Continuum Mechanics with Violations of Second Law of Thermodynamics

Martin Ostoja-Starzewski
Department of Mechanical Science & Engineering,
Institute for Condensed Matter Theory, and Beckman Institute
University of Illinois at Urbana-Champaign

[*Proc. Roy. Soc. A*, 2014]
[*Cont. Mech. Thermodyn.*, 2015]
[*J. Thermal Stresses*, 2016]
[*Entropy*, 2017]

Balance (conservation) laws of continuum mechanics

- mass
- linear momentum
- angular momentum
- energy

- second law of thermodynamics

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

provides restrictions on admissible forms of constitutive relations

reversible

irreversible

Physics: entropy production may spontaneously 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
- 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
- D.J. Evans & D.J. Searles, D.J. (2002). The fluctuation theorem, *Adv. Phys.* **51**(7), 1529-1585
- C. Jarzynski (2011). Equalities and inequalities: Irreversibility and the second law of thermodynamics at the nanoscale, *Annu. Rev. Condens. Matter Phys*. **2**, 329-51

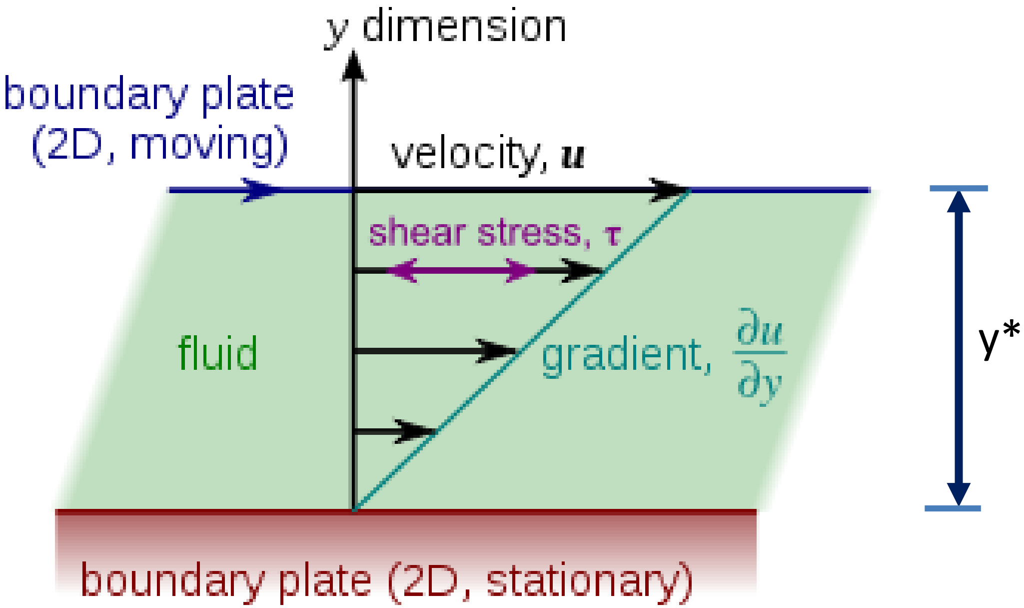
Maxwell: “*the second law is of the nature of strong probability … not an absolute certainty*”

$\Rightarrow$ need to revise thermodynamics of continuum mechanics

- modify the Clausius-Duhem inequality
- stochastic continuum thermomechanics
  - fluctuation theorem in place of 2nd law
  - entropy = submartingale
  - continuum mechanics axioms revisted
- applications in presence of 2nd law violations:
  - acceleration wavefront
  - stability of diffusion processes
  - permeability of random media
  - turbulence via micropolar fluid mechanics
  - …

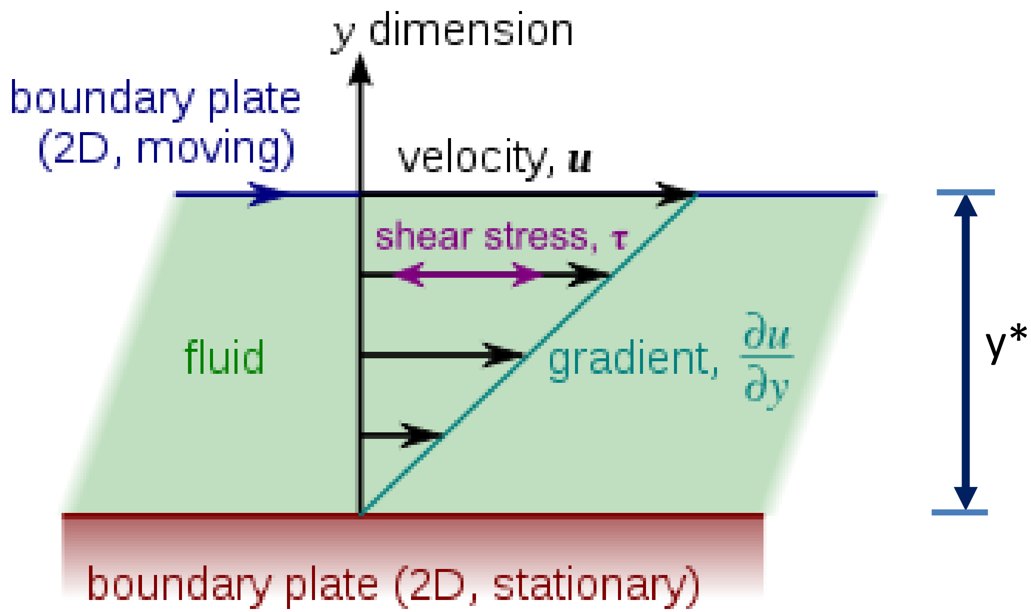
Couette flow

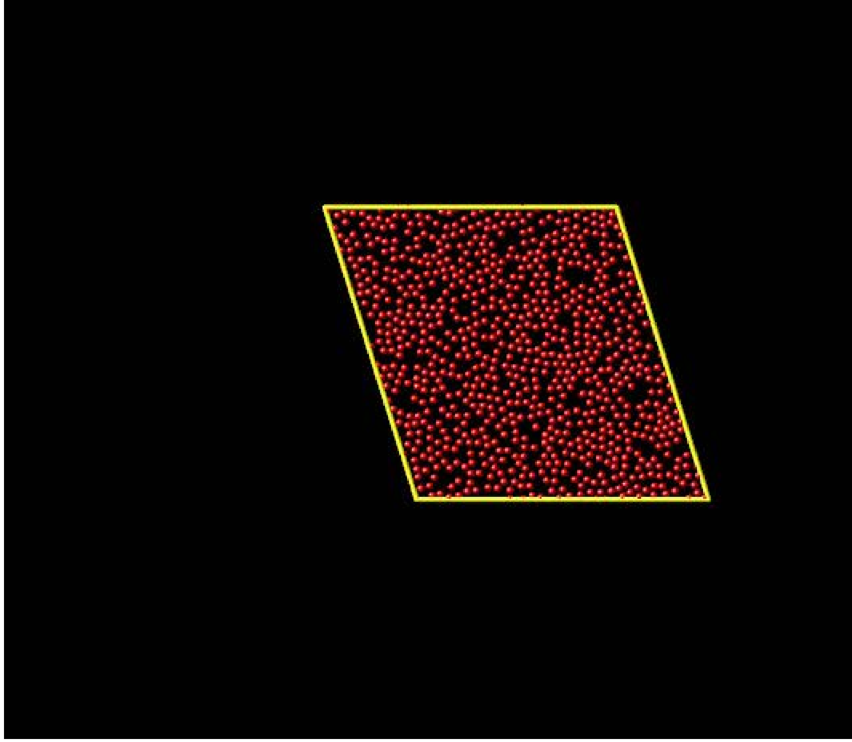
molecular dynamics via LAMMPS:

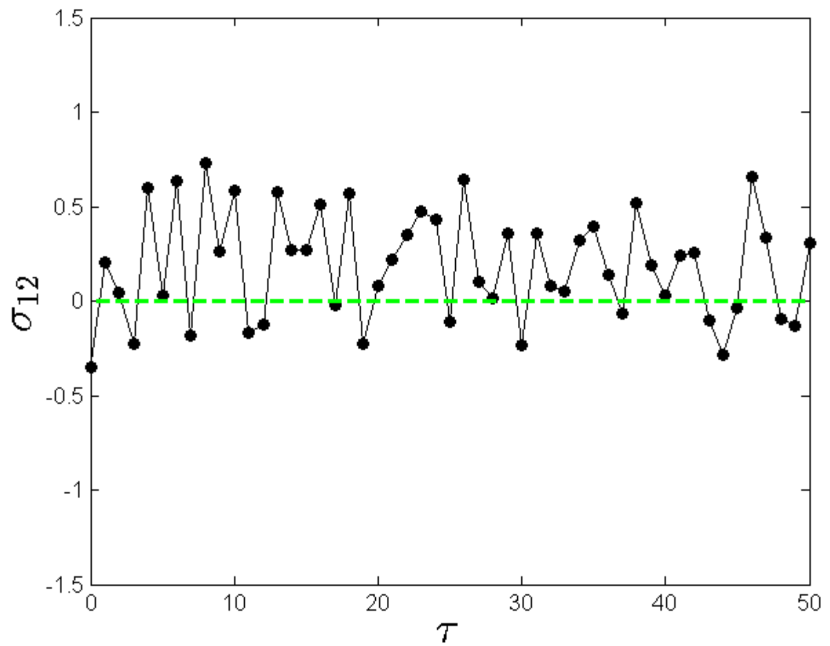


Couette flow

molecular dynamics via LAMMPS:

