Continuum Mechanics beyond the Second Law of Thermodynamics

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[*Proc. R. Soc. A*, 2014; *Cont. Mech. Thermodyn.*, 2015]

[NSF: CMMI-1030940, CMMI-1462749]

Balance (conservation) laws of continuum mechanics

- mass
- linear momentum
- angular momentum
- energy

- second law of thermodynamics

$$\dot{S} = \dot{S}^{(r)} + \dot{S}^{(i)} \quad \text{with} \quad \dot{S}^{(r)} = \dot{Q} / T, \quad \dot{S}^{(i)} \geq 0.$$

reversible

irreversible

provides restrictions on admissible forms of constitutive relations

Physics: entropy production may be negative on short time and v. small space scales

up to 3 sec. in cholesteric liquids…!

- D.J. Evans, E.G.D. Cohen & G.P. Morriss (1993). Probability of second law violations in steady states, *Phys. Rev. Lett*. **71(15**), 2401-2404
- D.J. Evans & D.J. Searles, D.J. (1994). Equilibrium microstates which generate second law violating steady states, *Phys. Rev. E* **50(2**), 1645-1648
- D.J. Evans & D.J. Searles, D.J. (2002). The fluctuation theorem, *Adv. Phys.* **51**(7), 1529-1585
- G.M. Wang, E.M. Sevick, E. Mittag, D.J. Searles & D.J. Evans (2002), Experimental demonstration of violations of the second law of thermodynamics for small systems and short time scales, *Phys. Rev. Lett.* **89**, 050601
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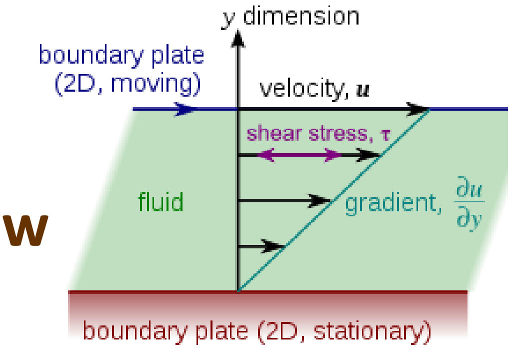
Maxwell: “*the second law is of the nature of strong probability … not an absolute certainty*”

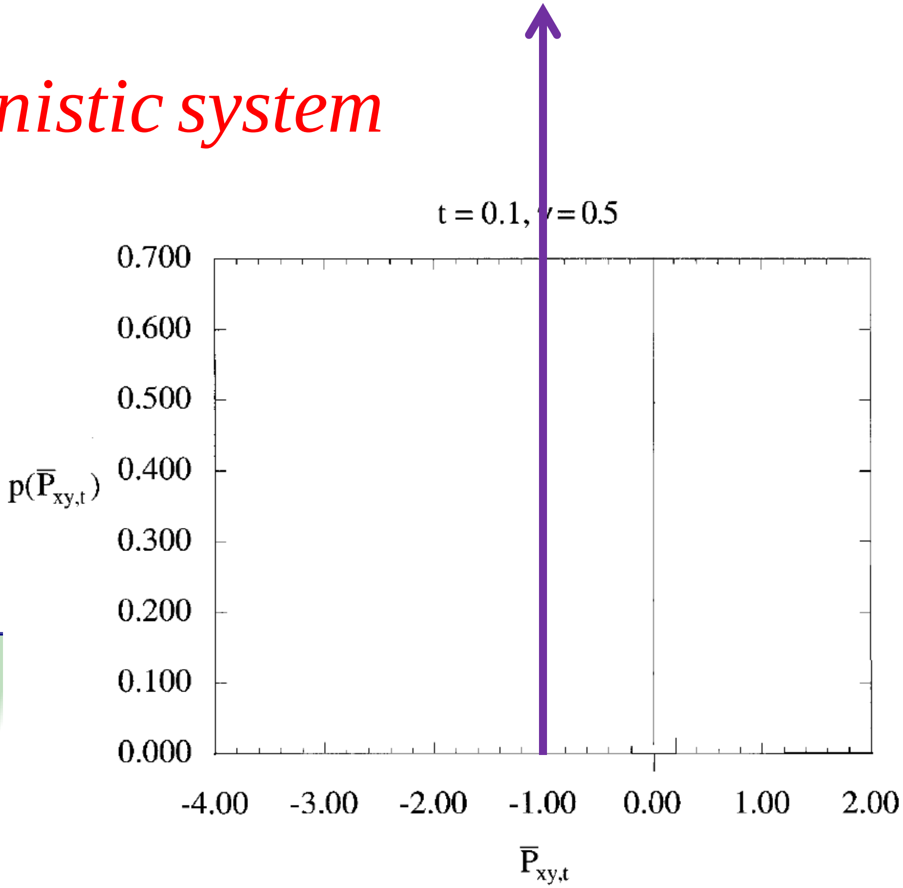
$\Rightarrow$ need to revise thermodynamics of continuum mechanics

- modify the Clausius-Duhem inequality
- stochastic continuum thermomechanics
  - fluctuation theorem in place of 2nd law
  - entropy = submartingale
  - random fields
- applications in presence of 2nd law violations:
  - permeability
  - acceleration wave
  - micropolar fluid mechanics
  - Lyapunov function in stochastic diffusion

in a deterministic system

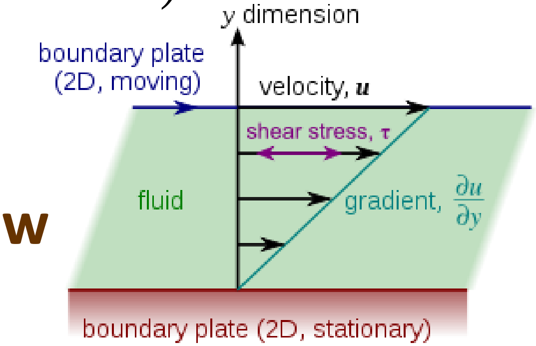
Couette flow

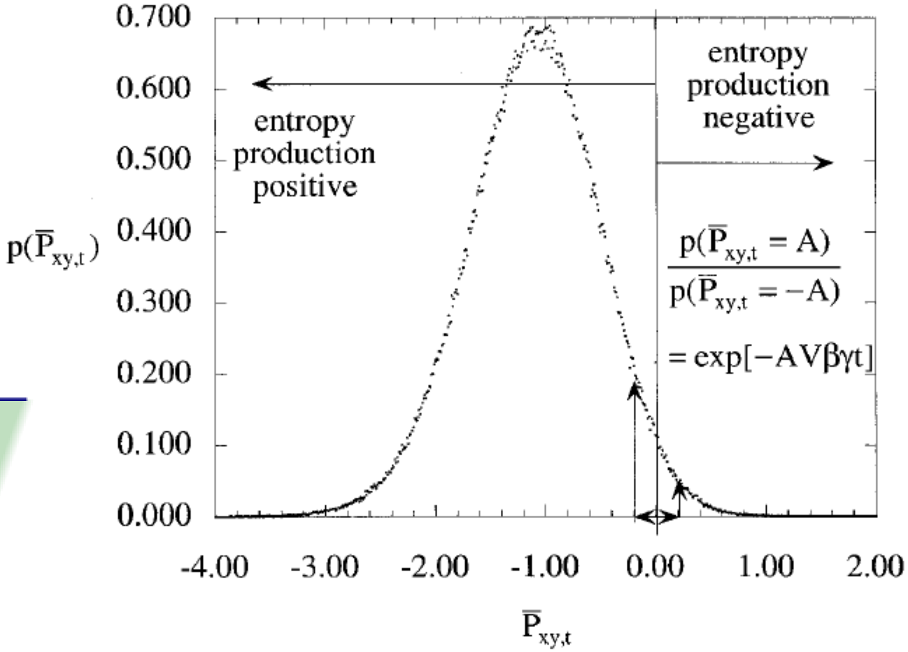




$$\frac{\mathrm{P}\left(\phi_t = A \pm dA\right)}{\mathrm{P}\left(\phi_t = -A \pm dA\right)} = e^{-At}$$

