# From Second Law Violations to Continuum Mechanics

**Martin Ostoja-Starzewski**

**Abstract** The violations of the Second Law become relevant as the length and/or time scales become very small. The Second Law then needs to be replaced by the fluctuation theorem and, mathematically, the irreversible entropy evolves as a submartingale. Next, a framework thermomechanics relying on stochastic functionals of energy and entropy is outlined. This allows a study of diffusion-type problems with random field constitutive coefficients not required to satisfy the positive definiteness everywhere. Finally, a formulation of stochastic micropolar fluid mechanics is developed, accounting for the lack of symmetry of stress tensor on molecular scales.

**Keywords** Continuum mechanics · Second law violations · Fluctuation theorem · Submartingale · Micropolar fluid

## 1 Motivation

The theory, simulations, and experiments of statistical mechanics over the past two decades indicate that violations of the Second Law of thermodynamics are relevant where/when the length and/or time scales become very small [5, 7, 9, 17, 19]. The Second Law must then be replaced by the *fluctuation theorem* or, strictly speaking, a group of such theorems. In effect, the Second Law holds on average, be it an ensemble average, or a spatial average over a sufficiently large domain, or a temporal average over a sufficiently large time interval. Interestingly, the Second Law violations may occur for up to 3 s (!) in cholesteric liquids. While the focus in statistical mechanics has been on stochastic thermodynamics, our interest is in introducing these results into continuum mechanics, i.e. in formulating stochastic continuum thermomechanics with spontaneous violations of the Second Law [12–14].

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So far, we have obtained these results:

- entropy evolution over time is a submartingale;
- classification of thermomechanical processes into four types depending on whether they are conservative or not and/or conventional continuum mechanical;
- stochastic generalizations of thermomechanics in the vein of either thermodynamic orthogonality [20] or primitive thermodynamics [4]; with explicit models formulated for Newtonian fluids with, respectively, parabolic or hyperbolic heat conduction;
- random field models of the martingale component, possibly including spatial fractal and Hurst effects;
- evolution of an acceleration wavefront randomly encountering regions with negative viscosity coefficient;
- Lyapunov function of a diffusion phenomenon where the random field coefficients do not satisfy the positive definiteness everywhere;
- spontaneous random fluctuations of the microrotation field in a viscous micropolar fluid model in the absence of random (turbulence-like) fluctuations of the classical (Cauchy) velocity field.

In this paper, following a brief account of the fluctuation theorem, we review some of the above results.

## 2 Background: Fluctuation Theorem

It has been established in statistical physics over the past two decades that the entropy production may be negative on short time and space scales, see reviews in [8, 15]. This is described by a so-called *fluctuation theorem* giving, in its basic form, an estimate of the relative probability of observing processes that have positive and negative total dissipation in non-equilibrium systems

$$\frac{\mathsf{P}\left(\phi_t = A\right)}{\mathsf{P}\left(\phi_t = -A\right)} = e^{At}. \tag{1}$$

Here $t$ is the time, while $\phi_t$ is the dissipation function quantifying the thermodynamic reversibility of a trajectory taken by a thermodynamic system, and $A$ is the value of $\phi_t$. To help explain it, in Fig. 1 we reproduce Fig. 1.1 from [8] giving the probability density histogram of fluctuations of the time-averaged shear stress $\sigma_{xy}$ in Couette flow. Note that (i) the fluctuations are not confined to the negative values of $\sigma_{xy}$, and (ii) for any pair of two points symmetrically distributed about 0.00 on the $\sigma_{xy}$ axis consistent with (1) the probability of a negative fluctuation [$\mathsf{P}\left(\phi_t = A\right)$] is greater than the probability of a positive fluctuation [$\mathsf{P}\left(\phi_t = -A\right)$].

