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The entropy production in stochastic thermodynamics

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April 14, 2014

Uniwersytet Jagielloński, Kraków

Antonio Celani, Stefano Bo, Ralf Eichorn, E.A., Phys Rev Lett (2012)
Stefano Bo, E.A., Ralf Eichhorn, Antonio Celani, EPL (2013)
Stefano Bo, Antonio Celani, J Stat Phys (2014)
Yueheng Lan, E.A., [to be submitted] (2014)

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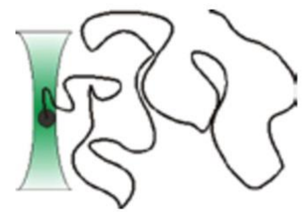
Terms to be explained:

The entropy production in stochastic thermodynamics

Thermodynamics in modern terms (Sekimoto, 2010)

$(k_B)T \approx 4nm \cdot pN$

The system: Of the whole world, a part which is properly cut out is called the system



work made ***on*** the system δW

$$\Delta U = \delta W + \delta Q$$

δQ heat given ***to*** the system

The external system: It is an agent which is capable of controlling macroscopically the system through a parameter *a* of the potential energy

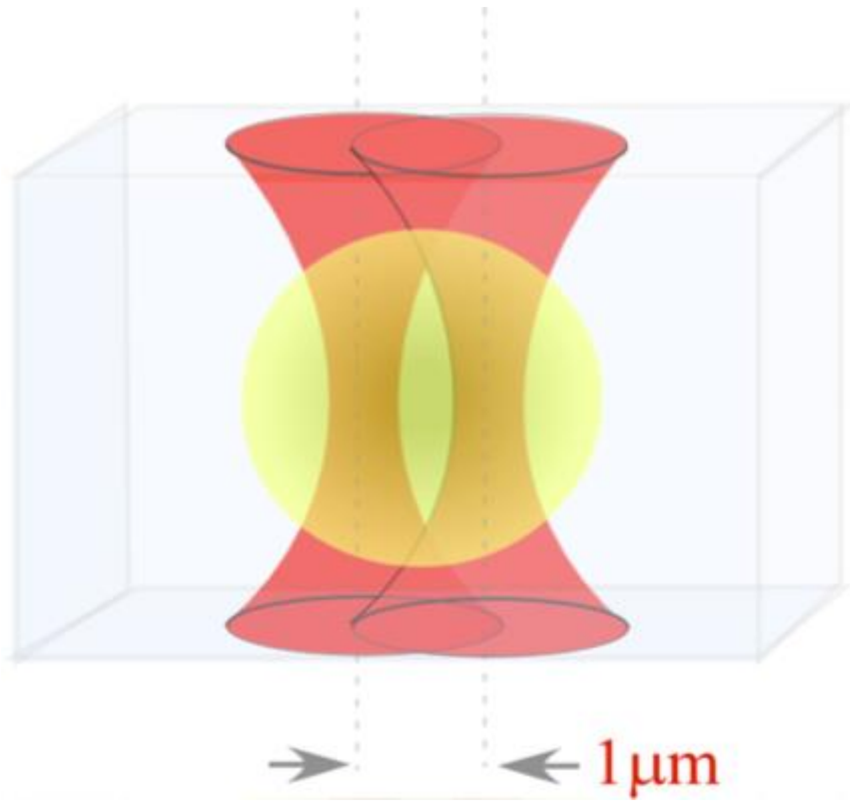
The thermal environment: The background to which the system is connected... ...keeps no memories of the systems's actions...

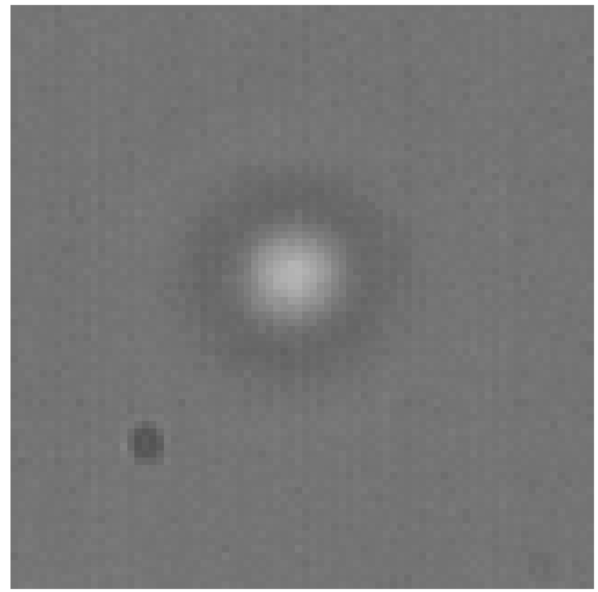
$$\delta S = -\delta Q / T$$

What is new about ”stochastic thermodynamics” is that it is a thermodynamics of single mesoscopic objects.

So a thermodynamics without the thermodynamic limit.

Example 1: micron-sized beads in water at room temperature





Antoine Bérut, Artak Arakelyan,
Artyom Petrosyan, Sergio Ciliberto, Raoul Dillenschneider and Eric Lutz
Nature (2012) **483**:187–189

