Nonequilibrium variational principles from dynamical fluctuations

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MRC, Warwick University, 18 May 2010

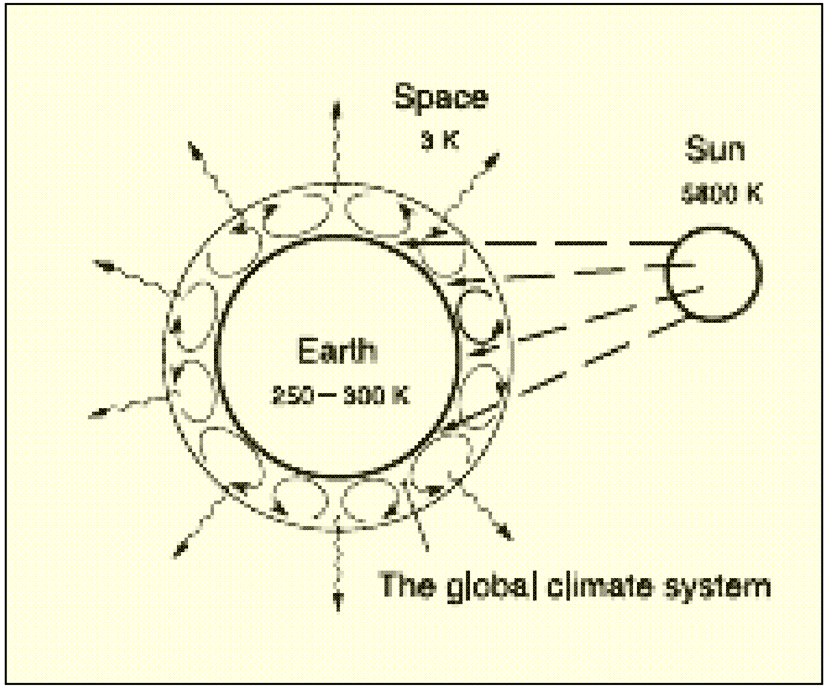
To be discussed

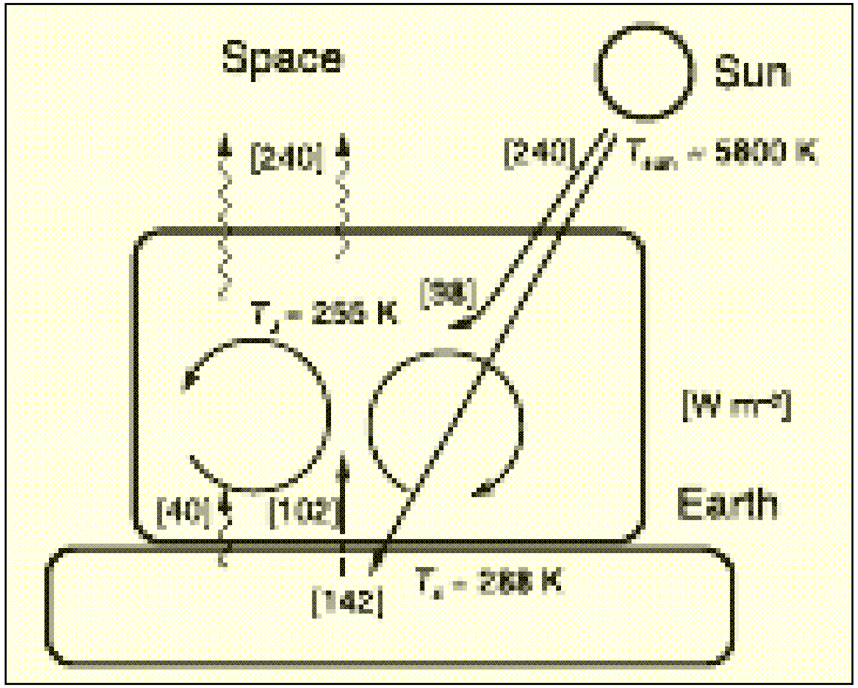
- Min- and Max-entropy production principles: various examples
- From variational principles to fluctuation laws: equilibrium case
- Static versus dynamical fluctuations
- Onsager-Machlup equilibrium dynamical fluctuation theory
- Stochastic models of nonequilibrium
- Conclusions, open problems, outlook,...

In collaboration with C. Maes,
B. Wynants, and S. Bruers
(K.U.Leuven, Belgium)

Motivation: Modeling Earth climate

[Ozawa et al, *Rev. Geoph.* **41** (2003) 1018]





$$\dot{S}_{\text{whole (univ)}} \approx \dot{S}_{\text{surr}} = \left(\frac{1}{T_a} - \frac{1}{T_{\text{sun}}}\right) 240 \approx 0.90\ (\text{W K}^{-1}\ \text{m}^{-2}) \quad = \dot{S}_{\text{turb}} + \dot{S}_{\text{abs (short,s)}} + \dot{S}_{\text{abs (short,a)}} + \dot{S}_{\text{abs (long,a)}}$$

$$= \left(\frac{1}{T_a} - \frac{1}{T_s}\right)102 + \left(\frac{1}{T_s} - \frac{1}{T_{\text{sun}}}\right)142 + \left(\frac{1}{T_a} - \frac{1}{T_{\text{sun}}}\right)98 + \left(\frac{1}{T_a} - \frac{1}{T_s}\right)40$$

Linear electrical networks

explaining MinEP/MaxEP principles

- Kirchhoff’s loop law:

$$\sum_k U_{jk} = \sum_k E_{jk}$$

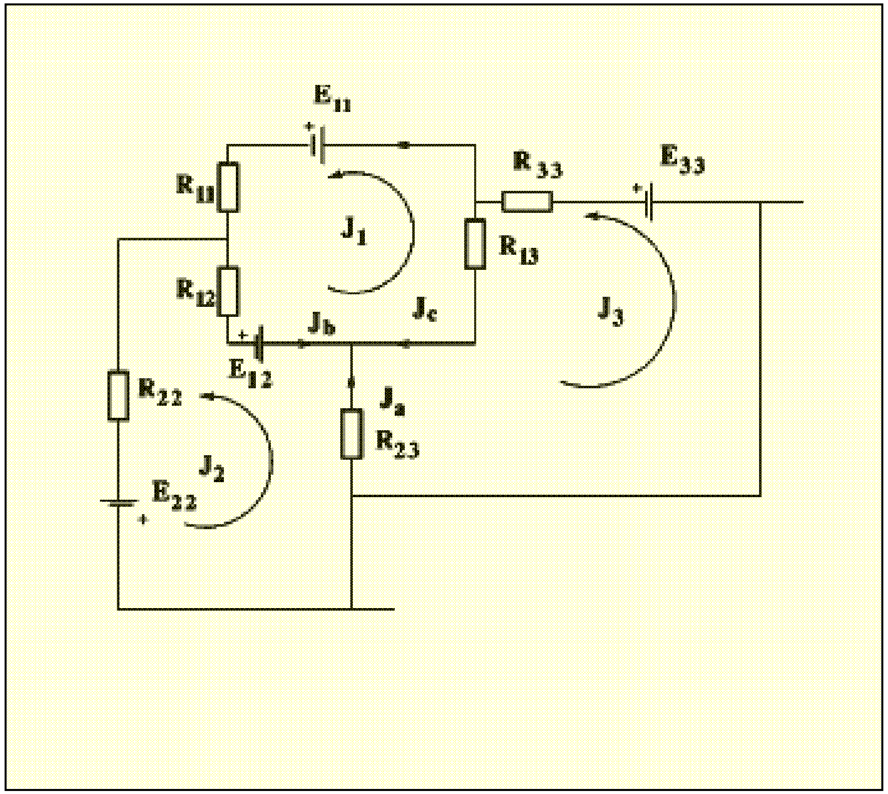
- Entropy production rate:

$$\sigma(U) = \beta Q(U) = \beta \sum_{j,k} \frac{U_{jk}^2}{R_{jk}}$$

- MinEP principle:

> *Stationary values of voltages minimize the entropy production rate*

- Not valid under inhomogeneous temperature!