Couette flow



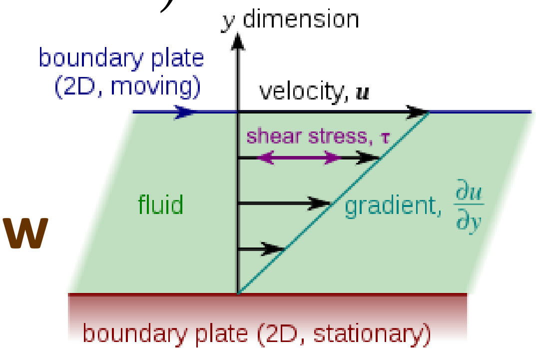


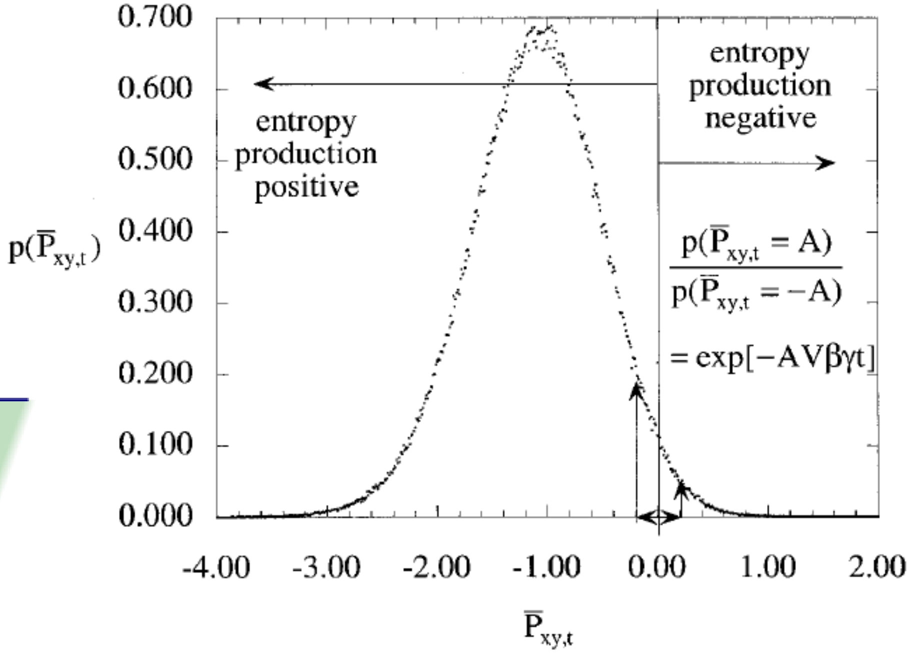
there exist fluctuations in shear stress for a molecular system in Couette flow

fluctuation theorem in place of 2nd law

$$\frac{\mathrm{P}\left(\phi_t = A \pm dA\right)}{\mathrm{P}\left(\phi_t = -A \pm dA\right)} = e^{-At}$$

Couette flow





an estimate of the relative probability of observing processes that have positive and negative total dissipation in non-equilibrium systems

"*In either the large system or long time limit the Steady State Fluctuation Theorem predicts that the Second Law will hold absolutely and that the probability of Second Law violations will be zero*." [Evans & Searles, 2002]

fluctuation theorem $\Rightarrow$

$$\mathrm{E}\{s^{(i)}(t+\Delta t) \,|\, \underset{history}{s^{(i)}(t)}\} \geq s^{(i)}(t)$$

in place of

$$s^{(i)}(t+\Delta t) \geq s^{(i)}(t)$$

(2nd law axiom in conventional thermodynamics and continuum theories)

… which random process can model the entropy evolution ?

- Markov process
- Processes homogeneous in time
  - wide-sense, or
  - narrow-sense
- Gaussian processes
- Martingale … $\mathbb{E}\{X(t+\Delta t)\,|\,\text{past}\} = X(t)$
- …

fluctuation theorem $\Rightarrow$

$$\mathbb{E}\{s^{(i)}(t+\Delta t) \mid \underset{history}{s^{(i)}(t)}\} \geq s^{(i)}(t)$$

in place of

$$s^{(i)}(t+\Delta t) \geq s^{(i)}(t)$$

$\Rightarrow$ irreversible entropy is a *submartingale*

[O-S & Malyarenko, *Proc. R. Soc. A*, 2014]

Doob decomposition $\Rightarrow \quad s^{(i)} = M_t + G_t$

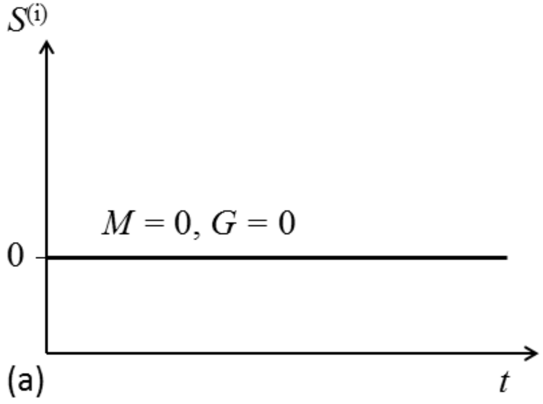
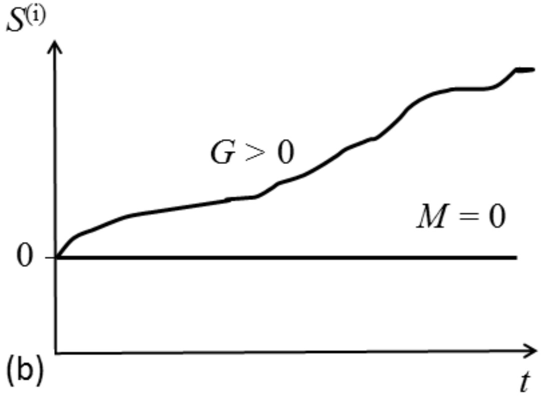
martingale

increasing process

$$E\{M(t+dt)\,|\,\text{past}\} := M(t)$$

(weakly monotonic f'n)

$\Rightarrow$ four distinct interpretations in continuum thermomechanics

	conservative phenomena	**quasi-conservative/dissipative phenomena**
continuum mechanics		

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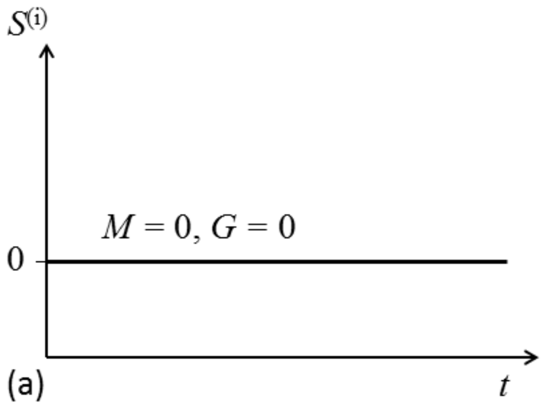
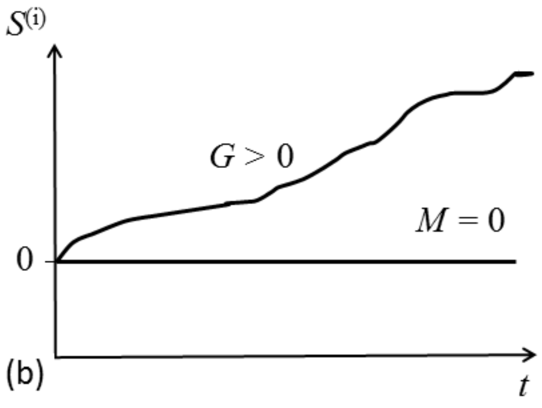
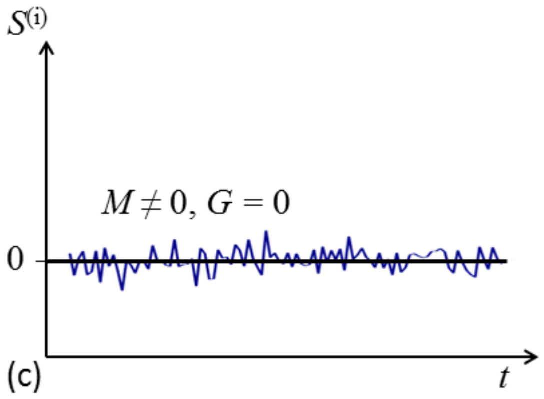
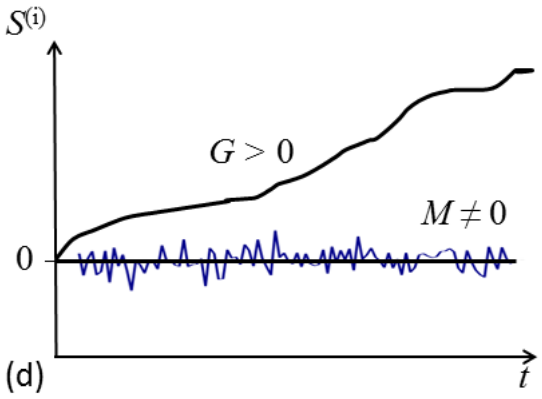
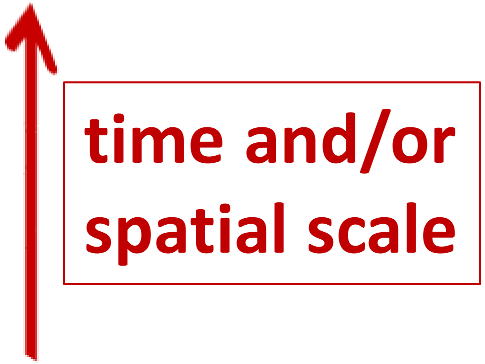
continuum mechanics		
statistical physics		



time and/or spatial scale

levels of thermodynamic models

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Drucker's Stability Postulate	• a classification only • many counterexamples (conceptual models and experiments)

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Second Law of Thermodynamics	• almost universally accepted as true • ... some materials (models and experiments) on very small time and space scales fall outside of it
fluctuation theorems	• account for negative entropy production

Fluctuation Theorems

Quantify probabilities of violations of Second Law

Are verifiable in laboratory

Can be used to derive the linear transport coefficients of, say, Navier-Stokes fluids (Green-Kubo relations)

