Continuum Physics with Violations of the Second Law of Thermodynamics

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Abstract As dictated by the modern statistical physics, the second law is to be replaced by the fluctuation theorem on very small length and/or time scales. This means that the deterministic continuum thermomechanics must be generalized to a stochastic theory allowing randomly spontaneous violations of the Clausius–Duhem inequality to take place anywhere in the material domain. This paper outlines possible extensions of stochastic continuum thermomechanics in coupled field problems: (i) thermoviscous fluids, (ii) thermo-elastodynamics, and (iii) poromechanics with dissipation within the skeleton, the fluid, and the temperature field. Linear dissipative processes are being considered, with the thermodynamic orthogonality providing the average constitutive response and the fluctuation theorem providing the violations of the second law of thermodynamics. Special attention is paid to the fact that one can develop hyperbolic theories (i.e. free of the paradox of infinite speeds of signal transmission) while working with the Fourier-type conduction for which the fluctuation theorem has already been developed.

1 Violations of the Second Law of Thermodynamics in Heat Conduction and Viscous Flow

In continuum thermomechanics (e.g. [1]), the second fundamental law may be written in terms of the reversible ($s^{*(r)}$) and irreversible ($s^{*(ir)}$) parts of entropy production rate ($\dot{s}$)

$$\dot{s} = s^{*(r)} + s^{*(ir)} \quad with \quad s^{*(r)} = -\left(\frac{q_i}{\theta}\right)_{,i} \quad and \quad s^{*(ir)} \geq 0. \tag{1}$$

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Here θ is the absolute temperature while q_i is the heat flux [Throughout we interchangeably use the subscript $(f_{i\ldots})$ and the symbolic $(\boldsymbol{f})$ notations for tensors, as the need arises; an overdot means the material time derivative.]. The inequality in $(1)_3$ is assumed to hold instantaneously, i.e. for all t.

In contemporary statistical physics (e.g. [2, 3]) the second law is replaced by the fluctuation theorem which gives the relative probability of observing processes that have positive (A) and negative $(-A)$ total dissipation in non-equilibrium systems:

$$\frac{\mathsf{P}\left(\phi_t = A\right)}{\mathsf{P}\left(\phi_t = -A\right)} = e^{At}. \tag{2}$$

Here ϕ_t is the total dissipation for a trajectory $\boldsymbol{\Gamma} \equiv \{q_1, p_1, ..., q_N, p_N\}$ of N particles originating at $\boldsymbol{\Gamma}(0)$ and evolving for a time t:

$$\phi_t\left(\boldsymbol{\Gamma}(0)\right) = \int_0^t \phi\left(\boldsymbol{\Gamma}(s)\right) ds. \tag{3}$$

The integral in (3) involves an instantaneous dissipation function:

$$\phi\left(\boldsymbol{\Gamma}(t)\right) = \frac{d\phi_t\left(\boldsymbol{\Gamma}(0)\right)}{dt}. \tag{4}$$

The second law of thermodynamics is recovered upon ensemble averaging, time averaging, or upscaling.

Note for future reference that the dissipation function ϕ, albeit on a coarser length scale, is also employed in continuum thermomechanics to describe the dissipative part of constitutive behavior of an elementary volume dV (or a corresponding elementary mass dm). That function is taken as a functional $\phi(\boldsymbol{V})$ over the space of velocities $\boldsymbol{V}$ (or as a functional $\phi(\boldsymbol{Y})$ over the space of dissipative forces $\boldsymbol{Y}$), such that its value equals the instantaneous irreversible entropy production:

$$\phi(\boldsymbol{V}) = s^{*(ir)}. \tag{5}$$

Effectively, the functional $\phi(\boldsymbol{V})$ or $\phi(\boldsymbol{Y})$ is employed to derive the constitutive laws of continua. As is well known, one of the simplest models of continuum physics is the linear (Fourier) heat conduction, whereby the functional becomes a quadratic form and the inequality $(1)_3$ implies the positive definiteness of the thermal conductivity tensor.

