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Entropy production mesoscopically and macroscopically

Erik Aurell

September 22, 2014
Angelo Vulpiani birthday party conference
“Strolling on Chaos, Turbulence and Statistical Mechanics”

Angelo the intellectual

Angelo the friend of the North

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Angelo the unpredictable, but *so* interested in predictability

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Happy Birthday!!!

Entropy production in stochastic thermodynamics [Sekimoto 2010]

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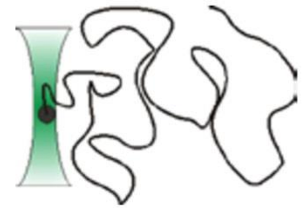
$$(k_B)T \approx 4nm \cdot pN$$

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...

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

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This entropy production is both physics and mathematics

As physics entropy production remains increased disorder in the environment and hence has to obey Clausius' law:

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

As mathematics it is also a ratio of path probabilities:

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

For stochastic kinetics the two definitions agree:

Jarzynski, Phys. Rev. E **56** 5018 (1997); Kurchan, J. Phys. A **31** 3719 (1998); Lebowitz & Spohn, J. Stat. Phys. **95** 333 (1999); Chétrite & Gawędzki, Comm. Math. Phys. (2008)

All fluctuation relations in classical stochastic systems follow from the definition as ratios of path probabilities:

Maes, J. Stat. Phys. **95** 367-392 (1999)
Gawędzki, arXiv:1308.1518 (2013)

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

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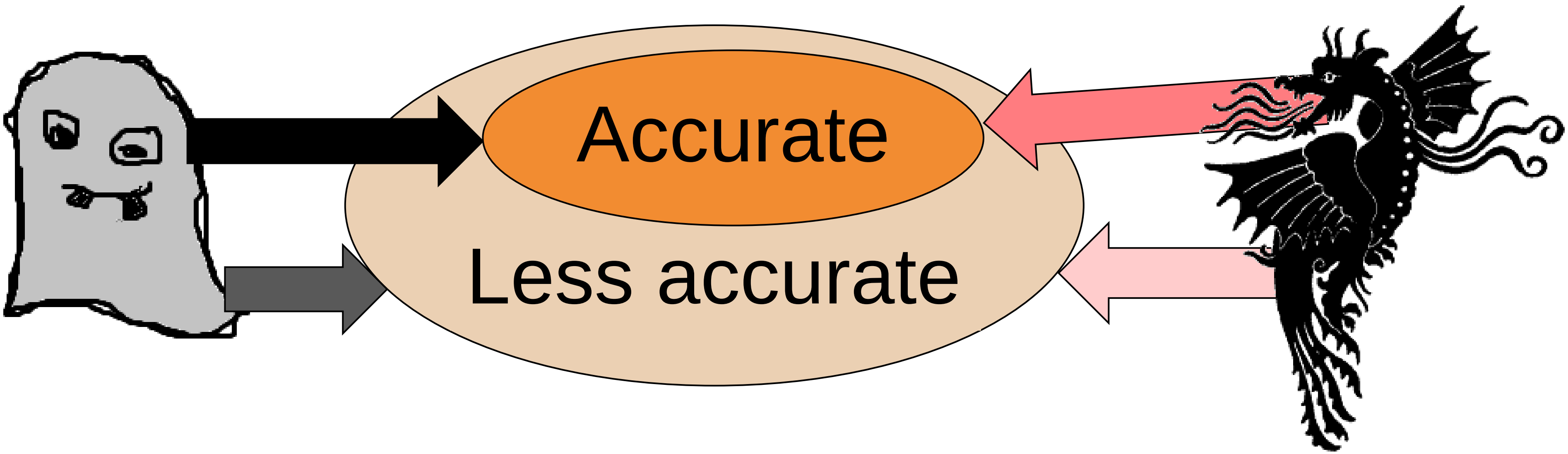
Suppose we can ”properly cut out a piece of the world” more or less accurately, as descriptions of ”The System”.



What happens to entropy production if we do this? Relations between macroscopics, mesoscopics, and, microscopics?