Valid in nonlinear regime, far from equilibrium

… Stochastic thermomechanics

$$\psi\left(T,\varepsilon_{ij}\right)=u\left(s,\varepsilon_{ij}\right)-sT \qquad \sigma_{ij}^{(d)}d_{ij}-q_k\frac{T,_k}{T}=\rho\phi\geq 0$$

free energy

dissipation function

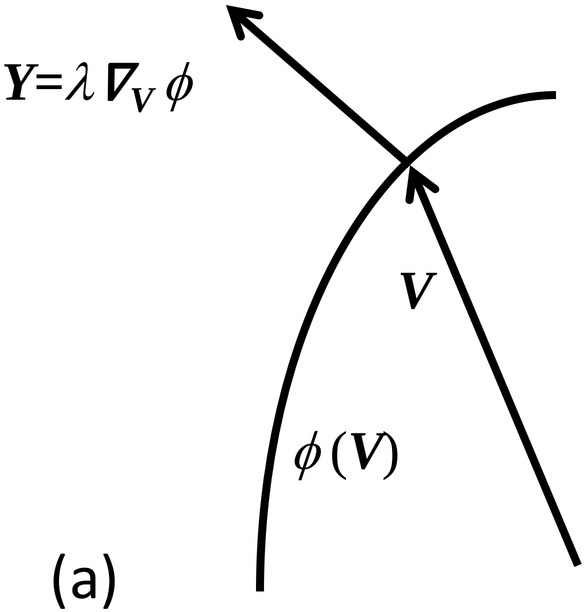
stochastic

$$\mathbf{Y}\cdot\mathbf{V}=\rho\ \phi(\mathbf{V},\omega)\geq 0 \quad \text{where} \quad \phi(\mathbf{V},\omega)=\phi_{\text{int}}(\mathbf{d},\omega)+\phi_{\text{th}}(\mathbf{q},\omega)$$

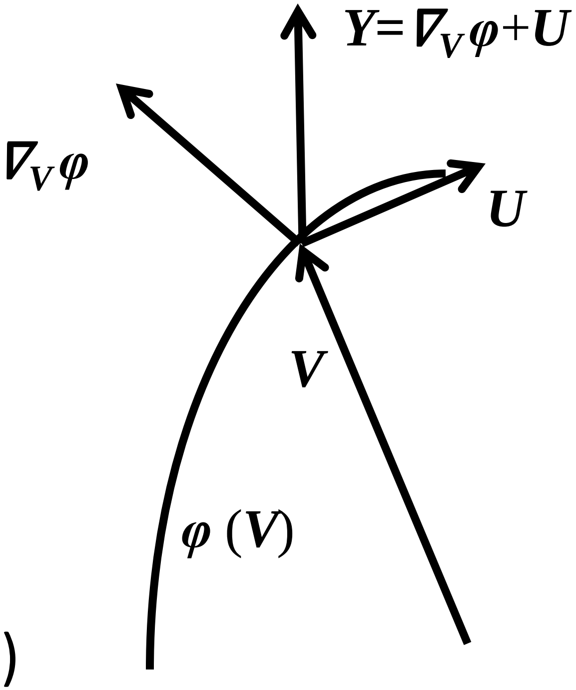
velocities $\mathbf{V}=\{d_{ij},\ T,_k\}$

dissipative forces $\mathbf{Y}=\{\sigma_{ij}^{(d)},\ \ -q_k/T\}$

$\Rightarrow$ Stochastic thermomechanics with internal variables (TIV)



(a)



(b)

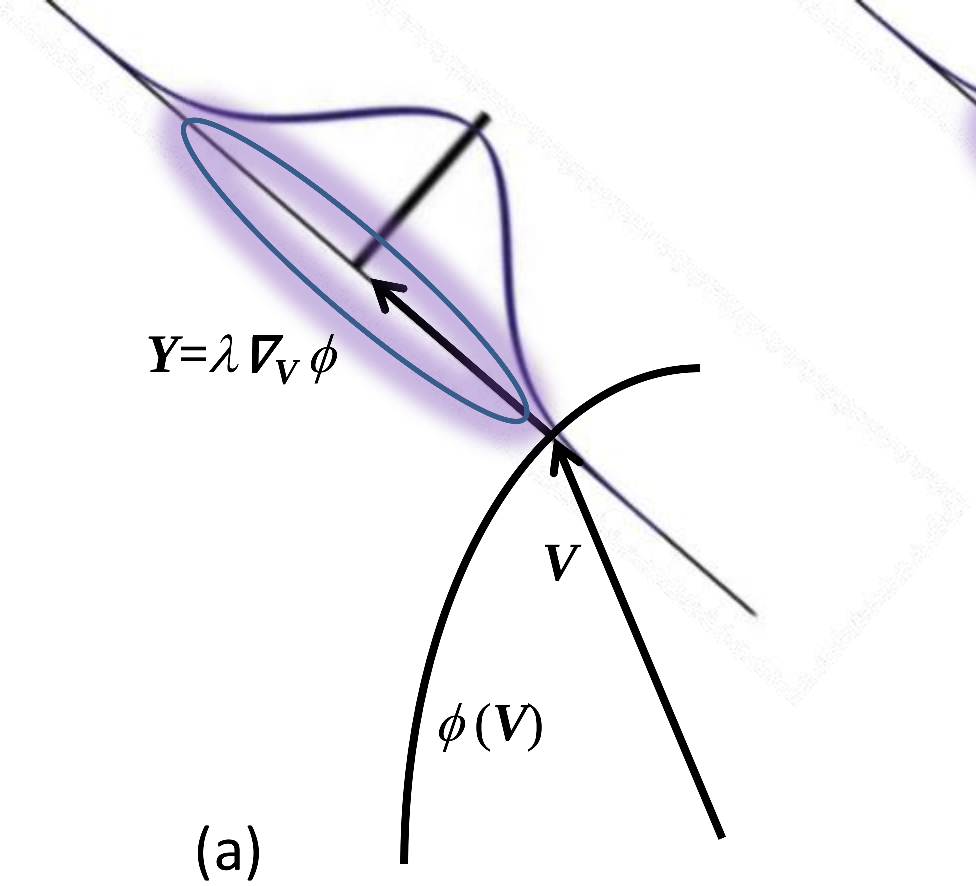
Thermodynamic Orthogonality
via convex analysis

Primitive Thermodynamics
with powerless vector
via Poincaré’s lemma

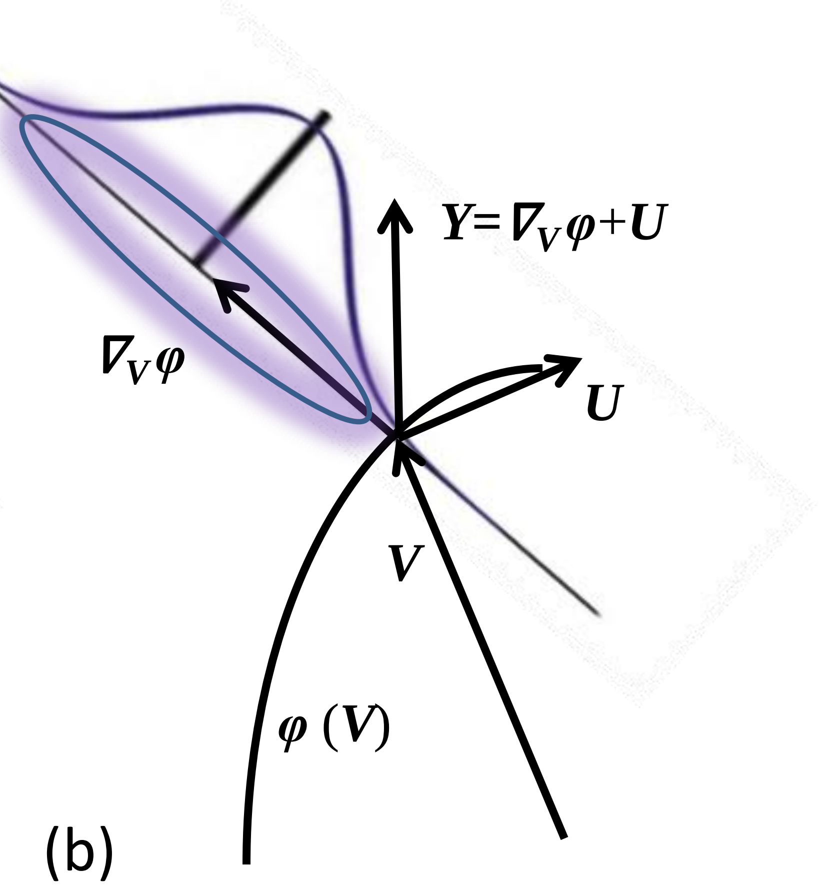
… or via maximum entropy in statistical physics:

Dewar (2005)

O-S & Zubelewicz
[*J. Phys. A: Math. Theor.* (2011)]