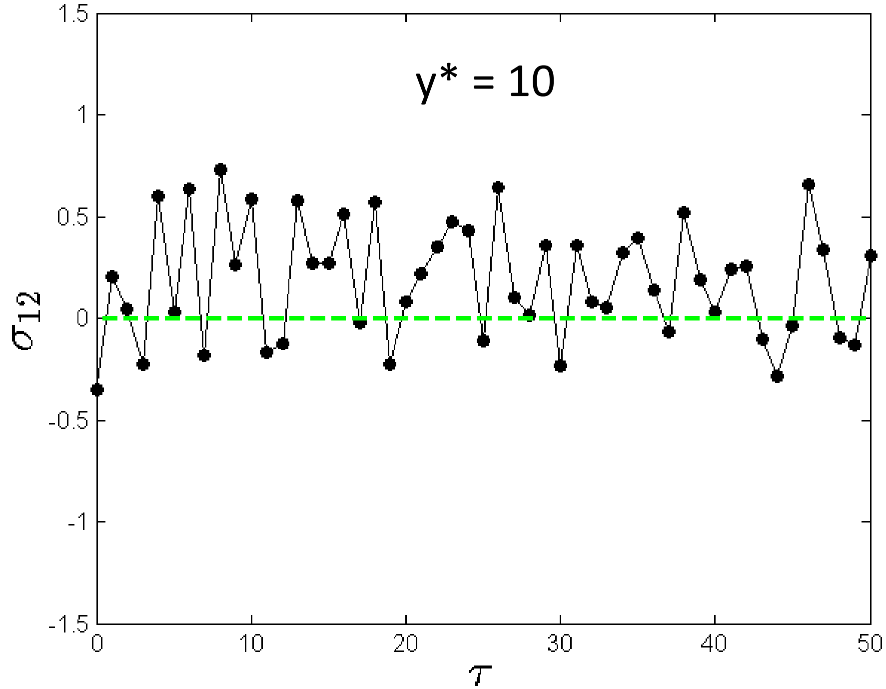


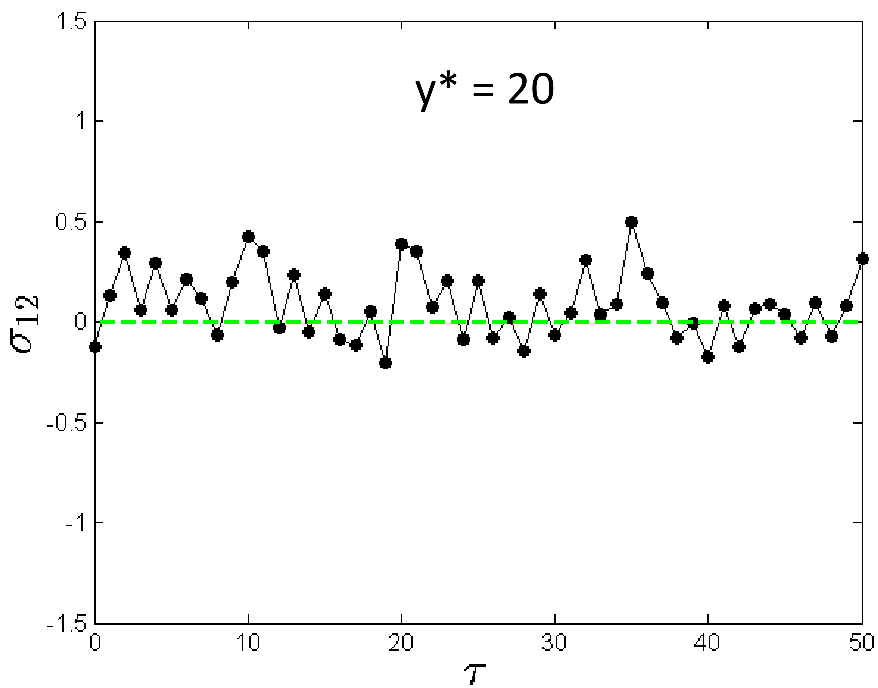


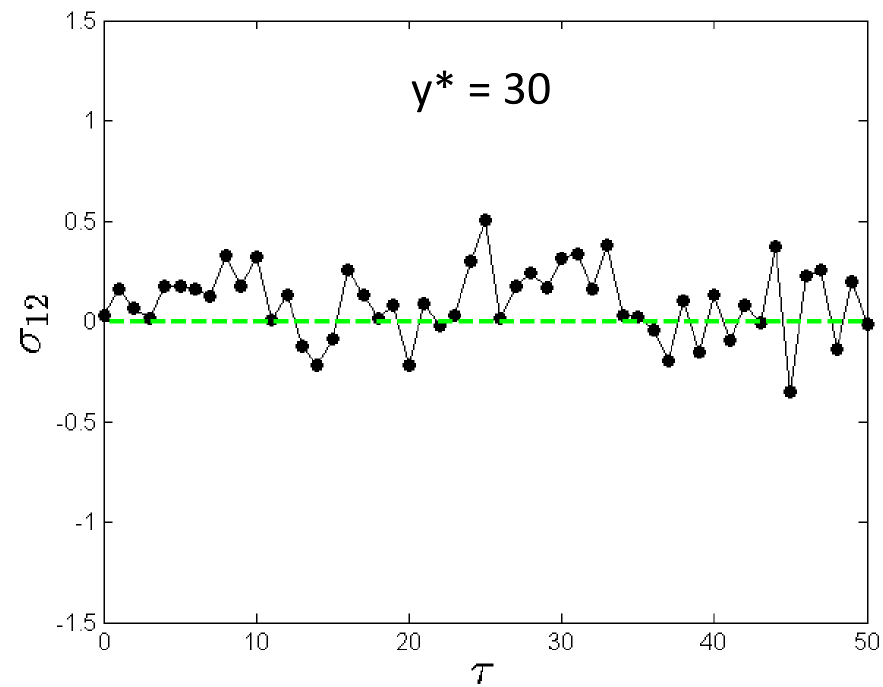


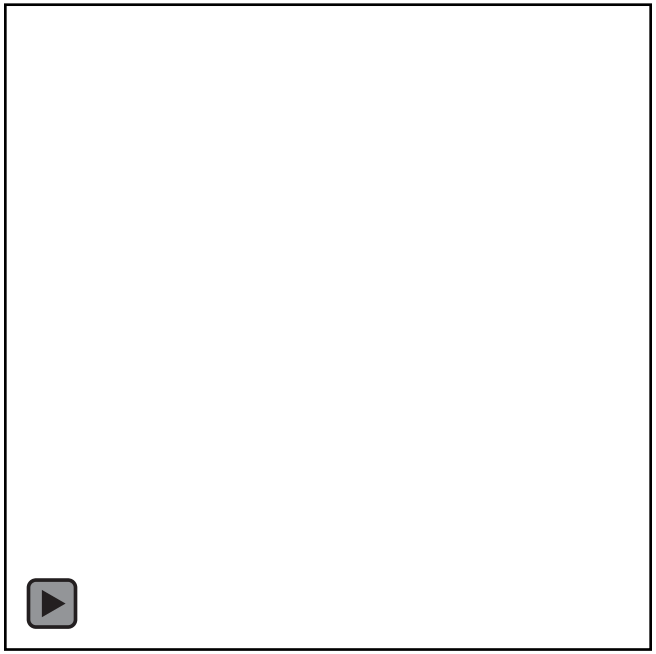
- Lennard-Jones potential
- Lees-Edwards boundary condition
- thermostatted system

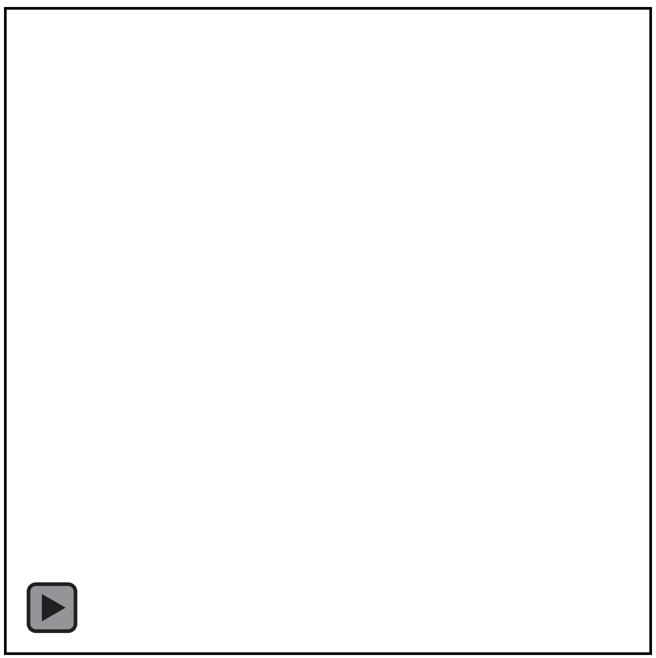
shear stress evolutions
for various channel heights

