Quantum corrections for Work

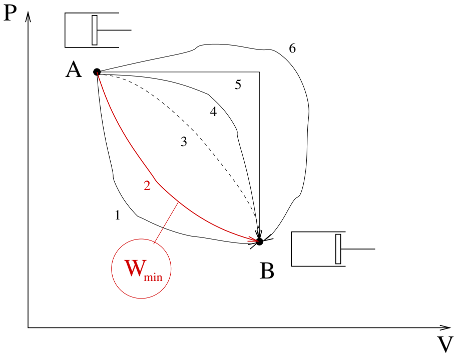
Olivier Brodier - L.M.P.T., Tours, France

in collaboration with
Kirone Mallick - Saclay, Paris.
Alfredo Ozorio de Almeida - C.B.P.F., Rio de Janeiro, Brésil

Plan

- ➙ Work in thermodynamics
- ➙ Jarzynski approach
- ➙ Quantum problem
- ➙ Different scenarii

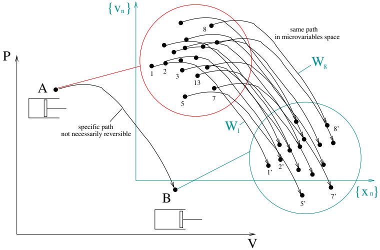
Work in thermodynamics



$T = T_0$ constant + second principle :

$$W \geqslant W_{\mathtt{min}} = \Delta F(T_0, V)$$

Jarzynski approach



Thermodynamics is intrinsically statistical and

$$"W" = \frac{1}{N}\sum_{n=1}^{N} W_n = \langle W \rangle$$

Jarzynski states that, if the initial state is a thermal state, then

$$\boxed{\langle e^{-\beta W} \rangle \equiv \int \frac{e^{-\beta H_0(x_0)}}{Z_0} e^{-\beta W(x_0 \to x_\tau)}\; dx_0 = e^{-\beta \Delta F} = \frac{Z_B}{Z_A}}$$

[Jarzynski 1996]

Some definitions

Time perturbation of a Hamiltonian :

$$H_t(x) = H_0 - \Phi_t \cdot q$$

with $\Phi_\tau = \Phi_0 = 0$, $x = (p, q)$ and Φ_t is a force.

$$W = \int_0^\tau \Phi_t \cdot \dot{q}_t \, dt$$

Integration by parts

$$W = 0 - \int_0^\tau \dot{\Phi}_t \cdot q_t \, dt$$

$$\boxed{W = \int_0^\tau \frac{\partial H_t}{\partial t}(x_t) \, dt}$$

General scheme of the proofs ([*Jarzynski PRE 1997*])

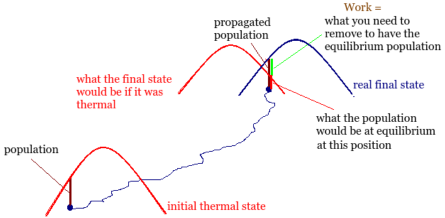
$$(1)\ \frac{d}{d\tau}\langle e^{-\beta W}\rangle_{x_\tau=x} = \int K_\tau(x,x')\langle e^{-\beta W}\rangle_{x_\tau=x'}\,dx' - \beta\frac{\partial H_\tau}{\partial\tau}\langle e^{-\beta W}\rangle_{x_\tau=x}$$

Thermal **equilibrium** state $\Pi_\tau = \frac{e^{-\beta H_\tau(x)}}{Z_\tau}$ verifies detailed balance :

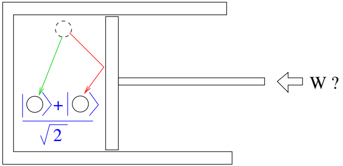
$$\int K_\tau(x,x')\Pi_\tau(x')\ dx' = 0$$

Hence $\frac{Z_\tau}{Z_0}\Pi_\tau(x)$ is a solution of (1) and

$$\frac{1}{Z_0}\int Z_\tau\Pi_\tau(x)\ dx = \int\langle e^{-\beta W}\rangle_{x_\tau=x}\ dx$$



Quantum problem



➡ Problem in defining a single work operator for the whole process.

➡ Work as the difference between final and initial energy in an adiabatical process.

➡ Work as a difference between final and initial energy of the operator ?

