Thinking beyond Entropy

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There are many entropies:

Clausius, Boltzmann, Gibbs, Shannon, von Neumann, Rényi,...,

thermodynamic, configurational, information, corporate,...

Many entropies:
Claude Shannon recalls...

My greatest concern was what to call it. I thought of calling it information, but the word was overly used, so I decided to call it uncertainty. When I discussed it with John von Neumann, he had a better idea. Von Neumann told me, You should call it entropy, for two reasons. In the first place your uncertainty function has been used in statistical mechanics under that name, so it already has a name. In the second place, and more important,...
nobody knows *what entropy really is, so in a debate you will always have the advantage.*

Clausius thermodynamic entropy:

The fundamental laws of the universe correspond to two fundamental theorems of the mechanical theory of heat:

1. The energy of the universe is constant.
2. The entropy of the universe tends to a maximum.

Rudolf Clausius
The Mechanical Theory of Heat (1867).

Second law consists of two statements:

2a) Clausius heat theorem: for reversible thermodynamic transformations

$$\mathrm{d}S = \frac{1}{T}\delta Q$$

2b) Maximal Carnot efficiency:

$$\mathrm{d}S_{\mathrm{total}} = \mathrm{d}S - \frac{1}{T}\delta Q \geq 0$$

There are almost as many formulations of the second law as there have been discussions of it.
P.W. Bridgman, (1941).

Kelvin statement:
No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

Boltzmann-Planck-Einstein statistical interpretation,

beginning of equilibrium fluctuation theory:

$$S = k_B \log W$$

The impossibility of an uncompensated decrease of entropy seems to be reduced to an improbability.
(Gibbs, quoted by Boltzmann)

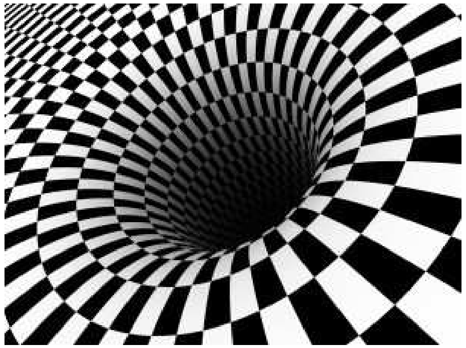
H-function: realization of $S = k_B \log W$ for dilute gases,

Boltzmann's H-theorem
in the context of the Boltzmann equation for dilute gases
is an extension of the second law:

In one respect we have even generalized the entropy principle here, in that we have been able to define the entropy in a gas that is not in a stationary state

Hence, the long search for some

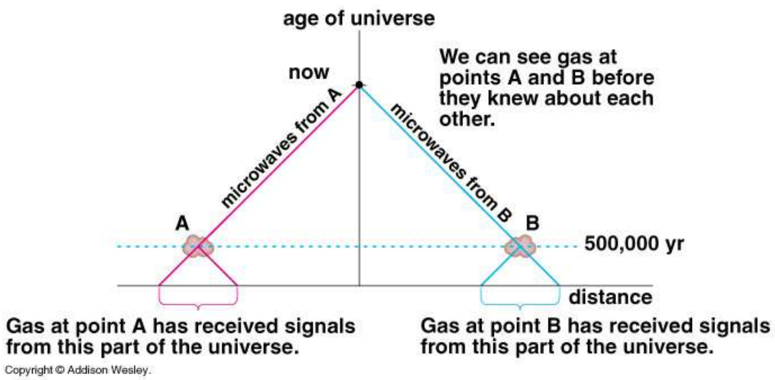
nonequilibrium entropy...



As an aside: *information paradox*

Loss of unitarity/determinism/reversibility need not be a problem,

e.g. dissipative evolutions are verified for reduced variables and for typical initial conditions,...



As an aside (2): *horizon problem*

Equilibrium need not be a matter of interactions or causal contact — equilibrium is **typical**, based on statistical/counting considerations,

i.e., maximum entropy for given constraints...

What can we mean by a nonequilibrium extension of the entropy concept?

- via Clausius heat theorem: entropy related to heat, possibly via exact differential,...
- via Boltzmann formula: entropy as rate of fluctuations, large deviations,...
- via H-theorem: entropy as Lyapunov functional,...

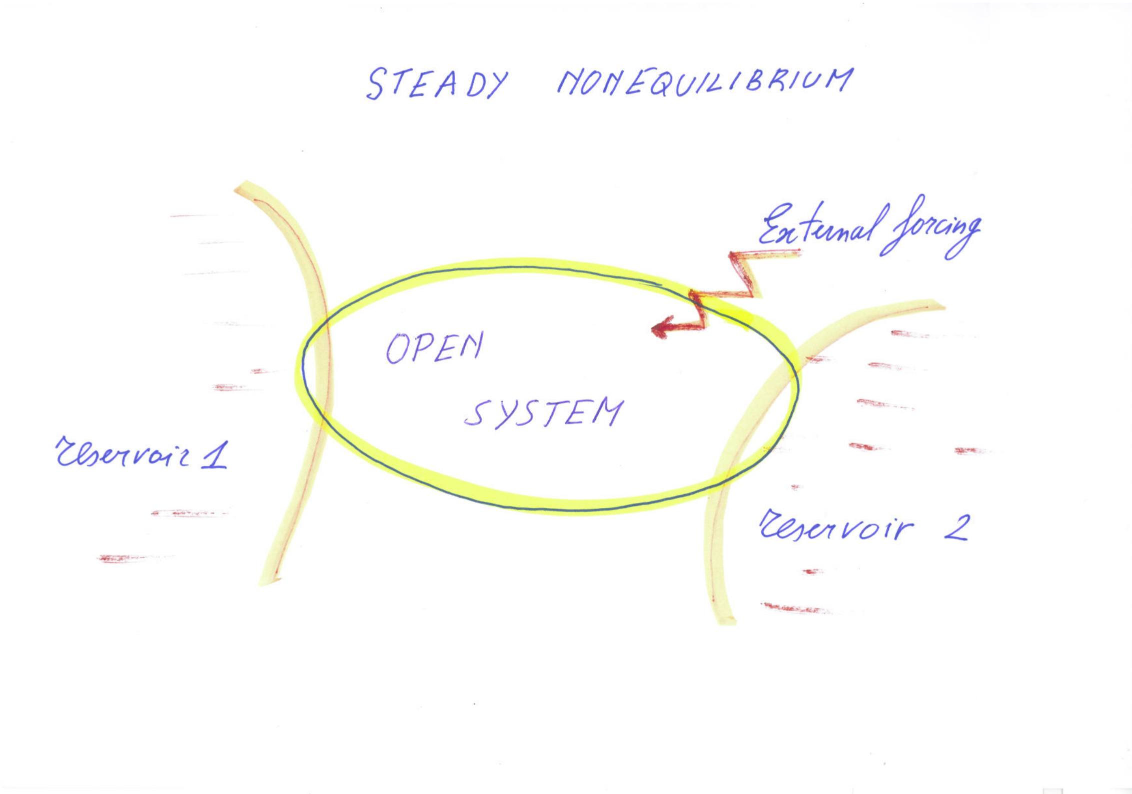
What can we mean by a nonequilibrium extension of the entropy concept?