That is, the fluctuation theorem compares the probability $\mathsf{P}\left(\phi_t = A \pm dA\right)$ of observing an arbitrary system trajectory having a dissipation total infinitesimally close to $A$ with that of the time reverse of that trajectory (its conjugate anti-trajectory)

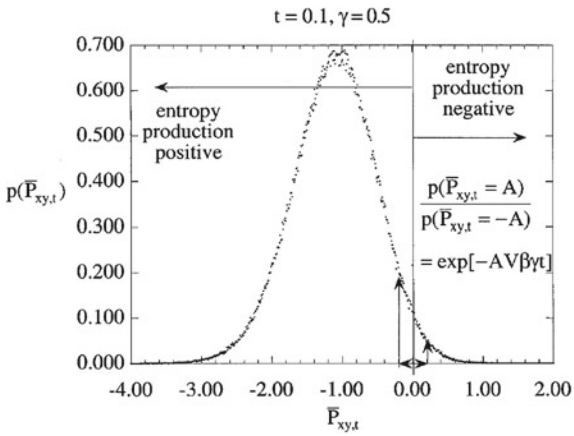


**Fig. 1** A histogram showing fluctuations in the time-averaged shear stress for a system undergoing Couette flow; figure taken from [8]

in the ensemble of trajectories:

$$\phi_t\left(\boldsymbol{\Gamma}(0)\right) = \ln \frac{\mathsf{P}\left(\boldsymbol{\Gamma}(0), 0\right)}{\mathsf{P}\left(\boldsymbol{\Gamma}^*(t), 0\right)} \tag{2}$$

More specifically, with $\boldsymbol{\Gamma} = (q_1, p_1, ...q_N, p_N)$ being the phase space vector of the system which corresponds to a system trajectory and $\boldsymbol{\Gamma}^*(t)$ being the result of a time reversal map applied to $\boldsymbol{\Gamma}(0)$, $\phi_t\left(\boldsymbol{\Gamma}(0)\right)$ is the total dissipation for a trajectory originating at 0 and evolving for a time $t$:

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

This integration involves an instantaneous dissipation function:

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

The fluctuation theorem as expressed by (1) states that (i) positive dissipation is exponentially more likely to be observed than negative dissipation, and (ii) upon ensemble averaging of $\phi_t$ (with $\mathsf{E}$ denoting the mathematical expectation), leading to

$$\mathsf{E}\left[\phi_t | \mathscr{F}_t\right] \geq 0. \tag{5}$$

Here $|\mathscr{F}_n$ indicates the conditioning on the past history and is discussed below. Considering that the time-integrated dissipation function $\phi_t$ equals the irreversible entropy production in continuum thermomechanics with internal variables (TIV), the inequality (5) is seen as a generalization of the Second Law of thermodynamics (i.e., the entropy production rate is non-negative). Note that $\phi$ in (3) and (4) is recognized as the irreversible entropy production rate.

## 3 Entropy Is a Submartingale

In view of the random fluctuations, $\phi_t$ is a stochastic process with a specific type of memory effect to be examined as follows. First, every stochastic process is defined with reference to a probability space $(\Omega, \mathscr{F}, \mathscr{P})$, where $\Omega$ is the sample space, $\mathscr{F}$ is the $\sigma$-field, and $\mathscr{P}$ the probability measure, the argument $\omega \in \Omega$ being employed to indicate an elementary event as well as the random character of $\phi_t$. We now switch from a continuous ($t$) to a discrete ($n$) time parametrization

$$\phi_n := \phi_{t=n}, \tag{6}$$

The point is that the analytical aspects of discrete-time stochastic processes are simpler than those of continuous-time processes; the integral in (3) is replaced by a summation, while the derivative in (4) is understood in a finite-difference sense.

Our growing knowledge of the process $\phi_n$ at the successive times (i.e., its history) is represented by a so-called *filtration* on $\Omega$: a sequence $\{\mathscr{F}_n : n = 0, 1, 2, \ldots\}$ of sub-sigma fields of $\mathscr{F}$ such that for all time instants $t_n$, $\mathscr{F}_n \subset \mathscr{F}_{n+1}$. In view of (5), we observe that this inequality is satisfied

$$\mathsf{E}\{\phi_{n+1} | \mathscr{F}_n\} \leq \phi_n, \tag{7}$$

which indicates that $\phi_n$ is a *submartingale*. On the technical side dictated by the probability theory, (7) has to be accompanied by two more conditions: (i) $\{\mathscr{F}_n; n = 0, 1, 2, \ldots\}$ is a filtration and $\phi_n$ is adapted to $\mathscr{F}_n$; (ii) for each $n$, $\phi_n$ is integrable.