➡ Master equation approach to generalize the notion of classical path in a non-adiabatical process

Master equation approach

$$\frac{\partial \widehat{\rho}_t}{dt} = -\frac{i}{\hbar}\left[\widehat{H}_t, \widehat{\rho}_t\right] + \frac{1}{2\hbar}\sum_n \left(2\widehat{L}_{n,t}\widehat{\rho}_t\left(\widehat{L}_{n,t}\right)^\dagger - \left(\widehat{L}_{n,t}\right)^\dagger \widehat{L}_{n,t}\widehat{\rho}_t - \widehat{\rho}_t\left(\widehat{L}_{n,t}\right)^\dagger \widehat{L}_{n,t}\right) = \mathcal{L}_t(\widehat{\rho}_t)$$

as $\mathcal{L}_t$ is time dependent, $\widehat{\Pi}_t$ is not solution, that is

$$\frac{\partial \widehat{\Pi}_t}{dt} \neq \mathcal{L}_t(\widehat{\Pi}_t)$$

- Find a superoperator $\mathcal{W}_t$ such that

$$\frac{d}{dt}\widehat{\Pi}_t = (\mathcal{L}_t + \mathcal{W}_t)(\widehat{\Pi}_t)$$

- With the assumption that $\widehat{\Pi}_t$ is "balanced" by $\mathcal{L}_t$, that is

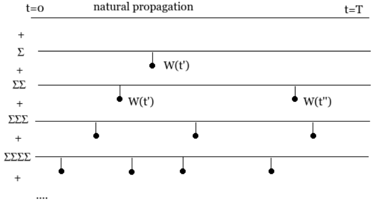
$$\mathcal{L}_t(\widehat{\Pi}_t) = 0,$$

then a brute force solution is then

$$\mathcal{W}_t(\widehat{\rho}) = \left(\frac{d}{dt}\widehat{\Pi}_t\right)\left(\widehat{\Pi}_t\right)^{-1}\widehat{\rho}$$

Expansion in $\mathcal{W}_t$

To obtain a Jarzynski-like equation one uses a Schwinger-Dyson expansion in $\mathcal{W}_t$ of the solution to the modified master equation



$$\mathcal{U}_{0,\tau}^{\mathcal{L}+\mathcal{W}} = \sum_n \int_{0\leqslant t_1 \leqslant \ldots \leqslant t_n \leqslant t} \left(\prod_{i=1}^{n} dt_i \right) \mathcal{U}_{0,t_1} \mathcal{W}_{t_1} \mathcal{U}_{t_1,t_2} \ldots \mathcal{W}_{t_n} \mathcal{U}_{t_n,t}$$

$$\boxed{\mathrm{Tr}\left(\widehat{\Pi}_\tau \widehat{A}\right) = \mathrm{Tr}\left(\widehat{\Pi}_0 \ \overrightarrow{e}^{\int_0^\tau \mathcal{W}_t^{\mathcal{L}} \ dt} \ (\widehat{A}_\tau)\right)}$$

[R.Chetrite and K.Mallick 2011]

Quantum work corrections

From Baker-Campbell-Hausdorff

$$\frac{d}{dt}(Z_t\widehat{\Pi}_t)\left(Z_t\widehat{\Pi}_t\right)^{-1} = -\beta\frac{\partial\widehat{H}_t}{\partial t} - \frac{\beta^2}{2!}\left[\frac{\partial\widehat{H}_t}{\partial t},\widehat{H}_t\right] - \frac{\beta^3}{3!}\left[\left[\frac{\partial\widehat{H}_t}{\partial t},\widehat{H}_t\right]\widehat{H}_t\right] - \dots$$

From Moyal expansion in Weyl representation

$$\mathcal{W}_t(x) = -\beta\left[\frac{\partial H_t}{\partial t}(x) + \frac{i\hbar\beta}{2}\left\{\frac{\partial H_t}{\partial t}(x), H_t(x)\right\} + \frac{(i\hbar\beta)^2}{6}\left\{\left\{\frac{\partial H_t}{\partial t}(x), H_t(x)\right\}, H_t(x)\right\} + \mathcal{O}\left((\hbar\beta)^3\right)\right]$$

Harmonic oscillator

$$\widehat{H}_t = \frac{\widehat{p}^2}{2m} + \frac{k_t}{2}\widehat{q}^2$$

In Weyl representation

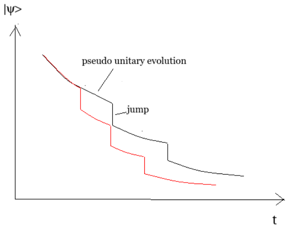
$$\mathcal{W}_t(p,q) = -\dot{\theta}\left[(1-f(\theta))\,\frac{p^2}{m\hbar\omega} + (1+f(\theta))\,\frac{m\omega q^2}{\hbar} + ig(\theta)\frac{pq}{\hbar}\right]$$