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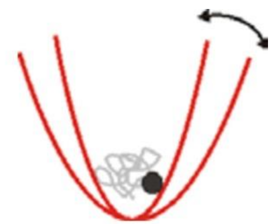
Test example: the underdamped Langevin equation...

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

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

force from the environment on the system...



$$V(z,t)$$

...which there is an opposite reaction force

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

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

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

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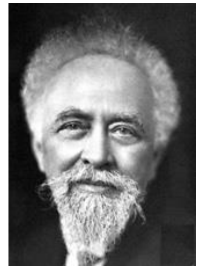
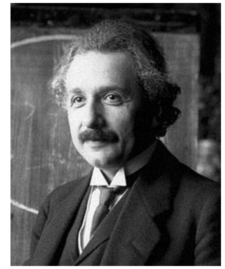
...compared to its overdamped limit.

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

Small time: $t_{\mathrm{r}} = m/\gamma$

Large length: L

Large time: $t_{\mathrm{f}} = L^2 / D$

Underdamped Kramers-Langevin (SDE) → Overdamped Kramers-Langevin (SDE)

$t_{\mathrm{r}}/t_{\mathrm{f}} = \varepsilon^2$

Underdamped Kramers-Langevin (SDE) ↓ Underdamped Fokker-Planck (PDE)

$\varepsilon = \ell / L$

Underdamped Fokker-Planck (PDE) → Overdamped Fokker-Planck (PDE)

Overdamped Fokker-Planck (PDE) ↑ Overdamped Kramers-Langevin (SDE)

Matsuo-Sasa (2010)

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

Expected entropy production

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

Fact 1: a "thermoentropic" force:

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

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

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

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

Fact 2: part of expected entropy production is not an expectation over (even corrected) force times distance. An "anomalous" contribution to the entropy production remains:

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

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

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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)]

The "anomalous" mesoscopic entropy production term is hence normal 3D macroscopic entropy

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

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

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

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)

Effects of rotation and asymmetry

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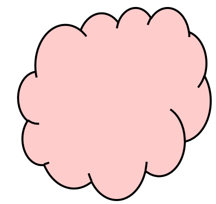
$$\dot{p} = -\partial_x V(x, \lambda_t) - \gamma \frac{p}{m} + \sqrt{2T\gamma}\dot{\eta}_t$$

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

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

Brownian particle of radius *R*. We 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 an anomalous contribution to the entropy production from the angular velocities with a mesoscopic thermal conductivity

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

Yueheng Lan, E.A., arXiv:1405.0663

And an analogous result if also γ is promoted to a metrix.

Raffele Marino, Ralf Eichhorn, E.A. (in preparation)

Mean flow and the advection-diffusion limit

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

Inertial particles limit: $\mathrm{Pe} \to \infty$ and St const. – too difficult (for us)

Advection-diffusion limit: $\mathrm{St} = \mathrm{Pe}^{-1} \to 0$ – one can do

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

Yueheng Lan, E.A., arXiv:1405.0663

This matches the other two terms in Landau-Lifshitz *Fluid Mechanics* 49.6

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

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

...and microscopics

Suppose that the microscopic entropy production is the change of the von Neumann entropy of a bath

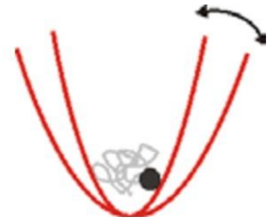
Esposito, Lindenberg, van den Broeck, New Journal of Physics **12** 013013 (2010)
Pucci, Esposito, Peliti. J. Stat. Mech. P4005 (2013)

Use Feynman-Vernon

A reminder: fluctuation relations in isolated quantum systems

Initial state of the system taken to be in equilbrium

Measurement E_i



$V(z,t)$ control

Measurement E_f

$$\rho^{eq} = |n\rangle\langle n| \frac{\exp(-\beta E_n)}{Z^{init}(\beta)} \Rightarrow |i\rangle\langle i| \Rightarrow \rho_f = \Phi(|i\rangle\langle i|) \Rightarrow |f\rangle\langle f|$$