In view of (2) above, the dissipation function is a stochastic (not deterministic) quantity which possibly and spontaneously takes negative values, so that the positive-definiteness does not absolutely hold. Therefore, we write (5) as

$$\boldsymbol{Y}(\omega) \cdot \boldsymbol{V} = \phi(\boldsymbol{V}, \omega) = s^{*(ir)}, \quad \omega \in \Omega, \tag{6}$$

where $\boldsymbol{Y}(\omega)$ are the dissipative forces conjugate to $\boldsymbol{V}$. Given that Ω is the set of possible outcomes, the argument ω indicates that $\phi(\boldsymbol{V}, \omega)$ is a stochastic functional, while $\boldsymbol{Y}(\omega)$ is a random quantity for a non-random (prescribed) velocity $\boldsymbol{V}$. An analogous picture holds for $\boldsymbol{Y}$ being prescribed and $\boldsymbol{V}$ the random outcome. It is tacitly assumed that Ω is equipped with a σ-algebra of observable events $\mathscr{A}$ and a probability measure P defined on $(\Omega, \mathscr{A})$.

The fluctuation theorem as expressed by (1) states that (i) positive dissipation is exponentially more likely to be observed than negative dissipation, and (ii) ensemble averaging of ϕ_t leads to

$$\langle \phi_t \mid \mathscr{F}_t \rangle \geq 0. \tag{7}$$

Here $\mid \mathscr{F}_t$ indicates the conditioning on the past and is discussed below, while $\langle f \rangle := \int f \, d\mathsf{P}$. Thus, the entropy production rate is non-negative on average. In view of the random fluctuations, ϕ_t is a stochastic process with a specific type of memory effect: a submartingale [4]. Treating time as a continuous parameter, we have

$$\langle \phi_{t+dt} \mid \text{past history} \rangle \geq \phi_t. \tag{8}$$

Next, we recall the Doob–Meyer decomposition to write ϕ_t as a sum of a martingale (M) and a "drift" process (G):

$$\phi_t(\boldsymbol{V}, \omega) = M + G \;\; and \;\; \phi(\boldsymbol{V}, \omega) = \dot{M} + \dot{G}. \tag{9}$$

Thus, $M \neq 0$ reflects the fluctuations of entropy production about the zero level $\left\langle s^{(i)} \right\rangle = 0$. The four different cases depending on whether $M = 0$ or $M \neq 0$ and $G = 0$ or $G > 0$ have been discussed in [4]. Overall, deterministic continuum mechanics is smoothly recovered as the time and/or spatial scale increases (so that $M \to 0$) or via ensemble averaging.

Note that one might also work with a discrete time formulation, making the mathematical analysis simpler.

There are three types of phenomena in classical physics where the fluctuation theorem is applicable: viscous [2], thermal [3], and electrical [2]. Here we concern ourselves with the first two, so that, contact with continuum thermomechanics is made by writing the scalar product $\boldsymbol{Y} \cdot \boldsymbol{V}$ as one involving the intrinsic mechanical dissipation (which includes the viscous effects) and thermal dissipation in spatial (Eulerian) description:

$$\phi(\boldsymbol{V}, \omega) = \phi_{th}(\boldsymbol{V}_1, \omega) + \phi_{mech}(\boldsymbol{V}_2, \omega), \quad \boldsymbol{V} \equiv (\boldsymbol{V}_1, \boldsymbol{V}_2) = \left(\frac{-\nabla\theta}{\theta}, \boldsymbol{d} \right). \tag{10}$$

Thus, the generalized velocity vector $\boldsymbol{V}$ is made up of two parts: the temperature gradient divided by the temperature $-\nabla\theta/\theta$ and the deformation rate $\boldsymbol{d}$. The reason we take the former as the argument of ϕ_{th} is that the fluctuation theorem for heat flow was derived for controllable temperature differences [3], with the heat flux being the stochastic outcome. Analogously, the fluctuation theorem for Couette and Poiseuille flows was derived for controllable velocities [3], with the Cauchy stress being the stochastic outcome. Thus, the dissipative force corresponding to $\boldsymbol{V}$ is made up of the heat flux and the dissipative stress

$$\boldsymbol{Y} \equiv (\boldsymbol{Y}_1, \boldsymbol{Y}_2) = \left(\boldsymbol{q}, \boldsymbol{\sigma}^{(d)}\right). \tag{11}$$

It is largely a matter of convenience whether $-\nabla\theta/\theta$ or $\boldsymbol{q}$ should be taken as a velocity or a dissipative force. In the section on thermoviscous fluids we work with the setup outlined above, while in the section on inviscid thermoelastic solids we invert the roles of $-\nabla\theta/\theta$ and $\boldsymbol{q}$.