$f(t) = \sinh(4t)/(4t)$
$g(t) = \sinh(2t)^2/t$
$\theta = \beta\hbar\omega$

$\hbar$ EXPANSION

$$\mathcal{W}_t(p,q) = -\beta\left[\frac{\dot{k}_t}{2}\widehat{q}^2 + i(\beta\hbar\omega)\frac{\dot{\omega}}{\omega}\omega p q + (\beta\hbar\omega)^2\frac{2}{3}\frac{\dot{\omega}}{\omega}(\frac{p^2}{2m} - \frac{k}{2}q^2) + \mathcal{O}\left((\beta\hbar\omega)^3\right)\right]$$

Quantum trajectory



during a time step δt the state $|\psi\rangle$ can chose between

- a jump with Lindblad operator (proba $p\delta t$)

$$|\Psi_t\rangle \longrightarrow \widehat{L}_k|\Psi_t\rangle$$

- or a pseudo-unitary evolution (proba $1 - p\delta t$) with effective non-Hermitian Hamiltonian $\widehat{H}_t^{\mathcal{L}}$

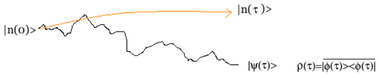
$$|\Psi_t\rangle \longrightarrow e^{-\frac{i\delta t}{\hbar}\widehat{H}_t^{\mathcal{L}}}|\Psi_t\rangle$$

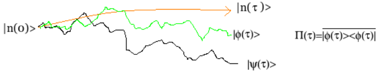
Then

$$\widehat{\rho}_t = \overline{|\Psi_t\rangle\langle\Psi_t|}$$

Quantum trajectory for the thermal state

$$\widehat{\Pi}_t = \sum_n |n_t\rangle e^{-\beta E_{n,t}} \langle n_t|$$





Modify $\widehat{H}_t^{\mathcal{L}}$ so that quantum trajectory follows $\widehat{\Pi}_t$

$$\widehat{H}_t^{\mathcal{L}} \longrightarrow H_t^{\mathcal{L}} + \widehat{H}_t^{\pi}$$

$$\frac{d}{dt}\widehat{\Pi}_t = -\frac{i}{\hbar}\left[\widehat{H}_t^{\pi}, \widehat{\Pi}_t\right] + \mathcal{L}_t(\widehat{\Pi}_t)$$

Quantum Work of the trajectory

- A possible expression is

$$\widehat{H}_t^{\pi} = i\hbar \sum_n |\dot{n}_t\rangle\langle n_t| - \frac{i\beta\hbar}{2} \sum_n \dot{E}_{n,t} |n_t\rangle\langle n_t| - \frac{i\hbar}{2} \frac{\dot{Z}_t}{Z_t}$$

- Example of the Harmonic oscillator $\widehat{H}_t = \frac{p^2}{2m} + \frac{k_t}{2} q^2$

$$\widehat{H}_t^{\pi} = -\frac{\dot{\omega}}{2\omega} \frac{\widehat{p}\widehat{q} + \widehat{q}\widehat{p}}{2} - \frac{i\beta\hbar}{2} \frac{\dot{\omega}}{\omega} \widehat{H}_t - \frac{i\hbar}{2} \frac{\dot{Z}_t}{Z_t}$$

- First term makes evolution of $|n_t\rangle$, and second term makes evolution of $E_{n,t}$. Third term is normalization.

PERSPECTIVES

- Find a more natural proof
- Unify the different approaches
- Treat a realistic system where work is an accessible quantity
- Give an experimental meaning to the "quantum work"

A simple proof

$$\langle e^{-\beta W} \rangle = \int \rho_0(x_0)\; e^{-\beta W(x_0, x_t)}\; dx_0$$

thermal initial state and adiabatic Hamiltonian system :

$$\langle e^{-\beta W} \rangle = \int \frac{e^{-\beta H_0(x_0)}}{Z_0}\; e^{-\beta [H_t(x_t) - H_0(x_0)]}\; dx_0$$

$$\langle e^{-\beta W} \rangle = \frac{1}{Z_0} \int e^{-\beta H_t(x_t)}\; dx_0$$

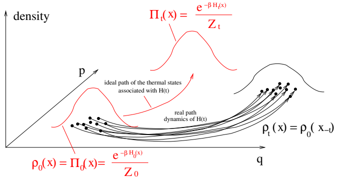
simplecticity :

$$\langle e^{-\beta W} \rangle = \frac{1}{Z_0} \int e^{-\beta H_t(x_t)}\; dx_t = \frac{Z_t}{Z_0}$$

with

$$Z_t = e^{-\beta F_t} = \int e^{-\beta H_t(x)}\; dx$$

General scheme of the proofs



Transport of the real state :

$$\frac{d}{dt}\left[\rho_t(x_t)\right] = \dot{\rho}_t(x_t) - \{H_t(x_t), \rho_t(x_t)\} = 0$$

$$\rho_\tau(x_\tau) = \rho_0(x_0)$$

Invariance by transport for the thermal **equilibrium** state :

$$\frac{d}{dt}\left[\Pi_t(x_t)\right] = \dot{\Pi}_t(x_t) - \{H_t(x_t), \Pi_t(x_t)\} = \left[-\beta \dot{H}_t(x_t) - \frac{\dot{Z}_t}{Z_t}\right] \Pi_t(x_t)$$

$$\Pi_\tau(x_\tau) = \Pi_0(x_0)\frac{Z_0}{Z_t} e^{-\beta \int_0^\tau \dot{H}_t(x_t)\ dt}$$