What NONEQUILIBRIUM?

Beyond close-to-equilibrium, beyond local equilibrium, beyond linear response, beyond transients,..,

Look at driven systems, open systems connected with stationary but conflicting reservoirs, causing steady currents to flow —
energy and particle transport.

new trends: nonequilibrium material science, bio-calorimetry, quantum relaxation, nonlinear electrical/optical circuits, coherent transport, early cosmology, active matter,...



(title talk) *Thinking beyond entropy* then means:

thinking beyond irreversible thermodynamics,
beyond local equilibrium,
beyond linear regime around equilibrium,
and stopping the obsession with entropy...

leaving space for some totally new concepts, in particular related to nonequilibrium kinetics and time-symmetric fluctuation sector.

Three examples of *thinking beyond*

3. in nonequilibrium heat capacities;
2. in dynamical fluctuation and response theory;
1. in stability analysis, as Lyapunov functional,...

Remember: nonequilibrium extension of the entropy concept

3. via Clausius heat theorem: entropy related to heat, possibly via exact differential,...
2. via Boltzmann formula: entropy as rate of fluctuations, large deviations,...
1. via H-theorem: entropy as Lyapunov functional,...

1. Excess in dynamical activity as new Lyapunov functional.

cf.
C. Maes, K. Netocny and B.Wynants: *Monotone return to steady nonequilibrium*, Phys. Rev. Lett. 107, 010601 (2011).
C. Maes, K. Netocny and B.Wynants: *Monotonicity of the dynamical activity*, arXiv:1102.2690v2 [math-ph].

Physics riddle:
It increases — what could it be?

typical answer: something entropic....

cf. H-theorems and the role of thermodynamic potentials as Lyapunov functions in irreversible macroscopic equations.

Examples of Lyapunov functions:

Cahn-Hilliard equation:

$$F[c] \equiv \int \mathrm{d}x \{(1 - c^2)^2 + \frac{\gamma}{2}|\nabla c|^2\}$$

Boltzmann equation:

$$H[f] \equiv - \int \mathrm{d}q \mathrm{d}p\, f(q,p) \log f(q,p)$$

Zooming in on Master equation

(linear Boltzmann equation - Markov processes):

$$\frac{\mathrm{d}}{\mathrm{d}t}\mu_t(x) = \sum_y \{k(y,x)\mu_t(y) - k(x,y)\mu_t(x)\}$$

say irreducible, with finite number of states x and unique stationary distribution ρ: well-known mathematical fact,

$$s(\mu_t|\rho) = \sum_x \mu_t(x)\ \log\frac{\mu_t(x)}{\rho(x)} \downarrow 0$$

What is the meaning of and how useful is this monotonicity of the relative entropy?

Mostly limited to processes satisfying detailed balance, in their approach to stationary equilibrium... because then

$$s(\mu|\rho) = F[\mu] - F[\rho]$$

$$F[\rho] = -\beta \log Z, \quad \rho(x) = \frac{1}{Z} e^{-\beta U(x)}$$

and so, under detailed balance with potential function $U(x)$, we are really speaking about the monotonicity of the free energy functional

$$F[\mu] = \sum_x \mu(x)U(x) + \sum_x \mu(x) \log \mu(x)$$

$$F[\mu_t] \downarrow - \beta \log Z$$

for μ_t solving the Master equation.

NEW IDEA

NONEQUILIBRIUM system as

caged system, kinematically constrained, much more dominated by noise and time-symmetric fluctuations.