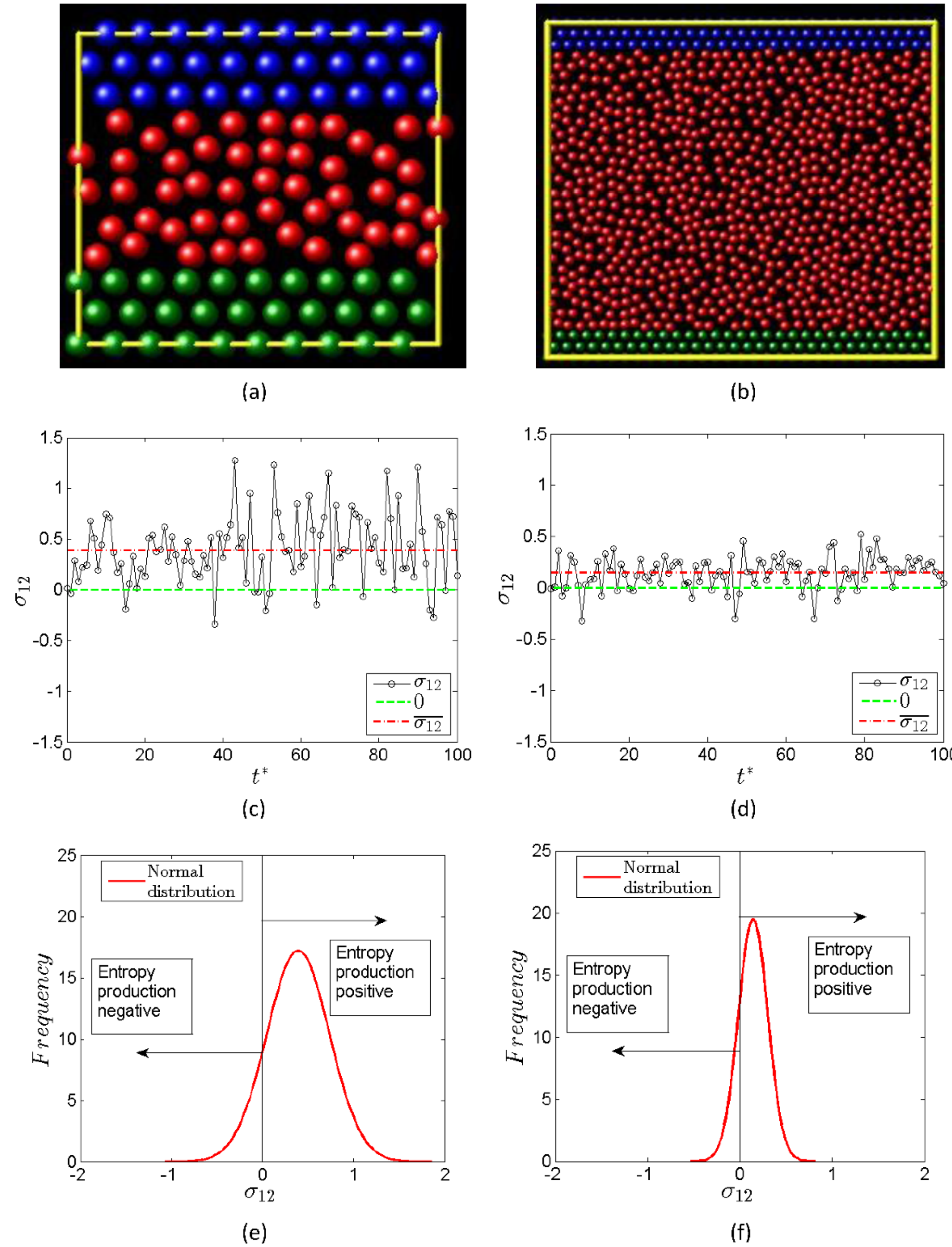








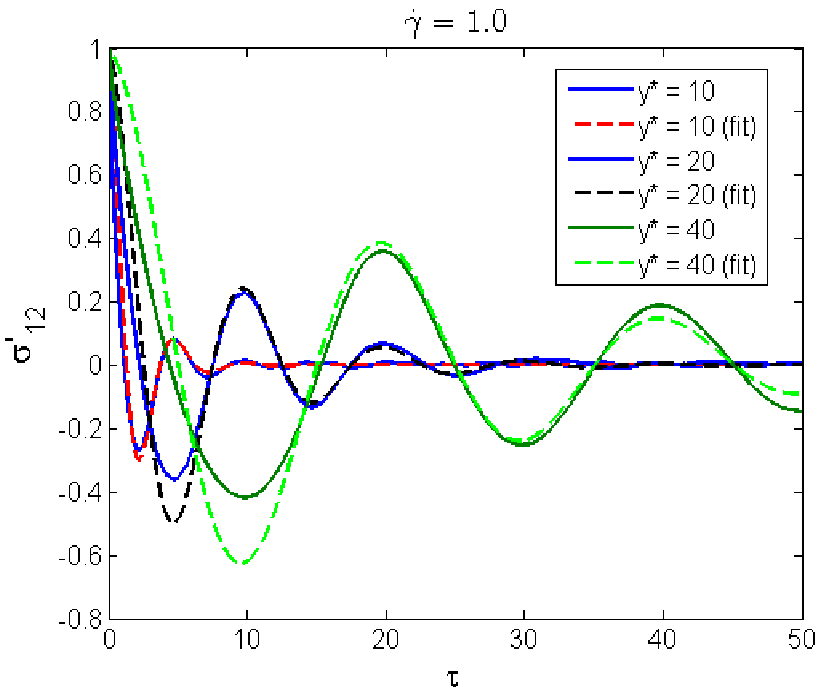




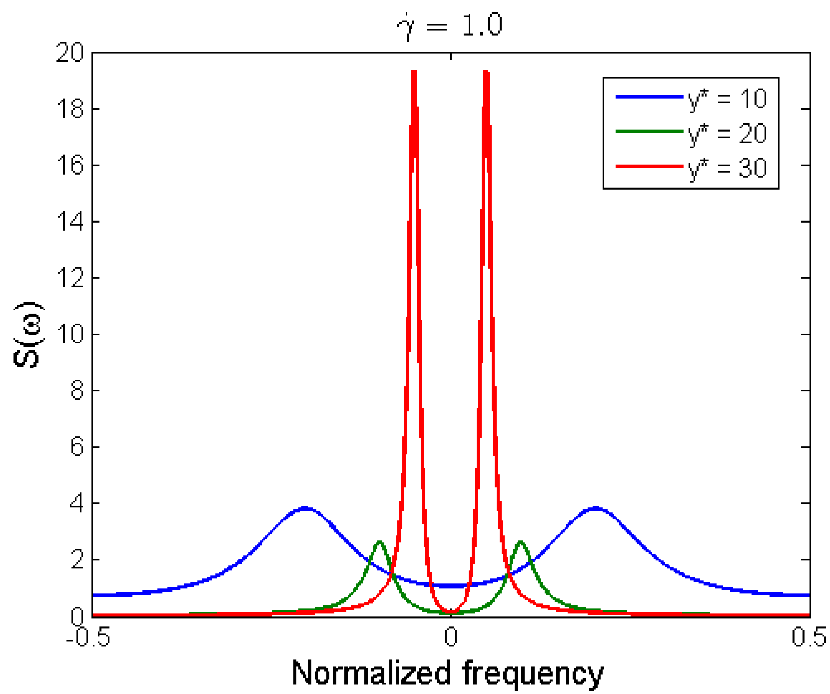
(a)
(b)
σ_{12}
t^*
σ_{12}
0
$\overline{\sigma_{12}}$
(c)
(d)
Normal distribution
Entropy production negative
Entropy production positive
$Frequency$
σ_{12}
(e)
(f)

autocorrelation of shear stress:

narrow-band random process



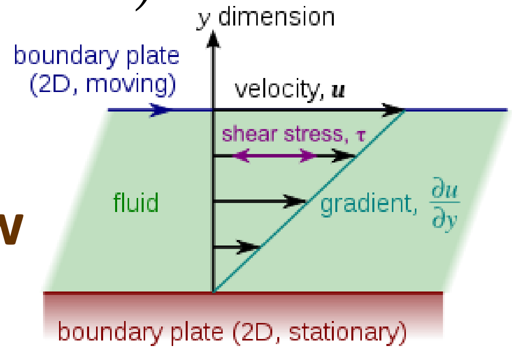
autocorrelation

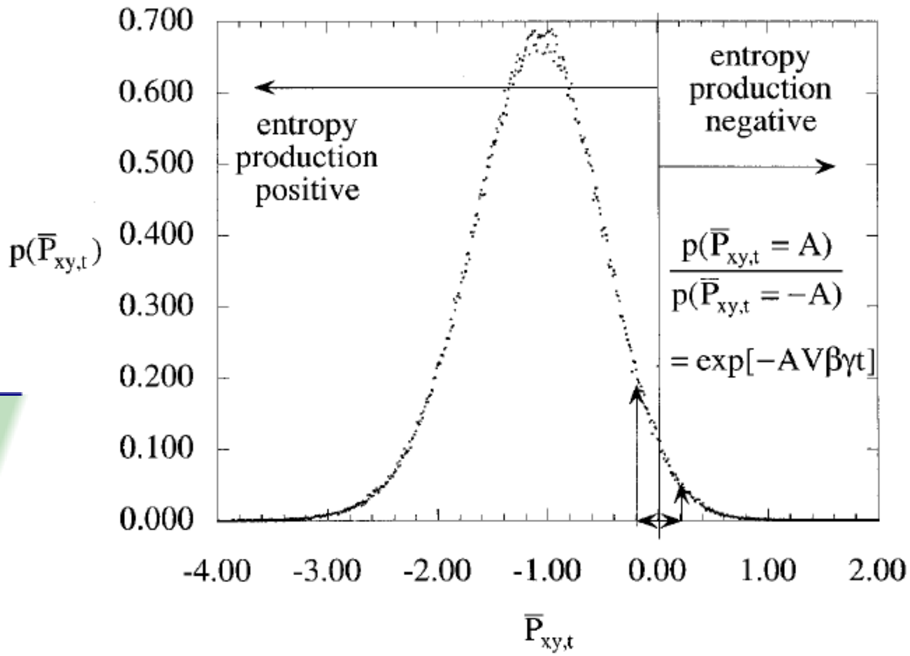


power spectral density

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

Couette flow



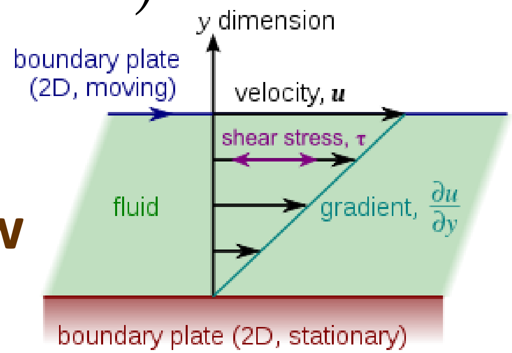


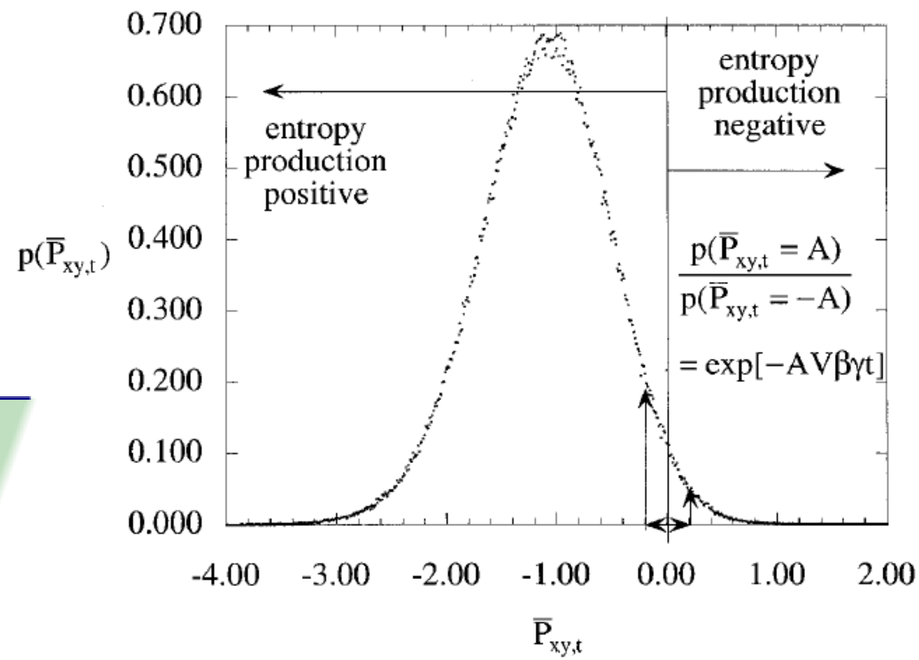
fluctuations in time-averaged shear stress for a molecular system in Couette flow