If the $\leq$ sign in (7) were replaced by an equality sign, we would have a so-called *martingale*. In fact, this observation acquires more light in view of the so-called *Doob decomposition* [3] saying that any submartingale is the sum of a martingale ($M$) and an increasing process ($G$): Let $\phi = \{\phi_n; n \geq 0\}$ be a submartingale relative to the filtration $(\mathscr{F}_n)$. Then there exists a martingale $M = \{M_n; n \geq 0\}$ and a process $G = \{G_n; n \geq 0\}$ such that

(i) $M$ is a martingale relative to $\mathscr{F}_n$;
(ii) $G$ is an increasing process: $G_n \leq G_{n+1}$ almost everywhere;
(iii) $G_n$ is $\mathscr{F}_{n-1}$-measurable $\forall n$;
(iv) $\phi_n = M_n + G_n$.

In [12] we have employed an analogous (Doob–Meyer decomposition) theorem in continuous time, also giving a unique decomposition of a submartingale into a martingale and a "drift" process. The discrete time case should be sufficient for most continuum physics applications, while allowing a simpler analytical treatment.

## 4 Violations of Second Law in Diffusion Problems

The partial differential equation of diffusion hinges on a coarse scale and a deterministic continuum approximation of a random medium. If we consider a very fine scale resolution where the violations of the Second Law relative to heat conduction occur [16], we must replace the deterministic picture by a stochastic one. Thus, the internal energy density $u$ (per unit volume) and the entropy $s$ (per unit volume) are random fields over the material ($\mathscr{D}$) and time ($T$) domains:

$$u : \mathscr{D} \times T \times \Omega \to \mathbb{R}, \quad s : \mathscr{D} \times T \times \Omega \to \mathbb{R}, \tag{8}$$

where we consider the heat conduction problem in a rigid (undeformable) conductor. With reference to Sect. 2, the Second Law of thermodynamics takes the ensemble averaged Clausius–Duhem form

$$\mathsf{E}\{\phi|\mathscr{F}_n\} \geq 0, \quad \phi = T\dot{s}^{(i)} = -q_k \frac{T_{,k}}{T} \equiv -\mathbf{q}\cdot\frac{\nabla T}{T}. \tag{9}$$

Here we recognize the pair of affinities: vector of velocity $T_{,k}$ conjugate to the vector of dissipative force $-q_k/T$ and introduce a dissipation function $\phi\,(q_k)$. Given the medium's randomness, $\phi$ is a random field

$$\phi : \mathscr{D} \times T \times \Omega \to \mathbb{R}. \tag{10}$$

At any given continuum point $\mathbf{x}$ in $\mathscr{D}$, $\phi$ is a random functional $\phi(\mathbf{q}, \omega)$, $\omega \in \Omega$. The randomness of $\phi$ disappears as the time and/or spatial scales become large and then $\phi$ reverts to a deterministic functional of a homogeneous continuum. According to the model outlined in Sect. 2,

$$\phi(\mathbf{q}, \omega) = \dot{G}(\mathbf{q}) + \dot{M}(\mathbf{q}, \omega), \tag{11}$$

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

$$\dot{G}(\mathbf{q}) = q_i \lambda_{ij} q_j \;\; \dot{M}(\mathbf{q}, \omega) = q_i \mathscr{M}_{ij}\,(\omega)\, q_j. \tag{12}$$

Here $\dot{G}(\mathbf{q})$ involves the thermal resistivity $\lambda_{ij}$ which is positive definite, and $\dot{M}(\mathbf{q}, \omega) = dM(\mathbf{q}, \omega)/dt$, with $M$ being the martingale modeling the random fluctuation according to (4). Clearly, the randomness residing in $M(\mathbf{d}, \omega)$ allows the total resistivity (and, hence, the total conductivity $\kappa_{ij} = \left(\lambda_{ij} + \mathscr{M}_{ij}\right)^{-1}$) to become negative since $\mathscr{M}_{ij}$ is not required to be positive definite, thus signifying the violations of the Second Law. More specifically, the second-rank tensor $\mathscr{M}_{ij} : \mathscr{V} \to \mathscr{V}$ (where $\mathscr{V}$ is a linear vector space) also is a second-order random field [12], such that

$$\mathscr{M}_{ij} : \mathscr{D} \times \Omega \to \mathscr{V}^2 \tag{13}$$

In view of the Gaussian character of fluctuations in Fig. 1, $\mathscr{M}_{ij}$ is a Gaussian random field.