There are two basic possibilities here:

- both processes in (10) may independently exhibit spontaneous random violations of the second law;
- both processes in (10) are coupled implying that the thermal and viscous violations of the second law are coupled, for which the relevant statistical physics has not yet been studied.

In what follows, we shall consider the first possibility above focusing on: (i) thermoviscous fluids with parabolic or hyperbolic type heat conduction, (ii) thermoelasticity with parabolic or hyperbolic type heat conduction, and (iii) poromechanics with dissipation within the skeleton, the fluid, and the temperature field. The reason we consider parabolic or hyperbolic cases is that the statistical physics has established the spontaneous violations of the Fourier type law [3], but a hyperbolic heat conduction in fluids and solids can still be modeled if a relaxation time in the entropy constitutive law is introduced. The theoretical developments below hinge on the fact that the balance laws apply irrespective of the conventional second law being obeyed or not. At the same time, we are interested in formulating models which are hyperelastic and hyperdissipative in ensemble average sense (or, for long time averages), thereby extending such class beyond the deterministic media fully obeying the second law [5, 6].

2 Random Fields

One of the key problems in constitutive modeling in continuum mechanics concerns the finding of a solution of (6), i.e. determining a constitutive relation linking $\boldsymbol{Y}$ with $\boldsymbol{V}$. The most effective and popular approach is based on a thermodynamic orthogonality [1] which also provides a stepping-stone to more complex models in continuum thermodynamics. To this end, take ϕ as a functional of $\boldsymbol{V}$, and obtain $\boldsymbol{Y}$ as its gradient in the velocity space:

$$\boldsymbol{Y} = \lambda \nabla_{\boldsymbol{V}} \phi \geq 0, \quad \lambda = \left(\boldsymbol{V} \cdot \nabla_{\boldsymbol{V}} \phi\right)^{-1} \phi. \tag{12}$$

The meaning of (11) is that, provided the dissipative force $\boldsymbol{Y}$ is prescribed, the actual velocity maximizes the dissipation rate $l^{(d)} = \boldsymbol{Y} \cdot \boldsymbol{V}$ subject to the side condition $\phi(\boldsymbol{V}) = \boldsymbol{Y} \cdot \boldsymbol{V} = l^{(d)} \geq 0$.

Replacing the deterministic picture by a stochastic one, the internal energy density u and the entropy s are real-valued random fields over the material ($\mathscr{D}$) and time (T) domains:

$$u : \mathscr{D} \times T \times \Omega \to \mathbb{R}, \quad s : \mathscr{D} \times T \times \Omega \to \mathbb{R}, \tag{13}$$

where we consider the heat conduction problem in a rigid (undeformable) conductor. The randomness disappears as the time and/or spatial scales become large: the field quantities simplify to deterministic functions of a homogeneous continuum.

Considering, say, the thermal dissipation in (10), we have

$$\phi_{th}\left(\frac{-\nabla\theta}{\theta}, \omega\right) = -q_k \frac{\theta_{,k}}{\theta} \equiv -\,\boldsymbol{q} \cdot \frac{\nabla\theta}{\theta}. \tag{14}$$

Given the stochastic violations of second law,

$$\phi_{th}(\boldsymbol{q}, \omega) = \dot{G}(\boldsymbol{q}) + \dot{M}(\boldsymbol{q}, \omega), \tag{15}$$

which, for the linear Fourier-type conductivity, becomes more explicit with

$$\dot{G}(\boldsymbol{q}) = \frac{1}{\theta} q_i \kappa_{ij} q_j, \; \dot{M}(\boldsymbol{q}, \omega) = \frac{1}{\theta} q_i \mathscr{M}_{ij}(\omega)\, q_j. \tag{16}$$

Here $\dot{G}(\boldsymbol{q})$ involves the thermal conductivity κ_{ij} which is positive definite, and $\dot{M}(\boldsymbol{q}, \omega) = dM(\boldsymbol{q}, \omega)/dt$, with M being the martingale modeling the random fluctuations according to (2). Clearly, the randomness residing in $M(\boldsymbol{d}, \omega)$ allows the total thermal conductivity $\kappa_{ij} + \mathscr{M}_{ij}$ to become negative since $\mathscr{M}_{ij}$ is not required to be positive definite, thus signifying the violations of the second law. More specifically, $\mathscr{M}_{ij} : \mathscr{V} \to \mathscr{V}$ (where $\mathscr{V}$ is a real vector space) is a second-order rank 2 tensor random field (e.g. [7, 8])

$$\mathscr{M}_{ij} : \mathscr{D} \times \Omega \to \mathscr{V}^2. \tag{17}$$

In view of the Gaussian character of nanoscale fluctuations, $\mathscr{M}_{ij}$ is a Gaussian tensor random field.

