Entropy Production and Time's Arrow Beyond the Second Law of Thermodynamics

Dissipation: The Phase-Space Perspective

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- Derivation of the formula
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Relevant topics to this school

Quantum Entropy, Quantum Relative Entropy, Trace Inequalities
Quantum Stein's Lemma, Information, ...

The Second Law of Thermodynamics

There exists no thermodynamic transformation whose *sole* effect is to extract a quantity of heat from a given heat reservoir and to convert it entirely into work.

William Thomson
Lord Kelvin
(1822-1873)

There exists no thermodynamic transformation whose *sole* effect is to extract a quantity of heat from a colder reservoir and to deliver it to a hotter reservoir.

Rudolf Clausius
(1822-1888)

Sir Arthur Eddington (1882-1944)

"The law that entropy always increases holds, I think, the supreme position among the laws of nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equation – then so much the worse for Maxwell's equations ... but if your theory is found to be against the second law of thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation." (1928)

"The second law of thermodynamics is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of the basic concepts, it will never be overthrown." (1949)
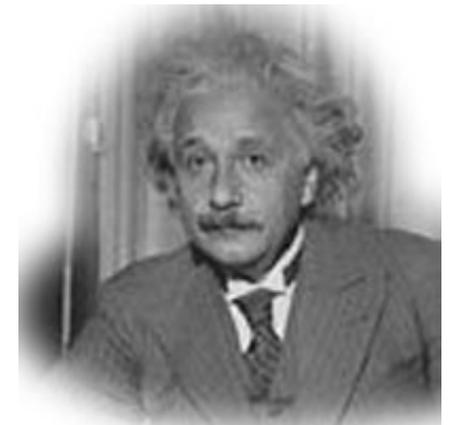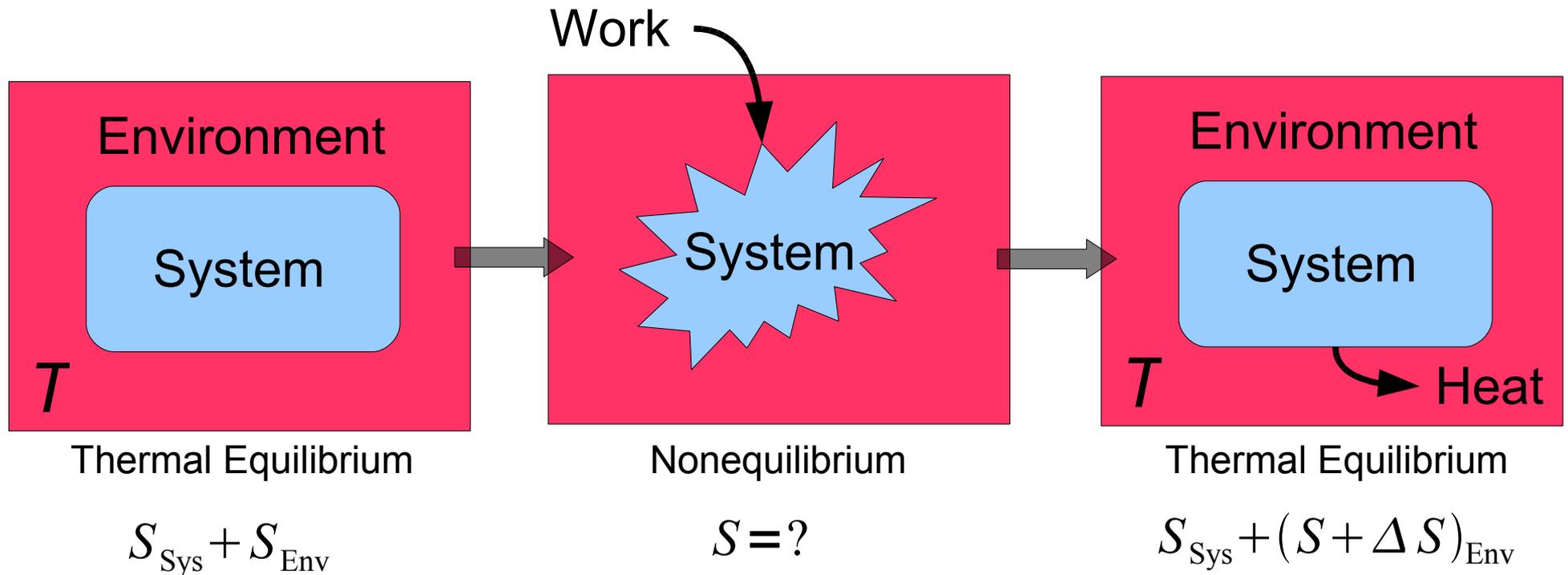
Albert Einstein (1879-1955)