Next, consider the evolution of energy in a spatial domain $\mathscr{D} \in \mathbb{R}^n$ ($n = 2$ or 3) having a boundary $\partial\mathscr{D} = \partial\mathscr{D}_q \cup \partial\mathscr{D}_T$ with both parts disjoint and such that $\partial\mathscr{D}_q$ is insulated and $\partial\mathscr{D}_T$ has a constant temperature prescribed on it:

$$\begin{array}{c} q_i n_i = 0 \quad \text{on} \quad \partial\mathscr{D}_q, \\ T = T_0 \quad \text{on} \quad \partial\mathscr{D}_T. \end{array} \tag{14}$$

Following [2], we observe from the energy balance that $u = -q_{i,i}$, and from the decomposition of entropy rate $\dot{s} = \dot{s}^{(r)} + \dot{s}^{(i)}$ (having the reversible part $\dot{s}^{(r)} = -(q_i/T)_{,i}$ and the irreversible part $\dot{s}^{(r)} = -q_i T_{,i}/T^2$) that $\dot{s} = -q_{i,i}/T$. Therefore,

$$\tfrac{d}{dt} \int_{\mathscr{D}} (u - T_0 s)\, dv = T_0 \int_{\mathscr{D}} \tfrac{q_i T_{,i}}{T^2} dv, \tag{15}$$

where the boundary conditions (14) have been employed. Noting, according to spontaneous violations of the Second Law mentioned in (11) and (12), that the scalar product $q_i T_{,i}$ takes random and possibly negative values, we cannot conclude that this is a Lyapunov function just like in diffusion systems obeying the Second Law considered in the aforementioned reference. It is upon taking the ensemble average of (15) that

$$\mathsf{E}\left\{\frac{d}{dt}\int_{\mathscr{D}} (u - T_0 s)\, dv\right\} = \mathsf{E}\left\{T_0 \int_{\mathscr{D}} \frac{q_i T_{,i}}{T^2} dv\right\} \leq 0 \tag{16}$$

which yields the Lyapunov function.

Interestingly, the result (17) does not depend on the heat conduction being linear. But, if that actually is the case (with $c$ being the specific heat capacity), the equation governing the temperature field is a stochastic partial differential one

$$\frac{\partial T}{\partial t} = \frac{1}{c}\left(\kappa_{ij}(\mathbf{x}, \omega)\, T_{,j}\right)_{,i}. \tag{17}$$

Next, upon ensemble averaging, the Clausius-Duhem inequality reduces to the condition of positive definiteness of the conductivity tensor $\kappa_{ij} = \lambda_{ij}^{-1}$ (with $\mathscr{M}_{ij} \to 0$), the second-order random field $\kappa_{ij}$ becomes a constant tensor field, and the diffusion equations for anisotropic and then isotropic homogeneous medium are obtained:

$$\frac{\partial T}{\partial t} = \frac{1}{c}\kappa_{ij} T_{,ji} \underset{\kappa_{ij}\to\kappa\delta_{ij}}{\to} \frac{\kappa}{c}\nabla^2 T. \tag{18}$$

# 5 Micropolar Fluid Model

## 5.1 Dissipation Functions

As noted in [6], the Cauchy stress tensor (i.e., the negative of the pressure tensor) generally lacks symmetry on length scales where the Second Law violations occur and this is the case with the molecular fluids. Indeed, the complete description of the hydrodynamics of molecular liquids must include angular momentum considerations and this challenge can naturally be met by using, instead of the classical (Cauchy) continuum, a micropolar continuum, Fig. 2a, b.