The same approach as in (15)–(17) may be used to introduce fluctuations in mechanical dissipation $\phi_{th}\,(\boldsymbol{d}, \omega)$ having spontaneously negative viscous responses.

3 Thermoviscous Fluid with a Thermal Relaxation Time

The internal energy u is taken as a function of the strain ε_{ij} and the entropy s:

$$u = u(\varepsilon_{ij}, s). \tag{18}$$

Switching from u to $\psi = u - \theta s$ by a Legendre transformation, we find

$$\psi = \psi(\varepsilon_{ij}, \theta) \quad and \quad s = s(\theta). \tag{19}$$

The first fundamental law (energy balance) is

$$\rho\dot{u} = \sigma_{ij} d_{ij} - q_{i},_{i}\ , \tag{20}$$

where the first term on the right is the specific power of deformation. The free energy function ψ (taken per unit mass), assuming no elastic response but the presence of a relaxation time t_0, is

$$\rho\psi(\varepsilon_{ij}, \theta) = \rho\psi_0 - \rho s_0 \vartheta - \frac{C_E}{2\theta_0}\vartheta^2 - \frac{C_E}{\theta_0} t_0 \vartheta \dot{\vartheta}, \quad \vartheta = \theta - \theta_0. \tag{21}$$

Here ψ_0 and s_0 are the free energy and entropy in the reference state, μ is the shear elastic modulus, C_E is the specific heat at constant strain, and $\vartheta = \theta - \theta_0$ is the temperature difference from the reference temperature θ_0. The last term on the right hand side is taken by analogy to the thermoelasticity with two relaxation times in the next section, so as to retain the Fourier-type heat conduction, but to obey the hyperbolic (finite speed) heat propagation. Also note that ψ does not depend on the strain ε_{ij}, so the resulting fluid does not poses any elasticity. In this section, an overdot denotes a material derivative $\mathscr{D}/\mathscr{D}t$ for absolute tensors (like the temperature gradient and deformation rate) and an Oldroyd derivative for tensor densities (like the heat flux and stress tensor).

The free energy being a potential for quasi-conservative stresses $\sigma_{ij}^{(q)}$ and the entropy s, we find

$$\begin{aligned} \sigma_{ij}^{(q)} &= \rho\frac{\partial\psi}{\partial\varepsilon_{ij}} = 0, \\ s = -\rho\frac{\partial\psi}{\partial\theta} &= \frac{C_E}{\theta_0}\vartheta + \frac{C_E}{\theta_0} t_0 \dot{\vartheta}. \end{aligned} \tag{22}$$

The relation $(22)_2$ is immediately identified as the constitutive equation for entropy. In view of the fluid's incompressibility, $\sigma_{ij}^{(q)}$ is taken as the deviatoric part of the quasi-conservative stress tensor, the corresponding spherical part being zero. As always in TIV [1],

$$\sigma_{ij} = \sigma_{ij}^{(q)} + \sigma_{ij}^{(d)}, \quad \beta_{ij}^{(q)} = -\beta_{ij}^{(d)}, \tag{23}$$

where $\sigma_{ij}^{(d)}$ is the dissipative stress. Also, $\beta_{ij}^{(q)}$ is the internal quasi-conservative stress and $\beta_{ij}^{(d)}$ is the internal dissipative stress, the first being conjugate to the internal variable α_{ij} and the second one to its rate $\dot{\alpha}_{ij}$. The fluid under consideration has no elastic response, so $\alpha_{ij} \equiv 0$.

The above Ansatz leads to the Clausius–Duhem inequality in the form

$$\rho\theta s^{*(ir)} = -\frac{q_i\theta,_i}{\theta} + \sigma_{ij}^{(d)} d_{ij} \geq 0, \tag{24}$$

where $\sigma_{ij}^{(d)}$ is the dissipative stress, which is now equal to the total stress σ_{ij} in view of $(22)_1$ and $(23)_1$. As discussed in the first two sections, the inequality (24) may spontaneously be violated.