On an isolated system, work done should be: $\delta W[i,f] = E_f - E_i$

Unitary time development implies: $\Phi(1) = 1$

$$\left\langle e^{-\beta\delta W}\right\rangle_{eq} = \sum_i \frac{e^{-\beta E_i}}{Z^{init}} \sum_f \langle f|\Phi(|i\rangle\langle i|)|f\rangle e^{-\beta(E_f - E_i)} = \frac{Z^{final}}{Z^{init}} = e^{-\beta\Delta F}$$

Jorge Kurchan, *A Quantum Fluctuation Theorem*, cond-mat/0007360

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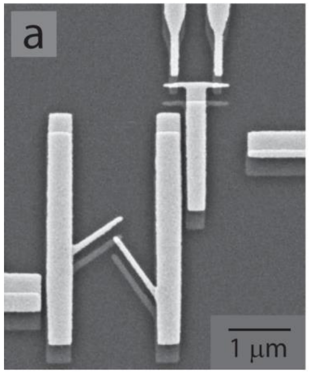
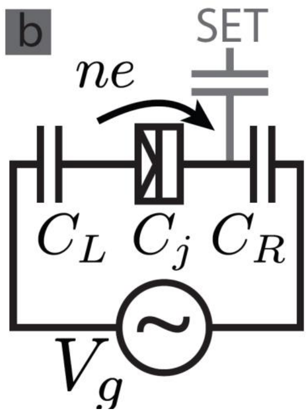
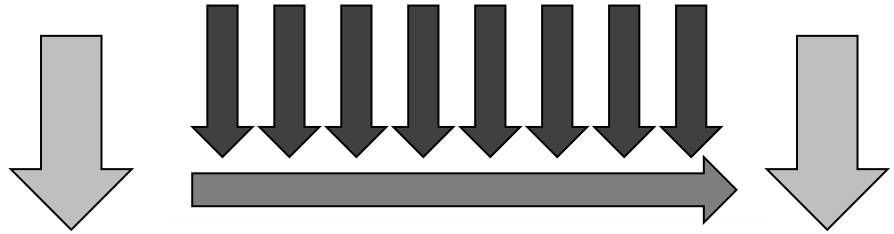
Other quantum fluctuation relations require frequent measurements

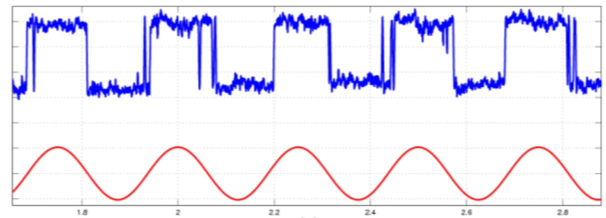




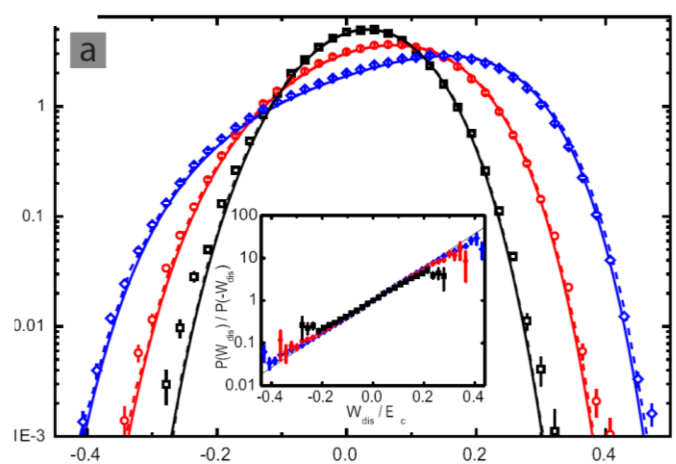


Detector current

Gate drive



Saira *et al*, *Test of Jarzynski and Crooks fluctuation relations in an electronic system*, PRL **109**, 180601 (2012); Koski *et al*, *Distribution of Entropy Production in a Single-Electron Box*, Nature Physics **9**, 644 (2013); Hekking & Pekola, *Quantum jump approach for work and dissipation in a two-level system*, PRL **111**, 093602 (2013); Horowitz & Parrondo, New J. Phys **15** 085028 (2013)