Fluctuation relations

Jarzynski relation allows to derive some fluctuation relations

$$\widehat{H}_t = \widehat{H}_0 + \lambda_t \widehat{V}$$

$$\mathrm{Tr}\left(\widehat{\Pi}_\tau \widehat{A}\right) = \mathrm{Tr}\left(\widehat{\Pi}_0 \; e^{\int_0^\tau \mathcal{W}_t^{\mathcal{L}} \; dt} \; \widehat{A}_\tau\right)$$

$$\frac{d}{d\lambda_t}\left[\mathrm{Tr}\left(\widehat{\Pi}_\tau \widehat{A}\right)\right] = \frac{d}{d\lambda_t}\left[\mathrm{Tr}\left(\widehat{\Pi}_0 \; e^{\int_0^\tau \mathcal{W}_t^{\mathcal{L}} \; dt} \; \widehat{A}_\tau\right)\right]$$

$$\boxed{0 = \langle\left(\mathcal{U}_{0,t}\frac{\partial \mathcal{W}_t}{\partial \lambda_t}\mathcal{U}_{t,\tau}\right)(\widehat{A}_\tau)\rangle|_{\lambda=0} - \frac{\partial}{\partial \lambda_t}\langle \widehat{A}_\tau\rangle|_{\lambda=0}}$$

Quantum work

$\mathcal{W}_t$ interpreted as some work rate operator.

A brute force solution is

$$\mathcal{W}_t\left(\widehat{\rho}\right) = \left(\frac{d}{dt}\widehat{\Pi}_t\right)\left(\widehat{\Pi}_t\right)^{-1}\widehat{\rho}$$

So that

$$\frac{d}{dt}\widehat{\Pi}_t = \mathcal{W}_t(\widehat{\Pi}_t) = \left(\mathcal{L}_t + \mathcal{W}_t\right)\left(\widehat{\Pi}_t\right)$$

Quantum trajectory

$$\widehat{\Pi}_t = \sum_n e^{-\beta E_{n,0}} \sum_{\gamma(n)} (\delta t)^{[\gamma]}\ \widehat{T}_N^{\gamma} \ldots \widehat{T}_1^{\gamma}\ |n_0\rangle\langle n_0|\ (\widehat{T}_1^{\gamma})^{\dagger} \ldots (\widehat{T}_N^{\gamma})^{\dagger}$$

with

$$[\gamma] = \text{number of jumps in trajectory } \gamma$$

The natural quantum trajectory is combined by episodes which track the thermal state

$$e^{-\frac{i\delta t}{\hbar}\widehat{H}_t^{\pi}}|n_t\rangle \simeq e^{-\frac{\beta\delta t}{2}\dot{E}_{n,t}}|n_{t+\delta t}\rangle$$

$$\widehat{\Pi}_t = \sum_n \int_{0\leqslant t_1\leqslant \ldots \leqslant t_n \leqslant t} \prod_{i=1}^{n} dt_i\ \widehat{U}_{t_n,t}^{\mathcal{L}+\pi}\widehat{L}_{t_n} \ldots \widehat{U}_{t_1,t_2}^{\mathcal{L}+\pi}\widehat{L}_{t_1}\widehat{U}_{0,t_1}^{\mathcal{L}+\pi}\widehat{\Pi}_0 \left(\widehat{U}_{0,t_1}^{\mathcal{L}+\pi}\right)^{\dagger} \widehat{L}_{t_1}^{\dagger} \left(\widehat{U}_{t_1,t_2}^{\mathcal{L}+\pi}\right)^{\dagger} \ldots \widehat{L}_{t_n}^{\dagger} \left(\widehat{U}_{t_n,t}^{\mathcal{L}+\pi}\right)^{\dagger}$$

Adiabatical case

where $\alpha_n(t)$ is Berry's phase.

$$\widehat{\Pi}_t = \sum_n e^{-\beta E_n} \sum_{\gamma(n)} (\delta t)^{[\gamma]} \, \widehat{T}_N^\gamma \ldots \widehat{T}_1^\gamma \, |n\rangle\langle n| \, (\widehat{T}_1^\gamma)^\dagger \ldots (\widehat{T}_N^\gamma)^\dagger$$

with

$$[\gamma] = \text{number of jumps in trajectory } \gamma$$