Consistent with (10), we take the specific (per unit mass) dissipation ϕ as:

$$\rho\theta s^{*(ir)} = \phi\left(-\frac{\theta,_i}{\theta}, d_{ij}\right). \tag{25}$$

Clearly, the inequality (24) may be stated in terms of the scalar product (6): $\boldsymbol{Y} \cdot \boldsymbol{V} \geq 0$.

Next, for the entropy production rate we adopt the dissipation functional in the space of velocity $\boldsymbol{V} = (-\theta^{-1}\nabla\theta, \boldsymbol{d})$:

$$\rho\theta s^{*(ir)} \equiv \rho\phi(\boldsymbol{V}) = \frac{\kappa}{\theta}\theta,_i \theta,_i + H d_{ij} d_{ij}, \tag{26}$$

where κ is the Fourier conductivity and H is the fluid viscosity. This is seen as a special case of (10) with both processes being effectively compound [1]. By thermodynamic orthogonality, (26) yields

$$\begin{aligned} -q_i &= \frac{1}{2}\rho\frac{\partial\phi}{\partial\theta,_i} = \kappa\theta,_i\,, \\ \sigma_{ij} = \sigma_{ij}^{(d)} &= \frac{1}{2}\rho\frac{\partial\phi}{\partial d_{ij}} = H d_{ij}. \end{aligned} \tag{27}$$

Collecting the three parts of the constitutive law: mechanical, Fourier law, and entropy:

$$\begin{aligned} q_i &= -\kappa\theta,_i\,, \\ \sigma_{ij} &= H d_{ij}, \\ s &= \frac{C_E}{\theta_0}\left(\vartheta + t_0\dot{\vartheta}\right), \end{aligned} \tag{28}$$

which shows that, while the Fourier-type law holds, there is a relaxation effect involved in the entropy. As a result, there also are violations according to [3], while the heat is conducted with finite speeds – i.e. not infinite speeds as would be the case with $t_0 = 0$. In other words, instead of having a parabolic (diffusion) equation for temperature, we have (by application of the energy balance (20) and the entropy-temperature relation $(28)_3$)

$$\kappa \vartheta_{,ii} = \rho C_E \left(\dot{\vartheta} + t_0 \ddot{\vartheta} \right). \tag{29}$$

Here we have also used the approximation of small temperature fluctuations. In effect, θ (just like ϑ) is governed by the telegraph (damped hyperbolic) Eq. (29), whose limiting case (for $t_0 \to 0$) is the conventional (parabolic) heat conduction equation.

4 Thermoelasticity with Two Relaxation Times

Conventional thermo-elastodynamics is hyperbolic in elastic response and parabolic in heat conduction. The standard way to obtain a purely hyperbolic (and still linear) thermo-elastodynamics is to replace the Fourier law by the Maxwell-Cattaneo law [9]. However, a fluctuation theorem for the latter type of thermal response does not (yet) exist and we need to work with a Fourier-type law. Thus, one may proceed by using the *theory of thermoelasticity with two relaxation times* [10, 11]. While the original derivation of that reference had used the free energy functional only, one may proceed by using a different free energy functional along with a dissipation functional. The approach is similar to that in the preceding section, although we take the heat flux and its rate as the argument of ϕ. First, we adopt the internal energy u as a function of the infinitesimal elastic strain ε_{ij} and the entropy s

$$u = u(\varepsilon_{ij}, s), \tag{30}$$

along with the (specific, per unit mass) dissipation functional ϕ as a function of the strain rate $\dot{\varepsilon}_{ij}$, the heat flux, and its rate

$$\phi = \phi(\dot{\varepsilon}_{ij}, q_i). \tag{31}$$

By the Legendre transformation $\psi = u - \theta s$, we now obtain

$$\dot{\psi} = \dot{u} - \dot{\theta} s - \theta \dot{s}, \tag{32}$$

whereas by the postulate of hyperelasticity for quasi-conservative stress and the entropy

$$\sigma_{ij}^{(q)} = \rho \frac{\partial \psi}{\partial \varepsilon_{ij}} \quad and \quad s = -\rho \frac{\partial \psi}{\partial \theta}. \tag{33}$$