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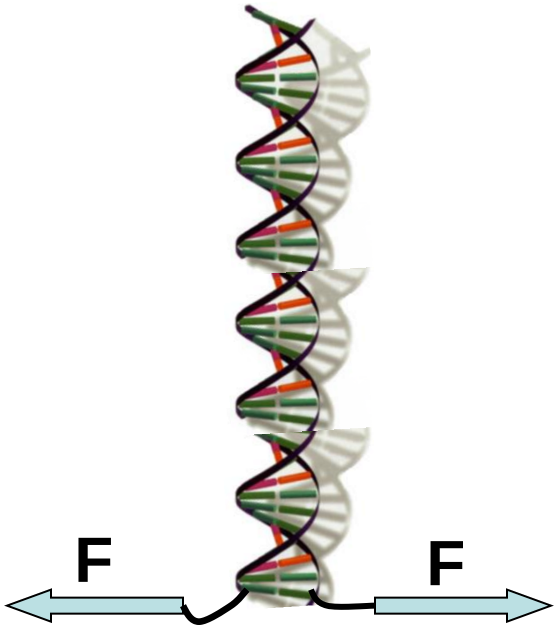
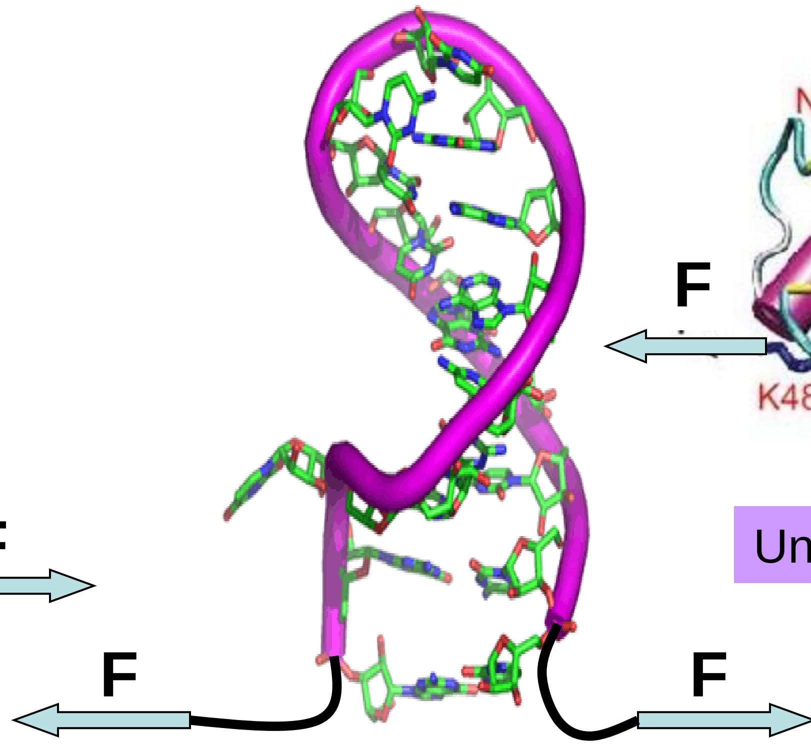
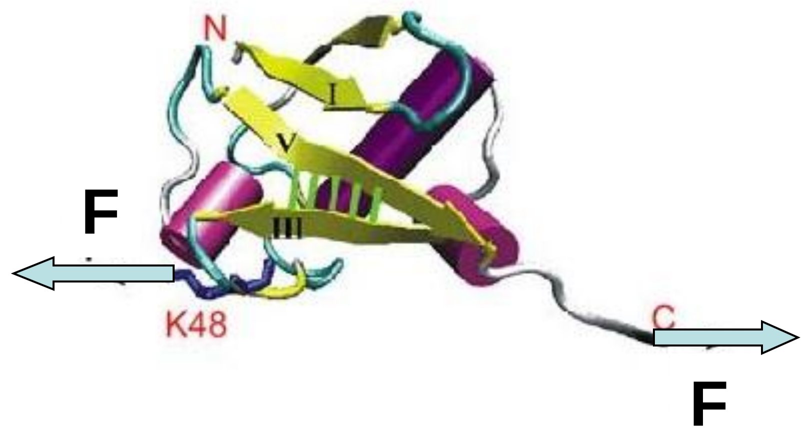
Example 2: molecular unzipping

B. Essevaz-Roulet, U. Bockelmann , F. Heslot F (1997) *Proc Natl Acad Sci* USA 94:11935-11940
M. Rief, H. Clausen-Schaumann, H.E. Gaub (1999) *Nat Struct Biol* 6:346-349
C. Danilowicz et al. (2003) *Proc Natl Acad Sci* USA 100:1694-1699



DNA unzipping (double stranded)





Unfolding of proteins

Unfolding of DNA and RNA hairpins (single stranded)

F. Ritort, J. Phys. (Cond. Matter) **18** R531 (2006))

Fluctuation relations

PHYSICAL REVIEW E VOLUME 56, NUMBER 5 NOVEMBER 1997

Equilibrium free-energy differences from nonequilibrium measurements: A master-equation approach

C. Jarzynski*
Theoretical Astrophysics, T-6, MS B288, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 18 June 1997)

In has recently been shown that the Helmholtz free-energy difference between two equilibrium configurations of a system may be obtained from an ensemble of *finite-time* (nonequilibrium) measurements of the work performed in switching an external parameter of the system. Here this result is established, as an identity, within the master equation formalism. Examples are discussed and numerical illustrations provided. [S1063-651X(97)10710-3]

$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}$$

"The free energy landscape between two equilibrium states is well related to the irreversible work required to drive the system from one state to the other"

Crooks' fluctuation relation

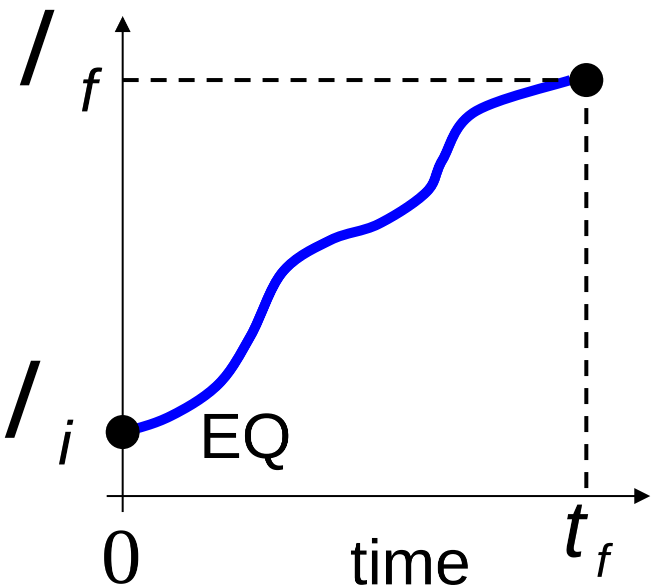
G. E. Crooks, Phys. Rev. E. 60, 2721 (1999)

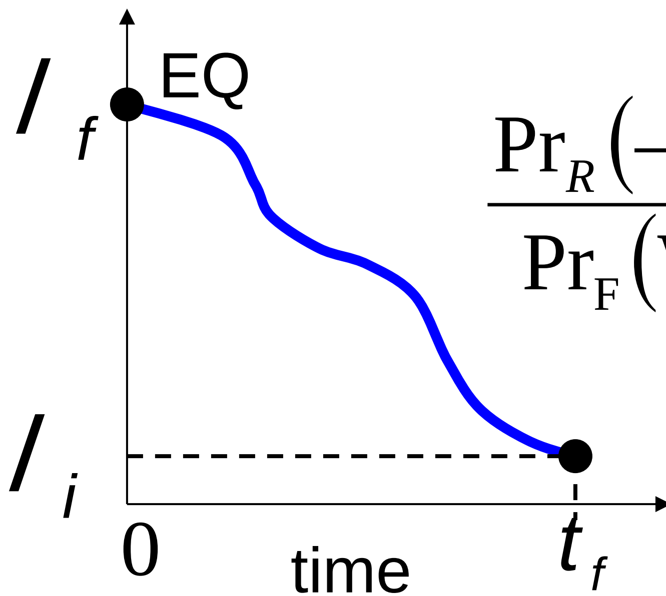
A more detailed version of the fluctuation theorem

$$\Pr(W) = \sum_{x_i, x_f} \rho^{eq}(x_i) \sum_{\text{paths from } i \text{ to } f} \delta(\delta W[\text{path}] - W)\Pr(\text{path})$$

