QUASISTATIC HEAT PROCESSES IN SMALL NONEQUILIBRIUM SYSTEMS

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From steady properties to *processes*

- Nonequilibrium steady state – static versus dynamic
- McLennan-Born nonequilibrium expansion
- Nonequilibrium processes: the concept of quasistatic limit
- Extended Clausius relation

Key technical point*: adding explicit time-dependence*

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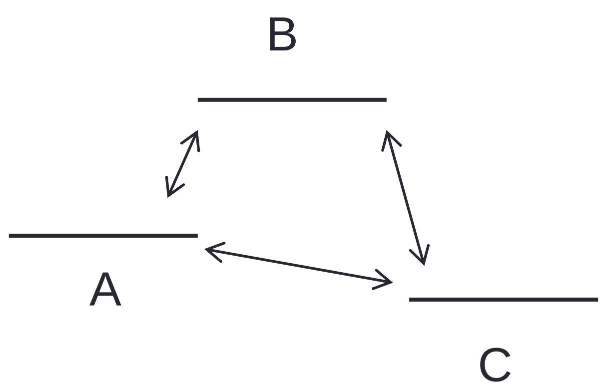
Generic nonequilibrium example

Ergodic continuous-time jump process with generator

$$\mathcal{L}A(x) = \sum_y \lambda(x,y)\,[A(y) - A(x)], \quad x = A, B, C, \ldots$$

Detailed balance $\Rightarrow$ rate asymmetry

$$\log \frac{\lambda(x,y)}{\lambda(y,x)} = \underbrace{\beta[E(x) - E(y)]}_{\text{entropy flux } \sigma(x,y)}$$



From *global* to *local* detailed balance:

- inhomogeneous temperature environment: $\beta = \beta(x,y)$
- extra non-potential force: $\sigma(x,y) = \beta[E(x) - E(y) + F(x,y)]$

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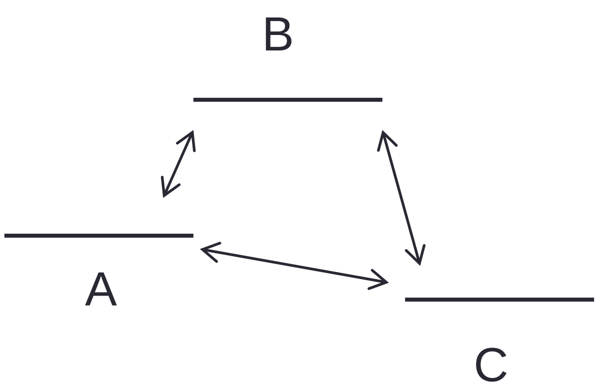

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$$\boxed{\sigma(x,y) \neq S(x) - S(y)}$$

Generic nonequilibrium example

From *global* to *local* detailed balance:

- inhomogeneous temperature environment: $\beta = \beta(x, y)$
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Possibly close to equilibrium in the perturbative sense

$$\beta(x, y) = \beta + \epsilon\beta_1(x, y) + \dots, \quad \text{or } F(x, y) = \epsilon F_1(x, y) + \dots$$

Many results are known up to first order, including:

✓variational characterization of steady state (MinEP/MaxEP principles)

✓McLennan(-Zubarev) stationary ensembles

✓Green-Kubo relations etc.

McLennan stationary ensemble

Question: What is the leading correction to the Boltzmann-Gibbs distribution beyond equilibrium?

$$\rho_F(x) = \frac{1}{Z_0} \exp[-\beta E(x) + \Delta(x)]$$

transient component of the entropy flux along relaxation started from x

- First derived for mechanical systems driven by coupling to two heat baths at different temperatures

Relates the stationary occupation to relaxation transport properties

Ref: J. A. McLennan Jr., *Phys. Rev.* **115,** 1405 (1959)

McLennan-Born expansion

Stationary problem $\rho_F(\mathcal{L}Y) = 0\ (\forall Y)$ can be solved perturbatively around a reference detailed balanced dynamics, $\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_1$:

$$\begin{aligned}\rho^s &= \rho^s_0 + \int_0^\infty dt\, e^{t\mathcal{L}^*}\,\mathcal{L}^*\,\rho^s_0 \\ &= \rho^s_0 - \frac{1}{\mathcal{L}_0}\,\mathcal{L}^*_1\rho^s_0 + \frac{1}{\mathcal{L}_0}\,\mathcal{L}^*_1\,\frac{1}{\mathcal{L}_0}\,\mathcal{L}^*_1\rho^s_0 - \dots\end{aligned}$$