fluctuation theorem in place of 2^{nd} 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 $\Rightarrow$

in place of

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

(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 … $\mathrm{E}\{X(t+\Delta t) \mid \mathrm{past}\} = X(t)$
- …

fluctuation theorem $\Rightarrow$

in place of

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

$\Rightarrow$ irreversible entropy is a *submartingale*

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

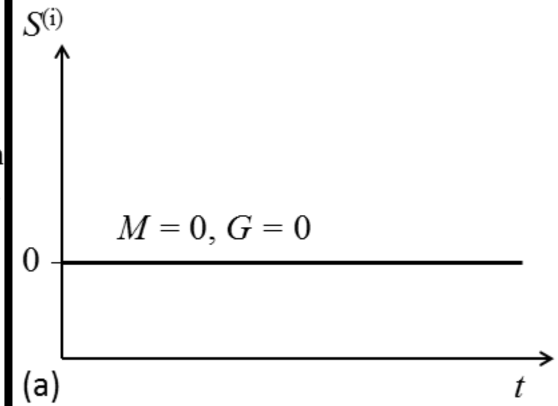
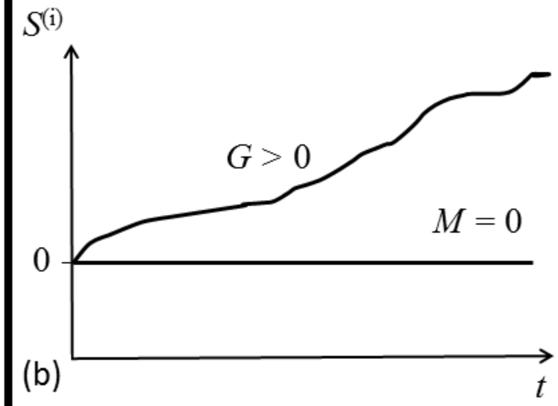
martingale

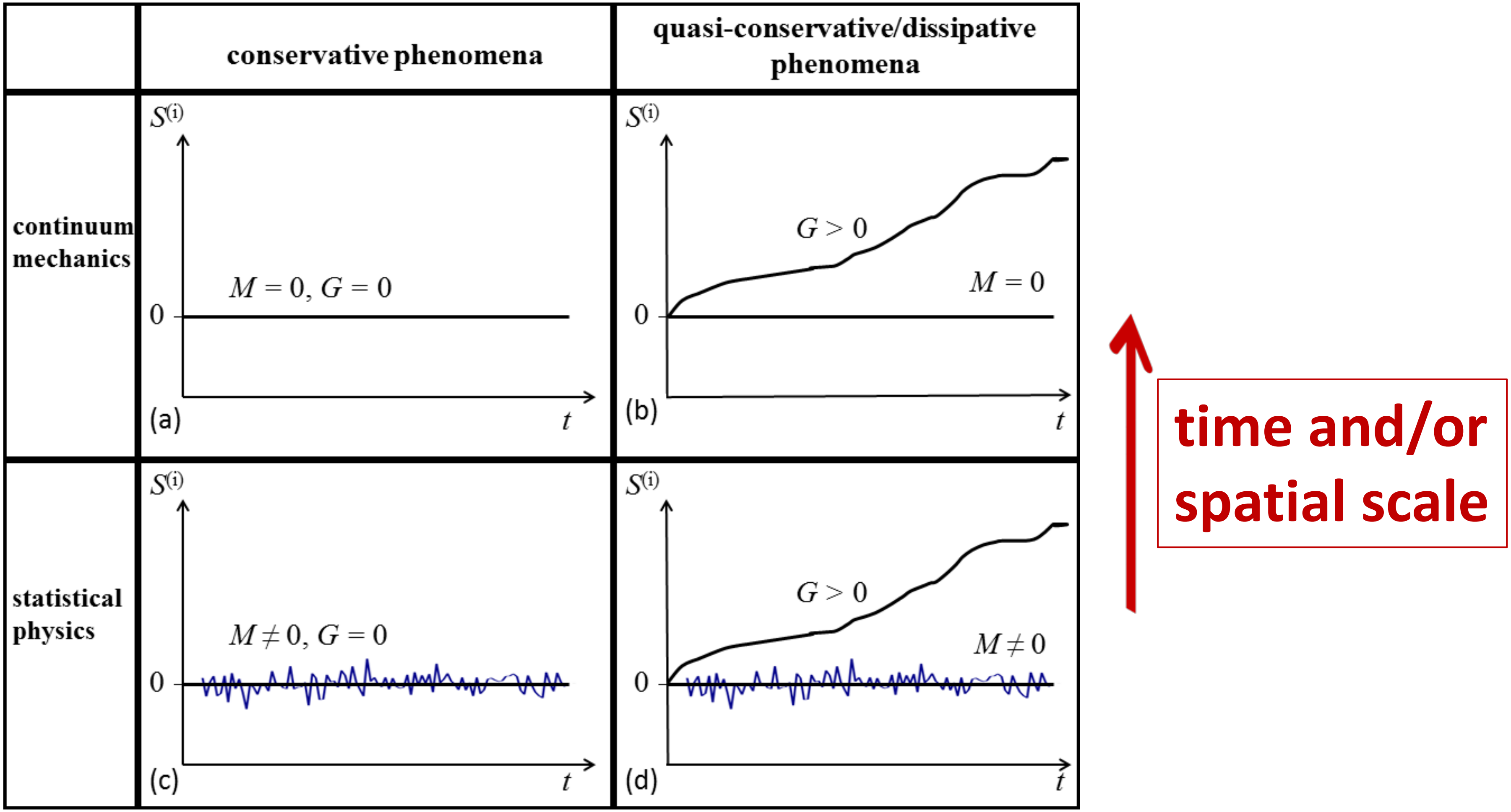
increasing process

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

(weakly monotonic f'n)

$\Rightarrow$ four distinct interpretations in continuum thermomechanics

<table>
<tr><th></th><th>conservative phenomena</th><th>quasi-conservative/dissipative phenomena</th></tr>
<tr><td>continuum mechanics</td><td>
</td><td>
</td></tr>
</table>


conservative phenomena
quasi-conservative/dissipative phenomena
continuum mechanics
statistical physics
$S^{(i)}$
$M = 0, G = 0$
$G > 0$
$M = 0$
$M \neq 0, G = 0$
$G > 0$
$M \neq 0$
0
t
(a)
(b)
(c)
(d)
time and/or spatial scale

levels of thermodynamic models

levels of thermodynamic models

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

levels of thermodynamic models

Drucker's Stability Postulate	• a classification only • many counterexamples (conceptual models and experiments)
Ziegler's Orthogonality Principle	• classifying principle for a wide range of solids, soils, and fluids (starts from energy and entropy production) • some materials (models and experiments) fall outside of it

levels of thermodynamic models

Drucker's Stability Postulate	• a classification only • many counterexamples (conceptual models and experiments)
Ziegler's Orthogonality Principle	• classifying principle for a wide range of solids, soils, and fluids (starts from energy and entropy production) • some materials (models and experiments) fall outside of it
Edelen's Primitive Thermomechanics	• accounts for dissipationless forces or fluxes • offers general solution consistent with 2nd law

levels of thermodynamic models

Drucker's Stability Postulate	• a classification only • many counterexamples (conceptual models and experiments)
Ziegler's Orthogonality Principle	• classifying principle for a wide range of solids, soils, and fluids (starts from energy and entropy production) • some materials (models and experiments) fall outside of it
Edelen's Primitive Thermomechanics	• accounts for dissipationless forces or fluxes • offers general solution consistent with 2nd law
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

levels of thermodynamic models

Drucker's Stability Postulate	• a classification only • many counterexamples (conceptual models and experiments)
Ziegler's Orthogonality Principle	• classifying principle for a wide range of solids, soils, and fluids (starts from energy and entropy production) • some materials (models and experiments) fall outside of it
Edelen's Primitive Thermomechanics	• accounts for dissipationless forces or fluxes • offers general solution consistent with 2nd law
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

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)

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*"

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.

advantages of 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 (via Green-Kubo relations)