Forward process: $\lambda(t)$

Reverse process: $\lambda(t_f - t)$





$$\frac{\Pr_R(-W)}{\Pr_F(W)} = e^{-\frac{W-F}{T}}$$

The basic fluctuation relations

$$\frac{\Pr_B(\text{path})}{\Pr_F(\text{path})} = e^{-\delta S_{env}}$$

The weighted probability of a path in a forward process is the probability of the path in the backward process

Kurchan, J Phys A (1998)
Lebowitz & Spohn, J Stat Phys (1999)
Chétrite & Gawędzki, Comm Math Phys (2008)

$$\delta S_{env} = -\delta Q / T$$

The weight is the entropy increase in the environment, proportional to heat released from the system

$$\left\langle e^{-\delta S_{env}} \right\rangle_{x_i}^{x_f} = \langle 1 \rangle_{x_f}^{x_i}$$

$$\langle \mathrm{F}(\text{path}) \rangle_{x_i}^{x_f} = \sum_{\text{paths from } i \text{ to } f} \mathrm{F}(\text{path}) \Pr(\text{path})$$

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Two simple derivations…

$$\int e^{-\beta E_f(x_f)} \left\langle e^{-\delta S_{env}} \right\rangle_{x_i}^{x_f} dx_i dx_f = \int e^{-\beta E_f(x_f)} \left\langle 1 \right\rangle_{x_f}^{x_i} dx_i dx_f = Z_f$$

but the left-hand side is $Z_i \int \rho_i^{eq}(x_i) \left\langle e^{-\beta\Delta E - \delta S_{env}} \right\rangle_{x_i}^{x_f} dx_i dx_f$

and then $-\beta\delta W = -\beta\Delta E - \delta S_{env}$ **gives** $\left\langle e^{-\beta\delta W} \right\rangle_{i,eq} = e^{-\beta\Delta F} \therefore$

$$\int \rho_f(x_f) \left\langle e^{-\delta S_{env}} \right\rangle_{x_i}^{x_f} dx_i dx_f = \int \rho_f(x_f) \left\langle 1 \right\rangle_{x_f}^{x_i} dx_i dx_f = 1$$

which means that we have $\left\langle e^{\log\rho_f - \log\rho_i - \delta S_{env}} \right\rangle_i = 1$

and by convexity of the exponential $\left\langle \delta S_{env} \right\rangle_i + S_f - S_i \geq 0 \therefore$

The entropy production in the environment is hence an important quantity in stochastic thermodynamics

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Mathematically, the general expression is well known for stochastic processes

$$\dot{\xi}_t = u_+ + u_- + v \qquad \langle v_t^i(x) v_s^j(y) \rangle = \delta(t-s) D_t^{ij}(x,y) \qquad D_t^{ij}(x) = D_t^{ij}(x,x)$$

$$\left\langle e^{-\delta S_{env}} \right\rangle_{x_i}^{x_f} = \left\langle 1^b \right\rangle_{x_f}^{x_i}$$

The fluctuation relations are satisfied by the Chétrite-Gawędzki functional Comm Math Phys (2008)

$$\delta S_{env} = \int 2\left(u_+ - \tfrac{1}{2}\partial_y \cdot D(x,y)\Big|_{y=x} \right) \cdot D^{-1}(x) \circ \left(\dot{\xi} - u_- \right) - \left(\nabla \cdot u_- \right) dt$$

Note however that this functional depends on the diffusion matrix at unequal spatial points *e.g.* **on temperature gradients.**

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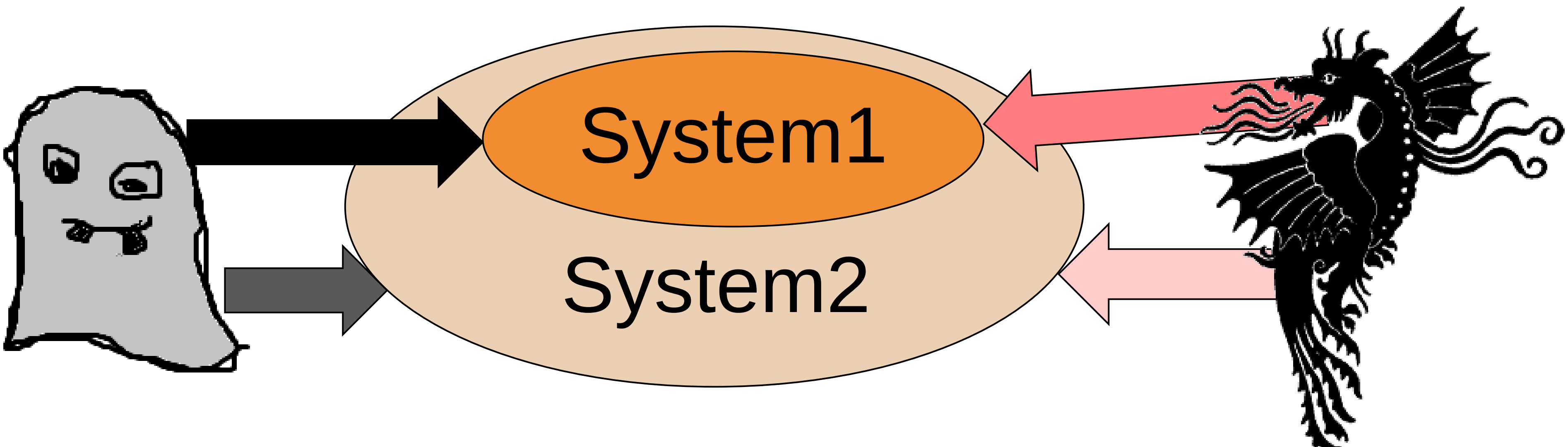
The problem of (Maxwell) demons and (thermal) dragons

Suppose we can "properly cut out of the world" both a larger and a smaller piece, both of which could be "The System".



Are there relations between mesoscopic heat, work and especially entropy production of the different systems?

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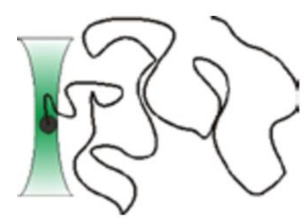
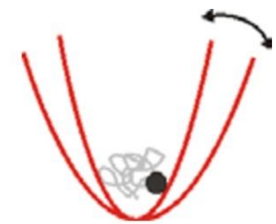
System 2: the under-damped Langevin eq in mesoscopics

$$\frac{dp}{dt} = -\partial_x V(x,\lambda_t) - \gamma \frac{p}{m} + \sqrt{2T\gamma}\,\dot{\omega}_t \qquad \frac{dx}{dt} = \frac{p}{m}$$

$$-\gamma \frac{p}{m} + \sqrt{2T\gamma}\,\dot{\omega}_t$$

force from the environment on the system...