To have a micropolar model, a couple traction $m_i^{(n)} = \mu_{ji} n_j$ is introduced in addition to the Cauchy traction $t_i^{(n)} = \tau_{ji} n_j$ on a unit surface of the outer normal $n_i$; the body force and body torque as being unimportant to our considerations. The kinematics of the continuum point is described by the displacement $u_i$ and the microrotation $\varphi_i$; their time rates, respectively, are $v_i$ and $w_i$. Also, the intrinsic angular momentum per unit mass is $l_i = I_{ik} w_k$, where $I_{ik}$ is the microinertia; for an isotropic micropolar fluid $I_{ik} = I\delta_{ik}$, where $I$ is the microintertia of a continuum fluid particle. The balance equations are:

the conservation of mass

$$\frac{D\rho}{Dt} = -\rho v_{i,i} , \tag{19}$$

the conservation of linear momentum

$$\rho \frac{Dv_i}{Dt} = \tau_{ji,j} , \tag{20}$$

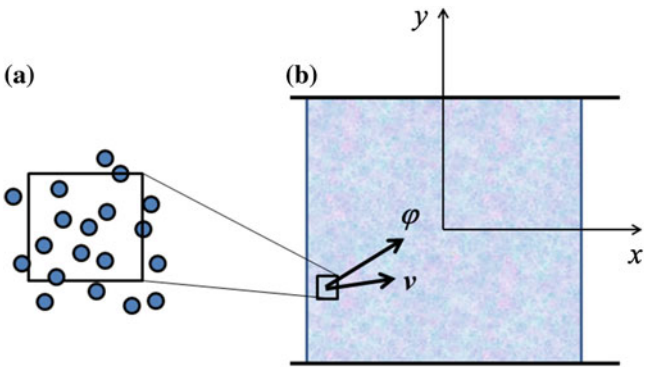


**Fig. 2** **a** Molecular fluid in which the stress tensor of continuum approximation is not symmetric; **b** $dV$ element of a micropolar continuum (with the velocity $v$ and microrotation $\varphi$ degrees of freedom) having spatial (and temporal) random field fluctuations. This is the basis for a study of Couette- or Poiseuille-type stochastic flow of a micropolar fluid in a channel

the conservation of angular momentum

$$\rho \frac{Dl_i}{Dt} = \mu_{ji},_j + e_{ijk}\tau_{jk}, \tag{21}$$

the conservation of internal energy

$$\rho \frac{Du}{Dt} = -q_i,_i + \tau_{ji}\left(v_i,_j - e_{kji}w_k\right) + \mu_{ji}w_i,_j + \rho g_i. \tag{22}$$

For an isotropic micropolar fluid $I_{ik} = I\delta_{ik}$, where $I$ is the microintertia of a continuum fluid particle. The special case of classical continuum mechanics is recovered when $\mu_{ji} = 0$, and $w_k = g_k = 0$.

In the presence of micropolar effects the constitutive equations are [11]

$$\begin{aligned}\tau_{ij} &= (-p + \lambda v_k,_k)\,\delta_{ij} + \mu\left(v_j,_i + v_i,_j\right) + \mu_r\left(v_j,_i - v_i,_j\right) - 2\mu_r e_{mij}w_m \\ \mu_{ij} &= c_0 w_k,_k\,\delta_{ij} + c_d\left(w_j,_i + w_i,_j\right) + c_a\left(w_j,_i - w_i,_j\right),\end{aligned} \tag{23}$$

where $\lambda$ and $\mu$ are the usual viscosity coefficients, $\mu_r$ is the dynamic microrotation viscosity, while $c_0$, $c_d$, and $c_a$ are the micropolar viscosity coefficients. Now, the governing equations (20)–(22) become

$$\rho \frac{Dv_i}{Dt} = -p,_i + (\lambda + \mu - \mu_r)\,v_j,_{ji} + (\mu + \mu_r)\,v_i,_{kk} + 2\mu_r e_{ijk}w_k,_j\,, \tag{24}$$

$$\rho I \frac{Dw_i}{Dt} = 2\mu_r\left(e_{mij}v_j,_i - 2w_i\right) + (c_0 + c_d - c_a)\,w_j,_{ji} + (c_d + c_a)\,w_i,_{kk}\,, \tag{25}$$

$$\rho \frac{Du}{Dt} = -q_i,_i - pv_i,_i + \rho\phi_{int}, \tag{26}$$

where $\phi_{int}$ is the intrinsic (i.e., fluid mechanical part of) dissipation function per unit mass, such that

$$\begin{aligned}\rho\phi_{int} = \lambda\left(v_{i,i}\right)^2 + 2\mu_{ij}d_{ij} + 4\mu_r\left(\frac{1}{2}e_{mij}v_{j,i} - w_i\right)^2 \\ + c_0\left(w_{i,i}\right)^2 + (c_d + c_a)\,w_{i,k}w_{i,k} + (c_d - c_a)\,w_{i,k}w_{k,i},\end{aligned} \tag{27}$$

where $d_{ij}$ is the deformation rate tensor. As discussed in [12], the intrinsic mechanical dissipation ($\phi_{int}$) is superposed with the thermal ($\phi_{th}$) dissipation

$$\phi = \phi_{int}\left[\left(v_i,_j - e_{kji}w_k\right), w_i,_j\,, \omega\right] + \phi_{th}(q_i, \omega). \tag{28}$$