Valid in nonlinear regime, far from equilibrium

Also apply to thermal and electrical phenomena

… 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

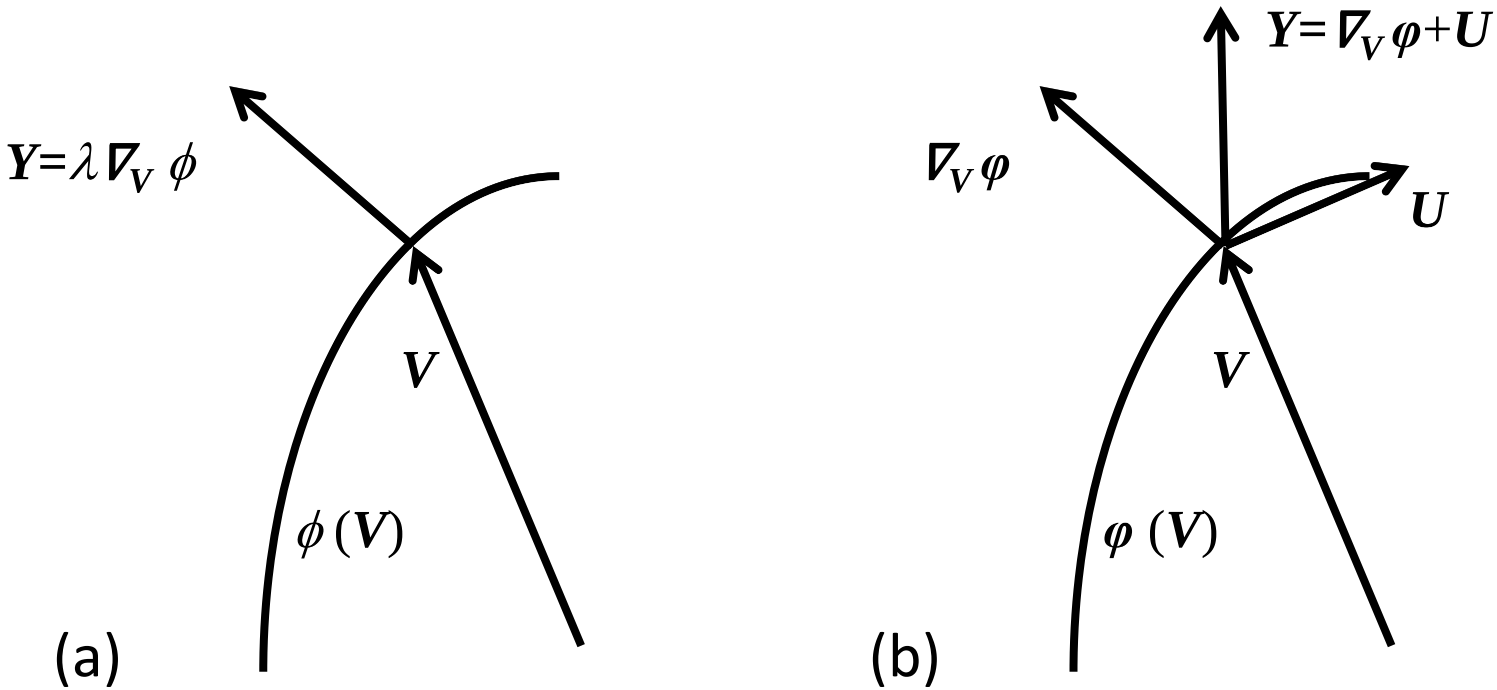
stochastic

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

$$\text{velocities} \qquad \mathbf{V}=\{d_{ij},\ T_{,k}\} \qquad \omega\in\Omega,\quad \left(\Omega,F,P\right)$$

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

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



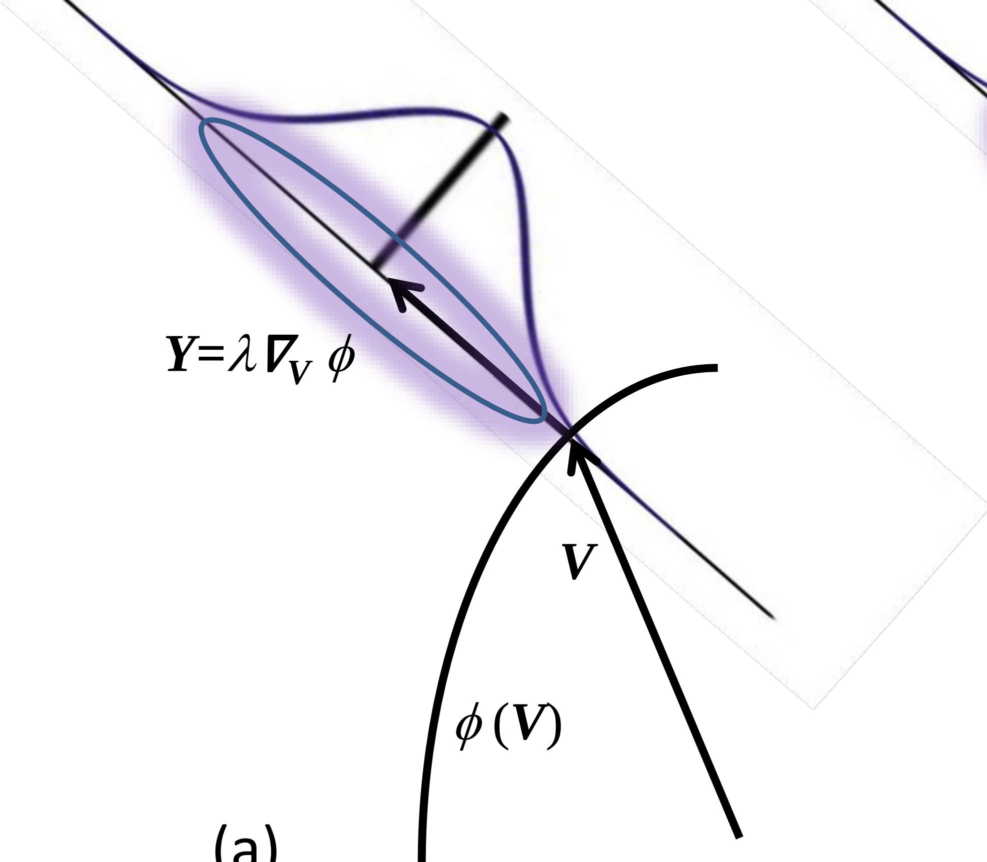
Thermodynamic Orthogonality
via convex analysis

(H. Ziegler, 1957)

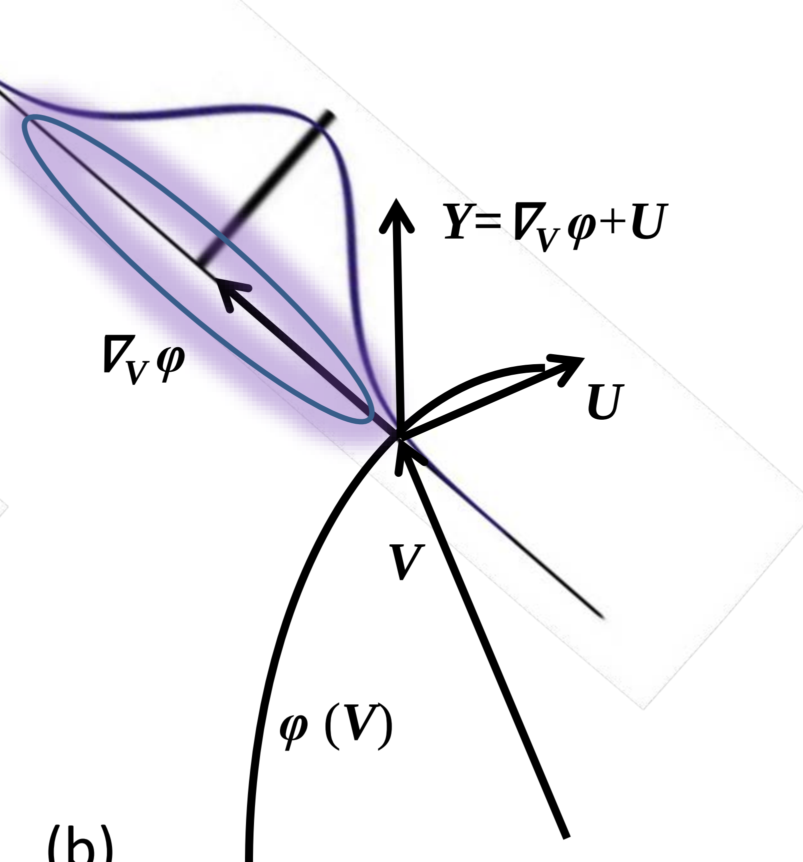
Primitive Thermodynamics
with powerless vector
via Poincaré's lemma

(D. Edelen, 1973)

… or via maximum information entropy in statistical physics:
Dewar (2005) O-S & Zubelewicz (2011) [*J. Phys. A: Math. Theor.*]



(a)



(b)

Thermodynamic Orthogonality
stochastic

Primitive Thermodynamics w/ powerless vector **stochastic**

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

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* $\alpha_c \neq \frac{\mu}{\beta}$ random

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

Acceleration waves with nanoscale wavefront thickness

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

Bernoulli equation

in random medium:

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

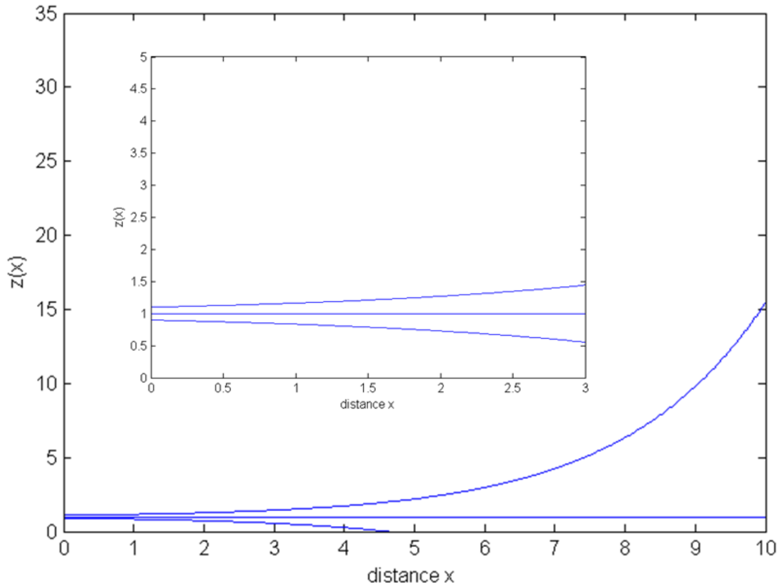
$\Rightarrow$ stochastic dynamical system driven by random viscosity

$$\frac{d\alpha}{dx} = \frac{G_0'\rho_R^{1/2}}{2G_0^{3/2}}\alpha - \frac{\rho_R \widehat{E}_0}{2G_0^2}\alpha^2$$