Detailed balance

$$L^*_0(\rho^s_0 Y) = \rho^s_0 L_0 Y$$

Pseudoinverse

$$\frac{1}{\mathcal{L}_0} = \int_0^\infty ds\,(P_{Ker\mathcal{L}_0} - e^{s\mathcal{L}_0})$$

McLennan-Born expansion

$$\rho^s = \rho_0^s + \int_0^\infty dt\, e^{t\mathcal{L}^*}\mathcal{L}^*\rho_0^s$$
$$= \rho_0^s - \frac{1}{\mathcal{L}_0}\mathcal{L}_1^*\rho_0^s + \frac{1}{\mathcal{L}_0}\mathcal{L}_1^*\frac{1}{\mathcal{L}_0}\mathcal{L}_1^*\rho_0^s - \ldots$$

The leading nonequilibrium correction has a simple interpretation in terms of the transient part of the work of nonpotential forces:

$$\langle W_F\rangle^{[0,T]} = \langle \textstyle\sum_j F(x_{t_{j-1}}, x_{t_j})\rangle^{[0,T]}$$
$$= \langle \int_0^T dt\, w(x_t)\rangle^{[0,T]}$$

Expected power of non-gradient forces

$$w(x) = \textstyle\sum_y \lambda(x,y)\, F(x,y)$$

Claim:

$$\mathcal{L}_1^*\rho_0^s = \beta w \rho_0^s + O(\epsilon^2)$$

- Due to local detailed balance, $\frac{\rho_0^s(x)\lambda(x,y)}{\rho_0^s(y)\lambda(y,x)} = e^{\beta[F(x)-F(y)]}$

McLennan-Born expansion

McLennan representation:

$$\rho^s = \frac{1}{Z_0}\exp[-\beta(E - \frac{1}{\mathcal{L}}w - X)], \quad X = O(\epsilon^2)$$

$$\frac{1}{\mathcal{L}}w(x) = \int_0^\infty [\langle w\rangle^s - e^{t\mathcal{L}}w(x)]\,dt = \Big\langle \int_0^\infty [\langle w\rangle^s - w(x_t)]\Big\rangle_x^{[0,\infty]}$$

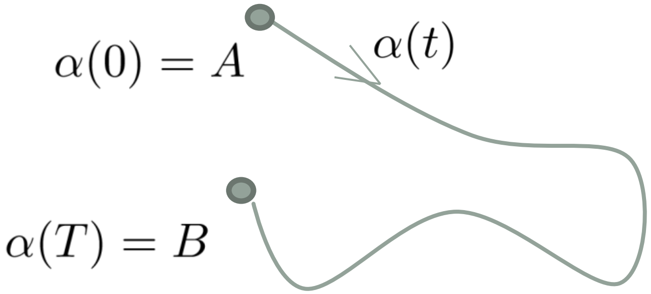
Transient part of the nongradient work when relaxing from state x

- This specific decomposition of the nonequilibrium correction appears useful when discussing quasistatic processes; see below
- It is a model-independent observation (no essential changes even when including inertial degrees of freedom)
- The first-order approximation already displays non-locality effects etc.
- The "genuine nonequilibrium correction" X can be expressed via a modified perturbation series and also in terms of correlations

C. Maes and K.N., *J. Math. Phys*. **51**, 015219 (2010)

Time-dependent processes

- Let $E = E_\alpha$ with some time-dependent protocol $\alpha(t)$
- A more general thermodynamic process is specified by $\gamma(t) = [\alpha(t), \beta(t), F(t)]$



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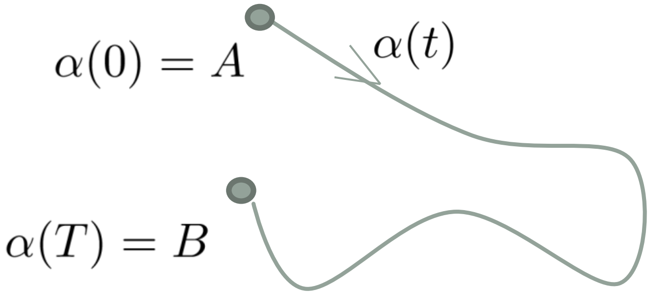
Is that all? **No!**



- In fact, the symmetric part of the rates also becomes relevant from the second order on!
  - ➢ The relevance of traffic/activity as an independent physical characterization of the nonequilibrium system