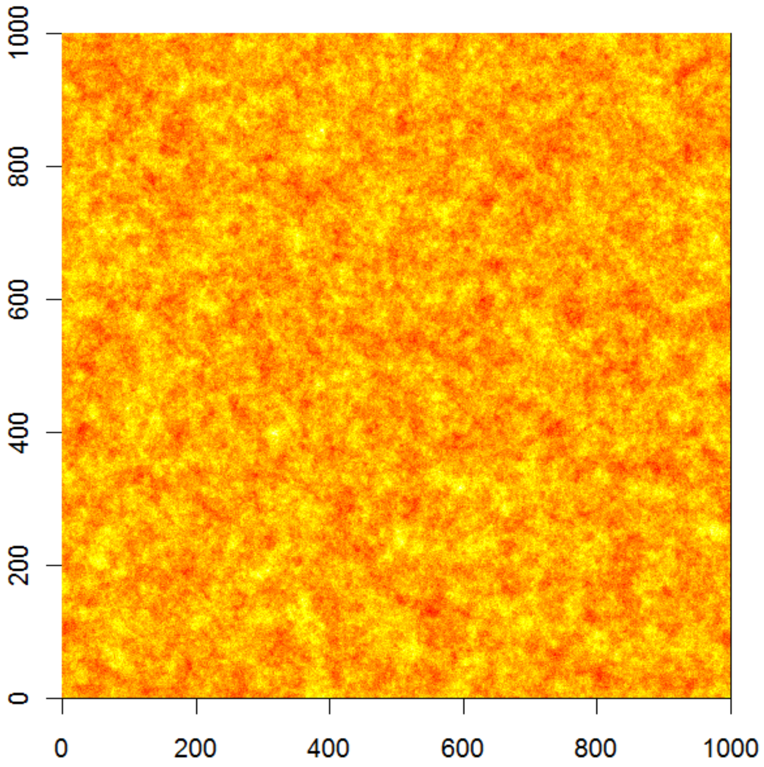


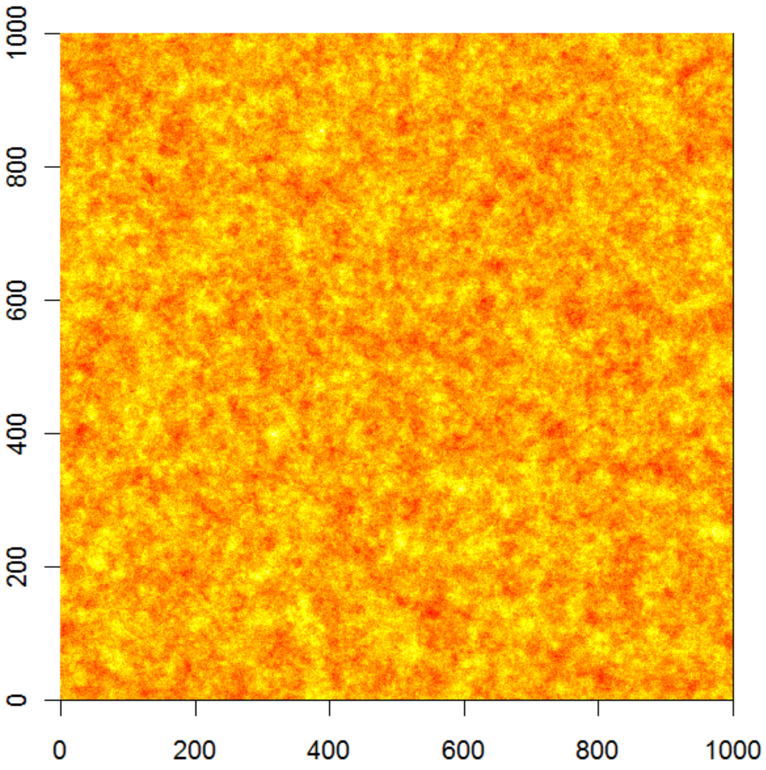
Thermodynamic Orthogonality
stochastic



Primitive Thermodynamics
w/ powerless vector **stochastic**

Martingale fluctuations in 2d: random fields

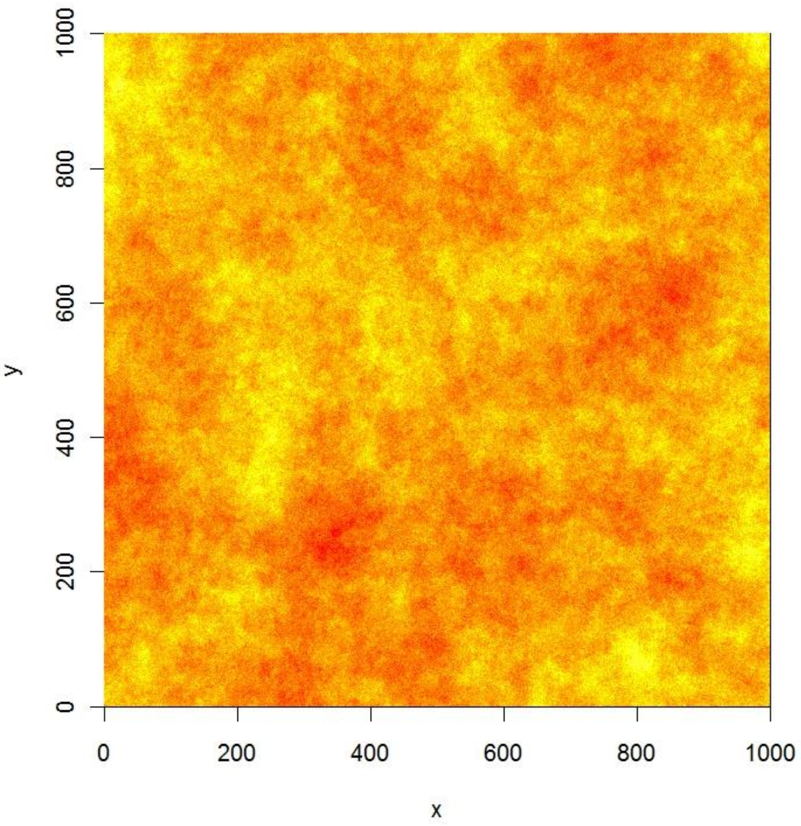


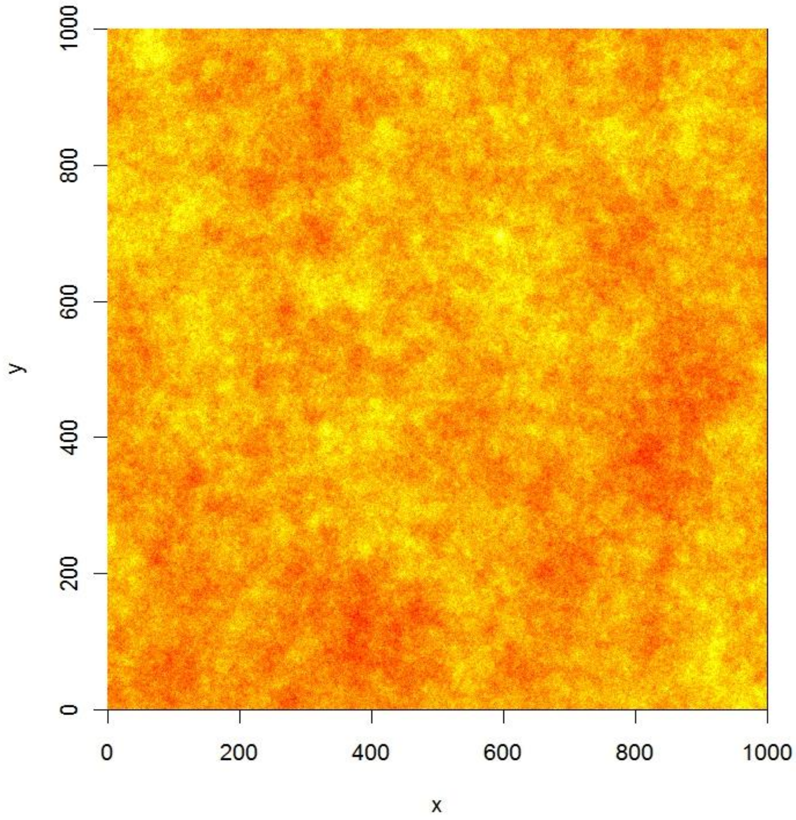


RFs with exponential or Gaussian correlation functions

$$C(x) = \exp[-Ax^{\alpha}], \quad A > 0, \quad 0 < \alpha \leq 2$$

Martingale fluctuations in 2d: random fields





RFs with fractal + Hurst effects

Cauchy

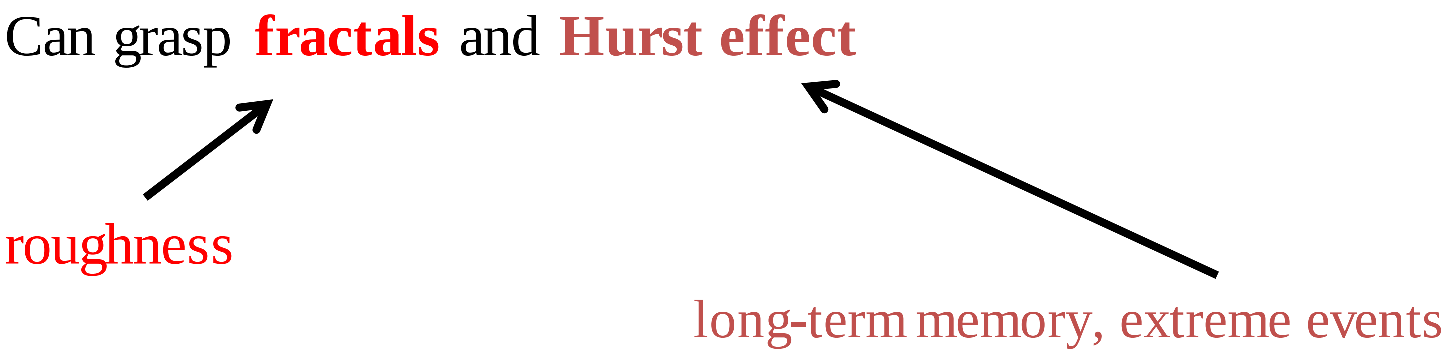
$$C_{\mathbf{C}}(r;\alpha,\beta):=\left(1+r^{\alpha}\right)^{-\beta/\alpha},$$