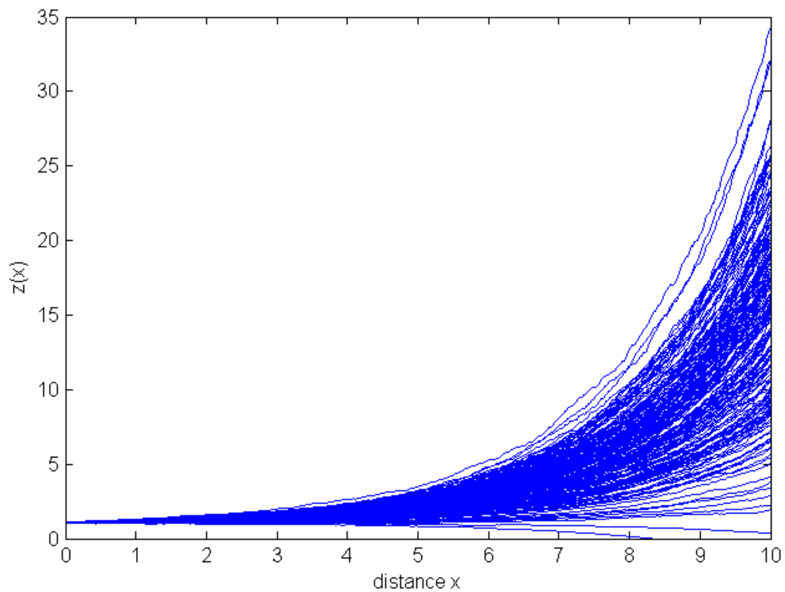
instantaneous modulus

instantaneous second-order tangent modulus

zero-mean Gaussian white noise



deterministic/homogeneous medium



random medium

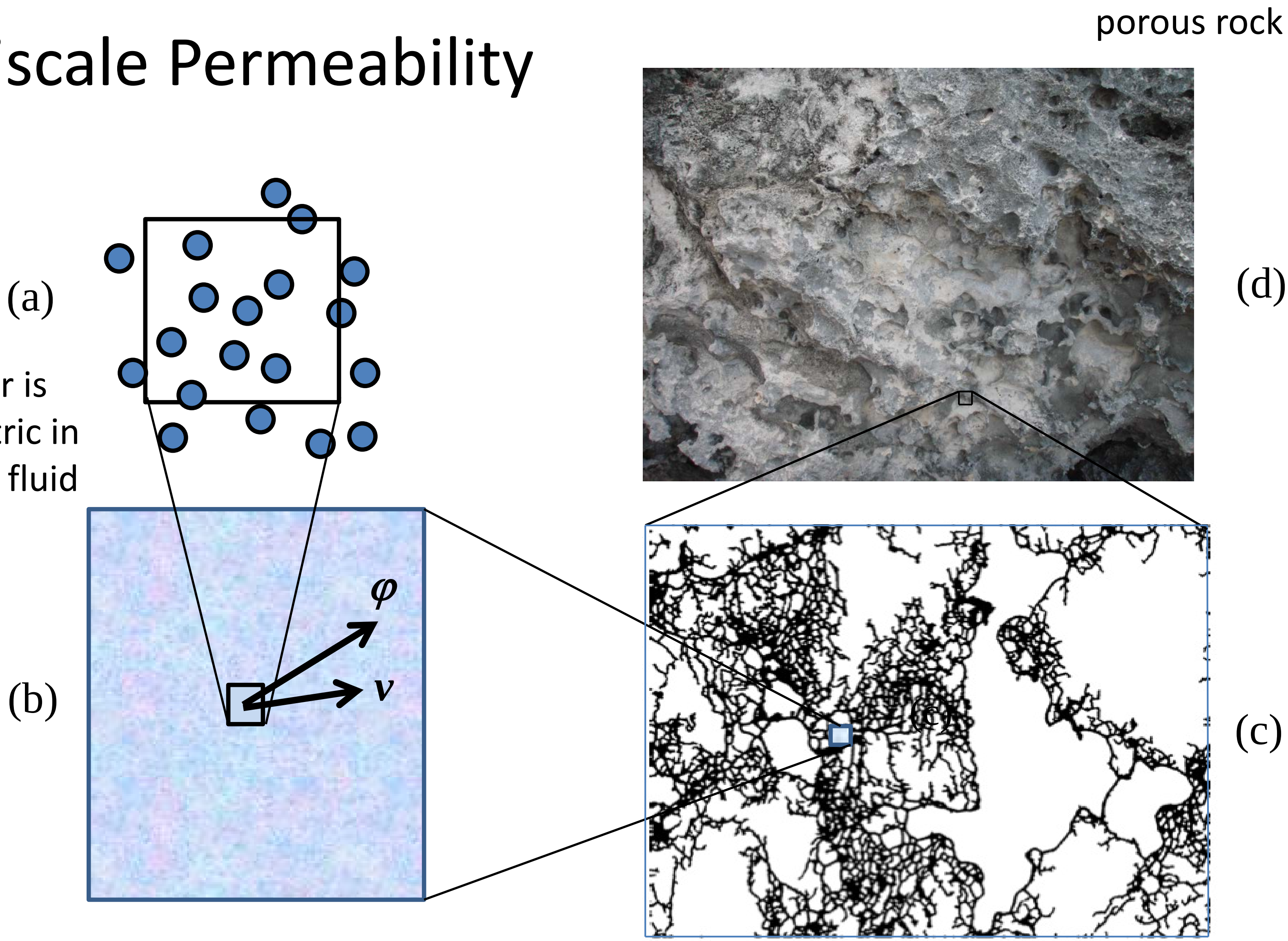
$$z := 1/\alpha$$

- Since the dissipation may become negative, the wave that started at the initial amplitude 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.

Multiscale Permeability

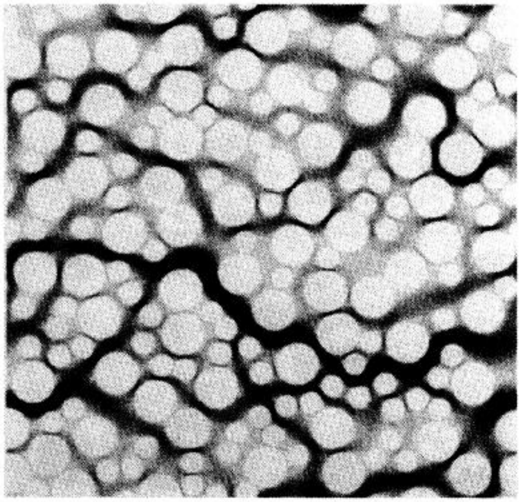


stress tensor is not symmetric in a molecular fluid

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

Flow in random porous media



Stokes' flow:

$$\mu \nabla^2 \vec{U} = \nabla p$$

$$\nabla \cdot \vec{U} = 0$$

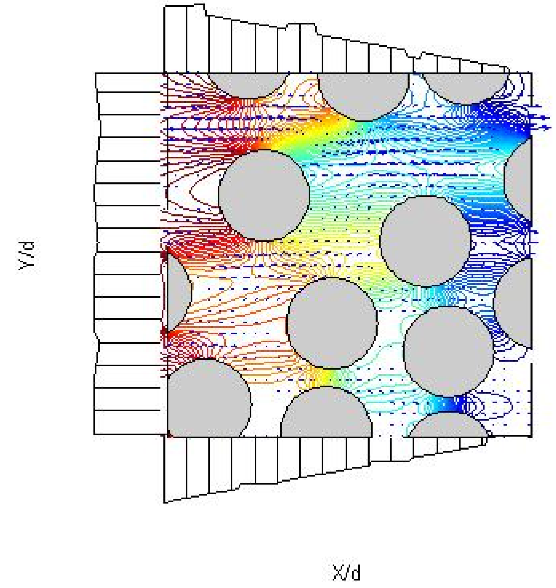
Darcy's Law (1876):

$$\vec{U}_D = -\frac{\tilde{\tilde{K}}}{\mu} \cdot \nabla p$$

$$\nabla \cdot \vec{U}_D = 0$$

…

$$\nabla \cdot (\tilde{\tilde{K}} \cdot \nabla p) = 0$$



After homogenization:

$$\nabla^2 p = 0$$

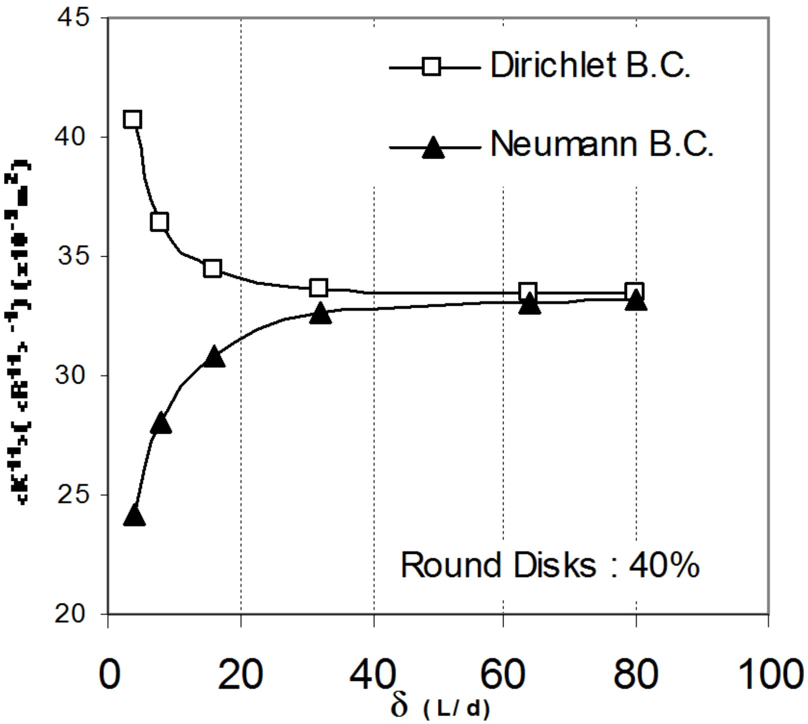
<u>Hill condition</u>: Equivalence of energetic and mechanical definitions of Darcy's law:

$$\overline{p_{,i}U_i} = \overline{p_{,i}}\,\overline{U_i} \Leftrightarrow \int_{\partial B} (p - \overline{p_{,j}}x_j)(U_i n_i - \overline{U_i}\, n_i) dS = 0$$