HEURISTICS

ENTROPY: volume of phase space region for values of reduced variables

DYNAMICAL ACTIVITY: surface (exit+entrance) of phase space region

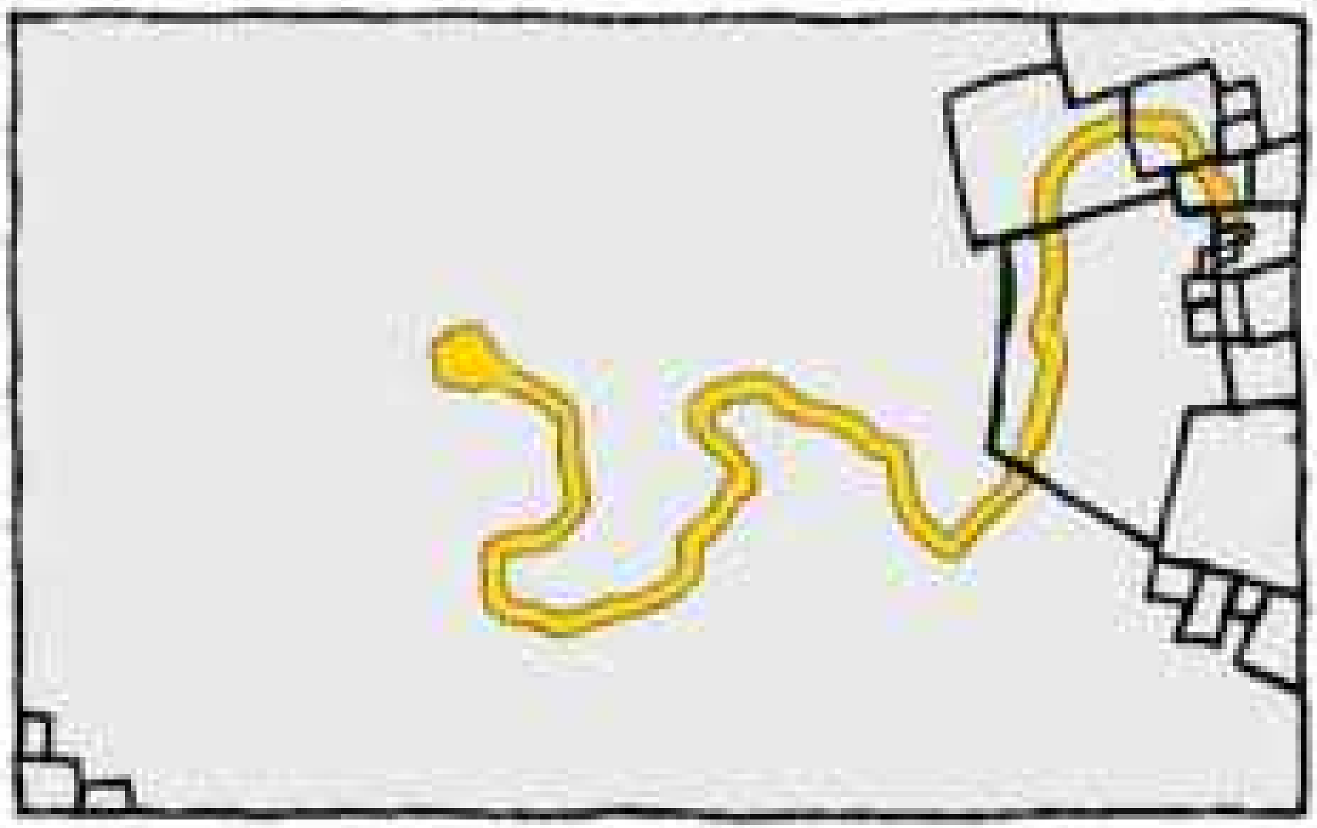


Figure 6: Wandering through boxes in phase space

Given reduced (mesoscopic) states $x, y, \ldots$ distributed with probability law μ.

The DYNAMICAL ACTIVITY in μ

depends on nonequilibrium driving,

and can change under opening additional dissipation channels.

The DYNAMICAL ACTIVITY in μ

$$D(\mu) = \sum_{x,y} \mu(x)\big[k(x,y) - k_V(x,y)\big]$$

where $V = V_\mu$ is the potential so that the dynamics with modified rates

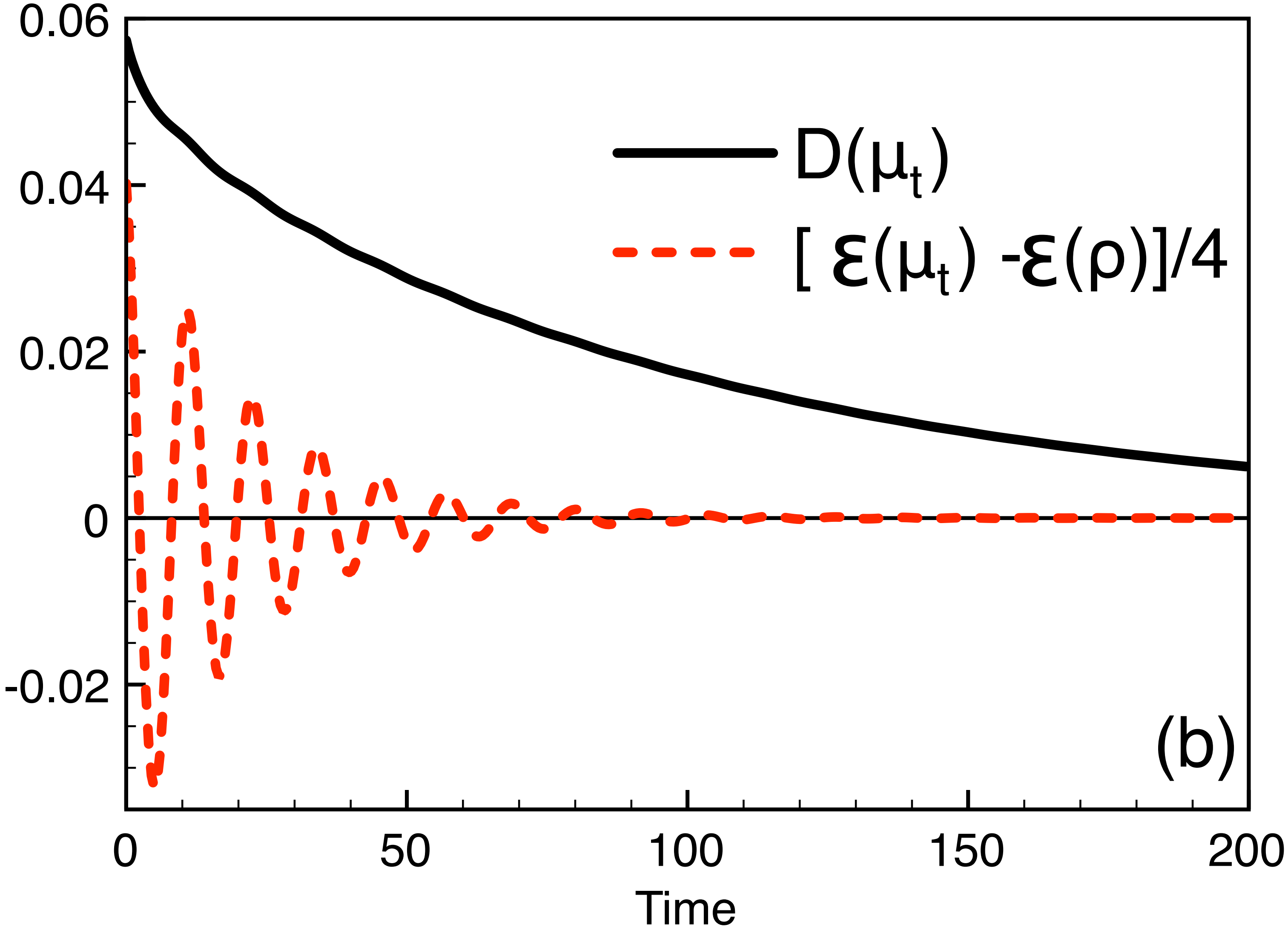
$$k_V(x,y) = k(x,y)\,\text{exp}\Big[\frac{V(y) - V(x)}{2}\Big]$$

leaves μ invariant.