$V(z,t)$

...which there is an opposite reaction force

$$-d'Q = dx \circ \left(\gamma \frac{p}{m} - \sqrt{2T\gamma}\,\dot{\omega}_t \right)$$

Ken Sekimoto, *Stochastic Energetics*, Lecture notes in Physics **799**, (Springer 2010)

[…] *heat is the work done by the retained degrees of freedom against the thermal environment that represents the eliminated degrees of freedom.*

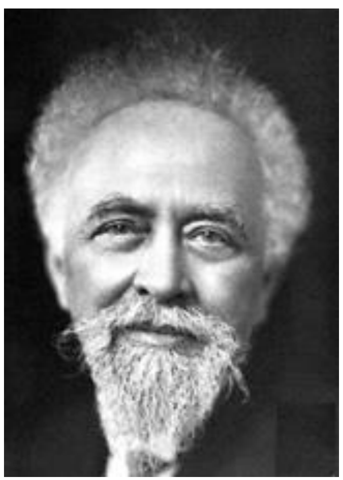
System 1: the overdamped limit of the Langevin equation

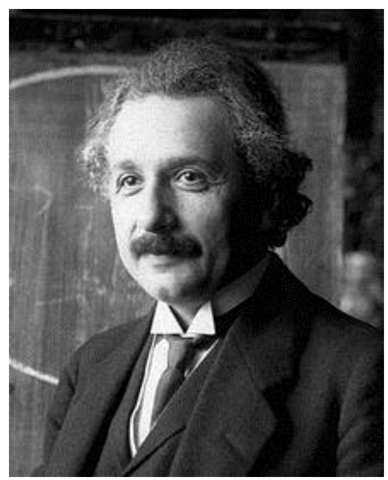
$$\dot{p} \approx 0$$

$$\dot{x} = -\frac{1}{\gamma}\partial_x V(x_t, \lambda_t) + \sqrt{2T/\gamma}\,\dot{\omega}_t$$

$$D = \frac{T}{\gamma}$$

This theory ignores inertia, and describes System 1 if times of order *m/γ* and shorter cannot be resolved.





No surprises when T and γ const.

$$U = p^2/2m + V(x) \qquad \text{Mesoscopic 1}^{\text{st}}\text{ Law} \quad \Delta U = \delta Q^{(2)} + \delta W$$

Sekimoto *Progr. Theor. Phys.* **180** (1998); Seifert *PRL* **95** (2005)

$$d'W = \partial_a V(x,a) \circ da \qquad d'Q^{(2)} = dx \circ \left(-\gamma \frac{p}{m} + \sqrt{2T\gamma}\,\dot{\omega}_t \right)$$

$$\frac{dp}{dt} = -\partial_x V(x,\lambda_t) - \gamma \frac{p}{m} + \sqrt{2T\gamma}\,\dot{\omega}_t \qquad \frac{dx}{dt} = \frac{p}{m}$$

...use the over-damped Langevin eq in the heat functional...

$$\delta Q^{(2)} = \int_{t_i}^{t_f} \left(-\gamma \dot{x} + \sqrt{2T\gamma}\,\dot{\omega}_t \right) \circ dx_t \rightarrow \delta Q^{(1)} = \int_{t_i}^{t_f} \partial_x V(x_t, \lambda_t) \circ dx_t$$

...and one gets again a 1st Law: $\delta Q^{(1)} + \delta W = \Delta V$

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If temperature and friction change in space diffusion is less obvious...

The correct over-damped limit of the Langevin eq at non-constant temperature [see Matsuo-Sasa (2000) for γ constant] **is**

$$dx_t = \left(-\partial_x V - \tfrac{1}{2}\partial_x T - \tfrac{1}{2}T\partial_x \log\gamma\right)\frac{dt}{\gamma} + \sqrt{2T/\gamma}\circ d\omega_t$$

Over-damped expected heat release is…

$$\delta Q^{over} = \int \partial_x V \circ dx_t$$

…but the fluctuation relations are satisfied by a δS_{env} with an extra term. Physical origin?

$$\delta S_{env}^{over} = \int \left(-\partial_x V/T - \partial_x T/T\right)\circ dx_t$$

The C-G functional if

$$D(x,y) = \sqrt{D(x)D(y)}$$

Solution: multi-scale expansions

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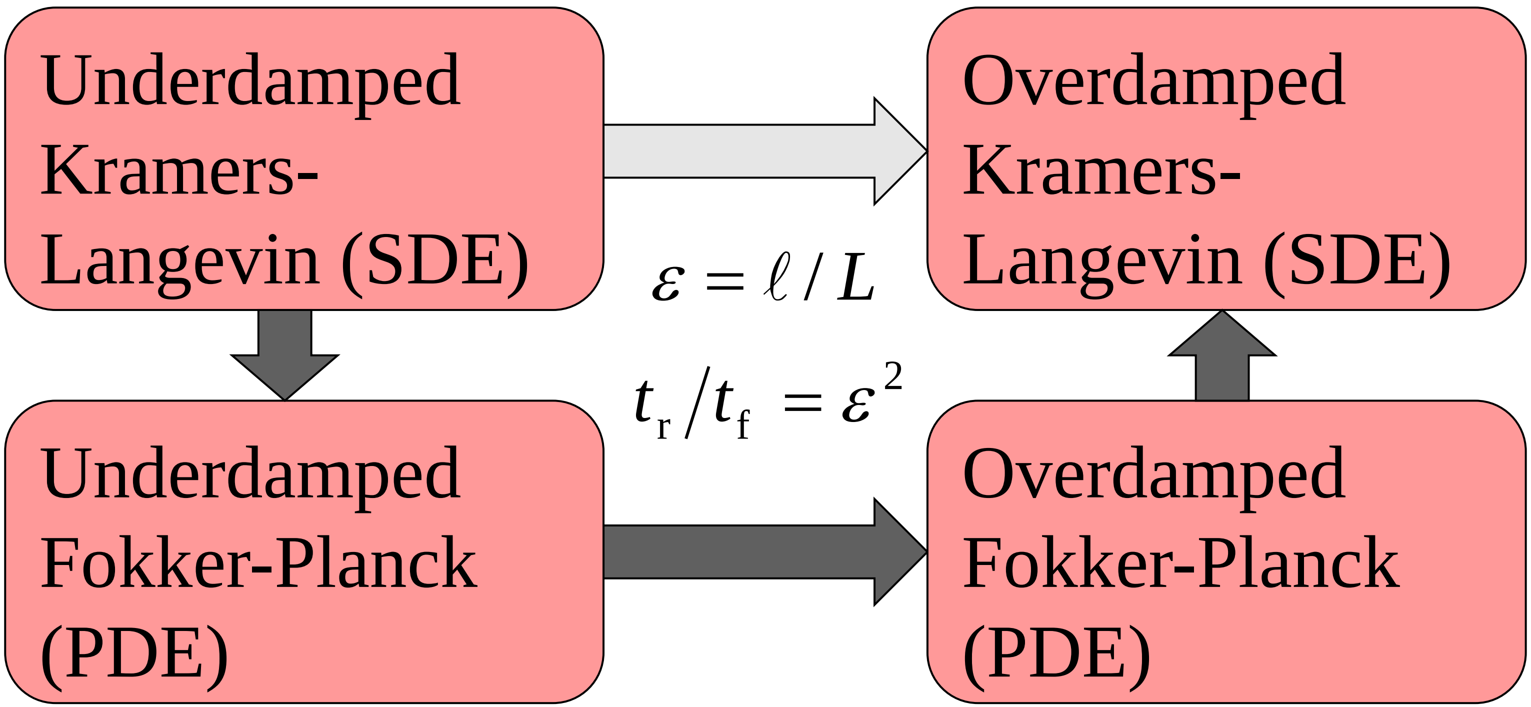
Small length: $\ell = v_{\mathrm{th}}\, m/\gamma$ **Large length:** L

Small time: $t_{\mathrm{r}} = m/\gamma$ **Large time:** $t_{\mathrm{f}} = L^2 / D$



The results first, how the calculations are done later.

