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The entropy change in a bath coupled to a driven quantum system

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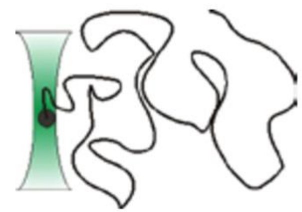
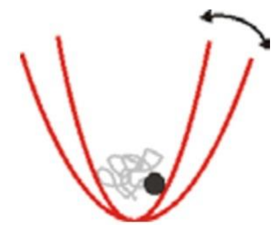
NORDITA program
“Quantum Engineering of States and Devices”

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...

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

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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"

Example: molecular unzipping

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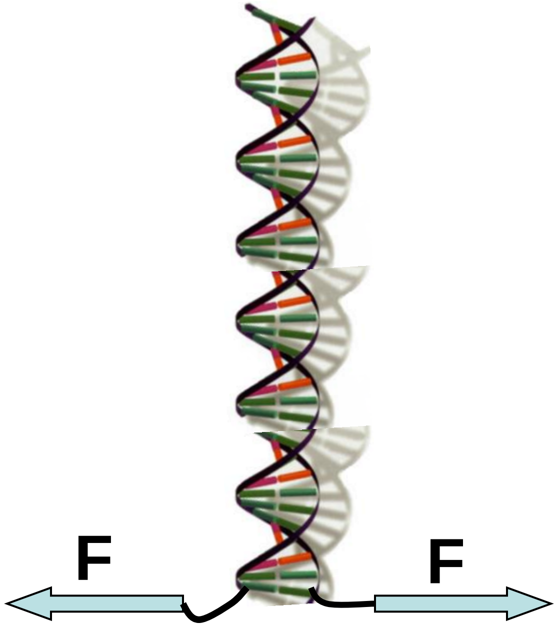
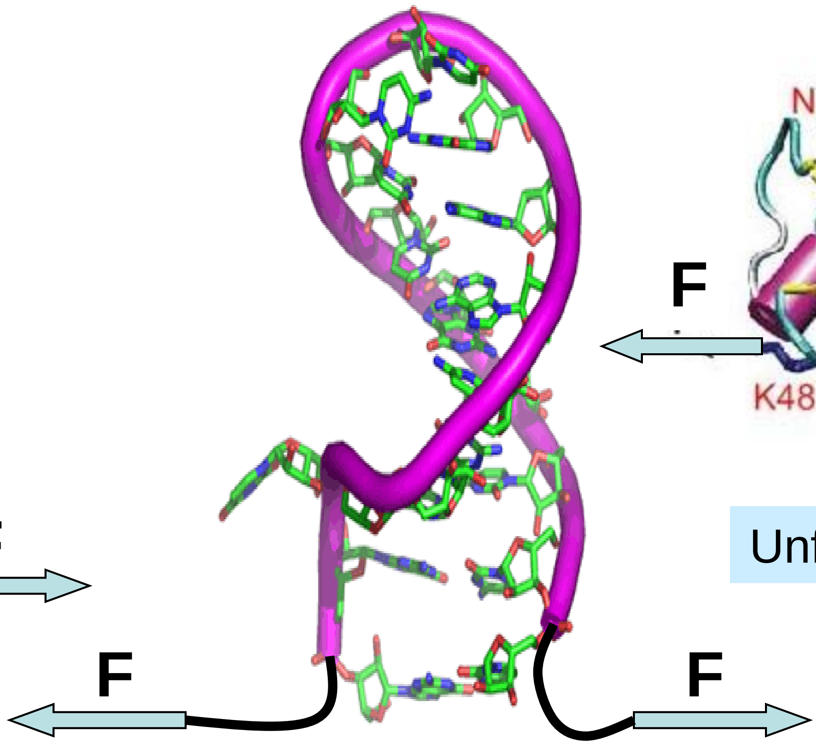
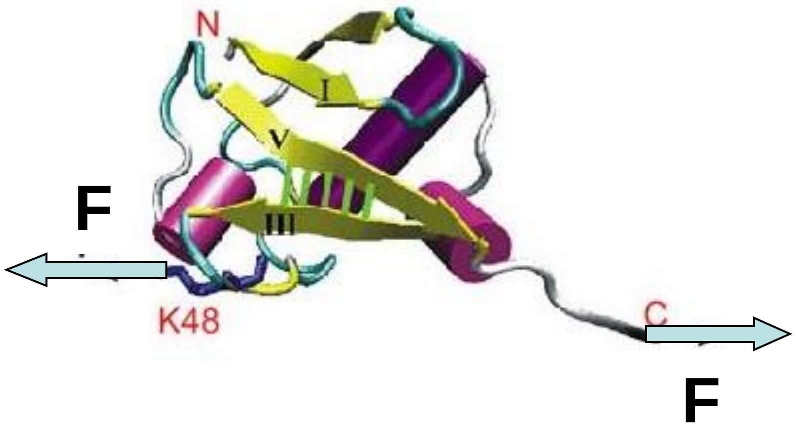
B. Essevaz-Roulet, U. Bockelmann , F. Heslot F (1997) *Proc Natl Acad Sci* USA 94:11935-11940
M. Rief, H. Clausen-Schaumann, H.E. Gaub (1999) *Nat Struct Biol* 6:346-349
C. Danilowicz et al. (2003) *Proc Natl Acad Sci* USA 100:1694-1699