New result: **Under** *normal linear response*,

$$D(\mu_t) \downarrow 0$$

monotone decay to zero, for large times t.


0.06
0.04
0.02
0
-0.02
0
50
100
150
200
Time
$D(\mu_t)$
$[\,\varepsilon(\mu_t)\ -\varepsilon(\rho)]/4$
(b)

2. Excess in dynamical activity as correction to fluctuation-dissipation theorem and as large deviation functional.

cf.

C. Maes, *Fluctuations and response out-of-equilibrium*. Progress of Theoretical Physics Supplement **184**, 318–328 (2010).

C. Maes, K. Netocny and B. Wynants, *On and beyond entropy production; the case of Markov jump processes*. Markov Processes and Related Fields **14**, 445–464 (2008).

Remember Kubo-theory: the linear response to a perturbation at equilibrium is directly related to the energy dissipation in the return to equilibrium.

$$\langle Q(t)\rangle^h - \langle Q(t)\rangle = \langle \mathsf{ENT}^{[0,t]}(\omega)\, Q(x_t)\rangle$$

where

$\mathsf{ENT}^{[0,t]}(\omega)$ is the entropy flux due to the decay of the perturbation over time-interval $[0,t]$.

Fluctuation-dissipation theorem

Suppose at $t = 0$ equilibrium system at β^{-1}. Add perturbation $-h_t V$, $t > 0$ to potential. Look at linear response:

$$\langle Q(t)\rangle^h = \langle Q(t)\rangle + \int_0^t \mathrm{d}s\, h_s R_{QV}(t,s) + o(h)$$

In equilibrium:

$$R_{QV}(t,s) = \beta \frac{\mathrm{d}}{\mathrm{d}s} \langle V(s) Q(t)\rangle$$

Major *motivation* and *subject*:

To know a system is to know its response to external stimuli.
If that response is related to the structure of (internal) fluctuations — that is even better.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NEW

The nonequilibrium formula takes the form

$$\langle Q(t)\rangle^h - \langle Q(t)\rangle = \frac{1}{2}\langle \mathrm{ENT}^{[0,t]}\, Q(t)\rangle + \frac{1}{2}\langle \mathrm{ESC}^{[0,t]}\, Q(t)\rangle$$

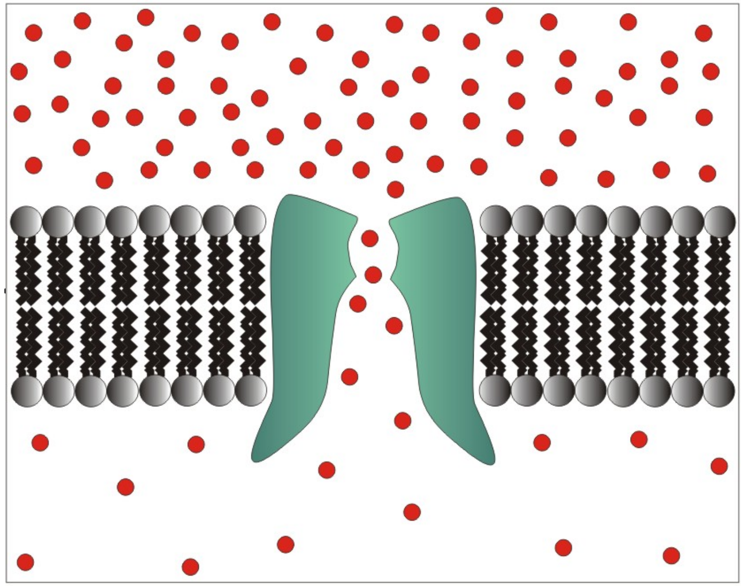
where

$\mathrm{ESC}^{[0,t]}$ is the excess in dynamical activity due to the decay of the perturbation over time-interval $[0,t]$.

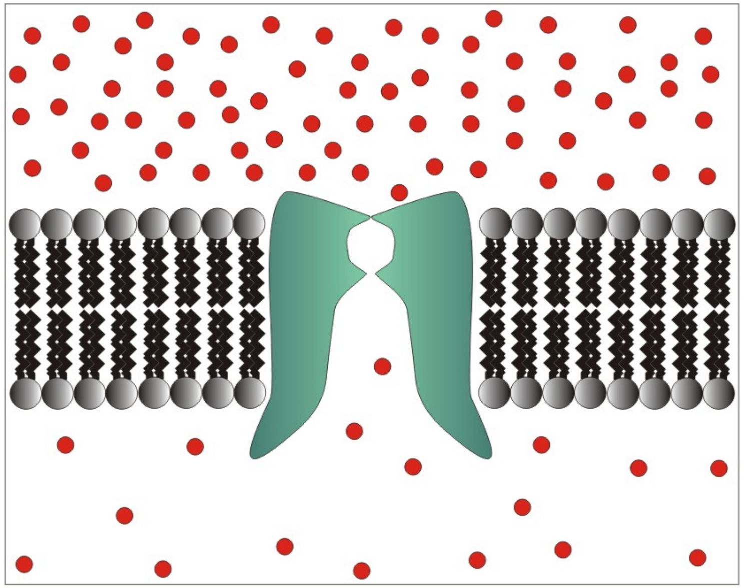
Example: boundary driven lattice gas in nonequilibrium steady state.
E.g. ions hopping through cell pore / ion channel

What happens to the density if you increase the chemical potentials *inside* and *outside* the cell?