$\beta > 0$ $\quad 0 < \alpha \le 2$

Dagum

$$C_{\mathbf{D}}(r;\beta,\gamma):=1-\left(1+r^{-\beta}\right)^{-\gamma/\beta},$$

$\gamma < 7\beta$ $\quad \beta^2 + \beta(5\gamma - 7) + \gamma < 0$



Can grasp **fractals** and **Hurst effect**

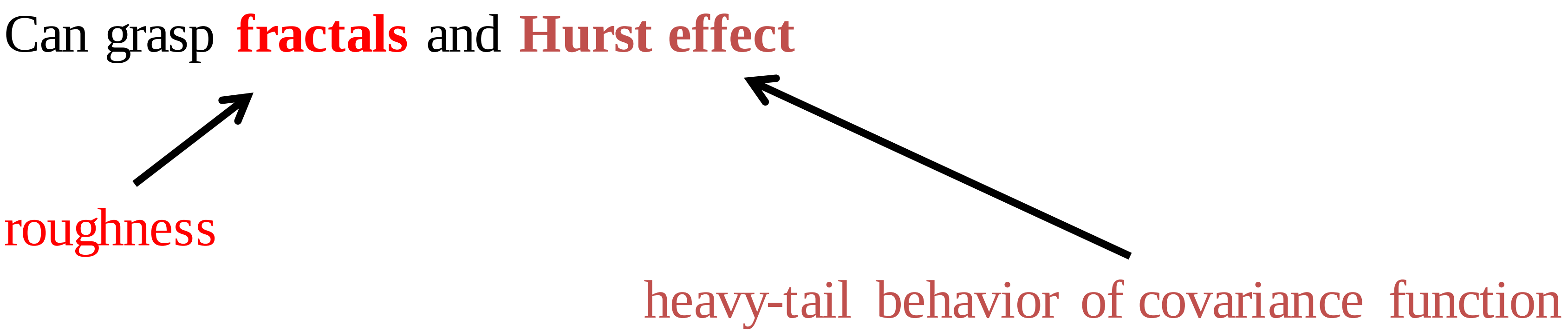
roughness

long-term memory, extreme events

$0 < H < 0.5$: time series with negative autocorrelation (a decrease between values will likely be followed by an increase)

$H = 0.5$: true random walk, w/o preference for a decrease or increase following any particular value

$0.5 < H < 1$: time series with positive autocorrelation (an increase between values followed by another increase)



Can grasp **fractals** and **Hurst effect**

roughness

heavy-tail behavior of covariance function

A random process Z_x is statistically self-similar if it obeys $Z_x = c^{-H} Z_{cx}$ for some constant c, where H is known as the *Hurst parameter*

- Crudely: when stretched by some factor c in x dimension, Z looks the same if stretched by c^{-H} in the Z dimension
- Most time series Z_t look “flat” if stretched like this

Acceleration waves in 1D media $\alpha \equiv \left[\left[a\right]\right] = a_2 - a_1$

Bernoulli equation

in deterministic medium: $$\frac{d\alpha}{dt} = -\mu\alpha + \beta\alpha^2$$

dissipation

elastic nonlinearity

competition

$\Rightarrow$ *critical amplitude* $$\alpha_c = \frac{\mu}{\beta}$$

$\Rightarrow$ *time to blow-up* $$t_\infty = -\frac{1}{\mu}\ln(1 - \frac{\mu}{\beta\alpha_0})$$

Acceleration waves with nanoscale wavefront thickness

$$\alpha \equiv \left[\left[a\right]\right] = a_2 - a_1$$

Bernoulli equation

in random medium:

$$\frac{d\alpha}{dt} = -\mu\alpha + \beta\alpha^2$$

dissipation

elastic nonlinearity

stochastic competition!

$\Rightarrow$ *critical amplitude* $\alpha_c \neq \dfrac{\mu}{\beta}$ random

$\Rightarrow$ *time to blow-up* $t_\infty \neq -\dfrac{1}{\mu}\ln(1-\dfrac{\mu}{\beta\alpha_0})$ random

Acceleration waves with nanoscale wavefront thickness

$$\alpha \equiv \left[\left[a\right]\right] = a_2 - a_1$$

Bernoulli equation

in random medium:

$$\frac{d\alpha}{dt} = -\mu\alpha + \beta\alpha^2$$

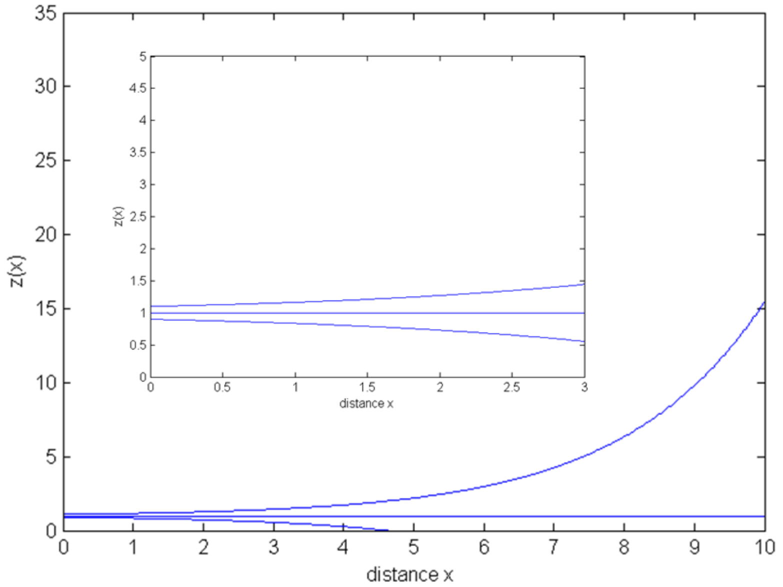
$\Rightarrow$ stochastic dynamical system driven by random viscosity G_0'

$$\frac{d\alpha}{dx} = \frac{G_0'\rho_R^{1/2}}{2G_0^{3/2}}\alpha - \frac{\rho_R E_0}{2G_0^2}\alpha^2$$

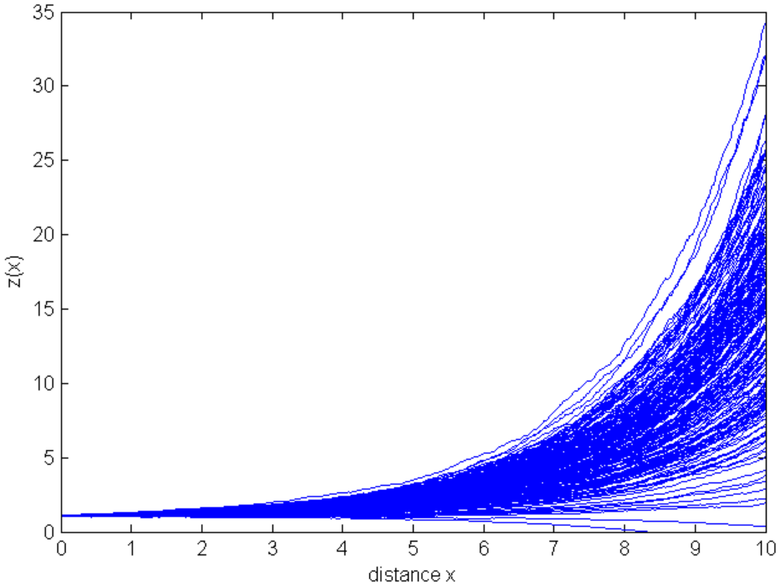
$$G_0' = \mathsf{E}\{G_0'\} + S\xi,$$

Start with Stratonovich interpretation of this stochastic differential equation

Work in terms of $z{:}=1/\alpha$



deterministic/homogeneous medium



random medium

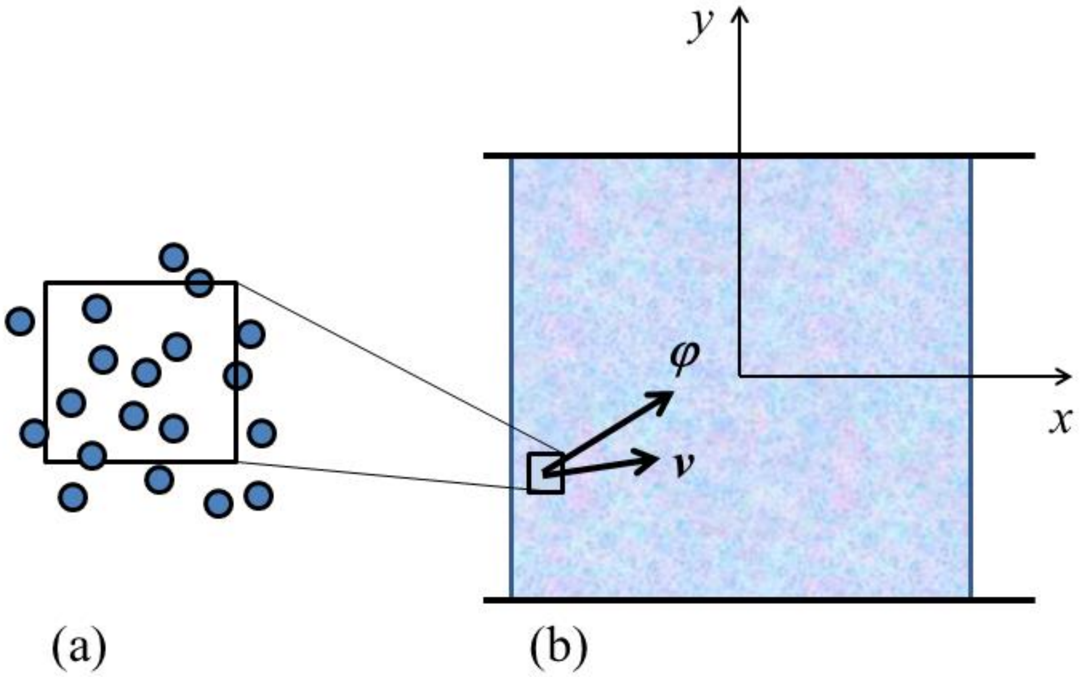
- Since the dissipation may become negative, the wave that started at the initial amplitude $\alpha_0 < \alpha_c$ can actually blow-up instead of exponentially die off.