Multi-scale for dynamics

$$\partial_t \rho + \partial \cdot \left((\rho/\gamma)(f - \partial T) \right) = \partial \cdot \left((T/\gamma) \partial \rho \right)$$

mass conservation by the drift from external force *f* $\quad \rho f/\gamma$

mass conservation by a thermophoretic drift term $\quad -\rho \partial T/\gamma$

mass conservation by diffusive flux with *D=T/γ* $\quad -T/\gamma\, \partial_x \rho$

The operator is the adjoint of $\quad \left(f/\gamma + T\partial\gamma^{-1} \right)\partial_x + T/\gamma\, \partial_{xx}$

Hence, this is also the Kolmogorov forward eq of an SDE:

$$dX_t = \left(f/\gamma - \tfrac{1}{2}\partial T/\gamma + \tfrac{1}{2} T\partial\gamma^{-1} \right) dt + \sqrt{2T/\gamma} \circ dW_t$$ **(Stratonovich)**

$$dX_t = \left(f/\gamma + T\partial\gamma^{-1} \right) dt + \sqrt{2T/\gamma} \bullet dW_t$$ **(Itô)**

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Multi-scale for the released heat

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expected **released heat conditioned on initial position**

$$\partial_t Q + \left(f/\gamma + T\partial\gamma^{-1}\right)\cdot\partial Q + T/\gamma\,\partial^2 Q = -\left(f/\gamma + T\partial\gamma^{-1}\right)\cdot f - \left(T/\gamma\right)\partial\cdot f$$

$$Q = E_{x,t}\left[\int_t^{t_f} f\bullet dX_t + \left(T/\gamma\right)\left(\partial\cdot f\right)dt\right] + C$$

$$dX_t = \left(f/\gamma + T\partial\gamma^{-1}\right)dt + \sqrt{2T/\gamma}\bullet dW_t$$

transforming from Itô to Stratonovich gives

$$Q = E_{x,t}\left[\int_t^{t_f} f\circ dX_t\right] + C$$

$$dX_t = \left(f/\gamma - \tfrac{1}{2}\partial T/\gamma + \tfrac{1}{2}T\partial\gamma^{-1}\right)dt + \sqrt{2T/\gamma}\circ dW_t$$

The over-damped limit of the expected heat release is normal.

$$\mathrm{E}_{x,v,t}\left[-\delta Q\right] = \mathrm{E}_{x,t}\left[\int_t^{t_f} f\circ dX_t\right]_0 + \Delta\mathrm{E}\left[\frac{mv^2}{2}\right] + O(\varepsilon)$$

the average over v^2 at the final time t_f yields d times spatial average of T w r t to final density ρ_f

Multi-scale for entropy production

$$\partial_t S + \left(f/\gamma + T\partial\gamma^{-1}\right)\cdot\partial S + T/\gamma\,\partial^2 S = -T/\gamma\,\partial\cdot\tilde{f} - \left(f/\gamma + T\partial\gamma^{-1}\right)\cdot\tilde{f} - A$$

The "thermoentropic" force correction

$$\tilde{f} = \left(f/T - (\partial T/T)\right)$$

$$\left\langle e^{-\int \tilde{f}\circ dX_t} \right\rangle_{x_i}^{x_f} = \left\langle 1^b \right\rangle_{x_f}^{x_i}$$

$$dX_t = \left(f/\gamma - \tfrac{1}{2}\partial T/\gamma + \tfrac{1}{2}T\partial\gamma^{-1}\right)dt + \sqrt{2T/\gamma}\circ dW_t$$

Chétrite-Gawędzki (2008) & Matsuo-Sasa (2010)

The over-damped limit of the expected entropy production is however anomalous. Part of it is not an expectation over force times distance (even corrected force) in the over-damped limit.

$$\mathrm{E}_{x,v,t}\left[\delta S_{env}\right] = \mathrm{E}_{x,t}\left[\int_t^{t_f} \tilde{f}\circ dX_t + A\,dt\right] + \Delta\mathrm{E}\left[\log\frac{e^{-\frac{mv^2}{2T}}}{(2\pi T/m)^{\frac{n}{2}}}\right] + O(\varepsilon)$$

$$A = \frac{(d+2)}{6\gamma T}\left|\partial T\right|^2$$

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The entropy production per unit volume of a fluid at rest but in a temperature gradient is

$$\kappa \frac{|\nabla T|^2}{T^2}$$

Landau-Lifshitz *Fluid Mechanics* 49.6
κ is the thermal conductivity of the medium
[κ has dimension 1/(length · time)]
κ of sea water at 27C is about 0.61 1/(m·s)

The "anomalous" mesoscopic entropy production term hence has a 3D macroscopic interpretation

$$E_{x,t}\left[\int_t^{t_f} A\,dt\right] = \left(t_i - t_f\right)\int \frac{5|\partial T|^2}{6\gamma T}\rho\, dV$$

as w/ equivalent mesoscopic thermal conductivity (5=3+2)

$$\kappa_{meso,3D} = 5T\rho/6\gamma$$

Detailed fluctuation relations

$$\frac{\Pr\left(\left[x,v\right]_{t_i,x_i,v_i}^{t_f,x_f,v_f}\right)}{\Pr^b\left(\left[x,-v\right]_{-t_f,x_f,-v_f}^{-t_i,x_i,-v_i}\right)} = \exp\left[\delta S_{env}^{over} + \delta S_{env}^{anom}\right]$$