Think of boundary driven Kawasaki dynamics in linear chain or of boundary driven Lorentz gas.



Open



Closed

Entropic contribution makes

$$\beta \frac{\mathrm{d}}{\mathrm{d}s} \langle \mathcal{N}(s)\mathcal{N}(t) \rangle$$

which amounts to local density fluctuations (as for response formulae in equilibrium)

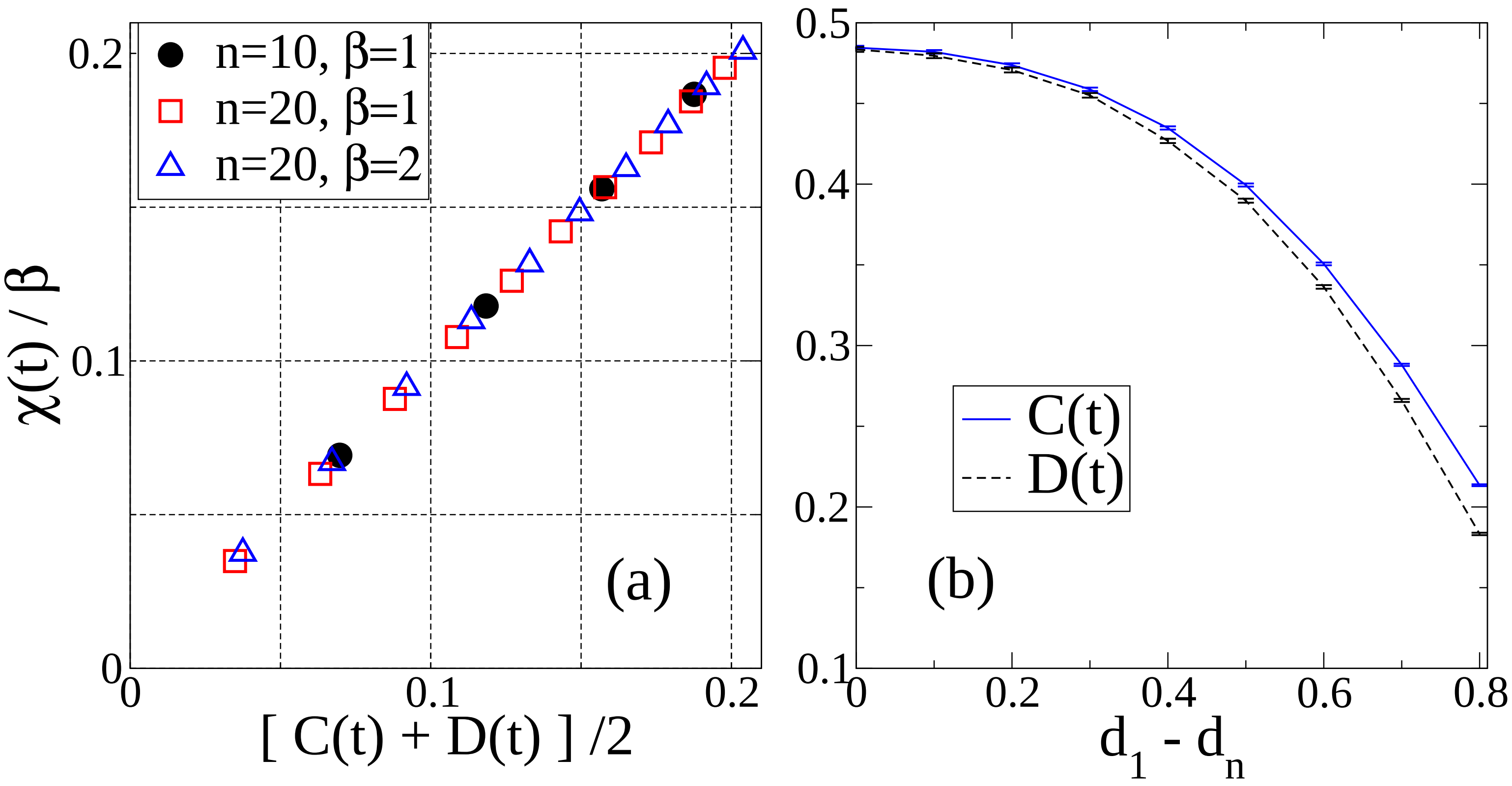
Frenetic contribution makes

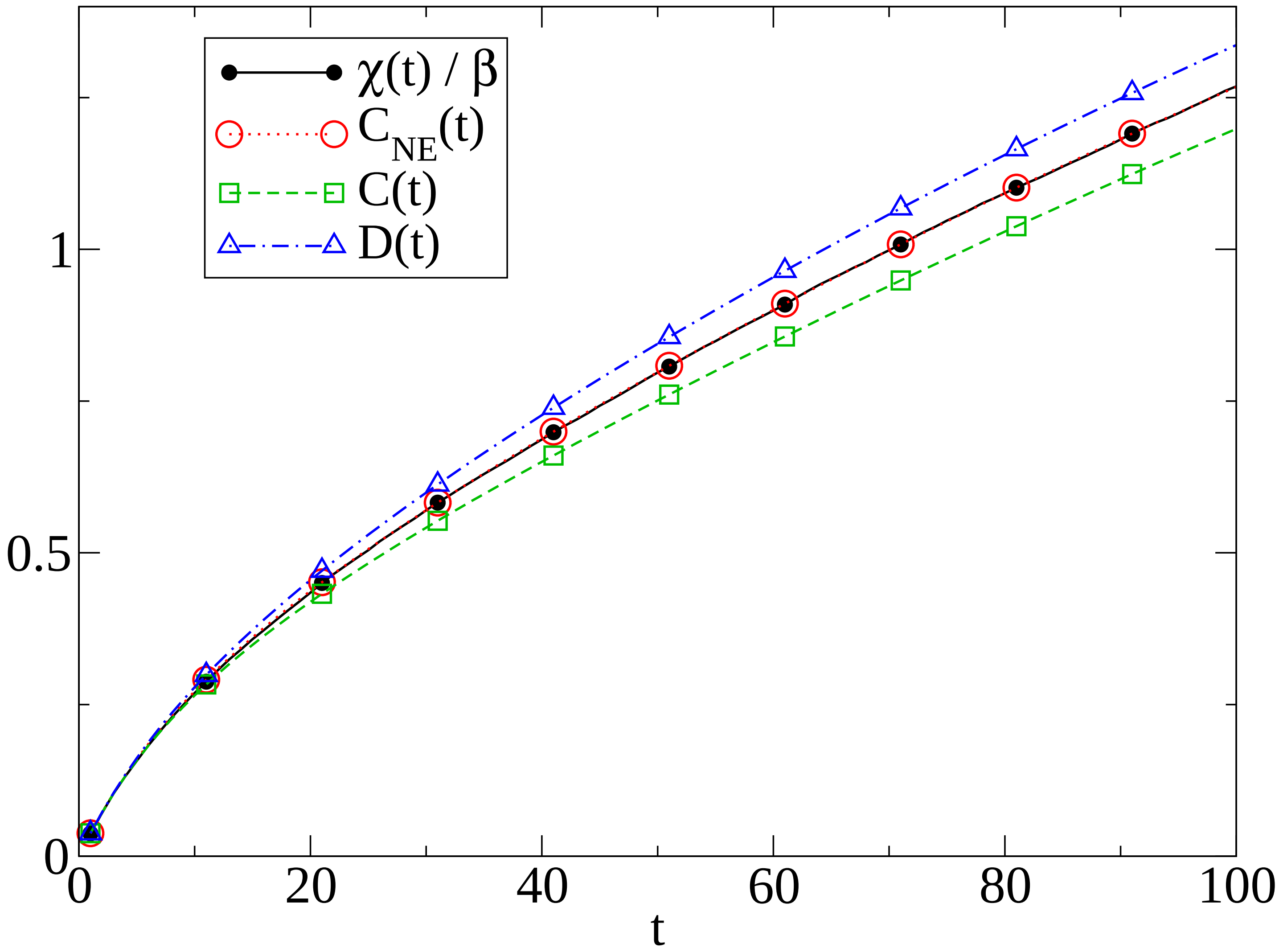
$$\beta \langle \mathcal{J}(s) \mathcal{N}(t) \rangle$$

for the instantaneous particle current J, the rate at which the total number of particles changes at each time.

Independent of all dynamical details, in the driven steady regime:

$$R_{\mathcal{N}\mathcal{N}}(t,s) - \beta \frac{\mathrm{d}}{\mathrm{d}s} \langle \mathcal{N}(X_s)\mathcal{N}(X_t)\rangle \quad = \quad \frac{\beta}{2} \langle \mathcal{N}(X_s)\, \mathcal{J}(X_t)\rangle - \frac{\beta}{2} \langle \mathcal{J}(X_s)\, \mathcal{N}(X_t)\rangle$$


n=10, β=1
n=20, β=1
n=20, β=2
χ(t) / β
[C(t) + D(t)] /2
(a)
0
0.1
0.2
C(t)
D(t)
(b)
$d_1 - d_n$
0.1
0.2
0.3
0.4
0.5
0.6
0.8


χ(t) / β
C_NE(t)
C(t)
D(t)
0
0.5
1
0
20
40
60
80
100
t

For example: boundary driven Lorentz gas

Example from work by Takahiro Nemoto and Shin-ichi Sasa:

Thermodynamic formula for the cumulant generating function of time-averaged current, Phys. Rev. E **84** (2011).

cumulant generating function

$$\log\langle\, \exp\{\lambda \cdot \text{ time-integrated current}\}\,\rangle$$

can be written (variationally) as a difference in dynamical activities.

All that is related to dynamical large deviation theory of Donsker-Varadhan (1975), where large deviation rate function for stationary occupation times involves differences in dynamical activities.

3. Time-symmetric sector in nonequilibrium heat capacities.

cf.
Eliran Boksenbojm, Christian Maes, Karel Netocny and Jirka Pesek:
Heat capacity in nonequilibrium steady states, Europhysics Letters **96**, 40001 (2011).

MAIN QUESTION:

how to make physical sense of

heat capacities

for steady nonequilibrium systems.

The main idea is to consider the excess heat when the environment temperature is changed.

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excess heat when the environment temperature is changed.

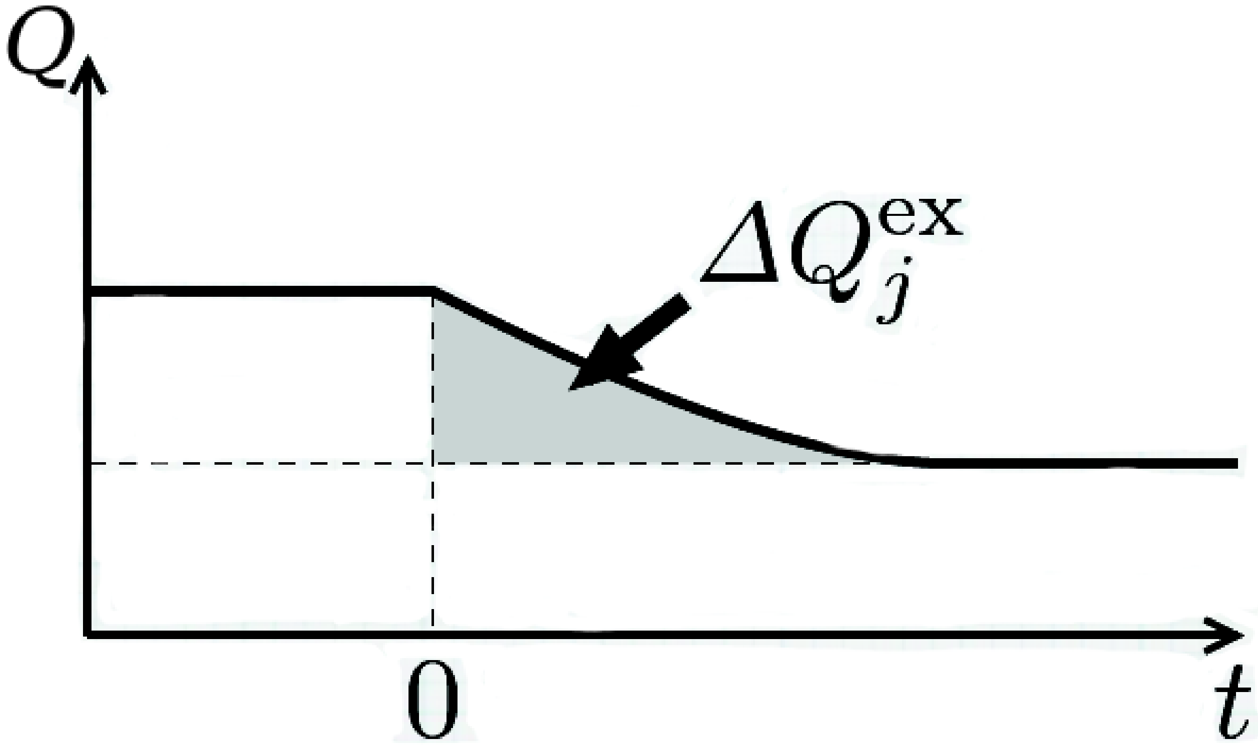
cf. previous **theoretical work** where the notion of excess heat was introduced in contrast with house-keeping heat:
papers by Oono-Paniconi (1998), Hatano-Sasa (2001), Ruelle (2003),
Komatsu-Nakagawa-Sasa-Tasaki (2008),...