$$\langle e^{-\beta(W-\Delta F)}\rangle = 1.03 \pm 0.03$$

The Feynman-Vernon theory

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$$\rho_{TOT}^{init} = \rho_S^{init} \otimes \rho_B^{eq} \qquad \rho_{TOT}^{final}$$

$$\rho_S^{init} = |i\rangle\langle i| \qquad \rho_S^{final} = \mathrm{Tr}_B\left[\rho_{TOT}^{final}\right] \longrightarrow |f\rangle\langle f|$$

$$\mathrm{P}_{if} = \int \psi_i(x_i)\psi_i^*(y_i)\psi_f^*(x_f)\psi_f(y_f)K_{FV}\left(x_i, y_i, x_f, y_f\right)dx_i dy_i dx_f dy_f$$

$$K_{FV} = \int dq_i dq'_i dq_f \mathcal{D}q\mathcal{D}q'\mathcal{D}x\mathcal{D}y e^{\frac{i}{\hbar}S_S[x]-\frac{i}{\hbar}S_S[y]+\frac{i}{\hbar}S_I[x,q]-\frac{i}{\hbar}S_I[y,q']+\frac{i}{\hbar}S_B[q]-\frac{i}{\hbar}S_B[q']}\rho_B^{eq}$$

$$K_{FV} = \int \mathcal{D}x\mathcal{D}y e^{\frac{i}{\hbar}S_S[x]-\frac{i}{\hbar}S_S[y]+i\Phi[x,y]}$$

Integrate out the bath…then assume it is harmonic oscillators and linear coupling…

$$i\Phi[x,y] = \frac{i}{\hbar}S_i[x,y] - \frac{1}{\hbar}S_r[x,y] = \frac{i}{\hbar}\iint_{u\le s}(x_s - y_s)(x_u + y_u)k_i(s-u) - \frac{1}{\hbar}\iint_{u\le s}(x_s - y_s)(x_u - y_u)k_r(s-u)$$

A remarkably simple final result…

$$k_i(s-u) = \sum_i \frac{C_i^2}{2m_i\omega_i}\sin\omega(s-u)$$

$$k_r(s-u) = \sum_i \frac{C_i^2}{2m_i\omega_i}\coth\frac{\omega_i\hbar\beta}{2}\cos\omega(s-u)$$

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Change of von Neumann entropy

$$|i\rangle\langle i| \quad \rho_{TOT}^{init} \longrightarrow \rho_{TOT}^{final} \quad |f\rangle\langle f|$$

$$\rho_{TOT}^{post} = \frac{|f\rangle\langle f| \otimes \langle f|\rho_{TOT}^{final}|f\rangle}{\mathrm{Tr}_B\left[\langle f|\rho_{TOT}^{final}|f\rangle\right]}$$

$$\rho_B^{post} = \frac{1}{P_{if}}\langle f|\rho_{TOT}^{final}|f\rangle$$

$$\delta\mathrm{Tr}\left[-\rho_B\log\rho_B\right] = -\frac{1}{P_{if}}\mathrm{Tr}\left[\langle f|\rho_{TOT}^{final}|f\rangle\log\rho_B^{eq}\right] + \mathrm{Tr}\left[\rho_B^{eq}\log\rho_B^{eq}\right] + O\left(\delta\rho^2\right)$$

$$\log\rho^{eq} = |n\rangle\langle n|\left(\beta F - \beta E_n\right) = \beta F|n\rangle\langle n| + \beta\frac{d}{d\varepsilon}\langle n|e^{-\varepsilon H_B}|n'\rangle\Big|_{\varepsilon=0}|n\rangle\langle n'|$$

$$\delta\mathrm{Tr}\left[-\rho_B\log\rho_B\right] = -\frac{\beta}{P_{if}}\frac{d}{d\varepsilon}\mathrm{Tr}\left[e^{-\varepsilon H_B}\langle f|\rho_{TOT}^{final}|f\rangle\right]\Big|_{\varepsilon=0} + \text{ simple terms}$$