Linear electrical networks

explaining MinEP/MaxEP principles

- Kirchhoff's current law:

$$\sum_j J_{jk} = 0$$

- Entropy production rate:

$$\sigma(J) = \beta Q(J) = \beta \sum_{j,k} R_{jk} J_{jk}^2$$

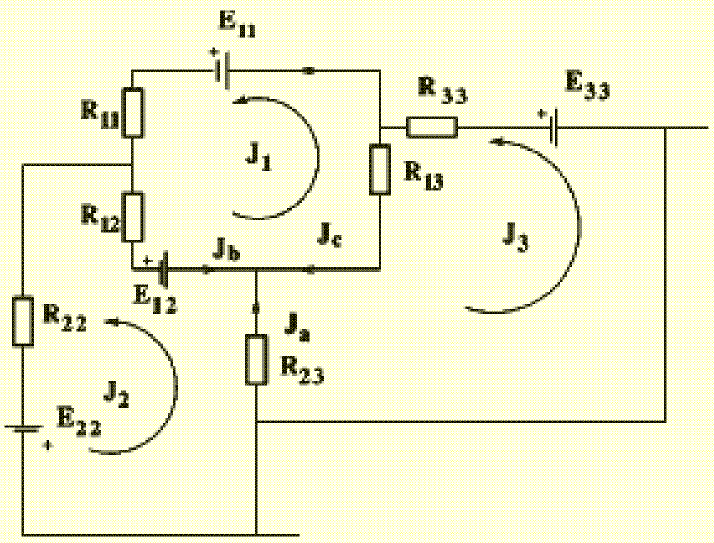
- Work done by sources:

$$W(J) = \sum_{jk} E_{jk} J_{jk}$$

- (Constrained) MaxEP principle:

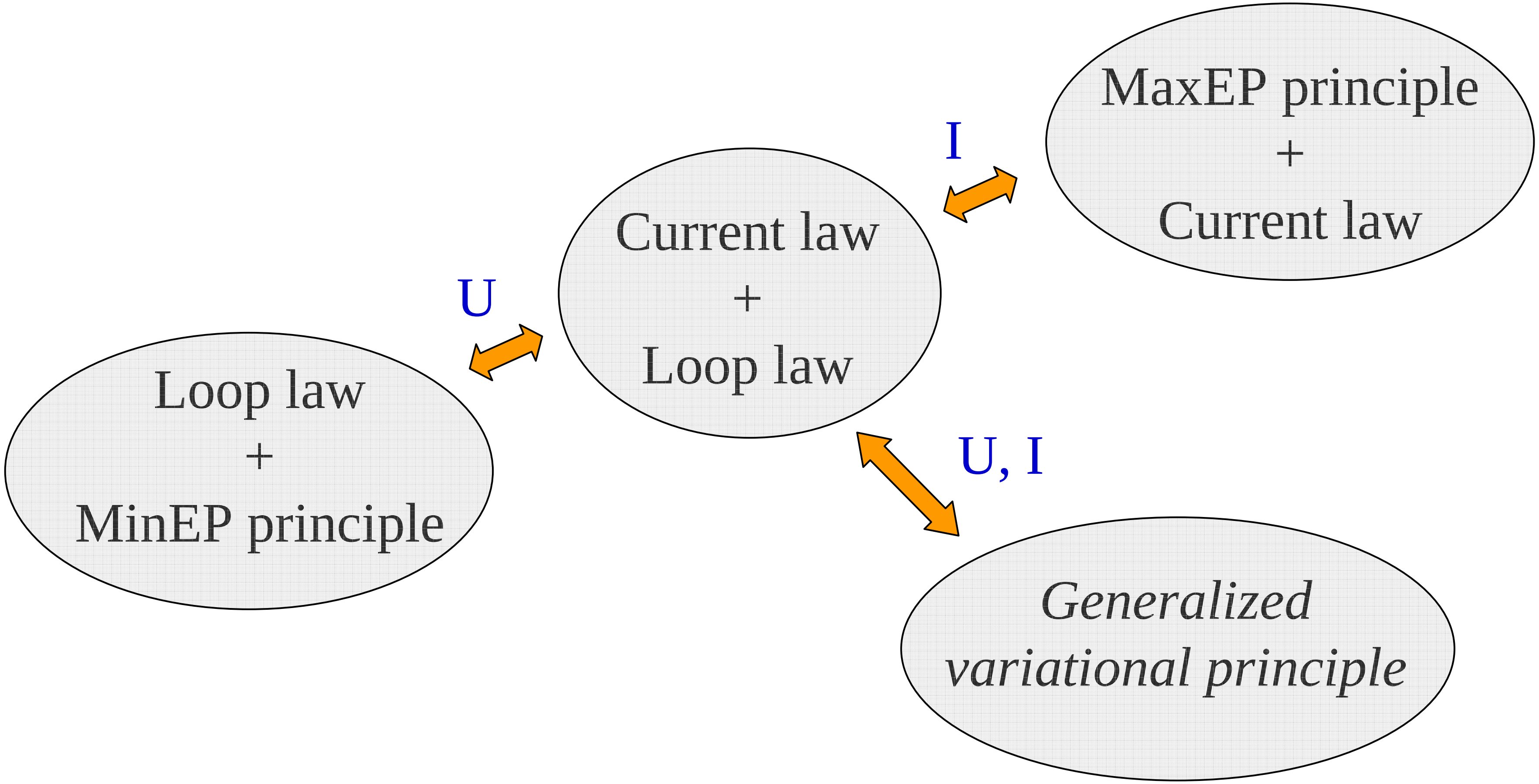
Stationary values of currents maximize the entropy production under constraint