START at time zero from steady regime at temperature T, and suddenly CHANGE THE TEMPERATURE to $T' = T + \mathrm{d}T$.
WAIT a time $\tau > \tau_r$ (relaxation time) and LOOK AT THE HEAT $Q := Q^{[0,\tau]}$ over times $t \in [0, \tau]$:

$$Q = E(x_\tau) - E(x_0) - \int_0^\tau F(x_t)\, \dot{x}_t \, \mathrm{d}t$$

for energy E and force F that acts on the system.
Denote $\langle Q \rangle$ the heat average over all trajectories in $[0, \tau]$, and $\langle Q \rangle_{T'}$ is the steady heat at temperature T'.
Then, heat capacity $C(T)$ is defined as

$$\langle Q \rangle - \langle Q \rangle_{T'} = C(T)\, \mathrm{d}T$$


Q
ΔQ_j^{ex}
0
t

Example

a Brownian particle driven through a toroidal trap, see e.g. the experimental realization and nonequilibrium response in the paper
Juan Ruben Gomez-Solano *et al*: Fluctuations and response in a non-equilibrium micron-sized system, Journal of Statistical Mechanics, P01008 (2011).

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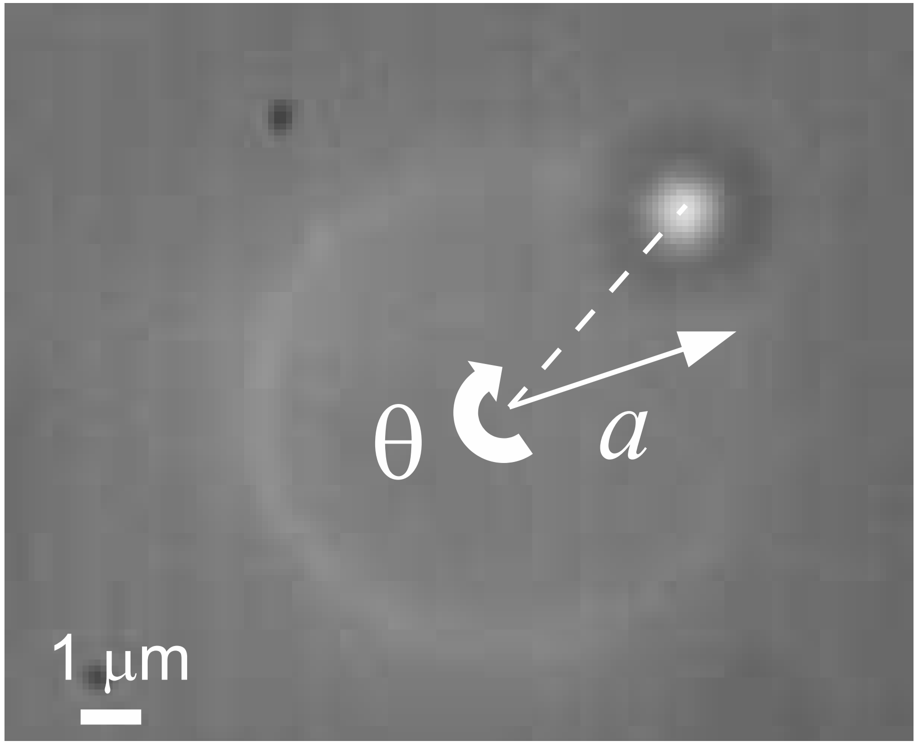
θ
a
1 μm

Interesting behavior at low temperatures and critical at $F = A$:

For $F < A$: localized regime, similar to equilibrium;
For $F > A$: conducting regime, energy-temperature response gets weaker.

$$\dot{x}_t = A \sin 2\pi x_t + F + \sqrt{2T}\,\xi_t$$

$$U(x) = \frac{A}{2\pi} \cos 2\pi x, \quad \xi_t = \text{ standard white noise}$$

For very **slowly varying** temperature T_t,

$$\dot{x}_t = A \sin 2\pi x_t + F + \sqrt{2T_t}\,\xi_t$$

and we ask for the nonequilibrium specific heat and
(1) how it relates to the temperature dependence of the dissipated power, and
(2) how it can be expressed as heat/activity fluctuations.

1. Relation with T-dependence of heat current:

Suppose $T_s - T = \varepsilon \sin(\omega s)$ with some small unit ε of temperature change.