Noting the balance of energy (20), (33) becomes

$$\rho\theta\dot{s} = \sigma_{ij}^{(d)}\dot{\varepsilon}_{ij} - q_{i,i}\,, \tag{34}$$

which, in view of (1), yields the Clausius–Duhem in standard form:

$$\rho\theta s^{*(ir)} = -\frac{q_i\theta_{,i}}{\theta} + \sigma_{ij}^{(d)}\dot{\varepsilon}_{ij} \geq 0. \tag{35}$$

Now, adopt the free energy (with $\vartheta = \theta - \theta_0$ as before)

$$\psi = \psi(\varepsilon_{ij}, \theta) = \frac{1}{2}\varepsilon_{ij}C_{ijkl}\varepsilon_{kl} + M_{ij}\varepsilon_{ij}\vartheta - \frac{C_E}{2\theta_0}\vartheta^2 - \frac{C_E}{\theta_0}t_0\vartheta\dot{\vartheta}, \tag{36}$$

so that

$$\sigma_{ij}^{(q)} = C_{ijkl}\varepsilon_{kl} + M_{ij}\vartheta \quad and \quad s = -M_{ij}\varepsilon_{ij} + \frac{C_E}{\theta_0}\vartheta + \frac{C_E}{\theta_0}t_0\dot{\vartheta}\ . \tag{37}$$

Also, adopt the dissipation function (this time in the space of heat flux and strain rate)

$$\phi(q_i, \dot{\varepsilon}_{ij}) = \rho\theta s^{*(ir)} = \frac{\lambda_{ij}}{\theta}q_iq_j + t_1M_{ij}\dot{\varepsilon}_{ij}\dot{\vartheta}, \tag{38}$$

so that, by treating both processes as compound [1],

$$-\frac{\theta_{,i}}{\theta} = \frac{1}{2}\frac{\partial\phi}{\partial q_i} = \frac{\lambda_{ij}}{\theta}q_j \quad and \quad \sigma_{ij}^{(d)} = \frac{\partial\phi}{\partial\dot{\varepsilon}_{ij}} = t_1M_{ij}\dot{\vartheta}. \tag{39}$$

On account of (23), we obtain

$$\begin{aligned} \sigma_{ij} = \sigma_{ij}^{(q)} + \sigma_{ij}^{(d)} &= C_{ijkl}\varepsilon_{kl} + M_{ij}(\vartheta + t_1\dot{\vartheta}), \\ \theta_0 s &= -\theta_0 M_{ij}\varepsilon_{ij} + C_E(\vartheta + t_0\dot{\vartheta}), \\ q_i &= -k_{ij}\vartheta_{,j}\,, \end{aligned} \tag{40}$$

where, again (recalling Sect. 2), $\kappa_{ij} + \mathscr{M}_{ij}$ is a random field of the Fourier thermal conductivity in space-time with spontaneous violations of positive-definiteness property. Note that k_{ij} in $(40)_3$ equals $\kappa_{ij} + \mathscr{M}_{ij}$, anisotropy being possible because we are now dealing with a solid, not fluid. It is well known that, (40) lead to coupled and hyperbolic-type equations for the (u_i, ϑ) pair

$$\begin{aligned} (C_{ijkl}u_{k,l})_{,j} - \rho\ddot{u}_i + [M_{ij}(\vartheta + t_1\dot{\vartheta})]_{,j} &= -b_i, \\ (k_{ij}\vartheta_{,j})_{,i} - C_E(\dot{\vartheta} + t_0\ddot{\vartheta}) + \theta_0 M_{ij}\dot{u}_{i,j} &= -r. \end{aligned} \tag{41}$$

Observe:

(i) The constitutive relations (40) are the same as those of the Green-Lindsay theory, but their derivation is based on treating the Fourier-type heat conduction as a purely dissipative process, and thus as a process described by the dissipation function rather than by the free energy function in [10, 11].

(ii) The inequalities $t_1 \geq t_0 \geq 0$ have to hold. By setting $t_1 = t_0 = 0$, we obtain the classical thermoelasticity. Also, one may only consider the limit $t_0 \to 0$, so that $(41)_2$ reduces to the conventional heat conduction equation.