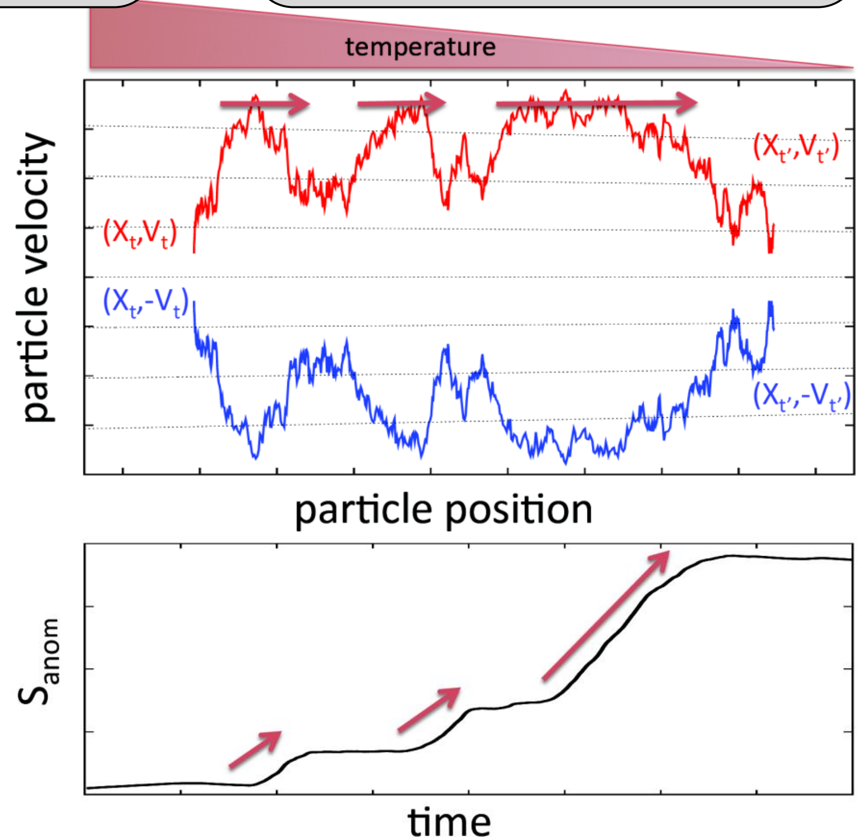
$$\frac{\Pr\left(\left[x\right]_{t_i,x_i}^{t_f,x_f}\right)}{\Pr^b\left(\left[x\right]_{-t_f,x_f}^{-t_i,x_i,}\right)} = \exp\left[\delta S_{env}^{over}\right]$$

in the overdamped limit, on the trajectory level; hence

$$\frac{\Pr\left(\left[v\mid x\right]_{t_i,x_i,v_i}^{t_f,x_f,v_f}\right)}{\Pr^b\left(\left[-v\mid x\right]_{-t_f,x_f,-v_f}^{-t_i,x_i,-v_i}\right)} = \exp\left[\delta S_{env}^{anom}\right]$$

and then in the usual way

$$\left\langle \exp\left[-\delta S_{env}^{anom}\right]\right\rangle = 1$$



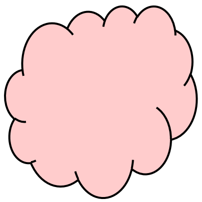
Effects of rotation and asymmetry

$$\dot{p} = -\partial_x V(x,\lambda_t) - \gamma \frac{p}{m} + \sqrt{2T\gamma}\,\dot{\eta}_t$$

$$\dot{x} = p/m \qquad I^i_j = \tilde{I}^i_j m R^2 \quad \Gamma^i_j = \tilde{\Gamma}^i_j \gamma R^2$$

$$Q^{-1}\frac{d(QI\omega)}{dt} = -\Gamma\omega + Q^{-1}M + \sqrt{2T}\,\sigma\dot{\xi}$$

Brownian particle of radius *R*. We do not have to assume that I and Γ commute. We need a friction matrix D (in general not a symmetric) and a diffusion matrix S.



$$D = I^{-1}\Gamma$$

$$S = I^{-1}\Gamma I^{-1}$$

A multi-scale analysis gives a contribution from the angular velocities of the same form, just another contribution to the mesoscopic heat conductivity

$$\kappa^{rot}_{meso,3D} = \frac{T\rho}{2\gamma}\mathrm{Tr}\left(1 + \frac{2m}{\gamma}D\right)^{-1}$$

Y. Lan, E.A. (2013) [in preparation]

The expression inside the trace is dimension-less. The rotations just acts to increase entropy production in the environment by "looping in the angles".

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Mean flow and the advection-diffusion limit. Time $t_u = L/u$.

Stokes number $\mathrm{St} = \frac{t_r}{t_u} = \frac{t_r u}{L}$ Péclet number $\mathrm{Pe} = \frac{t_f}{t_u} = \frac{Lu}{D}$ $\frac{\mathrm{St}}{\mathrm{Pe}} = \frac{t_r}{t_f} = \varepsilon^2$

$$\dot{p} = -\partial_x V(x,\lambda_t) - \gamma\left(\frac{p}{m} - u(x)\right) + \sqrt{2T\gamma}\,\dot{\omega}_t \qquad \dot{x} = p/m$$

$$\mathrm{Pe}\cdot\mathrm{St} = \frac{t_f t_r}{t_u^2} = \frac{v_{th}^2}{u^2}$$

Overdamped limit: $\mathrm{St} \rightarrow 0$ and Pe const. – gives no effects

Inertial particles limit: $\mathrm{Pe} \rightarrow \infty$ and St const. – too difficult at this stage

Advection-diffusion limit: $\mathrm{St} = \mathrm{Pe}^{-1} \rightarrow 0$ – we can handle

$$\mathrm{E}_{x,v,t}\left[\delta S_{env}^{AD(u)}\right] = \mathrm{E}_{x,t}\left[\int_t^{t_f} \frac{m}{2\gamma}\left(\partial_i u_j \partial_j u_i + \partial_j u_i \partial_j u_i\right)\right] + O(\varepsilon)$$

Y. Lan, E.A.

So we get also the entropy production due to internal friction

Landau-Lifshitz *Fluid Mechanics* 49.6
of course has two more terms
η is the dynamic viscocity [mass/(length · time)]
ζ is the bulk viscocity [mass/(length · time)]

$$\frac{\eta}{2T}\left(\partial_k u_i + \partial_i u_k - 1_{ik}\,\tfrac{2}{3}\,\partial\cdot u\right)^2$$

$$\frac{\varsigma}{T}\left(\partial\cdot u\right)^2$$

The macroscopic thermodynamics the fluid is the System and the Thermal Environment are reservoirs, typically at the boundaries. In stochastic thermodynamics for mesoscopic objects, the fluid on the other hand plays the role of the Thermal Environment. The entropy production in the environment of the mesoscopic object is thus the entropy production in the surrounding fluid, which is close to equilibrium on the time scales of the object (by assumption).

$$\eta_{meso,3D} = \frac{Tm\rho}{2\gamma} = \tfrac{1}{2}\,m\rho D$$

$$\varsigma_{meso,3D} = \frac{Tm\rho}{3\gamma} = \tfrac{1}{3}\,m\rho D$$

And it is therefore satisfying that the two concepts coincide.