Here the first two arguments of $\phi_{int}$ indicate its dependence on kinematic fields and its randomness and, similarly, the first argument of $\phi_{th}$ indicates its dependence on the heat flux. Furthermore, in the vein of probability theory, the $\omega$ parametrization (i.e. the third argument of $\phi_{int}$ and the second argument of $\phi_{th}$) indicate the stochastic character of these functionals. Thus

$$\phi\,(\mathbf{V},\omega) = \phi_{int}\,[\mathbf{V}_1,\mathbf{V}_2,\omega] + \phi_{th}(\mathbf{V}_3,\omega), \tag{29}$$

in which the velocity vector $\mathbf{V}$ has three components

$$\mathbf{V}_1 = \nabla\mathbf{v} - \mathbf{e}_j \times \mathbf{e}_i \cdot \mathbf{w}, \quad \mathbf{V}_2 = \nabla\mathbf{w}, \quad \mathbf{V}_3 = \mathbf{q}. \tag{30}$$

Corresponding to $\mathbf{V}$ there is the dissipative force $\mathbf{Y}$:

$$\mathbf{Y}_1 = \tau, \quad \mathbf{Y}_2 = \mu, \quad \mathbf{Y}_3 = -\frac{\nabla T}{T}. \tag{31}$$

Given the randomly occurring violations of the Second Law, just like in (4), the time integral of $\phi$ evolves as a submartingale: the entropy production inequality holds on average

$$\mathsf{E}\{\rho\,\phi(\mathbf{V},\omega)\} \geq 0. \tag{32}$$

By the Doob decomposition theorem, the submartingale is split into an increasing process and a martingale

$$\int_0^t \phi dt' = G + M \tag{33}$$

or, instantaneously,

$$\phi = \dot{G} + \dot{M}. \tag{34}$$

Clearly, $\dot{M}$ represents the microscale fluctuation, while $G$ represents the conventional (well-known) entropy growth. Thus, $\dot{G} \equiv dG/dt$ is identified with the average of the irreversible entropy rate ($\mathsf{E}\{s^{*(i)}\}$) and $\dot{M} \equiv dM/dt$ with its zero-mean random fluctuations. In terms of the irreversible entropy production, we have

$$\mathsf{E}\{s^{*(i)}\} = \dot{G}, \quad s^{*(i)} - \mathsf{E}\{s^{*(i)}\} = \dot{M}. \tag{35}$$

The fluid mechanics (intrinsic) part $\phi_{int}\,[\mathbf{V}_1,\mathbf{V}_2,\omega]$ of the random functional $\phi(\mathbf{V},\omega)$ is a superposition of two parts:

$$\phi_{int}(\mathbf{d},\omega) = \dot{G}(\mathbf{d}) + \dot{M}(\mathbf{d},\omega), \tag{36}$$

with the randomness residing in $M(\mathbf{d},\omega)$, and the viscosity coefficients assuring the positive-definiteness of $G$:

$$\begin{gathered} \mu \geq 0, \quad 3\lambda + 2\mu \geq 0, \\ c_d + c_a \geq 0,\ c_d + c_a \geq 0,\ 2c_d + 3c_0 \geq 0, \\ -(c_d + c_a) \leq c_d - c_a \leq (c_d + c_a)\,,\ \mu_r \geq 0. \end{gathered} \tag{37}$$

In general, the motion on microscale is turbulent. The micropolar fluid mechanics accounts for turbulence in terms of zero-mean perturbations about the means of both degrees of freedom ($\mathbf{v}$, $\mathbf{w}$) and pressure ($p$):

$$\begin{aligned} \mathbf{v} &= \overline{\mathbf{v}} + \mathbf{v}', \quad \overline{\mathbf{v}'} = 0, \\ \mathbf{w} &= \overline{\mathbf{w}} + \mathbf{w}', \quad \overline{\mathbf{w}'} = 0, \\ p &= \overline{p} + p', \quad \overline{p'} = 0. \end{aligned} \tag{38}$$