(iii) Transient phenomena (such as wavefronts), if occurring on very short length scales, are expected to deviate from the hyperbolic thermo-elastodynamics obeying the second law [11].

5 Violations of Second Law in Poromechanics

The preceding considerations apply to physics of porous media, in the sense that:

- the nanoscale dimensions of the porous channel network are nanoscale;
- the viscous fluid flow (Poiseuille and Couette type) in the channels violates the second law;
- the temperature field in the fluid occupying the channels violates the second law.

As a reference, in classical poromechanics obeying the second law [12], the Clausius–Duhem inequality is written in terms of irreversible entropy production $S^{*(ir)}$ $(= \rho s^{*(ir)})$ taking the form

$$\theta S^{*(ir)} = \theta S^{*(ir)}_{(th)} + \theta S^{*(ir)}_{(fluid)} + \theta S^{*(ir)}_{(skeleton)} \geq 0, \tag{42}$$

where three possible contributions to dissipation are identified:

1. thermal dissipation: $S^{*(ir)}_{(th)}$;
2. fluid dissipation: $S^{*(ir)}_{(fluid)}$;
3. skeleton dissipation: $S^{*(ir)}_{(skeleton)}$.

Conventionally, each of these contributions to dissipation is assumed to satisfy its own second law inequality. It now follows that, in case of poromechanics describing phenomena on very small space and time scales, the spontaneous violations of the second law can occur in either one or two or three processes, and these can be modeled according to what has been presented in the preceding sections.

6 Conclusions

The recent works [4, 13, 14] investigated extensions of continuum thermomechanics to account for spontaneous, random violations of the second law that become relevant on very small length and/or time scales... although in cholesteric liquids the time of such a violation may be up to 3 s. As dictated by modern statistical physics, the second law is then to be replaced by the fluctuation theorem. The particular phenomena and aspects included: Newtonian fluids with either parabolic or hyperbolic heat conduction, random field models including spatial fractal and Hurst effects, acceleration wavefront of nanoscale thickness, Lyapunov function for the heat field, random fluctuations of the microrotation field in a viscous micropolar fluid, Couette flow, and permeability of a medium with nanoscale pores.

This paper outlines possible extensions of stochastic continuum thermomechanics in coupled field problems: (i) thermoviscous fluids, (ii) thermoelastic solids, and (iii) poromechanics with dissipation within the skeleton, the fluid, and the temperature field. Special attention is paid to the fact that one can develop hyperbolic theories (i.e. free of the paradox of infinite speeds of signal transmission) while working with the Fourier-type heat conduction for which the fluctuation theorem has already been developed.

There are various directions in which this research may further be developed, of which we list two. On one hand, the details and extensions of what has been considered here need to be worked. On the other hand, one can start from the so-called Crooks Fluctuation Theorem (CFT) in statistical mechanics [15, 16] that relates the work done on a system during a non-equilibrium transformation to the free energy difference between the final and the initial state of the transformation. In general, the CFT says that, if the dynamics of the system satisfies microscopic reversibility, then the forward space-time trajectory $\boldsymbol{\Gamma}(t)$ is exponentially more likely than the time-reversed trajectory $\tilde{\boldsymbol{\Gamma}}(t)$, given that it produces entropy $s^{*(ir)}$,

$$\frac{\mathsf{P}\left[\boldsymbol{\Gamma}(t)\right]}{\mathsf{P}\left[\tilde{\boldsymbol{\Gamma}}(t)\right]} = e^{\sigma^{(ir)}(\boldsymbol{\Gamma})}. \tag{43}$$

Here $\sigma^{(ir)}(\boldsymbol{\Gamma})$ is the microscopic version of $\Delta S^{(ir)} = \Delta S - Q/\theta = (W - \Delta\Psi)/\theta$ written for the macroscopic system, whereby we also recall (1), the first law of thermodynamics, and the classical relation $\Psi = U - S\theta$, see [17]. The latter reference reviews this and many related issues as well as the fact that the CFT implies the so-called Jarzynski equality [18, 19]

$$\left\langle e^{-W/k_B\theta}\right\rangle = e^{-\Delta\Psi/k_B\theta}, \tag{44}$$

where k_B is the Boltzmann constant and θ is the initial temperature of the system in the reservoir. One step in the direction of extending the phenomenological non-equilibrium thermodynamics to account for that equality has been taken in [20].

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