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Here we can stop & thank

Stefano Bo

Antonio Celani

Ralf Eichhorn

Lan Yueheng

Academy of Finland

cnrs dépasser les frontières

Institut Pasteur

NORDITA

Vetenskapsrådet

Multi-scale expansions for the overdamped limit

I. Diffusion

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A non-dimensional Langevin eq

L **is a length scale of the problem (e.g. temperature variations) and** T_0 **is a reference temperature:**

$$x \to x/L \qquad v \to v/\sqrt{T_0/m} \qquad t \to t/\left(L/\sqrt{T_0/m}\right)$$

$$T \to T/T_0 \qquad \gamma \to \gamma L/\sqrt{T_0 m} \qquad f = -\partial_x V/T_0/L$$

$$\dot{x} = v \qquad \dot{v} = f - \gamma v + \sqrt{2T\gamma}\,\dot{\omega}_t$$

The over-damped approximation $1/\gamma = \sqrt{T_0 m}/\gamma L = \varepsilon/\gamma_0 \to 0$ **can be achieved by taking either *m* to zero or γ to infinity**

non-dimensional time	ε	ε^0	ε^{-1}
dimensional time	m/γ	L/v_{therm}	L^2/D

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The over-damped limit forwards

$$\partial_t P = L^* P + 1/\varepsilon\, M^* P$$

$$L^* P = \partial_x(-vP) + \partial_v(-fP)$$
$$M^* P = \partial_v(\gamma_0 v P) + \partial_v^2(T\gamma_0 P)$$

…expansion of *P* and *t* in the small parameter ε….

$$P = P_0 + \varepsilon P_1 + \varepsilon^2 P_2 + \ldots \qquad t = \varepsilon^{-1}\theta + t + \varepsilon\tau + \ldots$$

…solve order by order and assume relaxation….

$$\partial_\theta P_0 = M^* P_0 \Rightarrow P_0 \in \ker M^* \Leftrightarrow P_0 = \rho(x,t,\tau)\exp\left(-\tfrac{1}{2}v^2/T\right)/(2\pi T)^{\frac{d}{2}}$$

$$\partial_\theta P_1 = -\partial_t P_0 + L^* P_0 + M^* P_1 \Rightarrow \left(\partial_t - L^*\right)P_0 \in \operatorname{Im} M^* \Leftrightarrow \perp \ker M$$

$$\partial_\theta P_2 = -\partial_\tau P_0 - \partial_t P_1 + L^* P_1 + M^* P_2 \Rightarrow \partial_\tau P_0 + \left(\partial_t - L^*\right)P_1 \perp \ker M$$

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The over-damped Fokker-Planck

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Solvability condition on first order is straight-forward… …but then one also needs to *solve* the for the first order because that enters in second order solvability condition:

$$L^* P_0 \perp \ker M \Rightarrow \partial_t \rho = 0$$

$$\psi_{k_1,k_2,\dots k_d} = \prod_{i=1}^{d} H_{k_i}\left(v_i / \sqrt{T}\right) \exp\left(-\tfrac{1}{2} v^2 / T\right) \Big/ \left(2\pi T\right)^{\frac{d}{2}}$$

$$M^* \psi_{k_1,k_2,\dots k_d} = -\gamma\left(\sum k_i\right)\psi_{k_1,k_2,\dots k_d}$$

$$P_1 = \left(r - \frac{1}{\gamma_0}(v \cdot \partial_x \rho) + \frac{\rho}{\gamma_0 T}(v \cdot (f - \partial T)) + \frac{\rho\left((d+2)T - v^2\right)}{6\gamma_0 T^2}(v \cdot \partial T) \right) \frac{\exp(-\frac{1}{2} v^2 / T)}{(2\pi T)^{\frac{d}{2}}}$$

Fortunately, the first and last term here cancel on second order

$$\partial_\tau P_0 + \left(\partial_t - L^*\right) P_1 \perp \ker M \Rightarrow \partial_\tau \rho + \partial \cdot \left(\frac{\rho}{\gamma_0}(f - \partial T)\right) = \partial \cdot \left(\frac{T}{\gamma_0} \partial \rho\right)$$

Interpreting this Fokker-Planck

$$\partial_t \rho + \partial \cdot \left((\rho/\gamma)(f - \partial T) \right) = \partial \cdot \left((T/\gamma) \partial \rho \right)$$

mass conservation by the drift from external force *f* $\rho f / \gamma$

mass conservation by a thermophoretic drift term $-\rho \partial T / \gamma$

mass conservation by diffusive flux with *D=T/γ* $-T/\gamma \, \partial_x \rho$

This F-P operator is the adjoint of $\left(f/\gamma + T \partial \gamma^{-1} \right) \partial_x + T/\gamma \, \partial_{xx}$

Hence, the F-P is also the Kolmogorov forward eq of the SDE:

$$dX_t = \left(f/\gamma - \tfrac{1}{2} \partial T/\gamma + \tfrac{1}{2} T \partial \gamma^{-1} \right) dt + \sqrt{2T/\gamma} \circ dW_t$$ **(Stratonovich)**

$$dX_t = \left(f/\gamma + T \partial \gamma^{-1} \right) dt + \sqrt{2T/\gamma} \bullet dW_t$$ **(Itô)**

Multi-scale expansions for the overdamped limit

II. Expected heat release

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The over-damped limit backwards

appears when we consider expected released heat

$$-\delta Q = \int\left(\gamma v - \sqrt{2T\gamma}\,\dot{\omega}_t\right)\circ dx = \int\left(f dt - dv\right)\circ v$$

(here written in the non-dimensional variables). Expectation values are over the process from now (*t*) up to a final time t_f

$$E_{x,v,t}\left[-\delta Q\right] = \tfrac{1}{2}v^2 - E_{x,v,t}\left[\tfrac{1}{2}v^2(t_f)\right] + E_{x,v,t}\left[\int_t^{t_f} f v dt\right] = \tfrac{1}{2}v^2 + Q(x,v,t)$$

$$Q = Q_0 + \varepsilon Q_1 + \varepsilon^2 Q_2 + \ldots \quad t = \varepsilon^{-1}\theta + t + \varepsilon\tau + \ldots$$

$$\partial_t Q + LQ + 1/\varepsilon\, MQ = -fv$$

$$\lim_{t\to t_f} Q(x,v,t) = -\tfrac{1}{2}v^2$$

$$LQ = v\partial_x Q + f\partial_v Q$$

$$MQ = -\gamma_0 v\partial_v Q + T\gamma_0\partial_v^2 Q$$

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Formally the expansion is similar

