

$$\mathscr{P}^{inn} := \operatorname{sym}\left((\nabla v)T^T + BA + \mathbf{b}^t\mathbf{m}\right),$$

and we identify it as a *tensor density of internal power*.

3. Fluctuations and heat

In this section we pursue the tender to take χ as a measure of heat, as the energy required to moment of momentum balance to deprive it by the disturbing influence of chained higher velocity distribution moments. When such a principle is invoked in 'rational' theories, terms used in its formulation are left to the informed reader to interpret rather than specified in terms of concepts (such as 'power' and 'evolution equation') clearly available from rational continuum mechanics. Not only 'heat' but also 'thermodynamic process' needs to be asseverated. Once those words are given mathematical substance, the first principle will become the evolution rule sought for χ.

Actually, one must overcome another obstacle: heat rate of change cannot be expressed as the derivative of another primitive function. We, nevertheless, pursue the goal, although within some restrictions, which will be made fully clear. Firstly, we specify that the body to which the principle is intended to apply is the bunch of molecules belonging to the loculus $\mathfrak{e}$ at time τ. Then, the heat stored in that body is measured by the kinetic energy associated with the velocities $c(\tau,x;y)$. The latter choice is certainly a severe restriction, but it allows us to trace a road through the maze and to specify the tools required perhaps for a later more satisfactory process. For our next pilgrimage we must chart a map for the region involved, which is the functional space Σ of $c(\tau,x;\cdot)$, in which we take paths parameterized, for each x and τ, by a variable t, ranging in some interval $\mathscr{I}$ of the type $[0,\bar{\tau}]$, each path taken as defining a thermodynamic process. Along every path, the heat rate of change is measured by the rate of change of χ. A *thermodynamic heat-like process* is a path $t \longmapsto c_t(x,\tau;\cdot)$ in the space of fields $c(x,\tau;\cdot)$, parameterized by t. We neglect the residual fluctuations $w - w_*$. Specifically, $c(x,\tau;\cdot)$ is a field, depending on y over the loculus $\mathfrak{e}(x)$ at the instant τ. In the particle-to-continuum analysis proposed by Noll (1955) (see the translation by Lehoucq and Von Lilienfeld-Toal 2010), Noll attributes to the kinetic energy pertaining to fluctuations beyond average velocity the origin of heat flux. Here these fluctuations contribute partially to the description of mechanics. As we have discussed in our work (Capriz and Mariano 2019), in essence we mean for heat the macroscopic collective effect of phenomena left out from the representation of motion, even in the generalized sense suggested by the description of material microstructures. In this sense, the conceptual boundary beyond which we start speaking of heat rather than referring only to mechanics is variable in the sense dictated by the level of detail at which we describe body morphology and its changes.

Notice that, at variance of standard approaches involving heat, $\tilde{\chi}(x,\tau)$ appears in the tensor moment of momentum balance for it emerges from consideration of the effects pertaining to residual fluctuations. Such a peculiar feature determines the way we construct the evolution equation for $\tilde{\chi}(x,\tau)$. Specifically, we presume existence of a flux $\mathfrak{q} \in \mathbb{R}^3$ and scalar source $\mathfrak{r}$ driving the variation in time of $\tilde{\chi}(x,\tau)$, assumed to be sufficiently smooth to satisfy at least in weak sense the following evolution equation:

$$\dot{\chi} - \sigma\chi = \mathrm{tr}\mathscr{P}^{inn} + \mathfrak{r} - \mathrm{div}\mathfrak{q}.$$

We interpret such an equation as the *first principle* of the thermodynamics pertinent to sparse phases in the description proposed here. The term $\dot{\chi} - \sigma\chi$ is the time derivative of χ accounting for relative volume variations between outer and inner loculus scales (see Capriz and Mariano 2014, 2018) for the formal derivation of such a derivative for scalar

and tensor entities). The right-hand side term of the latter equation includes source and heat flux. They require constitutive structures not investigated here. Looking at the tensor moment of momentum balance, we notice that its common vector version is associated with the skew-part of K, which does not include χI. Such an aspect tells us that

$$\rho\chi = \frac{1}{3}\mathrm{trsym}(\rho\overset{\circ}{K} - O + A - \mathrm{div}\mathbf{m}),$$

so that

$$\dot{\chi} = \overbrace{\frac{1}{3\rho}\mathrm{trsym}(\rho\overset{\circ}{K} - O + A - \mathrm{div}\mathbf{m})}^{\cdot},$$

which make sense provided appropriate regularity of the fields involved, the one of K emerging, if it is sufficient, from the analysis of balance equations, which requires, to be pursued (if possible), the preliminary assignment of constitutive structures, an aspect not tackled in the present preamble.

In molecular dynamics, it is customary to look at phenomena within a spatial cell (Hansen and McDonald 2013). Molecules, intended as mass points, interact through a potential depending on molecule from the distance of its first neighbor. The derivative of such potential is the force acting on each molecule, which undergoes conservative dynamics. In this way, periodic boundary conditions assure that the statistical ensemble considered is microcranonical. If, in addition, we consider such a cell as fixed once and for all, we find severe obstacles in describing crystal structure transformations. To overcome such a difficulty Parrinello and Rahman (1980, 1981) suggested to consider a time-varying cell that follows the motion. They maintained the microcanonical structure and adopted an explicit expression of the Lagrangian, which implies, as shown by Podio-Guidugli (2010), that the referential inertial tensor of molecular cluster in the cell be considered spherical and constant in time; also that choice rests on considering cell fluctuations to be irrotational.

At variance, we consider the loculus as a grand canonical statistical ensemble; we leave fixed the loculus but - being it grand canonical - we consider mass variations inside it and adopt a time derivative following the relative motion between macro (outer loculus) and mesoscopic (inner loculus) scales. We can move from our grand canonical approach towards the microcanonical one along a reduction-type path, *e.g.*, by accepting approximations as those proposed by Di Carlo (2019), in which the starting point is a decomposition of the velocity equal to the one used in all our previous works referenced here, with B defined according to Capriz's proposal (Capriz 2008, p. 290). A time threshold of event detectability may allow one to assume conditions in which the mass variation at mesoscopic (inner loculus) scale is small. Then one may reach microcanonical ensemble conditions in this approximated sense (the ergodic assumption bridges phase-space and space-time averages).

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