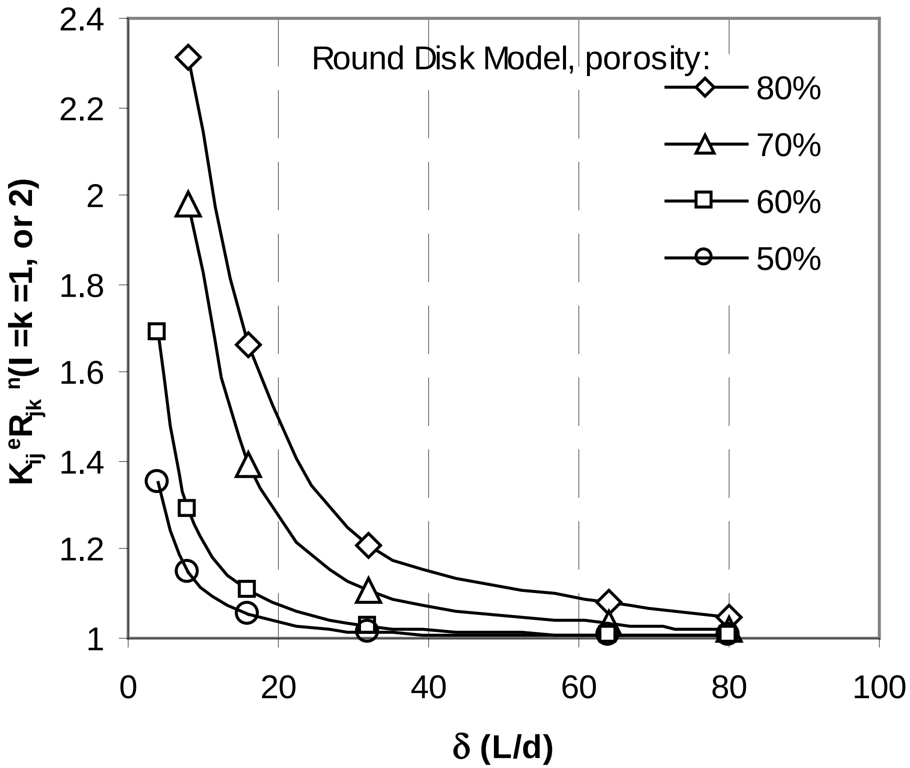
$$\left.\begin{array}{ll}
\text{(i)} & p = \overline{\nabla p} \cdot \vec{x} \quad \text{or} \quad p = \overline{p_{,i}} x_i \\
\text{(ii)} & \vec{U} \cdot \vec{n} = \vec{U}_0 \cdot \vec{n} \quad \text{or} \quad U_i n_i = U_{0i} n_i \\
\text{(iii)} & (p - \overline{p_{,i}} x_i)(U_i n_i - U_{0i} n) = 0 \\
\text{or} & (p - \overline{\nabla p} \cdot \vec{x}) \cdot (\vec{U} \cdot \vec{n} = \vec{U}_0 \cdot \vec{n}) = 0
\end{array}\right\} \text{on} \quad \partial B$$

$$\left\langle \tilde{\tilde{K}}_{\delta}{}^{e} \right\rangle \geq \left\langle \tilde{\tilde{K}}_{2\delta}{}^{e} \right\rangle \geq \cdots \geq \tilde{\tilde{K}}^{eff} = (\tilde{\tilde{R}}^{eff})^{-1} \geq \cdots \geq \left\langle \tilde{\tilde{R}}_{2\delta}{}^{n} \right\rangle^{-1} \geq \left\langle \tilde{\tilde{R}}_{\delta}{}^{n} \right\rangle^{-1}$$

[*Proc. R. Soc. A*, 2006; *Adv. Appl. Mech*, 2016]



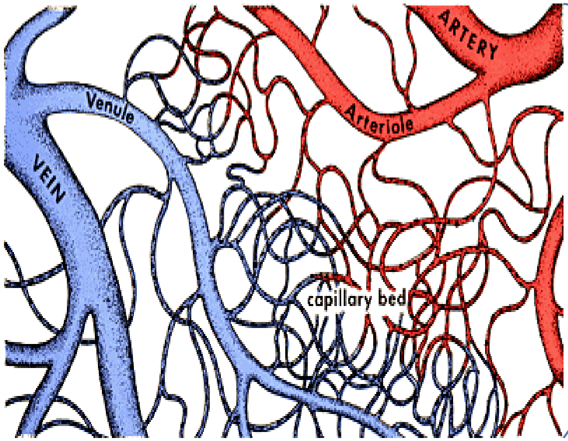
Effect of increasing window scale on the convergence of the permeability/resistance tensor hierarchy (upper/lower bounds under Dirichlet/Neumann b.c.).

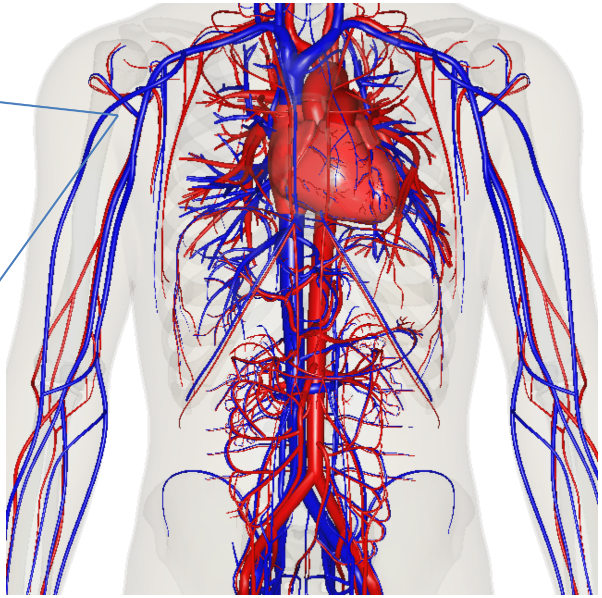


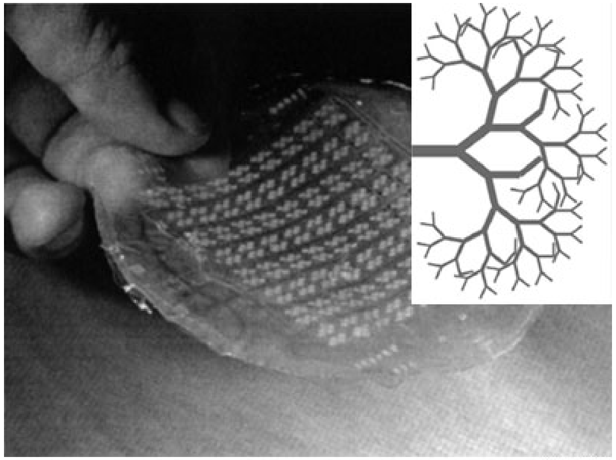
Finite-size scaling of the product of ***K*** and ***R***.

In view of violations of the 2nd law
the smaller are the channels, the better is the permeability!

… flows in biomechanics







Source: MIT

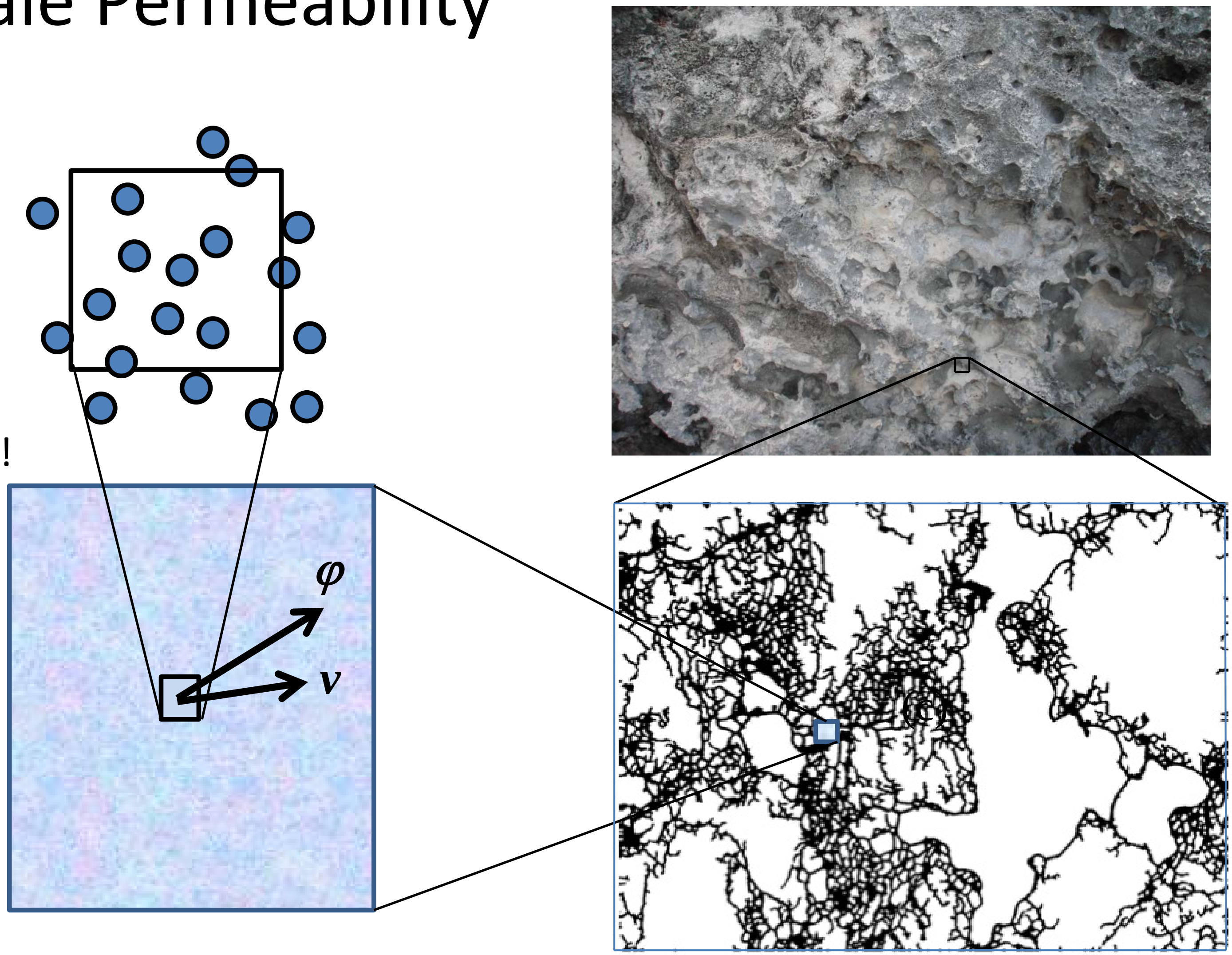
Multiscale Permeability

porous rock

(a)

stress tensor is not symmetric in a molecular fluid!