DNA unzipping
(double stranded)



Unfolding of DNA and RNA hairpins (single stranded)



Unfolding of proteins

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

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The fluctuation relations formally arise from trivial identities

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

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

As an immediate consequence:

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

The physical problem is to show that such a formal mathematical expression really is standard entropy production, which is also

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

For stochastic kinetics models this is indeed so

Jarzynski, Phys. Rev. E **56** 5018 (1997); Kurchan, J. Phys. A **31** 3719 (1998); Lebowitz & Spohn, J. Stat. Phys. **95** 333 (1999); Gawędzki (2013)

Using the trivial identities…

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

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** $\left\langle e^{-\beta \delta W} \right\rangle_{i,eq} = e^{-\beta \Delta F} \therefore$

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

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 $\left\langle \delta S_{env} \right\rangle_i + S_f - S_i \geq 0 \therefore$

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For isolated quantum systems:

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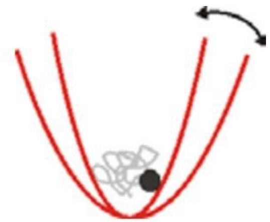
Initial state of the system taken to be in equilbrium

Measurement E_i



$V(z,t)$ control

Measurement E_f

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

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

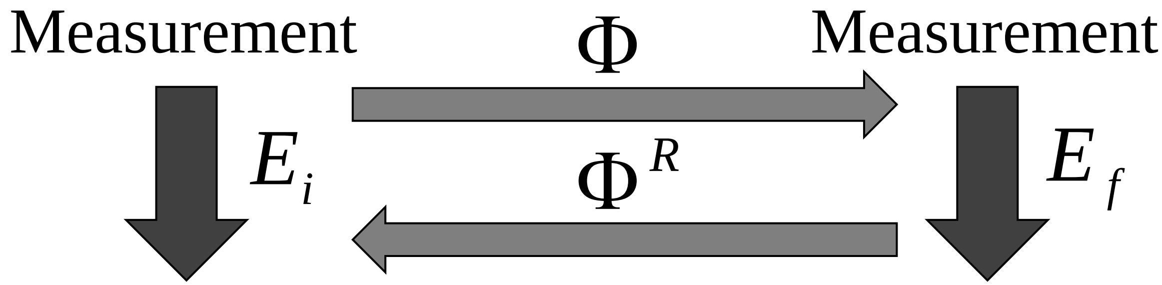
Unitary time development implies: $\Phi(\mathbf{1}) = \mathbf{1}$

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

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

For open quantum systems…

...one can still do the formal side of the argument...



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

If entropy production $\delta S[i,f] = \log \frac{\langle f|\Phi(|i\rangle\langle i|)|f\rangle}{\langle i|\Phi^R(|f\rangle\langle f|)|i\rangle}$ and $\delta W = \Delta E + k_B T \delta S$

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

Implicit, for instance, in Jordan Horowitz & Juan Parrondo, *Entropy production along nonequilibrium quantum jump trajectories*, New J. Phys **15** 085028 (2013)

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Experiments from Pekola group