- The blow-up event becomes impossible as the wavefront thickness gets larger.

- Taking other spatial correlations of the random field viscosity than white-noise does not fundamentally change the results.

In general, the motion on microscale is turbulent

- Are non-zero microrotational disturbances $\mathbf{w}'$ possible for vanishing classical flow disturbances $\mathbf{v}'$?



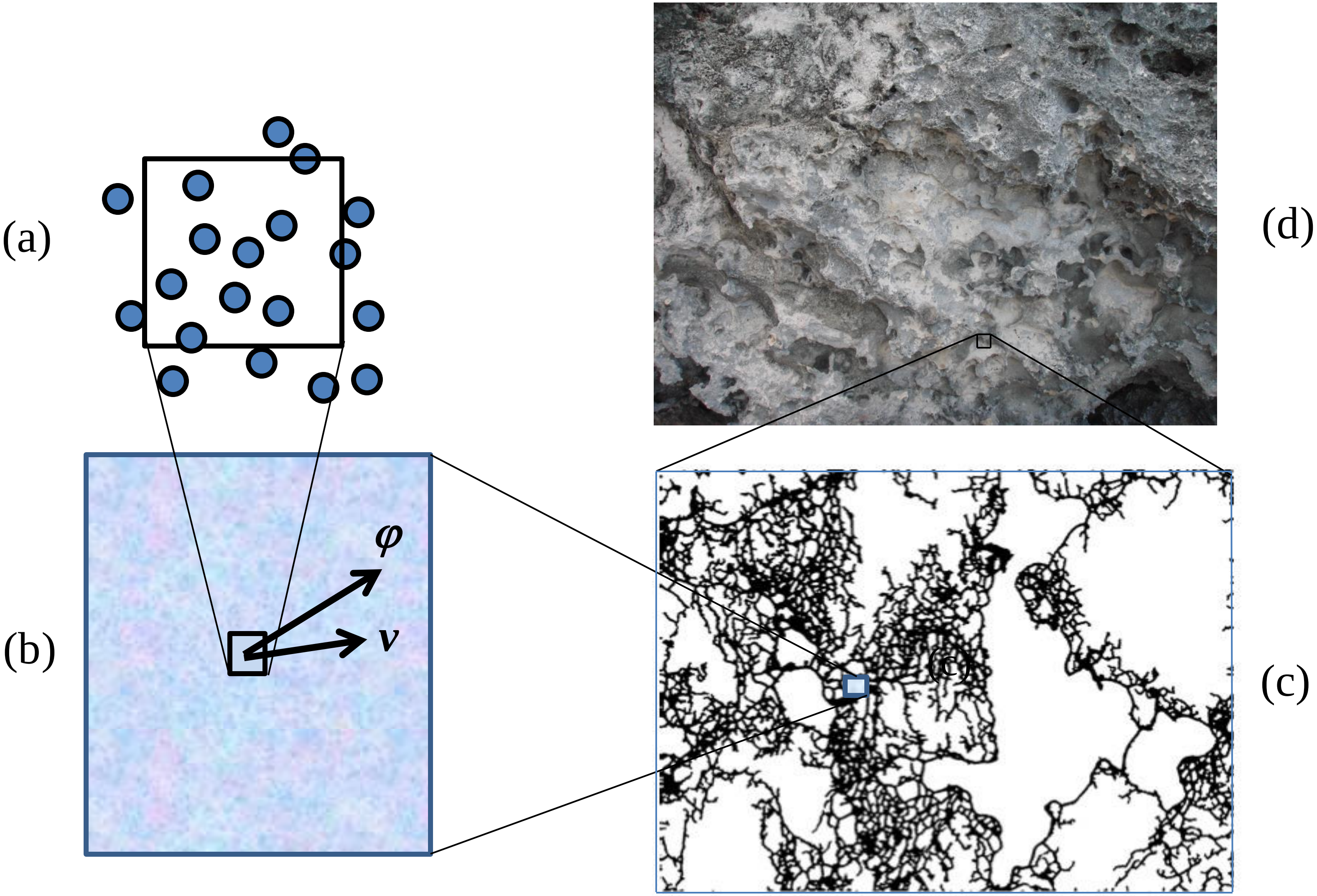
$$\mathbf{v} = \bar{\mathbf{v}} + \mathbf{v}', \qquad \overline{\mathbf{v}'} = 0,$$

$$\mathbf{w} = \bar{\mathbf{w}} + \mathbf{w}', \qquad \overline{\mathbf{w}'} = 0,$$

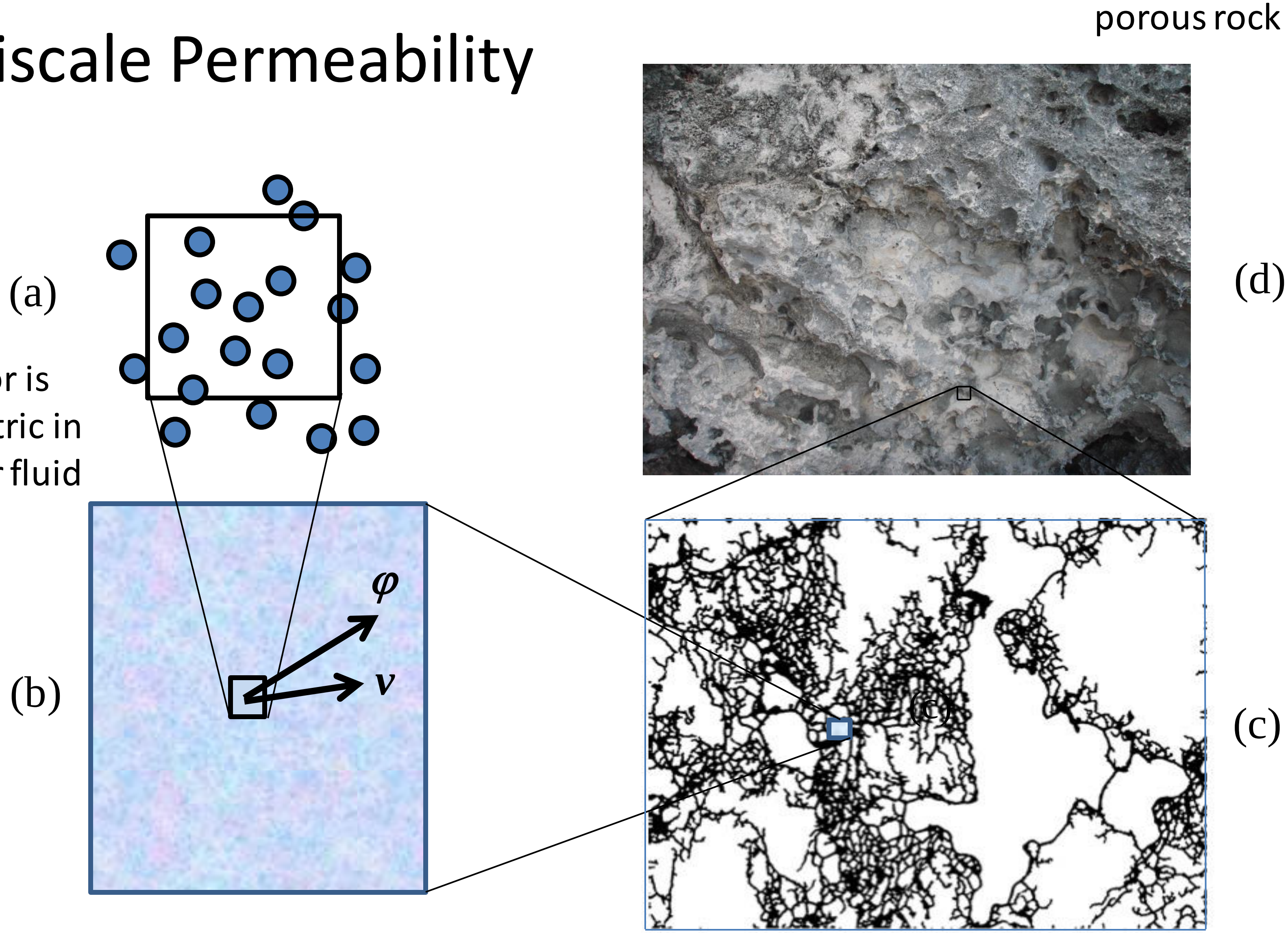
$$p = \bar{p} + p', \qquad \overline{p'} = 0.$$

- According to the analysis of steady parallel flows (Liu, 1970), assuming the conventional Second Law holds, **No**.

- In light of the Fluctuation Theorem, non-zero microrotational disturbances <u>may spontaneously arise</u>, … but not on average.