For finite ε the integrals over the bath are, as in Feynman-Vernon, Gaussian, and...

$$\delta\mathrm{Tr}\left[-\rho_B\log\rho_B\right] = -\frac{\beta}{P_{if}}\frac{d}{d\varepsilon}\mathrm{Tr}_{if}\int\mathcal{D}x\mathcal{D}y\, e^{\frac{i}{\hbar}S_S[x]-\frac{i}{\hbar}S_S[y]+\frac{i}{\hbar}S_i[x,y]-\frac{1}{\hbar}S_r[x,y]-\varepsilon(P+Q+R)+\dots}\Big|_{\varepsilon=0} + O\left(\delta\rho^2\right)$$

Explicitly…

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$$\rho_B^{eq} \otimes |i\rangle\langle i| \quad \rightarrow \quad \rho_{TOT}^{final} \qquad \rho_B^{post} = \frac{1}{P_{if}} \langle f | \rho_{TOT}^{final} | f \rangle$$

$$\delta \mathrm{Tr}\left[-\rho_B \log \rho_B\right] = -\frac{\beta}{P_{if}} \frac{d}{d\varepsilon} \mathrm{Tr}_{if} \int \mathcal{D}x\mathcal{D}y e^{\frac{i}{\hbar}S_S[x] - \frac{i}{\hbar}S_S[y] + \frac{i}{\hbar}S_i[x,y] - \frac{1}{\hbar}S_r[x,y] - \varepsilon(P+Q+R)+\ldots}\Big|_{\varepsilon=0} + O\left(\delta\rho^2\right)$$

$$P[x,y] = \iint_{u\le s} (x_s - y_s)(x_u - y_u)\, p(s-u) = \tfrac{d}{d\beta}\left(\tfrac{1}{\hbar} S_r\left[x,y\right]\right)$$

$$p(s-u) = -\sum_i \frac{C_i^2}{4m_i} \sinh^{-2} \frac{\omega_i \hbar \beta}{2} \cos \omega_i (s-u)$$

$$Q[x,y] = \iint_{u\le s} (x_s y_u + x_u y_s)\, q(s-u)$$

$$q(s-u) = \sum_i \frac{C_i^2}{2m_i} \cos \omega_i (s-u)$$

$$R[x,y] = \iint_{u\le s} (x_s y_u - x_u y_s)\, r(s-u)$$

$$r(s-u) = i \sum_i \frac{C_i^2}{2m_i} \coth \frac{\omega_i \hbar \beta}{2} \sin \omega_i (s-u)$$

P, Q and R are new terms, of similar type but not the same as in Feynman-Vernon.

Caldeira-Leggett model…

$$\sum_i \to \int_0^{\Omega} f(\omega) d\omega$$

Ohmic spectral density of the bath oscillators

$$\frac{f(\omega)C^2(\omega)}{m(\omega)} = \frac{2\eta\omega^2}{\pi}$$

First spectral cut-off Ω is taken large. Then a high-temperature limit is taken such that

$$\Omega\hbar\beta << 1$$

$$S_i[x,y] = -\tfrac{\eta}{2}\int (x_s - y_s)(\dot{x}_s - \dot{y}_s) \text{ + potential renormalization}$$

$$S_r[x,y] = \tfrac{\eta}{\hbar\beta}\int (x_s - y_s)^2$$

$$\delta \mathrm{Tr}\left[-\rho_B \log \rho_B\right] = -\frac{\beta}{P_{if}} \frac{d}{d\varepsilon} \mathrm{Tr}_{if} \int \mathcal{D}x\mathcal{D}y e^{\frac{i}{\hbar}S_S[x] - \frac{i}{\hbar}S_S[y] + \frac{i}{\hbar}S_i[x,y] - \frac{1}{\hbar}S_r[x,y] - \varepsilon(P+Q+R) + \dots}\Big|_{\varepsilon=0} + O\left(\delta\rho^2\right)$$