…the only difference is that the operators *L* and *M* and their adjoints change roles…

$$\partial_\theta Q_0 = -MQ_0 \Rightarrow Q_0 \in \ker M \Leftrightarrow Q_0 = \eta(x,t,\tau)$$

$$\partial_\theta Q_1 = -\partial_t Q_0 - LQ_0 - MQ_1 - fv \Rightarrow (\partial_t + L)Q_0 + fv \in \operatorname{Im} M$$

$$Q_0 = \eta(x,\tau)$$

$$Q_1 = M^{-1}\left(-\partial_t Q_0 - LQ_0 - fv\right) + q_1(x,t,\tau)$$

$$\partial_\theta Q_2 = -\partial_\tau Q_0 - \partial_t Q_1 - LQ_1 - MQ_2 \Rightarrow \partial_\tau Q_0 + (\partial_t + L)Q_1 \perp \ker M^*$$

and after turning the crank one gets to order ε^1

$$\partial_\tau \eta + f/\gamma_0 \,\partial\eta + T\partial\left(1/\gamma_0 \partial\eta\right) = -T\partial\left(f/\gamma_0\right) - f^2/\gamma_0$$

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Interpreting this PDE for the heat

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re-written for convenience a little on right hand side

$$\partial Q + \left(f/\gamma + T\partial\gamma^{-1}\right)\cdot \partial Q + T/\gamma\,\partial^2 Q = -\left(f/\gamma + T\partial\gamma^{-1}\right)\cdot f - (T/\gamma)\partial\cdot f$$

$$Q = E_{x,t}\left[\int_t^{t_f} f \bullet dX_t + (T/\gamma)(\partial\cdot f)dt\right] + C$$

$$dX_t = \left(f/\gamma + T\partial\gamma^{-1}\right)dt + \sqrt{2T/\gamma}\bullet dW_t$$

transforming from Itô to Stratonovich gives

$$Q = E_{x,t}\left[\int_t^{t_f} f \circ dX_t\right] + C$$

$$dX_t = \left(f/\gamma - \tfrac{1}{2}\partial T/\gamma + \tfrac{1}{2}T\partial\gamma^{-1}\right)dt + \sqrt{2T/\gamma}\circ dW_t$$

The over-damped limit of the expected heat release is normal.

$$E_{x,v,t}[-\delta Q] = E_{x,t}\left[\int_t^{t_f} f \circ dX_t\right]_0 + \frac{v^2}{2} - \tfrac{d}{2}\langle T\rangle_{\rho_f} + O(\varepsilon)$$

the average over v^2 at the final time t_f yields d times spatial average of T w r t to final density ρ_f

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Multi-scale expansions for the overdamped limit

III. Expected entropy production

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Another over-damped limit

…differs from that for heat if T is not constant…

$$\delta S_{env} = \int \left(\frac{fdt}{T} - \frac{dv}{T} \right) \circ v = \int \frac{fv}{T} dt - d\left(\frac{v^2}{2T} \right) + \frac{v^2}{2} \circ d\left(\frac{1}{T} \right)$$

$$E_{x,v,t}\left[\delta S_{env}\right] = \frac{v^2}{2T} - E_{x,v,t}\left[\frac{v^2(t_f)}{2T} \right] + E_{x,v,t}\left[\int_t^{t_f} \frac{fv}{T} dt - \frac{v^2}{2T^2}\left(\partial_t T + v \cdot \partial T\right) dt \right]$$

$$S = S_0 + \varepsilon S_1 + \varepsilon^2 S_2 + \ldots \qquad t = \varepsilon^{-1}\theta + t + \varepsilon\tau + \ldots$$

$$\partial_t S + LS + 1/\varepsilon\, MS = -\frac{fv}{T} + \frac{v^2}{2T^2}\left(\partial_t T + v \cdot \partial T\right)$$

$$\lim_{t \to t_f} S(x,v,t) = -\frac{v^2}{2T}$$

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A more painful expansion...

The difference to the previous case is in the more complex source terms of order ε⁰ and ε¹. Also we have to assume that *T* only depends directly on slow time τ.

$$\partial_\theta S_0 = -MS_0 \Rightarrow S_0 \in \ker M \Leftrightarrow S_0 = \xi(x,t,\tau)$$

$$\partial_\theta S_1 = -\partial_t S_0 - LS_0 - MS_1 - \frac{fv}{T} + \frac{v^2}{2T^2}(v \cdot \partial T) \Rightarrow Condition$$

$$S_1 = M^{-1}\left(-\partial_t S_0 - LS_0 - \frac{fv}{T} + \frac{v^2}{2T^2}(v \cdot \partial T) \right) + s_1(x,t,\tau)$$

$$\partial_\theta S_2 = -\partial_\tau S_0 - \partial_t S_1 - LS_1 - MS_2 + v^2 / 2T^2 \partial_\tau T \Rightarrow Condition$$

Turning the crank is now a bit more laborious.

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But the calculation can be done

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$$\partial S + \left(f/\gamma + T\partial\gamma^{-1}\right)\cdot\partial S + T/\gamma\,\partial^2 S = -T/\gamma\,\partial\cdot\tilde{f} - \left(f/\gamma + T\partial\gamma^{-1}\right)\cdot\tilde{f} - A$$

A "thermoentropic" force correction

$$\tilde{f} = \left(f/T - (\partial T/T)\right)$$

$$\left\langle e^{-\int \tilde{f}\circ dX_t} \right\rangle_{x_i}^{x_f} = \left\langle 1^b \right\rangle_{x_f}^{x_i}$$

$$dX_t = \left(f/\gamma - \tfrac{1}{2}\partial T/\gamma + \tfrac{1}{2}T\partial\gamma^{-1}\right)dt + \sqrt{2T/\gamma}\circ dW_t$$

Chétrite-Gawędzki (2008) & Matsuo-Sasa (2010)

The over-damped limit of the expected entropy production is however anomalous. Part of it cannot be reduced to a expected functional of the over-damped dynamics.

$$E_{x,v,t}\left[\delta S_{env}\right] = E_{x,t}\left[\int_t^{t_f} \tilde{f}\circ dX_t + A dt\right] + \frac{v^2}{2T} - \frac{d}{2} + O(\varepsilon)$$

$$A = \frac{(d+2)}{6\gamma T}\left|\partial T\right|^2$$

Recovering fluctuation relations…

$$\delta S_{env} = \Delta\left(\frac{v^2}{2T} + \tfrac{d}{2}\log T\right) + \int \frac{fv}{T}dt + \frac{dT - v^2}{2T^2}\left(\partial_t T + v \cdot \partial_x T\right)dt$$

$$\tilde{f} = \frac{f - \partial_x T}{T}$$

FRs can be looked at through generating functions

$$G_s\left(t_f, x_f, v_f \mid t_i, x_i, v_i\right) = \left\langle e^{-s\int \tilde{f}\circ dX_t - s\int \frac{\left(dT - v^2\right)}{2T^2}\partial_t T dt - s\int \frac{\left((d+2)Tv - v^2 v\right)}{2T^2}\partial_x T dt} \right\rangle_{x_i, v_i}^{x_f, v_f}$$

The overdamped limit can be taken for these functions as well...

$$\partial_t G_s = \ldots + \frac{s(1-s)(d+2)}{6\gamma T}\left|\partial_x T\right|^2 G_s + O(\varepsilon)$$

...the anomaly vanishes at s=0 and s=1 – preserving FR