$$Q(J) = W(J)$$



Linear electrical networks

summary of MinEP/MaxEP principles



MaxEP principle
+
Current law

Current law
+
Loop law

Loop law
+
MinEP principle

Generalized variational principle

From principles to fluctuation laws

Questions and ideas

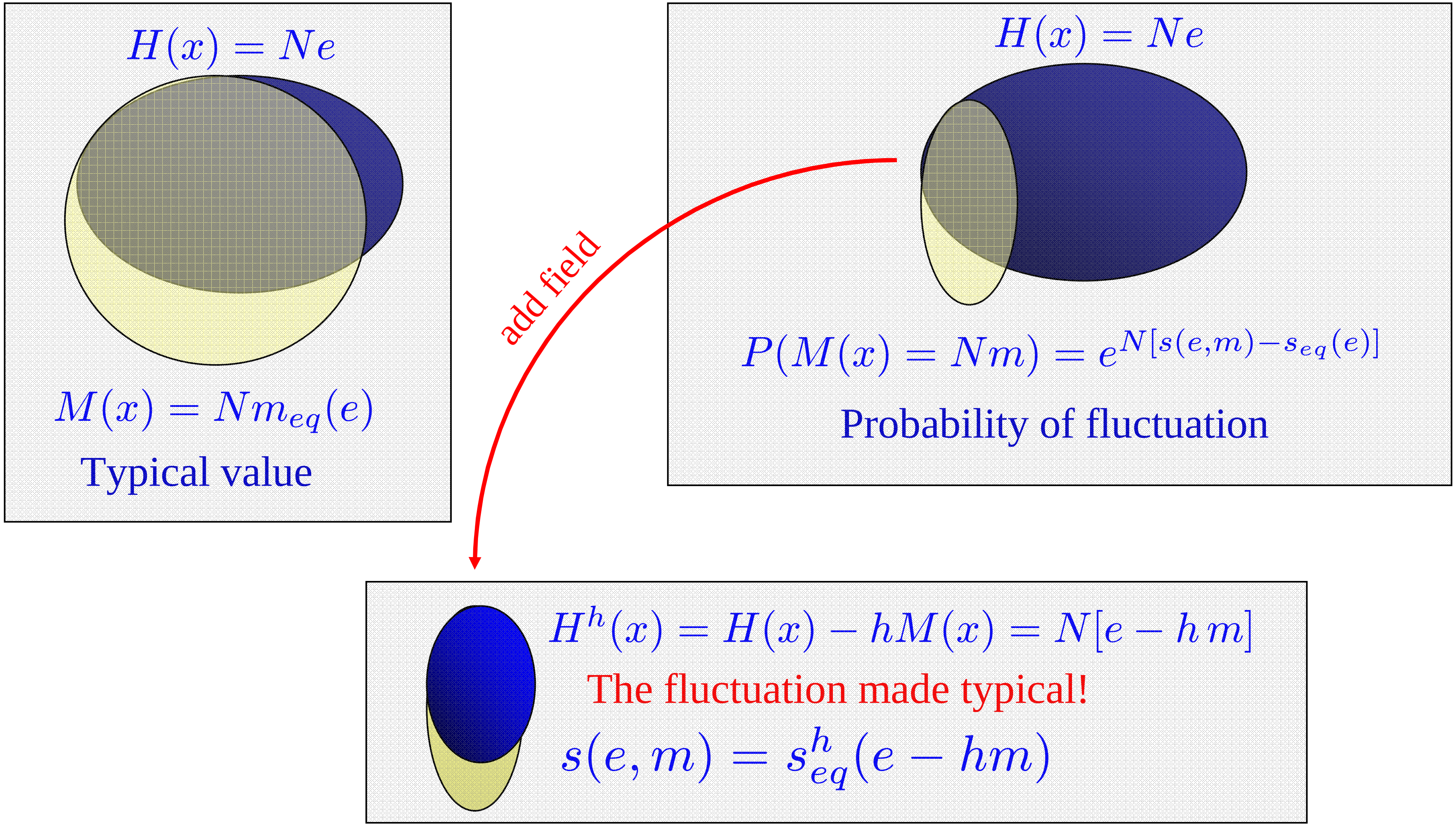
- How to go beyond approximate and *ad hoc* thermodynamic principles?
- Inspiration from thermostatics:

> *Equilibrium variational principles are intimately related to the structure of equilibrium fluctuations*

- Is there a nonequilibrium analogy of thermodynamical fluctuation theory?