$$p(s-u) \approx -\tfrac{2\eta}{\hbar^2\beta^2}\delta(s-u)$$

$$P[x,y] = -\tfrac{\eta}{\hbar^2\beta^2}\int (x_s - y_s)^2 = -\tfrac{1}{\beta\hbar} S_r[x,y]$$

$$q(s-u) \approx -2\eta\ddot{\delta}(s-u)$$

$$Q[x,y] = \eta\int \dot{x}_s \dot{y}_s \text{ + boundary terms}$$

$$r(s-u) \approx -i\tfrac{2\eta}{\hbar\beta}\dot{\delta}(s-u)$$

$$R[x,y] = \tfrac{i\eta}{\hbar\beta}\int \dot{x}_s y_s - x_s \dot{y}_s = \tfrac{2i}{\hbar\beta} S_i[x,y] \text{ + bound. terms}$$

Simple consequence

$$\delta \mathrm{Tr}\left[-\rho_B \log \rho_B\right] = -\frac{\beta}{P_{if}} \frac{d}{d\varepsilon} \mathrm{Tr}_{if} \int \mathcal{D}x\mathcal{D}y e^{\frac{i}{\hbar}S_S[x]-\frac{i}{\hbar}S_S[y]+\frac{i}{\hbar}S_i[x,y]-\frac{1}{\hbar}S_r[x,y]-\varepsilon(P+Q+R)+\ldots}\Big|_{\varepsilon=0} + O\left(\delta\rho^2\right)$$

The most divergent new term in exponent is

$$Q[x,y] = \eta \int \dot{x}_s \dot{y}_s$$

This gives a contribution to the entropy change

$$\frac{1}{P_{if}} \left\langle \beta\eta \int \dot{x}_s \dot{y}_s \right\rangle_i^f$$

Compare the work done *on* the system by a friction force (heat transferred *from* a bath)

$$\int (-\eta v) dx = \int -\eta v^2 dt$$

By Clausius' formula the entropy production *in* the bath by reaction to the friction force is then

$$\delta S_{env} = \int \beta\eta v^2 dt$$

The same!

The other (sub-leading) contributions are more tricky to compute…

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The two sorts of entropy production in Feynman-Vernon

$$\delta S\left[i,f\right] = -\log \frac{P_{fi}^R}{P_{if}}$$

Φ

Φ^R

$$\delta \mathrm{Tr}\left[-\rho_B \log \rho_B\right] = \frac{\beta \langle P+Q+R\rangle_{if}}{P_{if}}$$

$$P_{fi}^R = \int \psi_f(x_f)\psi_f^*(y_f)\psi_i^*(x_i)\psi_i(y_i) K_{FV}^R\left(x_f, y_f, x_i, y_i\right) dx_i dy_i dx_f dy_f$$

$$= \mathrm{Tr}_{\mathrm{fi}} \int \mathcal{D}x\mathcal{D}y e^{\frac{i}{\hbar}S_S^R[x] - \frac{i}{\hbar}S_S^R[y] + \frac{i}{\hbar}S_i^R[x,y] - \frac{1}{\hbar}S_r^R[x,y]}$$

The two sides have different structure. At best, if there are frequent measurements…

$$\delta S[i,f] \approx -\frac{\left\langle \Delta S_S[x] + \Delta S_S[y] + \Delta S_i[x,y] + \Delta S_r[x,y]\right\rangle_{if}}{P_{if}}$$

And in this case (frequent measurements) one can get equality between the two sides if time reversal leads to…

$\Delta S_S\left[x\right] = \Delta S_S\left[y\right] = 0$ …kind of natural

$\Delta S_i\left[x,y\right] = -\beta R$ …can actually be true

$\Delta S_r\left[x,y\right] = -\beta(P+Q)$ …not true for friction

Thanks

Ralf Eichhorn

Antonio Celani

Stefano Bo

Yueheng Lan

Raffaele Marino

Karol Życzkowski

Jakub Zakrzewski

Jukka Pekola

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Happy birthday Angelo!