Quasistatic limit

- Introducing a slow-time by rescaling

$$\gamma(t) \longrightarrow \gamma(\varepsilon t), \quad 0 \leq t \leq T/\varepsilon, \quad \varepsilon \to 0$$

- The evolution equation

$$\frac{\partial \rho_t^\varepsilon}{\partial t} = \mathcal{L}^*_{\gamma(\varepsilon t)} \rho_t^\varepsilon$$

has the well known adiabatic-limit solution

$$\lim_{\varepsilon \downarrow 0} \rho^\varepsilon_{t/\varepsilon} = \rho^s_{\gamma(t)}$$

with $\rho^s_{\gamma(t)}$ stationary w.r.t. $\mathcal{L}_{\gamma(t)}$

But for path quantities we need a next correction!

An extension of adiabatic theorem

- Time-integrated non-adiabatic correction reads

$$\lim_{\varepsilon\downarrow 0} \int_0^{T/\varepsilon} [\rho_t^\varepsilon - \rho^s_{\gamma(\varepsilon t)}]\, dt = \int_{A\rightsquigarrow B} d\gamma \cdot \frac{1}{L^*_\gamma} \nabla_\gamma \rho^s_\gamma$$

Integration runs along the geometric shape of $\gamma(t)$

- It can be used to calculate quasistatic expectations of the excess parts of path observables and it proves its purely geometrical nature

$$\lim_{\varepsilon\downarrow 0} \left\langle \int_0^{T/\varepsilon} Y^{ex}_{\gamma(\varepsilon t)}(x_t)\, dt \right\rangle^{[0,T/\varepsilon]} = - \int_{A\rightsquigarrow B} d\gamma \cdot \left\langle \nabla_\gamma \left(\frac{1}{L_\gamma} Y_\gamma \right) \right\rangle^s_\gamma$$

$$Y^{ex}_\gamma = Y_\gamma - \langle Y_\alpha \rangle^s_\gamma$$

Some more insight

- The formula can be recognized as a (quasi-static) balance equation for the observable $\Phi_\gamma = \frac{1}{\mathcal{L}_\gamma} Y_\gamma$

$$\langle \Phi_B \rangle_B - \langle \Phi_A \rangle_A = \int_{A \rightsquigarrow B} d\gamma \cdot \langle \nabla_\gamma \Phi \rangle_\gamma^s + \lim_{\varepsilon \downarrow 0} \Big\langle \int_0^{T/\varepsilon} (\mathcal{L}\Phi)_{\gamma(\varepsilon t)}(x_t)\, dt \Big\rangle^{[0,T/\varepsilon]}$$

$$||$$

Counts changes along jumps

$$\lim_{\varepsilon \downarrow 0} \Big\langle \int_0^{T/\varepsilon} dt\, \frac{d\gamma(\varepsilon t)}{dt} \cdot \nabla_{\gamma(\varepsilon t)} \Phi \Big\rangle^{[0,T/\varepsilon]}$$

Counts changes along flat pieces of the trajectory

Example: For $\Phi_\alpha \equiv E_\alpha$ this is the decomposition of energy changes into the work of potential forces and the rest (= work of non-potential forces + heat)

Application: Work of non-potential forces

- The work of non-potential force comes (in the present model) only from jumps, and its expectation reads

$$W_F = \left\langle \int_0^T w(x_t)\, dt \right\rangle^{[0,T]}, \quad w(x) = \sum_y \lambda(x,y)\, F(x,y)$$

- In the quasistatic limit it diverges as $1/\varepsilon$ but it has a well defined geometrical finite-part:

$$W_F = \frac{1}{\varepsilon} \int_0^T dt\, \langle w \rangle^s_{\gamma(t)} - \int_{A \rightsquigarrow B} d\gamma \cdot \left\langle \nabla_\gamma \left(\frac{1}{\mathcal{L}_\gamma} w_\gamma \right) \right\rangle^s_\gamma + O(\varepsilon)$$

Excess component $W_F^{ex} = \int \delta W_F^{ex}$

- Recall that $\frac{1}{\mathcal{L}_\alpha} w_\alpha$ is the leading nonequilibrium correction to the Boltzmann-Gibbs distribution

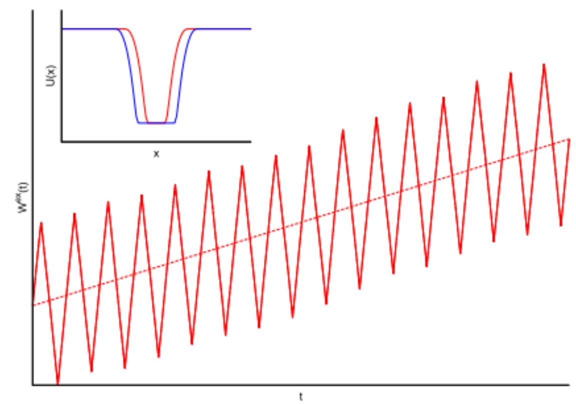
Measuring excess work?