From principles to fluctuation laws

Equilibrium fluctuations



$H(x) = Ne$

$M(x) = Nm_{eq}(e)$

Typical value

add field

$H(x) = Ne$

$P(M(x) = Nm) = e^{N[s(e,m) - s_{eq}(e)]}$

Probability of fluctuation

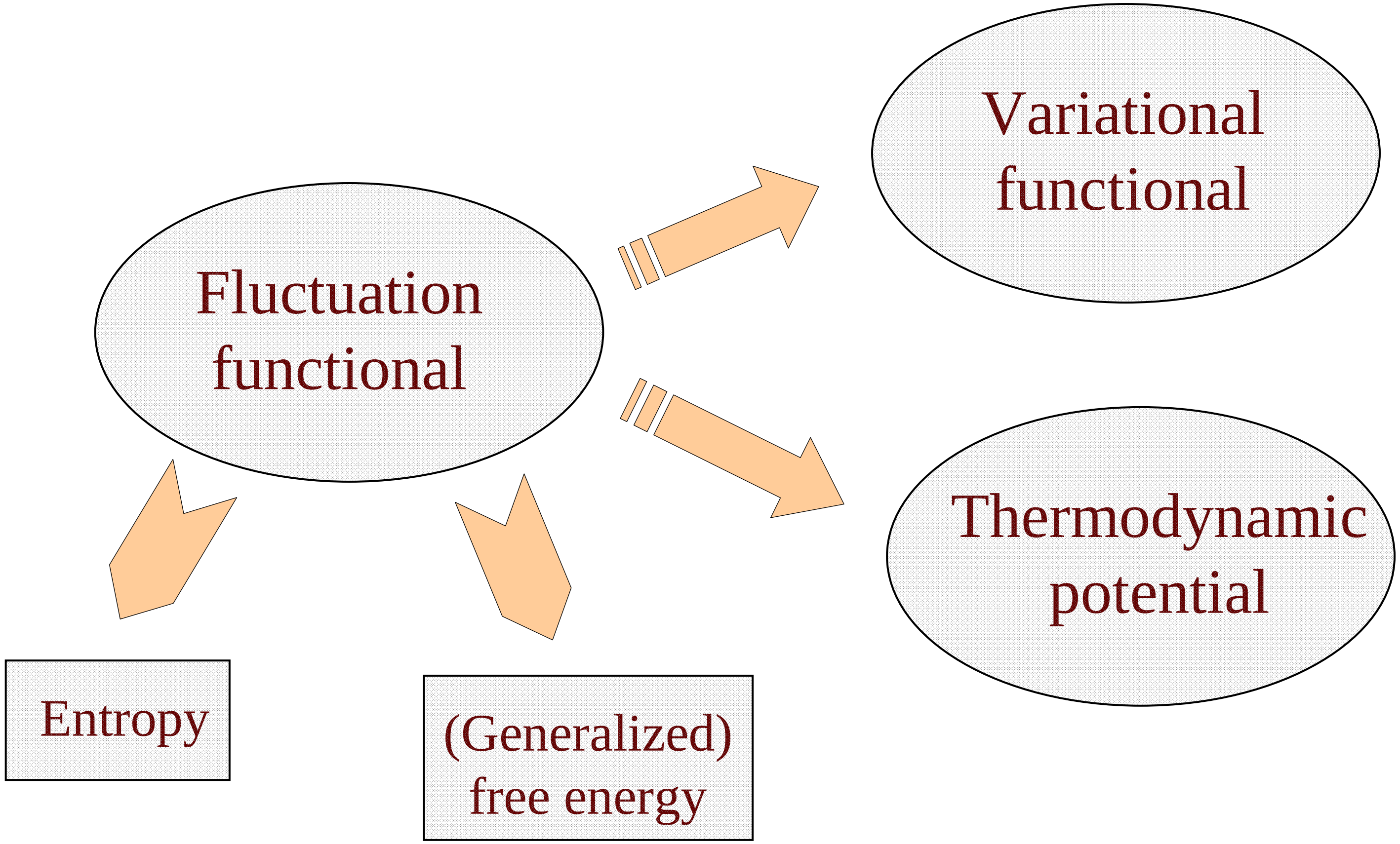
$H^h(x) = H(x) - hM(x) = N[e - h\,m]$

The fluctuation made typical!

$s(e,m) = s^h_{eq}(e - hm)$

From principles to fluctuation laws

Equilibrium fluctuations



Fluctuation functional

Variational functional

Thermodynamic potential

Entropy

(Generalized) free energy

From principles to fluctuation laws

Static versus dynamical fluctuations

- Empirical time average:

$$\bar{m}_T = \frac{1}{T}\int_0^T m(x_t)\,dt$$

- Ergodic property:

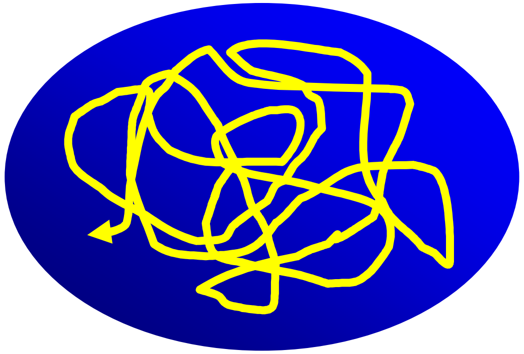
$$\bar{m}_T \to m_{eq}(e), \quad T \to \infty$$

- Dynamical fluctuations:

$$P(\bar{m}_T = m) = e^{-T\,I(m)}$$

- Interpolating between static and dynamical fluctuations:

$$P\Big(\frac{1}{n}\sum_{k=1}^{n} m(x_{\tau k}) = m\Big) = e^{-n\,I^{(\tau)}(m)}$$



$H(x) = Ne$

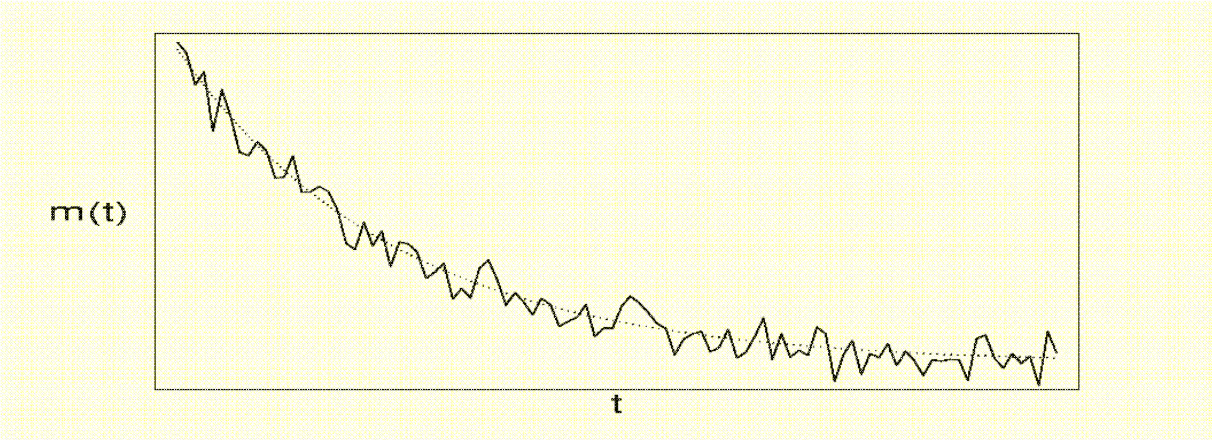
Static: $\tau \to \infty$

$I^{(\infty)}(m) = s(e) - s(e,m)$

Dynamic: $\tau \to 0$

Effective model of macrofluctuations

Onsager-Machlup theory



- Dynamics: $$R\,dm_t = -s\,m_t\,dt + \sqrt{\frac{2R}{N}}\,dB_t$$
- Equilibrium: $$P(m_\infty = m) \propto e^{-\frac{1}{2}N\,s\,m^2}$$

$S(m) - S(0)$

- Path distribution: $$P(\omega) = \exp\Big[-\frac{N}{4}\int_0^T \frac{R}{2}\Big(\frac{dm_t}{dt} + \frac{s}{R}m_t\Big)^2\Big]$$

Effective model of macrofluctuations

Onsager-Machlup theory

- Dynamics: $R\,dm_t = -sm_t\,dt + \sqrt{\frac{2R}{N}}dB_t$
- Path distribution:

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- Dynamical fluctuations:

$$P(\bar{m}_T = m) = P(m_t = m;\, 0 \le t \le T) = \exp\left[-T\frac{Ns^2}{8R}m^2\right]$$

- (Typical immediate) entropy production rate:

$$\sigma(m) = \frac{dS(m_t)}{dt} = \frac{Ns^2}{2R}m^2$$

Effective model of macrofluctuations

Onsager-Machlup theory

- Dynamics: $R\,dm_t = -s m_t\,dt + \sqrt{\frac{2R}{N}}dB_t$
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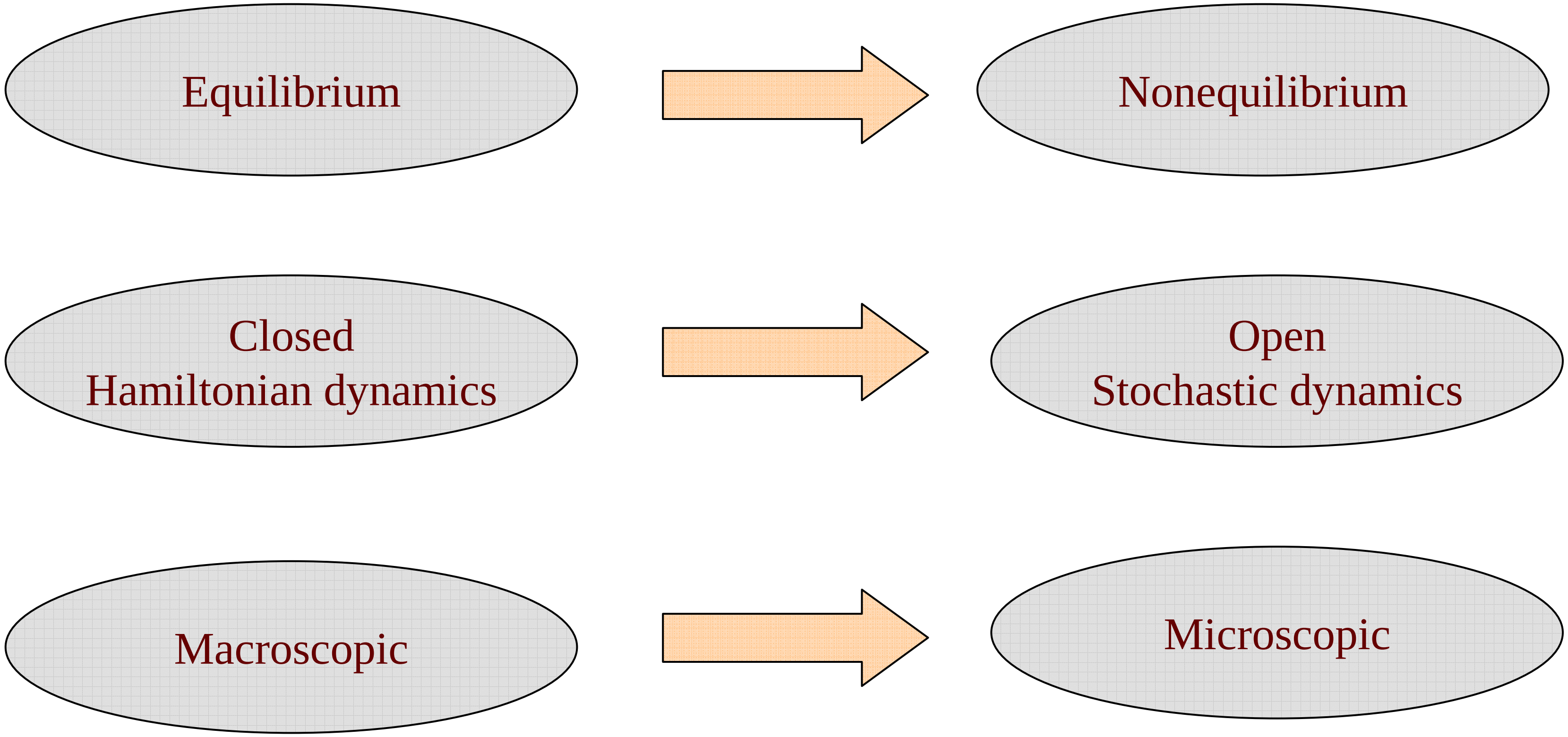
$$I(m) = \frac{1}{4}\sigma(m)$$

- (Typical immediate) entropy production rate:

$$\sigma(m) = \frac{dS(m_t)}{dt} = \frac{Ns^2}{2R}m^2$$

Towards general theory



Equilibrium → Nonequilibrium

Closed
Hamiltonian dynamics → Open
Stochastic dynamics

Macroscopic → Microscopic

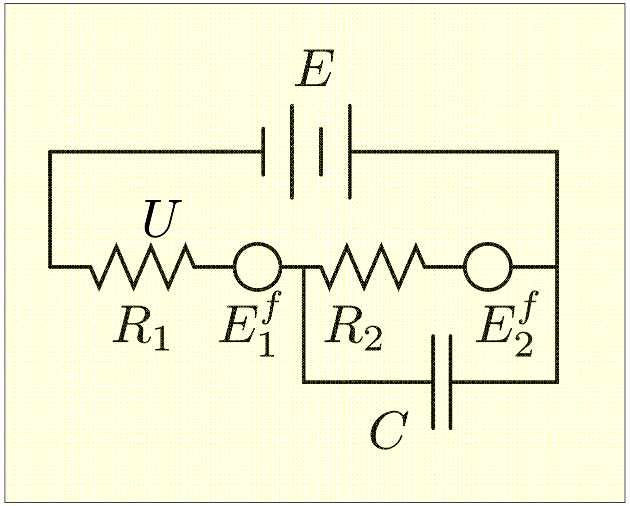
Linear electrical networks revisited

Dynamical fluctuations

- Fluctuating dynamics:

$$E = U + R_2 J + E_2^f$$

$$J = C\dot{U} + \frac{U - E_1^f}{R_1}$$



- Johnson-Nyquist noise:

$$E_t^f = \sqrt{\frac{2R}{\beta}}\,\xi_t$$

white noise

- Empirical time average:

$$\bar{U}_T = \frac{1}{T}\int_0^T U_t\,dt$$

- Dynamical fluctuation law:

$$-\frac{1}{T}\log P(\bar{U}_T = U) = \frac{1}{4}\frac{\beta_1\beta_2(R_1+R_2)}{\beta_1 R_1+\beta_2 R_2}\left[\frac{U^2}{R_1} + \frac{(E-U)^2}{R_2} - \frac{E^2}{R_1+R_2}\right]$$

Linear electrical networks revisited

Dynamical fluctuations

- Fluctuating dynamics:

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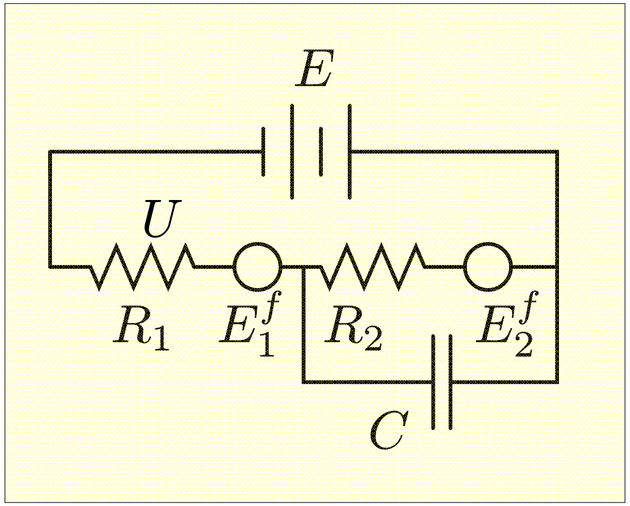


- Johnson-Nyquist noise:

$$E_t^f = \sqrt{\frac{2R}{\beta}}\,\xi_t$$

white noise

- Empirical time average:

$$\bar{U}_T = \tfrac{1}{T}\int_0^T U_t\,dt$$

total dissipated heat

- Dynamical fluctuation law:

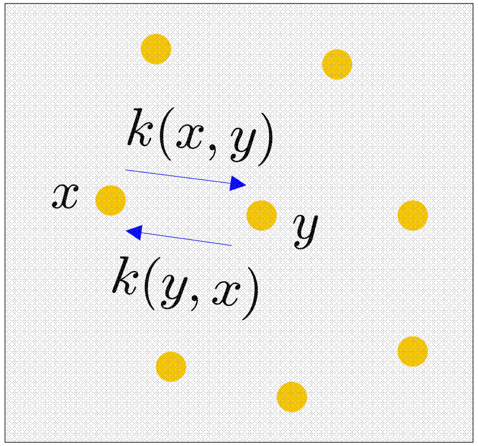
$$-\tfrac{1}{T}\log P(\bar{U}_T = U) = \tfrac{1}{4}\,\tfrac{\beta_1\beta_2(R_1+R_2)}{\beta_1 R_1+\beta_2 R_2}\left[\tfrac{U^2}{R_1} + \tfrac{(E-U)^2}{R_2} - \tfrac{E^2}{R_1+R_2}\right]$$

Stochastic models of nonequilibrium

breaking detailed balance

- Local detailed balance:

$$\log \frac{k(x,y)}{k(y,x)} = \Delta s(x,y) = -\Delta s(y,x)$$



- Global detailed balance generally broken:

$$\Delta s(x,y) = s(y) - s(x) + \epsilon F(x,y)$$

- Markov dynamics:

$$\frac{d\rho_t(x)}{dt} = \sum_y [\rho_t(y)k(y,x) - \rho_t(x)k(x,y)]$$

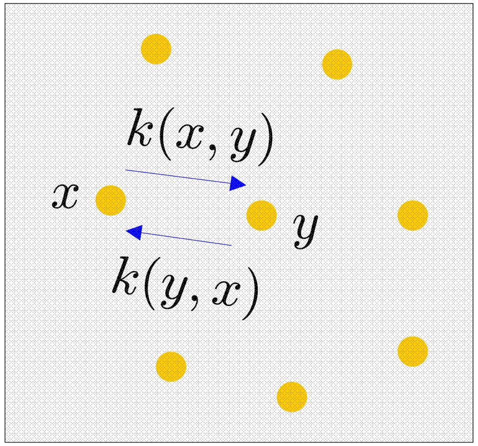
Stochastic models of nonequilibrium

breaking detailed balance

- Local detailed balance:

$$\log\frac{k(x,y)}{k(y,x)} = \Delta s(x,y) = -\Delta s(y,x)$$

entropy change
in the environment



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Stochastic models of nonequilibrium

breaking detailed balance

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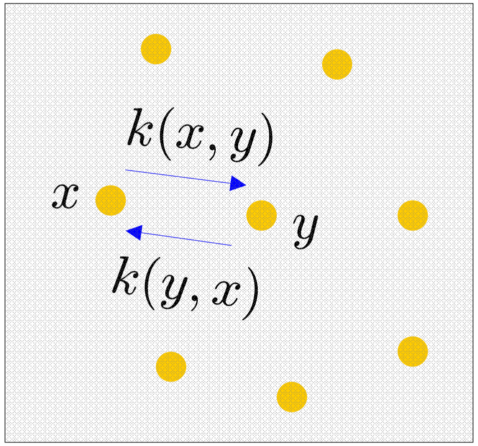

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entropy change in the environment

- Global detailed balance generally broken:

$$\Delta s(x,y) = s(y) - s(x) + \epsilon F(x,y)$$

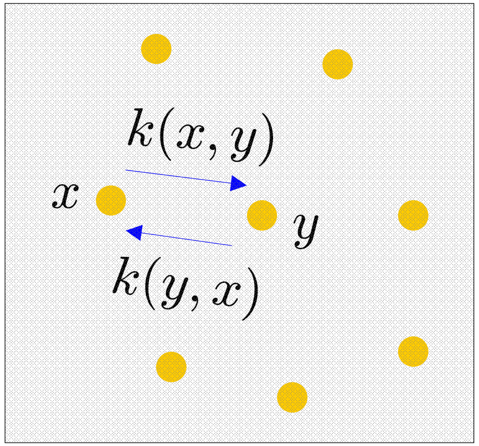
breaking term

- Markov dynamics:

$$\frac{d\rho_t(x)}{dt} = \sum_y [\rho_t(y)k(y,x) - \rho_t(x)k(x,y)]$$

Stochastic models of nonequilibrium

entropy production



- Entropy of the system:

$$S(\rho) = -\sum_x \rho(x) \log \rho(x)$$

- Mean currents:

$$J_\rho(x,y) = \underbrace{\rho(x)k(x,y) - \rho(y)k(y,x)}_{\text{zero at detailed balance}}$$

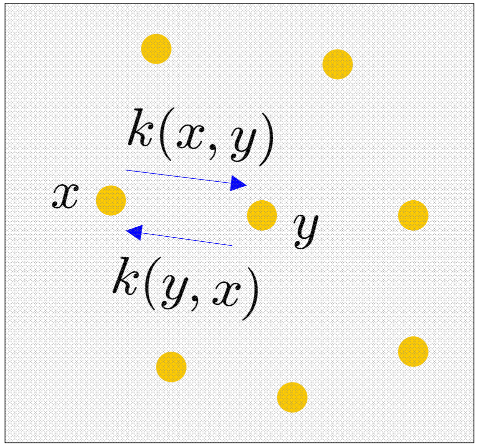
- Mean entropy production rate:

$$\sigma(\rho) = \frac{dS(\rho_t)}{dt} + \frac{1}{2}\sum_{(x,y)} J_\rho(x,y)\Delta s(x,y)$$

$$= \sum_{x,y} \rho(x)k(x,y) \log \frac{\rho(x)k(x,y)}{\rho(y)k(y,x)}$$

Stochastic models of nonequilibrium

entropy production



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- Mean entropy production rate:

$$\sigma(\rho) = \frac{dS(\rho_t)}{dt} + \frac{1}{2}\sum_{(x,y)} J_\rho(x,y)\Delta s(x,y)$$

$$= \sum_{x,y} \rho(x)k(x,y) \log \frac{\rho(x)k(x,y)}{\rho(y)k(y,x)} \geq 0$$

Warning:
Only for time-reversal
symmetric observables!

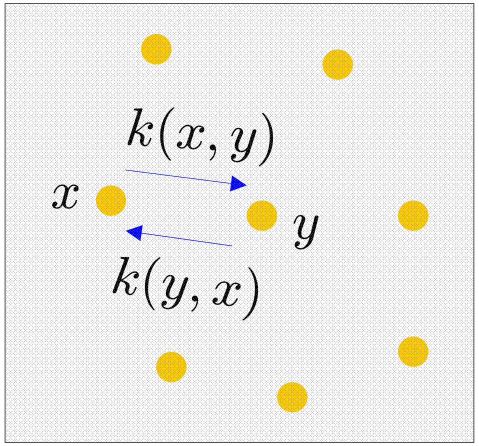
Stochastic models of nonequilibrium

MinEP principle

- ("Microscopic") MinEP principle:

In the first order approximation around detailed balance

$$\sigma(\rho) = \min \quad \Rightarrow \quad \rho = \rho_s + O(\epsilon^2)$$



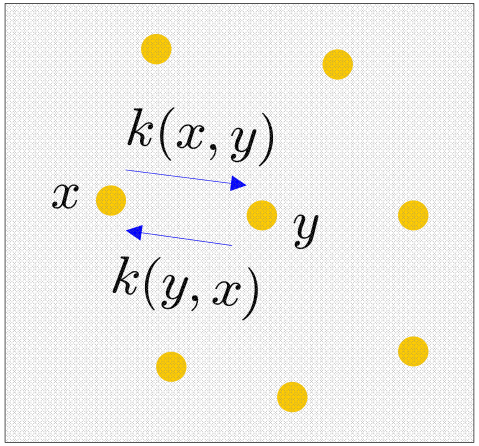
- Can we again recognize entropy production as a fluctuation functional?