Then, the low-frequency asymptotics of the heat current response is

$$J_t^Q = J_0^Q + \varepsilon\,[\sigma \sin(\omega t) - C(T)\,\omega \cos(\omega t) + O(\omega^2)]$$

and the (quasistatic) steady heat capacity provides the leading low-frequency (out-phase) correction to the steady (in-phase) linear temperature-heat relation. This also indicates how the steady heat capacity can possibly be detected and measured from the response to slow periodic temperature variations.

2. Relation with fluctuation theory:

In equilibrium: heat capacity in the canonical ensemble (fixed volume and particle number) $\propto$ energy variance;

In nonequilibrium: heat/activity fluctuations:

$$C(T) = \frac{1}{2k_B T^2} \langle \{Q^- - Q^+\} \{ \int_0^\infty \mathrm{d}s \, A(x_s) + Q(\omega) \} \rangle$$

where Q is heat and A is a state function, expressing nonequilibrium kinetics, which originates from the time-symmetric sector.

One consequence: heat capacity can become negative.

Example: overdamped motion of star in dense cluster with differential rotation,

$$\dot{x}_t = F - \nabla U + \sqrt{2T}\,\xi_t$$

$$U(r,\theta) = \frac{\lambda}{2} r^2, \qquad F(r,\theta) = \kappa\, r^{\alpha}\, \vec{e}_{\theta}, \qquad \alpha > -1$$

quadratic central potential U and angular driving F.

The heat capacity as defined via the quasi-static excess heat is given by

$$C_F = \frac{\partial \langle U \rangle}{\partial T} + \Delta C_F,$$

with "correction"

$$\Delta C_F = \frac{\alpha \dot{S}}{2\lambda} \propto T^{\alpha - 1}$$

linear in steady entropy production rate $\dot{S}$.

The heat capacity C_F becomes negative whenever $\alpha < 0$ and driving large enough or T small enough.

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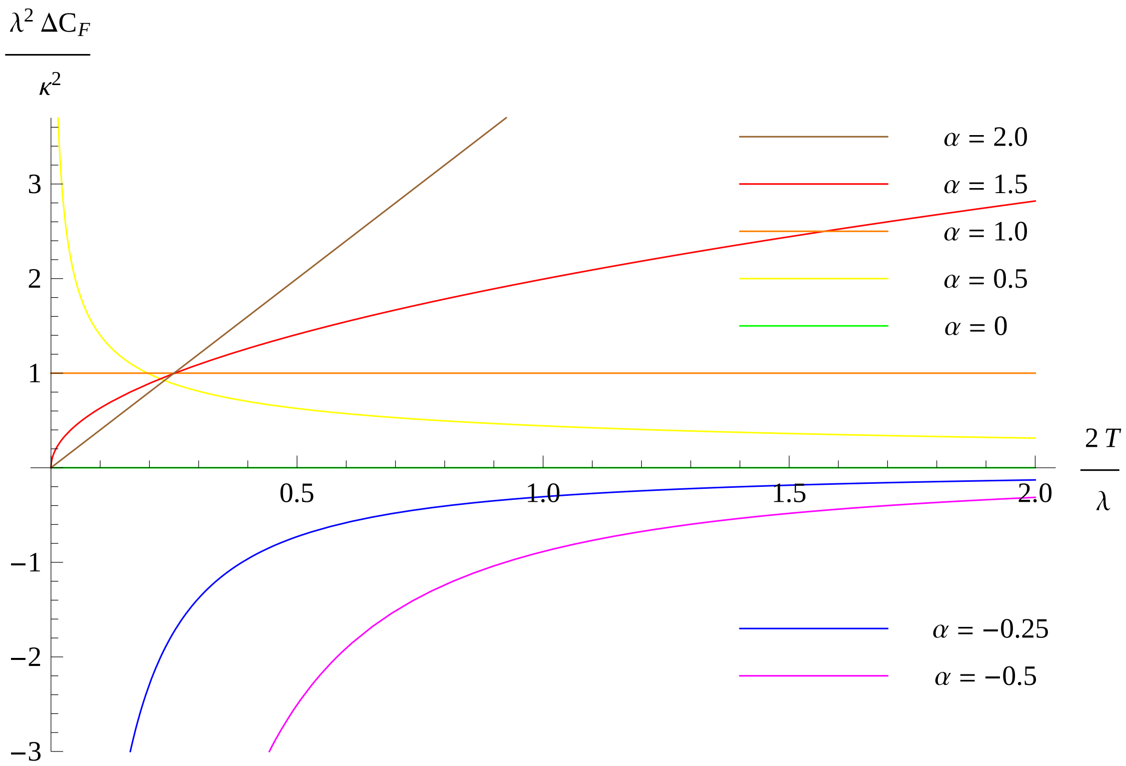

$\frac{\lambda^2 \Delta C_F}{\kappa^2}$
3
2
1
−1
−2
−3
0.5
1.0
1.5
2.0
$\frac{2T}{\lambda}$
α = 2.0
α = 1.5
α = 1.0
α = 0.5
α = 0
α = −0.25
α = −0.5

To first order

in the nonequilibrium driving,

$$C = \frac{\mathsf{d}}{\mathsf{d}T}\langle E\rangle - \frac{1}{T}\big(\langle E\rangle - \langle E\rangle_{\mathsf{eq}}\big)$$

which adds **two responses.**
Right-hand side is purely steady state property — no process property.

Experimental explorations on steady nonequilibrium heat capacities:

papers by Sevilla group such as by
del Cerro-Ramos (1993),
Del Cerro-Martin-Ramos (1996).

Conclusions:
There is a world and even life beyond entropy...

We see it in
- new H-theorems — Lyapunov function;
- new fluctuation-dissipation-activity theorem;
- new effects in nonequilibirum heat capacity.

Moreover:

Entropy *defocuses* in nonequilibrium physics as
- dynamical fluctuations not expressed in terms of heat dissipation;
- entropy gets curvature — non-scalar thermodynamic potentials.

see also many other similar observations, such as in "Geometrical Clausius Equality for Steady State Thermodynamics" by Takahiro Sagawa, Hisao Hayakawa.

paper download from

`http://itf.fys.kuleuven.be/~christ/`

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