Divergent and finite components behave differently under the protocol reversal $\gamma(t) \mapsto \gamma(T-t)$

$$W_F = \underbrace{\frac{1}{\varepsilon}\int_0^T dt\,\langle w\rangle^s_{\gamma(t)}}_{\text{even}} - \underbrace{\int_{A\rightsquigarrow B} d\gamma \cdot \left\langle \nabla_\gamma \left(\frac{1}{\mathcal{L}_\gamma} w_\gamma\right)\right\rangle^s_\gamma}_{\text{odd}} + O(\varepsilon)$$

$$W_F - W_F^{reversed} = 2W_F^{ex} + O(\epsilon)$$

Necessary to adjust the speed of the process and the number of cycles to control the errors!



Quasistatic energetics

- Quasistatic work of potential forces is well defined and geometric:

$$W_E = \int_{A \rightsquigarrow B} \langle \nabla_\alpha E \rangle_\alpha^s \cdot d\alpha$$

- The excess heat is defined so that to have energy balance in the form of the First Law:

$$\langle E_B \rangle_B - \langle E_A \rangle_A = W_E + W_F^{ex} + Q^{ex}$$

- All quantities are well defined already on the path-level

- Main question: What can we say about Q^{ex} ?

Extended Clausius relation

$$Q^{ex} = \int_{A \rightsquigarrow B} \beta^{-1} dS_\gamma + \int_{A \rightsquigarrow B} d\gamma \cdot \langle \nabla_\gamma X \rangle_\gamma^s + O(\epsilon^3)$$

Second-order correction

$$S_\gamma = -\langle \ln \rho_\gamma^s \rangle_\gamma^s$$

Nonequilibrium (Shannon) entropy

- Clausius relation remains valid up to first order
- The second-order correction vanishes if assuming $\Delta\alpha = O(\epsilon)$ and $\Delta\beta = O(\epsilon)$
- The latter can also be given in terms of correlations

- D. Ruelle, *Proc. Nat. Acad. Sci. USA* **18**, 3054 (2003)
- T. S. Komatsu et al, *Phys. Rev. Lett.* **100**, 230602 (2008)
- K. N. and J. Pešek, in preparation

Nonequilibrium heat capacity

Let α and F are kept fixed:

$$dQ^{ex} = d\langle E\rangle^s - dW_F^{ex}$$

$$= d\langle E\rangle^s + \langle w\,\frac{1}{\mathcal{L}_0}E\rangle_0^s\,d\beta$$

Corresponding heat capacity:

$$C = \left.\frac{dQ^{ex}}{d(1/\beta)}\right|_{\alpha,F} = \frac{\partial\langle E\rangle^s}{\partial(1/\beta)} - \beta^2\langle w\frac{1}{\mathcal{L}_0}E\rangle_0^s$$

$$= \frac{\partial\langle E\rangle^s}{\partial(1/\beta)} - \beta\big[\langle E\rangle^s - \langle E\rangle_0^s\big]$$

$$= \frac{\partial\langle E\rangle^s}{\partial(1/\beta)} - \beta F\,\frac{\partial\langle E\rangle^s}{\partial F}$$

all up to $O(\epsilon)$

Conclusions

- Equilibrium thermodynamics allows for a natural extensions “slightly away” from equilibrium
- Quasistatic limit well defined for path observables in terms of excess components – measurable *in principle*
- Clausius formulation of the Second Law remains generally valid up to first (respectively second) order in the degree of detailed balance breaking
- Excess heat naturally gives rise to a generalized heat capacity with leading nonequilibrium correction related with an unconvential equilibrium linear response coefficient

Needs to be understood:

- The structure of higher-order contributions breaking the Clausius relation (sufficient conditions for the existence of integrability factors,…)
- Role of fluctuations in the quasistatic regime


Thank You
for Your Attention!