Stochastic models of nonequilibrium

dynamical fluctuations

- Empirical occupation times:

$$\bar{p}_T(x) = \frac{1}{T}\int_0^T \chi(\omega_t = x)\,dt$$



- Ergodic theorem:

$$\bar{p}_T(x) \to \rho_s(x), \quad T \to \infty$$

- Fluctuation law for occupation times?

$$P(\bar{p}_T = p) = e^{-T\,I(p)}$$

- *Note:* $I(\rho_s) = 0$

Stochastic models of nonequilibrium

dynamical fluctuations

- *Idea*: Make the empirical distribution typical by modifying dynamics:

$$k(x,y) \longrightarrow k_v(x,y) = k(x,y)\, e^{[v(y)-v(x)]/2}$$

- The “field” v is such that distribution p is stationary distribution for the modified dynamics:

$$\sum_y \left[p(y)k_v(y,x) - p(x)k_v(x,y)\right] = 0$$

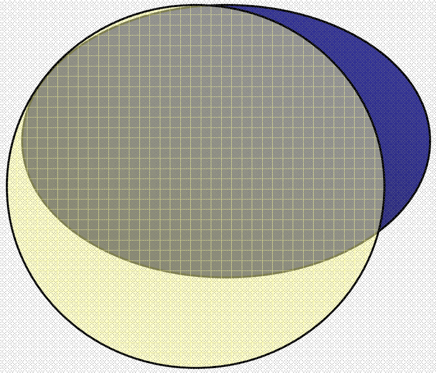
- Comparing both processes yields the fluctuation law:

$$\boxed{I(p) = \sum_{x,y} p(x)\left[k(x,y) - k_v(x,y)\right]}$$

Recall

Equilibrium fluctuations

$$H(x) = Ne$$

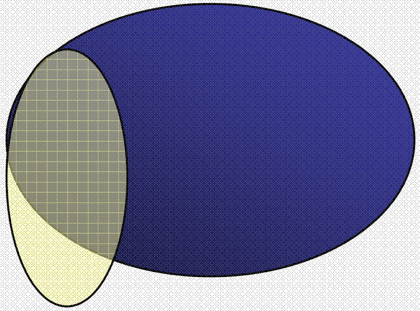


$$M(x) = Nm_{eq}(e)$$

Typical value

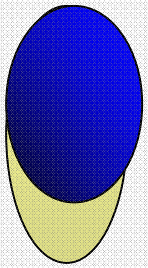
add field

$$H(x) = Ne$$



$$P(M(x) = Nm) = e^{N[s(e,m) - s_{eq}(e)]}$$

Probability of fluctuation



$$H^h(x) = H(x) - hM(x) = N[e - h\,m]$$

The fluctuation made typical!

$$s(e,m) = s^h_{eq}(e - hm)$$

Stochastic models of nonequilibrium

dynamical fluctuations

- *Idea*: Make the empirical distribution typical by modifying dynamics:

$$k(x,y) \longrightarrow k_v(x,y) = k(x,y)\, e^{[v(y)-v(x)]/2}$$

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$$I(p) = \sum_{x,y} p(x)\left[k(x,y) - k_v(x,y)\right]$$

Stochastic models of nonequilibrium

dynamica

- *Idea:*
  modi
  $k($
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  $$\sum_{y}$$

Traffic = mean dynamical activity:

$$\mathcal{T} = \frac{1}{2}\sum_{x,y} p(x)k(x,y) + p(y)k(y,x)$$

$$\Downarrow$$

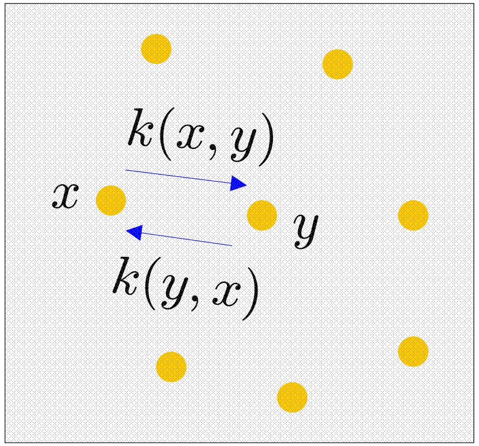
$$\text{I(p)} = \text{excess in traffic}$$

- Comparing both processes yields the fluctuation law:

$$I(p) = \sum_{x,y} p(x)\big[k(x,y) - k_v(x,y)\big]$$

Stochastic models of nonequilibrium

Recall: entropy production functional



- Entropy of the system:

$$S(\rho) = -\sum_x \rho(x)\log\rho(x)$$

- Mean currents:

$$J_\rho(x,y) = \underbrace{\rho(x)k(x,y) - \rho(y)k(y,x)}_{\text{zero at detailed balance}}$$

- Mean entropy production rate:

$$\sigma(\rho) = \frac{dS(\rho_t)}{dt} + \frac{1}{2}\sum_{(x,y)} J_\rho(x,y)\Delta s(x,y)$$

$$= \sum_{x,y} \rho(x)k(x,y)\log\frac{\rho(x)k(x,y)}{\rho(y)k(y,x)}$$

Stochastic models of nonequilibrium

dynamical fluctuations close to equilibrium

- General observation:

> *In the first order approximation around detailed balance*
>
> $$I(p) = \frac{1}{4}\left[\sigma(p) - \sigma(\rho_s)\right] + o(\epsilon^2)$$

- The variational functional is recognized as an approximate fluctuation functional
- *A consequence*: A natural way how to go beyond MinEP principle is to systematically analyze appropriate fluctuation laws

Stochastic models of nonequilibrium

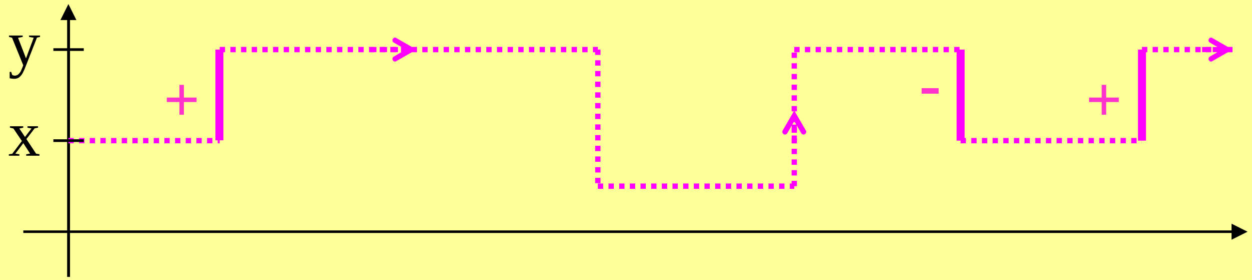
dynamical fluctuations close to equilibrium