With reference to the analysis of Couette- and Poiseuille-type flows conducted in [10], we ask: Are non-zero microrotational disturbances $\mathbf{w}'$ possible for vanishing classical flow disturbances $\mathbf{v}'$? According to the analysis of steady parallel flows, assuming the conventional Second Law of thermodynamics holds, the answer is in the negative. However, given the spontaneous violations of the Second Law, non-zero fluctuations $\mathbf{w}'$ will also spontaneously appear (!) under imposed zero fluctuation field ($\mathbf{v}' = \mathbf{0}$) of the velocity field $\mathbf{v}$ [14].

## 5.2 *Upscaling from Stochastic to Deterministic Media*

As the spatial scale increases, the micropolar effects tend to vanish, and the fluid becomes classical Newtonian, so that only the first line of these inequalities remains relevant. As is well known, for incompressible response, the Newtonian fluid simplifies to a Navier–Stokes fluid in the special case of a vanishing bulk viscosity: $\lambda + \frac{2}{3}\mu \to 0$. The upscaling from the molecular level to stochastic and then deterministic continua involves the gradual replacement of field equations (20)–(22) by the equations of conventional continuum mechanics, whereby $\mu_{ji} = 0$ and $w_k = g_k = 0$, so that

$$\begin{aligned} &\text{conservation of linear momentum} && \rho\frac{Dv_i}{Dt} = \sigma_{ji},_j\,, \\ &\text{conservation of angular momentum} && e_{ijk}\sigma_{jk} = 0, \\ &\text{conservation of internal energy} && \rho\frac{Du}{Dt} = -q_i,_i + \sigma_{ji}d_{ji}. \end{aligned} \tag{39}$$

Note that, since $dV$ is a statistical volume element (SVE), not a representative volume element (RVE), the response depends on the type of loading. To this end, guided by the analogy to upscaling of a spatially random micropolar elastic continuum [18], we set up a homogenization condition of Hill-Mandel type for a micropolar fluid medium [a generalization of the Hill-Mandel condition]:

$$\overline{\sigma_{ij}d_{ij} + \beta_{ij}\alpha_{ij} + \mu_{ij}\dot{\kappa}_{ij}} = \overline{\sigma}_{ij}\,\overline{d}_{ij} + \overline{\beta}_{ij}\,\overline{\alpha}_{ij} + \overline{\mu}_{ij}\,\overline{\kappa}_{ij}\,, \tag{40}$$

where $\overline{f} \equiv \frac{1}{V} f dV$ denotes the volume average. The quantities appearing here are defined by first introducing decompositions of the generally non-symmetric velocity gradient $l_{ij}$ and the generally non-symmetric Cauchy stress $\tau_{ij}$ according to

$$l_{ij} = d_{ij} + \alpha_{ij}, \qquad \tau_{ij} = \sigma_{ij} + \beta_{ij}\,, \tag{41}$$

where $d_{ij}$ is the deformation rate and $\sigma_{ij}$ is the symmetric Cauchy stress.

$$\begin{aligned} d_{ij} = \tfrac{1}{2}(v_{i,j} + v_{j,i}), \qquad \alpha_{ji} = \tfrac{1}{2}(v_{i,j} - v_{j,i}) - e_{kij}\dot{\varphi}_k, \\ \sigma_{ij} = \tfrac{1}{2}(\tau_{ij} + \tau_{ji}), \qquad \beta_{ji} = \tfrac{1}{2}(\tau_{ij} - \tau_{ji}) \end{aligned} \tag{42}$$

Similar to the aforementioned reference, a computational study using molecular dynamics, under boundary conditions consistent with (40), will reveal the quantitative scaling of classical and micropolar viscosities in terms of the SVE size $\sqrt[n]{dV}$ in either $n = 2$ or 3 dimensions.