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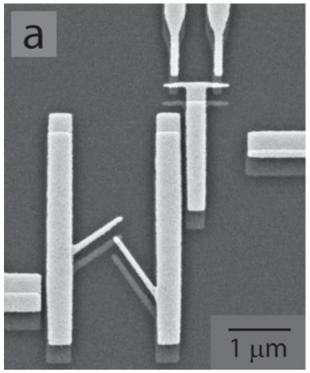
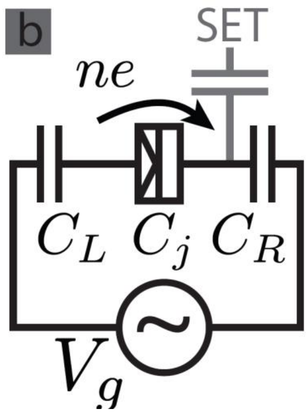
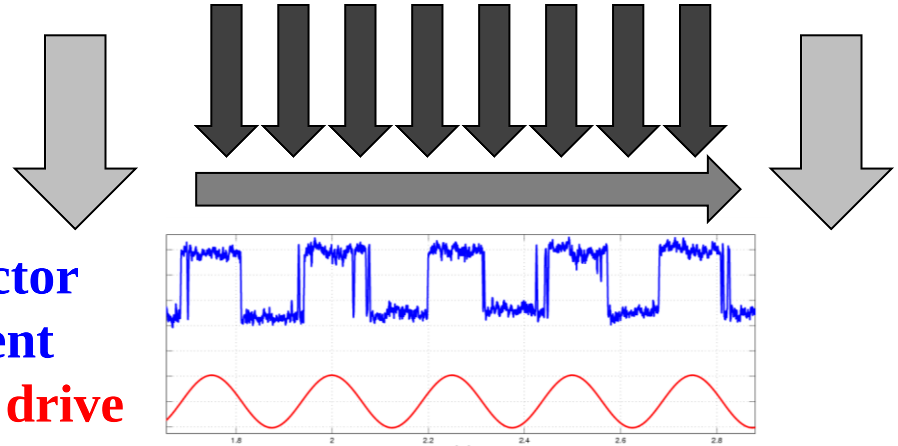


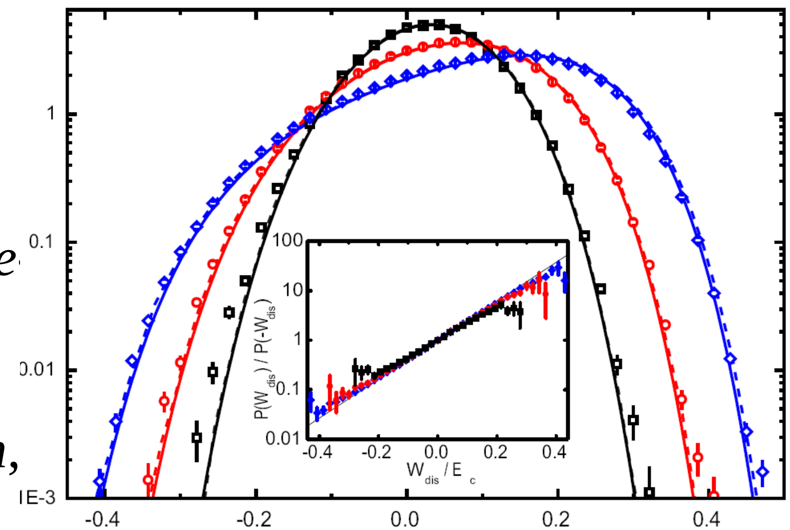


Detector current

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)



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

Define δS_{env} as the change of von Neumann entropy of the bath.

Esposito, Lindenberg, van den Broeck, New Journal of Physics **12** 013013 (2010)

Is this then the same entropy change as given by the formal argument?

The Feynman-Vernon theory

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

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

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

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

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

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…

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

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

Change of von Neumann entropy

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

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

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

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

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

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

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

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

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Explicitly…

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

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

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

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

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

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

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

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

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

Caldeira-Leggett model…

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

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

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

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

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

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

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

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

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

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

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

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

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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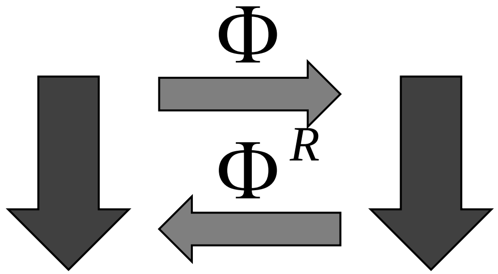
The formal argument stated in the Feynman-Vernon theory

$$\delta S[i,f] = -\log \frac{P^R_{fi}}{P_{if}}$$



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

$$P^R_{fi} = \int \psi_f(x_f)\psi^*_f(y_f)\psi^*_i(x_i)\psi_i(y_i) K^R_{FV}(x_f, y_f, x_i, y_i)\, dx_i dy_i dx_f dy_f$$

$$= \mathrm{Tr}_{\mathrm{fi}} \int \mathcal{D}x\mathcal{D}y\, e^{\frac{i}{\hbar}S^R_S[x] - \frac{i}{\hbar}S^R_S[y] + \frac{i}{\hbar}S^R_i[x,y] - \frac{1}{\hbar}S^R_r[x,y]}$$

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

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

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

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

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

$\Delta S_r[x,y] = -\beta(P + Q)$ …unclear

Thanks

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