- General observation:

In the first order approximation around detailed balance

Empirical currents:

$$\bar{J}_T(x,y) = \frac{1}{T}\big[\#\{\text{jumps } x \to y \text{ in } [0,T]\} - \#\{\text{jumps } y \to x\} \text{ in } [0,T]\big]$$



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Stochastic mo

dynamical fluctuations

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In the fir
detailed

Empirical currents:

$$\bar{J}_T(x,y) = \frac{1}{T}\left[\#\{\text{jum}\right.$$

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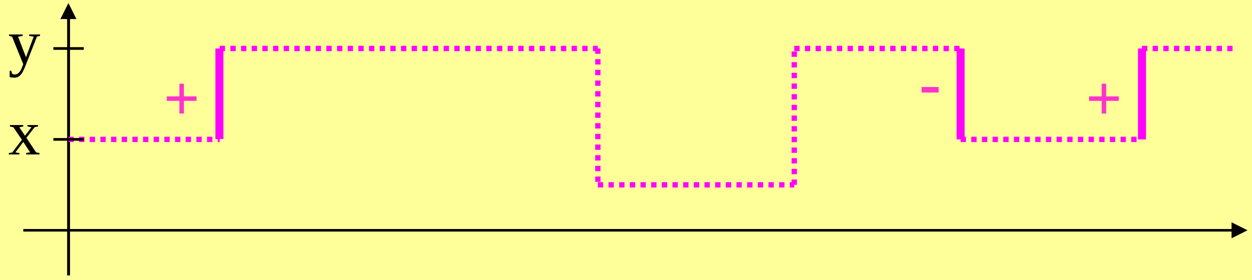

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tion laws

Typically,

$$\bar{J}_T(x,y) \to \rho_s(x)k(x,y) - \rho_s(y)k(y,x)$$

$$J_s(x,y)$$

Fluctuation law:

$$P(\bar{J}_T = J) = e^{-T\,G(J)}$$

- *with the fluctuation functional*

$$G(J) = \frac{1}{4}\left[\dot{S}(J_s) - \dot{S}(J)\right] + o(\epsilon^2)$$

on stationary currents satisfying

$$\dot{S}(J) = D(J)$$

Stochastic mo

dynamical fluctuations

- General observa

In the fir
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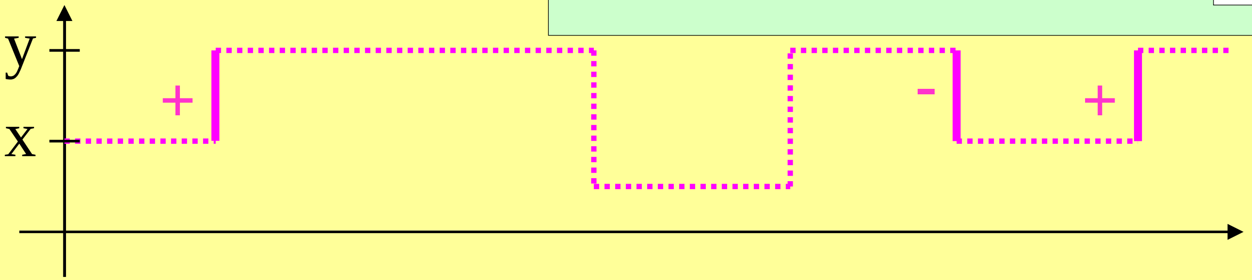

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$$\bar{J}_T(x,y) \to \rho_s(x)k(x,y) - \rho_s(y)k(y,x)$$

Fluctuation law:

$$P(\bar{J}_T = J) = e^{-T\,G(J)}$$

Entropy flux
$\frac{1}{2}\sum_{x,y} J(x,y)\,\Delta s(x,y)$

- *with the fluctuation functional*

$$G(J) = \frac{1}{4}\big[\dot{S}(J_s) - \dot{S}(J)\big] + o(\epsilon^2)$$

on stationary currents satisfying

$$\dot{S}(J) = D(J)$$

Onsager dissipation function

Stochastic models of nonequilibrium

towards general fluctuation theory

- It is useful to study the occupation time statistics and current statistics jointly
- Joint occupation-current statistics has a canonical structure

Driving-parameterized dynamics

$$k_F(x,y) = k_0(x,y)\, e^{F(x,y)/2}$$

Reference equilibrium

anti-symmetric

Current potential function

$$H(p,F) = 2[\mathcal{T}_F(p) - \mathcal{T}_0(p)]$$

Traffic

- Canonical equations

$$\left.\frac{\delta H}{\delta F(x,y)}\right|_{p,F} = J_F(x,y) \qquad \overset{\text{Legendre}}{\longleftrightarrow} \qquad \left.\frac{\delta G}{\delta J(x,y)}\right|_{p,J_F} = F(x,y)$$

- Joint occupation-current fluctuation functional

$$\mathcal{I}_F(p,J) = \frac{1}{2}\left[G(p,J) + H(p,F) - \dot{S}(F,J)\right]$$

Driving-parameterized dynamics

$$k_F(x,y) = k_0(x,y)\, e^{F(x,y)/2}$$

Reference equilibrium

anti-symmetric

Current potential function

$$H(p,F) = 2[\mathcal{T}_F(p) - \mathcal{T}_0(p)]$$

Traffic

Stochastic models of nonequilibrium

consequences of canonical formalism

- Functional G describes (reference) equilibrium dynamical fluctuations
- Fluctuation symmetry immediately follows:

$$\mathcal{I}_F(p,-J) - \mathcal{I}_F(p,J) = \dot{S}(F,J)$$

- Symmetric (p) and antisymmetric (J) fluctuations are coupled away from equilibrium, but:

Decoupling between p and J

- for small fluctuations
- close to equilibrium

General conclusions

what we know

- Both MinEP and MaxEP principles naturally follow from the fluctuation laws for empirical occupation times and empirical currents, respectively
- The validity of both principles is restricted to the close-to-equilibrium regime and it is essentially a consequence of
  - decoupling between time-symmetric and time-antisymmetric fluctuations
  - intimate relation between traffic and entropy production for Markovian dynamics close to detailed balance
- Time-symmetric fluctuations are in general governed by the traffic functional (nonperturbative result!)
- Joint occupation-current fluctuations have a general canonical structure, generalizing the original Onsager-Machlup theory
- Our approach can be extended to semi-Markov systems with some similar conclusions, cf. [6]

General conclusions

what we would like to know

- What is the operational meaning of new quantities (traffic,…) emerging in the dynamical fluctuation theory?
- Are there useful computational schemes for the fluctuation functionals and can one systematically improve on the EP principles beyond equilibrium?
- What is the relation between static and dynamical fluctuations?
- Could the dynamical fluctuation theory be a useful approach towards building nonequilibrium thermodynamics beyond close-to-equilibrium?

…and still many other things would be nice to know…

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Thank You
for Your Attention!