## 6 Conclusions

That "*the Second Law is of the nature of strong probability … not an absolute certainty*" was already recognized by J.C. Maxwell. However, it is only in the past two decades that statistical physics has come out in support of that statement. The fundamental fact is that there is a non-zero probability of negative entropy production rate on very small scales and (very) short times. To this end, the fluctuation theorem replaces the Second Law of thermodynamics (and Clausius-Duhem inequality) as a weaker (and stochastic) restriction to be placed on the dependent fields and material properties. In turn, this leads to a generalization of continuum (thermo)mechanics. Next, given the lack of symmetry of stress tensor on molecular scales, a stochastic micropolar fluid is proposed a more appropriate model of hydrodynamics on very small levels; consequences relating to fine scale turbulent motions and upscaling to a deterministic continuous medium are then reviewed. On the history of mechanics side, while finalizing this paper, the author became aware of the study [1], where a microcrack density function was modeled as a submartingale.

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## References

1. Augusti, G., Mariano, P.M.: Stochastic evolution of microcracks in continua. Comp. Meth. Appl. Mech. Eng. **168**, 155–171 (1999)
2. Ball, J.M.: Dynamical Systems and Energy Minimization. http://people.maths.ox.ac.uk/ball/Teaching/dynenergy2013.pdf (2014)
3. Doob, J.L.: Stochastic Processes. Wiley (1953)
4. Edelen, D.G.B.: Primitive thermodynamics: a new look at the Clausius-Duhem inequality. Int. J. Eng. Sci. **12** (1974)

5. Evans, D.J., Cohen, E.G.D., Morriss, G.P.: Probability of second law violations in steady states. Phys. Rev. Lett. **71** (1993)
6. Evans, D.J., Morriss, G.P.: Statistical Mechanics of Nonequilibrium Liquids. Cambridge University Press (2008)
7. Evans, D.J., Searles, D.J.: Equilibrium microstates which generate second law violating steady states. Phys. Rev. E **50**, 1645 (1994)
8. Evans, D.J., Searles, D.J.: The fluctuation theorem. Adv. Phys. **51**(7), 1529–1585 (2002)
9. Jarzynski, C.: Equalities and inequalities: irreversibility and the second law of thermodynamics at the nanoscale. Annu. Rev. Condens. Matter Phys. **2**, 329–351 (2011)
10. Liu, C.Y.: On turbulent flow of micropolar fluids. Int. J. Eng. Sci. **8**, 457–466 (1970)
11. Łukaszewicz, G.: Micropolar Fluids: Theory and Applications. Birkhäuser (1999)
12. Malyarenko, A., Ostoja-Starzewski, M.: Statistically isotropic tensor random fields: correlation structures. Math. Mech. Comp. Syst. (MEMOCS) **2**(2), 209–231 (2014)
13. Ostoja-Starzewski, M., Malyarenko, A.: Continuum mechanics beyond the second law of thermodynamics. Proc. R. Soc. A **470**, 20140531 (2014)
14. Ostoja-Starzewski, M.: Second law violations, continuum mechanics, and permeability, Continuum Mech. Thermodyn., in press (2015)
15. Reid, J.C., Brookes, S.J., Evans, D.J., Searles, D.J.: The dissipation function: its relationship to entropy production, theorems for nonequilibrium systems and observations on its extrema. In: Dewar, R.C., et al. (eds.) Beyond the Second Law, Understanding Complex Systems. Springer, Berlin (2014)
16. Searles, D.J., Evans, D.J.: Fluctuation theorem for heat flow. Int. J. Thermophys. **22**(1), 123–134 (2001)
17. Seifert, D.J.: Stochastic thermodynamics, fluctuation theorems and molecular machines. Rep. Prog. Phys. **75**, 126001 (58pp) (2001)
18. Trovalusci, P., Ostoja-Starzewski, M., de Bellis, M.L., Muralli, A.: Scale-dependent homogenization of random composites as micropolar continua. Europ. J. Mech./A: Solids **49**, 396–407 (2014)
19. Wang, G.M., Sevick, E.M., Mittag, E., Searles, D.J., Evans, D.J.: Experimental demonstraiton of violations of the second law of thermodynamics for small systems and short time scales. Phys. Rev. Lett. **89**, 050601 (2002)
20. Ziegler, H., Wehrli, C.: The derivation of constitutive relations from the free energy and the dissipation functions. Adv. Appl. Mech. **25**, 183–238 (1987)