(a)
(b)
φ
v
(d)
(c)
(c)

Multiscale Permeability



stress tensor is not symmetric in a molecular fluid

dV element of micropolar continuum (with velocity v and microrotation φ DOFs) having random field fluctuations

(fractal) porous network within which the micropolar fluid flow takes place

Balance equations of micropolar fluids

$$\frac{D\rho}{Dt} = -\rho v_i,_i$$

$$\rho \frac{Dv_i}{Dt} = \tau_{ji},_j + \rho f_i$$

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

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

classical continuum mechanics is recovered for: $\mu_{ji} = 0 \quad w_k = g_k = 0$

Balance equations of micropolar fluids

linear viscous fluid model (generalizes Navier-Stokes)

$$\tau_{ij} = \left(-p + \lambda v_{k},_{k}\right)\delta_{ij} + \mu\left(v_{j},_{i} + v_{i},_{j}\right) + \mu_r\left(v_{j},_{i} - v_{i},_{j}\right) - 2\mu_r e_{mij} w_m$$

$$\mu_{ij} = c_0 w_{k},_{k}\,\delta_{ij} + c_d\left(w_{j},_{i} + w_{i},_{j}\right) + c_a\left(w_{j},_{i} - w_{i},_{j}\right)$$

$$\rho\frac{Dv_i}{Dt} = -p,_{i} + \left(\lambda + \mu - \mu_r\right)v_{j},_{ji} + \left(\mu + \mu_r\right)v_{i},_{kk} + 2\mu_r e_{ijk} w_{k},_{j}$$

$$\rho\frac{Dl_i}{Dt} = 2\mu_r\left(e_{mij} v_{j},_{i} - 2w_i\right) + \left(c_0 + c_d - c_a\right)w_{j},_{ji} + \left(c_d + c_a\right)w_{i},_{kk}$$

$$\rho\frac{Du}{Dt} = -q_{i},_{i} - p v_{i},_{i} + \rho\phi_{\text{int}}$$

$$\rho\phi_{int} = \lambda(v_{i,i})^2 + 2\mu d_{ij}d_{ij} + 4\mu_r\left(\tfrac{1}{2}e_{mij}v_{j,i} - w_i\right)^2$$
$$+c_0(w_{i,i})^2 + (c_d + c_a)w_{i,k}w_{i,k} + (c_d - c_a)w_{i,k}w_{k,i},$$

intrinsic
dissipation function

Hold on average:

$$\mu \geq 0, \quad 3\lambda + 2\mu \geq 0,$$

$$c_d + c_a \geq 0, \quad c_d + c_a \geq 0, \quad 2c_d + 3c_0 \geq 0,$$

$$-(c_d + c_a) \leq c_d - c_a \leq (c_d + c_a), \quad \mu_r \geq 0.$$

Thermodynamic orthogonality:
… from a molecular fluid to a continuum

$$\varphi_{\mathrm{int}}(\mathbf{d},\omega) = \dot{G}(\mathbf{d}) + \dot{M}(\mathbf{d},\omega)$$

$$\dot{G} = 2\mu d'_{(2)}, \qquad \sigma_{ij}^{(q)} = -p\delta_{ij}, \qquad \sigma_{ij}^{(d)} = 2\mu d'_{ij}$$

for Fourier-type heat conduction

Primitive thermodynamics:
… from a molecular fluid to a continuum

$$\mathbf{Y} = \nabla_{\mathbf{V}}\varphi(\mathbf{V},\mathbf{w}) + \mathbf{U}(\mathbf{V},\mathbf{w})$$

$$\mathbf{V}\cdot\mathbf{U} = 0, \quad \mathbf{U}\left(\mathbf{0},\mathbf{w}\right) = \mathbf{0}$$

$$\mathbf{Y} = [\boldsymbol{\sigma}^{(d)}, -\frac{\nabla T}{T}, -\nabla_{\mathbf{q}}\psi], \quad \mathbf{V} = [\mathbf{d},\mathbf{q},\dot{\mathbf{q}}], \quad \mathbf{U} = \left[\mathbf{u}_1,\mathbf{u}_2,\mathbf{u}_3\right]$$

for Maxwell-Cattaneo heat conduction

Violations of second law in diffusion problems

e.g. in heat conduction [Searles DJ, Evans DJ (2001) Fluctuation theorem for heat flow. *Int. J. Thermophys.* **22**(1), 123-134]

RFs of internal energy and entropy:

$$u : \mathcal{D} \times T \times \Omega \to \mathbb{R}, \qquad s : \mathcal{D} \times T \times \Omega \to \mathbb{R},$$

Second Law on average:

$$\mathsf{E}\{\phi|\mathcal{F}_n\} \geq 0, \qquad \phi = T\dot{s}^{(i)} = -q_k \frac{T,_k}{T} \equiv -\mathbf{q} \bullet \frac{\nabla T}{T}.$$

$$\phi : \mathcal{D} \times T \times \Omega \to \mathbb{R}.$$

Dissipation function:

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

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

$$\mathbf{M}_{ij} : \mathbf{D} \times \Omega \to \mathbf{V}^2$$

Violations of second law in diffusion problems

in heat conduction
on finite domain:

$$q_i n_i = 0 \quad \text{on} \quad \partial\mathbf{D}_q$$
$$T = T_0 \quad \text{on} \quad \partial\mathbf{D}_T$$

$$\Rightarrow \quad \frac{d}{dt}\int_{\mathbf{D}}\left(u - T_0 s\right)dv$$
$$= \int_{\mathbf{D}}\left(\frac{T_0}{T} - 1\right)q_i,_i\, dv$$
$$= \int_{\mathbf{D}}\left[\left(\left(\frac{T_0}{T} - 1\right)q_i\right),_i + T_0\frac{q_i T,_i}{T^2}\right]dv$$
$$= \int_{\mathbf{D}}\left(\frac{T_0}{T} - 1\right)q_i n_i dS + T_0\int\frac{q_i T,_i}{T^2}dv$$
$$= T_0\int_{\mathbf{D}}\frac{q_i T,_i}{T^2}dv$$

$$\Rightarrow \quad \mathrm{E}\left\{\frac{d}{dt}\int_{\mathcal{D}}(u - T_0 s)dv\right\} = \mathrm{E}\left\{T_0\int_{\mathcal{D}}\frac{q_i T,_i}{T^2}dv\right\} \leq 0$$

$\Rightarrow$ Lyapunov function: $V = \mathrm{E}\left\{T_0\int_{\mathcal{D}}\frac{q_i T,_i}{T^2}dv\right\} \leq 0$

if SL holds: $\dfrac{\partial T}{\partial t} = \dfrac{1}{c}\left(\kappa_{ij}\left(\mathbf{x},\omega\right)T,_j\right),_i$ $\qquad$ $\dfrac{\partial T}{\partial t} = \dfrac{1}{c}\kappa_{ij}T,_{ji} \underset{\kappa_{ij}\to\kappa\delta_{ij}}{\to} \dfrac{\kappa}{c}\nabla^2 T.$

How can axioms of thermomechanics admit negative entropy production?

Fundamental role in physics is played by free energy and dissipation function.

That role is not played - as classically done in rational continuum mechanics – by the quartet of stress σ, heat flux q, free energy ψ, and entropy s.

… a very wide range of continuum constitutive behaviors may be derived from thermomechanics with internal variables (TIV)

… fundamentally based on the free energy and dissipation functions.

Axiom of Determinism is to be replaced by Axiom of Causality: "*The future state of the system depends solely on the probabilities of events in the past*"

or "*the probability of subsequent events can be predicted from the probabilities of finding initial phases and a knowledge of preceding changes in the applied field and environment of the system*."

Fluctuation Theorem (FT) is derived from the Axiom of Causality.

Second Law is obtained as a special case of FT.

Eventually, this justifies the Axiom of Determinism.