(b)



(d)

(c)

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

Stress tensor is not symmetric

$\Rightarrow$ use micropolar fluid mechanics

[Eringen, Łukaszewicz]

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

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

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

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

classical continuum mechanics is recovered for:

Balance equations of micropolar fluids

linear viscous fluid model (generalizes Navier-Stokes)

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

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

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

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

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

intrinsic
dissipation function

Hold on average:

Violations of second law in diffusion problems

in heat conduction
on finite domain:

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

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

Lyapunov function:

if SL holds:

Observations

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

Thermodynamic orthogonality:
… from a molecular fluid to a continuum

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

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

for Fourier-type heat conduction

Primitive thermodynamics:
… from a molecular fluid to a continuum

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

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

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:

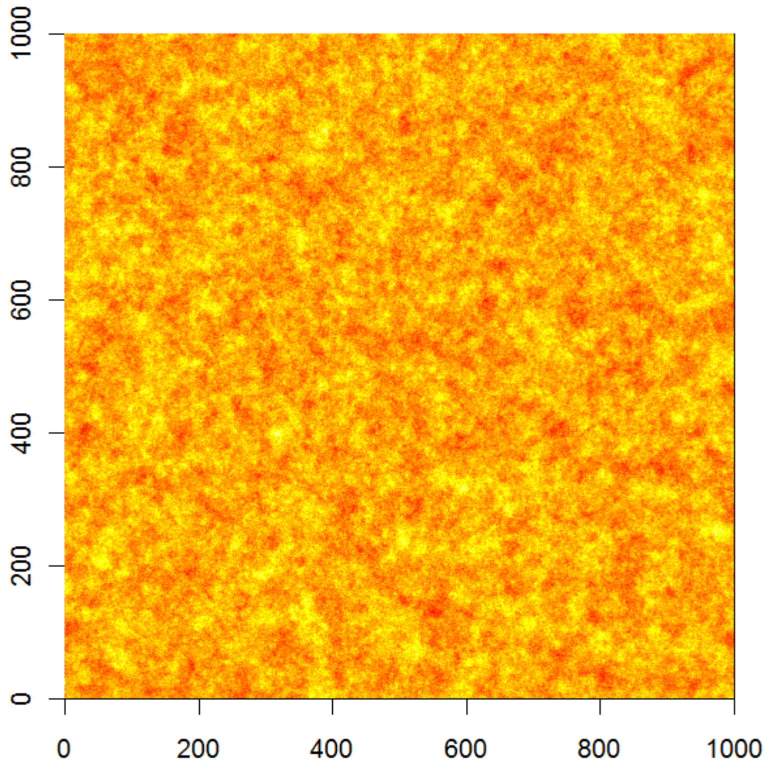
Second Law on average:

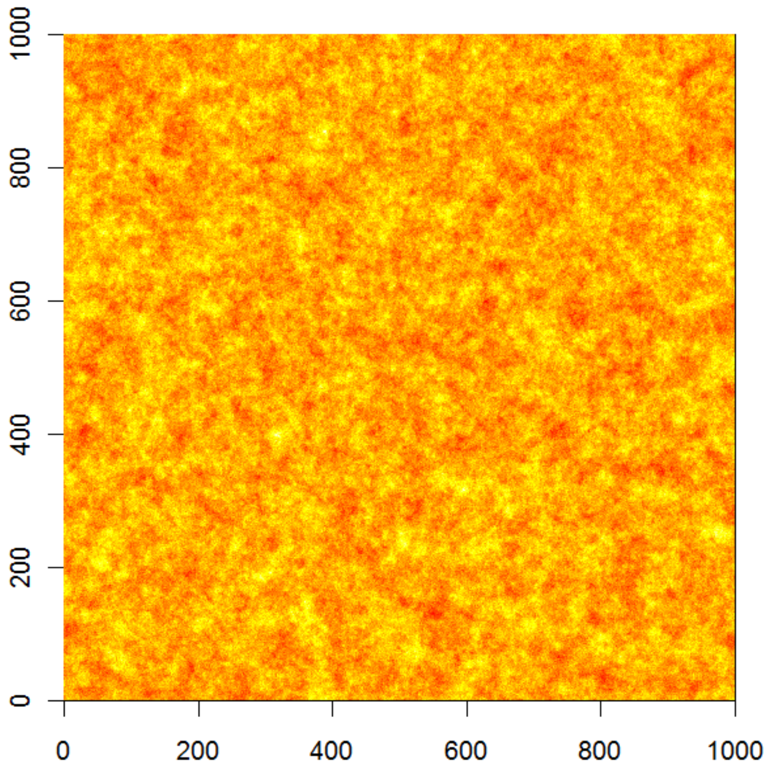
Dissipation function:

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

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

Martingale fluctuations in 2d: random fields

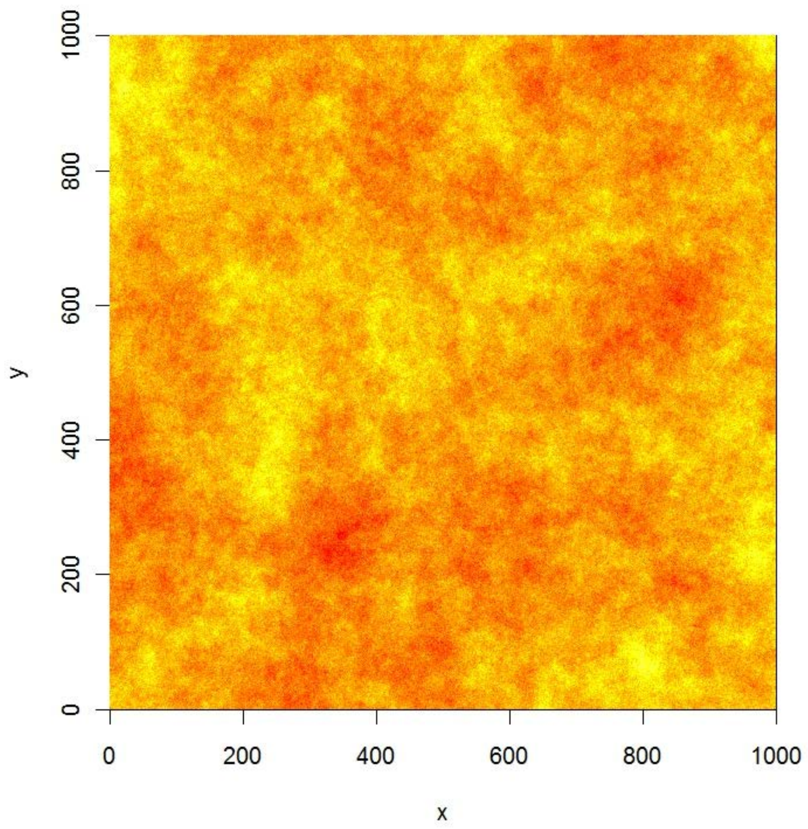


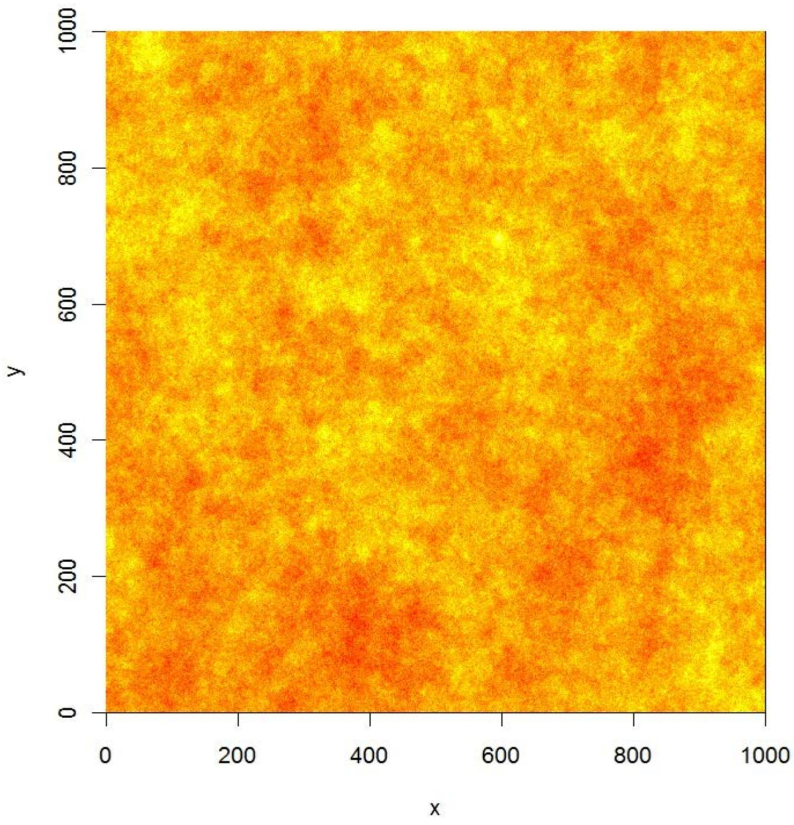


RFs with exponential or Gaussian correlation functions

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

Martingale fluctuations in 2d: random fields





RFs with fractal + Hurst effects

Cauchy

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

$\beta > 0 \qquad 0 < \alpha \leq 2$

Dagum

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

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