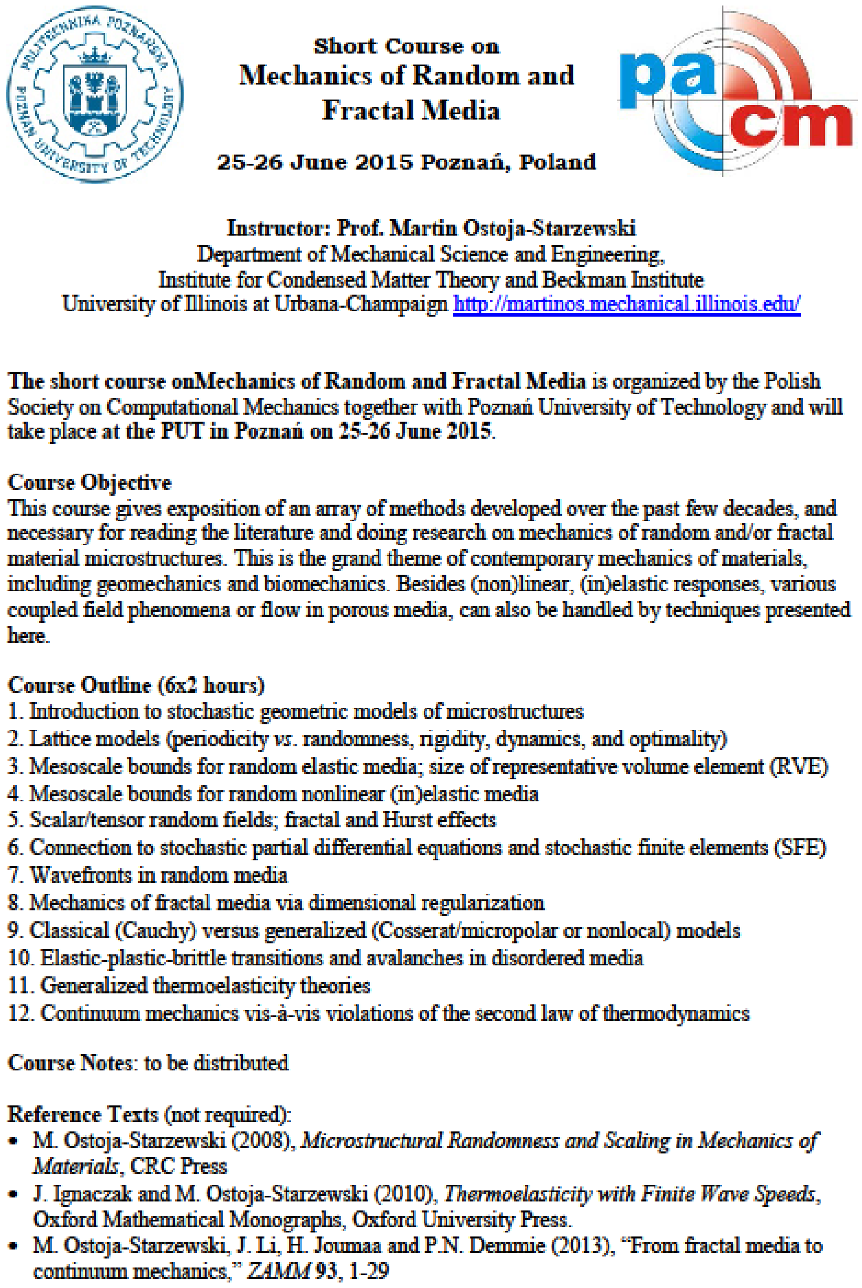
Axiom of Local Action is to be replaced by the scale dependence of adopted continuum approximation. Reference to microstructure is needed.

Axiom of Equipresence is to be abandoned since the violation of Second Law may occur in one physical process present in constitutive relations, not all.

Conclusions

- Non-zero probability of negative entropy production rate on very small time and space scales motivates a revision of continuum mechanics.
- Fluctuation theorem replaces 2nd law as a restriction on dependent fields and material properties.
- Entropy evolves as a submartingale.
- Stochastic generalizations of thermomechanics.
- Effect of violations when the phenomena occur on spatial and/or time scales where the 2nd law may spontaneously be violated

…such as **life**



Short Course on

Mechanics of Random and Fractal Media

25-26 June 2015 Poznań, Poland

Instructor: Prof. Martin Ostoja-Starzewski
Department of Mechanical Science and Engineering,
Institute for Condensed Matter Theory and Beckman Institute
University of Illinois at Urbana-Champaign http://martinos.mechanical.illinois.edu/

The short course onMechanics of Random and Fractal Media is organized by the Polish Society on Computational Mechanics together with Poznań University of Technology and will **take place at the PUT in Poznań on 25-26 June 2015**.

Course Objective

This course gives exposition of an array of methods developed over the past few decades, and necessary for reading the literature and doing research on mechanics of random and/or fractal material microstructures. This is the grand theme of contemporary mechanics of materials, including geomechanics and biomechanics. Besides (non)linear, (in)elastic responses, various coupled field phenomena or flow in porous media, can also be handled by techniques presented here.

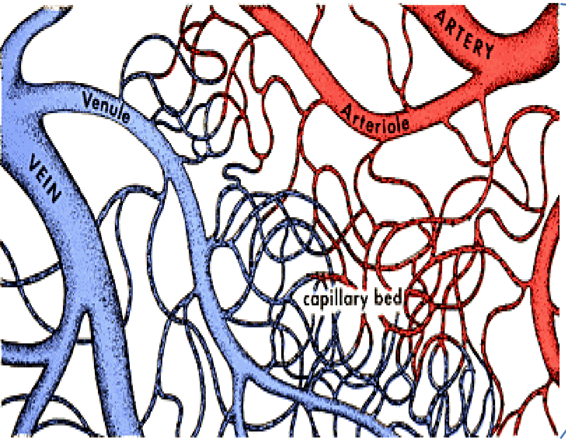
Course Outline (6x2 hours)

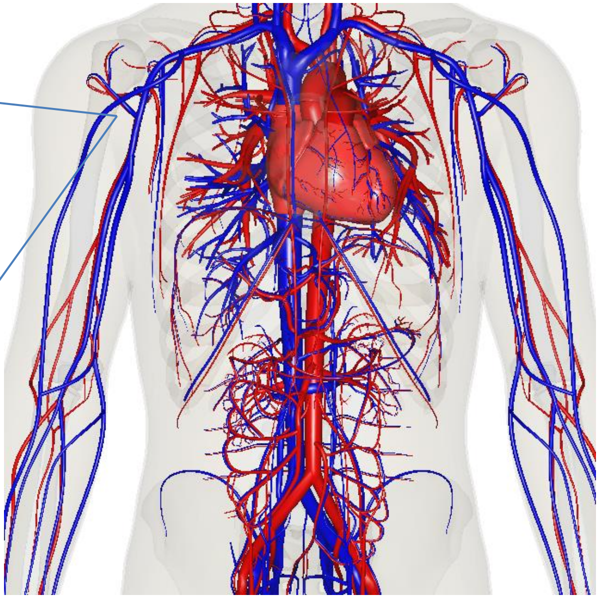
1. Introduction to stochastic geometric models of microstructures
2. Lattice models (periodicity *vs*. randomness, rigidity, dynamics, and optimality)
3. Mesoscale bounds for random elastic media; size of representative volume element (RVE)
4. Mesoscale bounds for random nonlinear (in)elastic media
5. Scalar/tensor random fields; fractal and Hurst effects
6. Connection to stochastic partial differential equations and stochastic finite elements (SFE)
7. Wavefronts in random media
8. Mechanics of fractal media via dimensional regularization
9. Classical (Cauchy) versus generalized (Cosserat/micropolar or nonlocal) models
10. Elastic-plastic-brittle transitions and avalanches in disordered media
11. Generalized thermoelasticity theories
12. Continuum mechanics vis-à-vis violations of the second law of thermodynamics

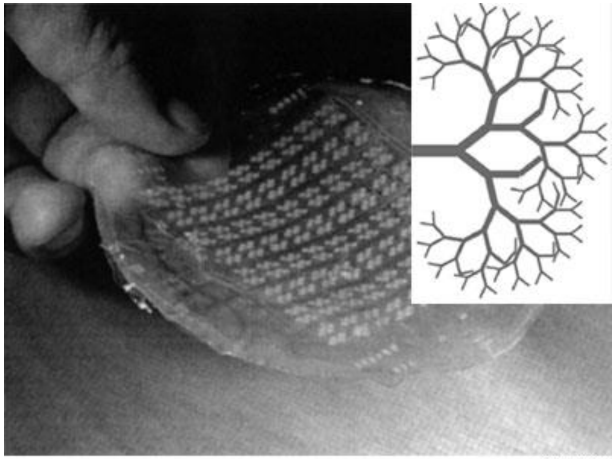
Course Notes: to be distributed

Reference Texts (not required):

- M. Ostoja-Starzewski (2008), *Microstructural Randomness and Scaling in Mechanics of Materials*, CRC Press
- J. Ignaczak and M. Ostoja-Starzewski (2010), *Thermoelasticity with Finite Wave Speeds*, Oxford Mathematical Monographs, Oxford University Press.
- M. Ostoja-Starzewski, J. Li, H. Joumaa and P.N. Demmie (2013), "From fractal media to continuum mechanics," *ZAMM* 93, 1-29



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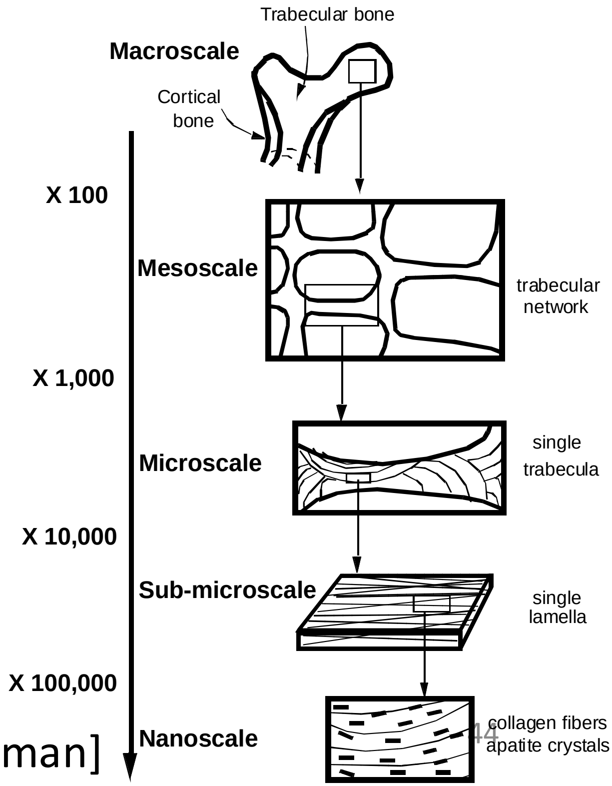

continuum fluid and solid mechanics
is enriched by multiscale models
especially, in fractal systems
and biomechanics

Iwona Jasiuk
[MechSE, IGB, Beckman]