Entropy Production and the Second Law

$$\Delta S \geq 0$$

$$(\Delta S \equiv S_{\text{fin}} - S_{\text{ini}}; \quad S \equiv \text{Entropy at an equilibrium state})$$

Work

Environment

System

T

Thermal Equilibrium

$$S_{\text{Sys}} + S_{\text{Env}}$$

System

Nonequilibrium

$$S = ?$$

Environment

System

T

Heat

Thermal Equilibrium

$$S_{\text{Sys}} + (S + \Delta S)_{\text{Env}}$$

Time reversed process cannot happen spontaneously.

Second Law ⟶ **Time's Arrow**

Microscopic Definition of Entropy

Boltzmann $\qquad S_B = k \log W$

Gibbs $\qquad S_G = -k \int \rho \ln \rho \, d\Gamma$ $\qquad \Longrightarrow \quad \Delta S = 0$

Von Neumann $\quad S_N = -k \operatorname{Tr}(\rho \ln \rho)$

k = Boltzmann constant

These expressions valid only for equilibrium systems.

$\Delta S = $
$$ \boxed{\begin{array}{c} \text{I say} \\ k\, D\big(\rho_F(t) \,\|\, \tilde{\rho}_B(t)\big) \end{array}} \geq 0 $$

Ludwig E. Boltzmann
(1844-1906)

Minimal Prerequisites I. Quantum Mechanics

State of the system

Density Operator ρ

Non-negative operator on a Hilbert space H

$\mathrm{Tr}\,\rho = 1$

Time evolution of the system

$$i\hbar \frac{d\rho}{dt} = [H, \rho]$$

$\hbar$: Planck constant

H: Hamiltonian (self-adjoint operator on H)

$$[A, B] = AB - BA$$

$$\rho(t) = U\,\rho(t_0)\,U^{-1}$$

U: Unitary operator on H

For example

$$U = e^{-iH(t-t_0)/\hbar}$$

Minimal Prerequisites II. Measurement

Observables and Statistical Average

Physical Quantity: Ω (self-adjoint operator on H)

Expectation Value: $\langle\Omega\rangle=\mathrm{Tr}(\Omega\rho)$

Example: Energy of the system $E=\langle H\rangle=\mathrm{Tr}(H\rho)$

Spectral representation $\quad \Omega=\sum_i \omega_i \mathcal{P}_i, \qquad \mathcal{P}_i^2=\mathcal{P}_i, \qquad \sum_i \mathcal{P}_i=I$

Probability to obtain ω_i upon measurement $\quad p_i=\mathrm{Tr}(\mathcal{P}_i\rho)$

$$\langle\Omega\rangle=\mathrm{Tr}(\Omega\rho)=\sum_i \omega_i \mathrm{Tr}(\mathcal{P}_i\rho)=\sum_i \omega_i p_i$$

Minimal Prerequisites III. Thermal Equilibrium

Thermal Equilibrium at Temperature T

$$\rho_{eq} = \frac{1}{Z} e^{-\beta H} \qquad \beta = \frac{1}{kT}, \qquad Z = \mathrm{Tr}\, e^{-\beta H} \text{ (Partition Function)}$$

$$\frac{d\rho_{eq}}{dt} = 0 \quad ([H, e^{-\beta H}] = 0)$$

$$S_N = -k\,\mathrm{Tr}(\rho_{eq} \ln \rho_{eq}) = \frac{1}{T}\Big[\mathrm{Tr}(H\rho_{eq}) + kT \ln Z\Big] = \frac{E - F}{T}$$

$$F \equiv -kT \ln Z \text{ (Free Energy)} \qquad\qquad F = E - S_N T$$

Minimal Prerequisites IV. Time Reversal Symmetry

Θ : Time Reversal Operator

$\Theta \lambda = \bar{\lambda} \Theta \quad (\lambda \in \mathbb{C})$ anti-unitary $t = 0$ $t = \tau$

$\Theta \dfrac{\mathrm{d}}{\mathrm{d}t} \Theta^{-1} = -\dfrac{\mathrm{d}}{\mathrm{d}t}$

v v

$\Theta p \Theta^{-1} = -p$
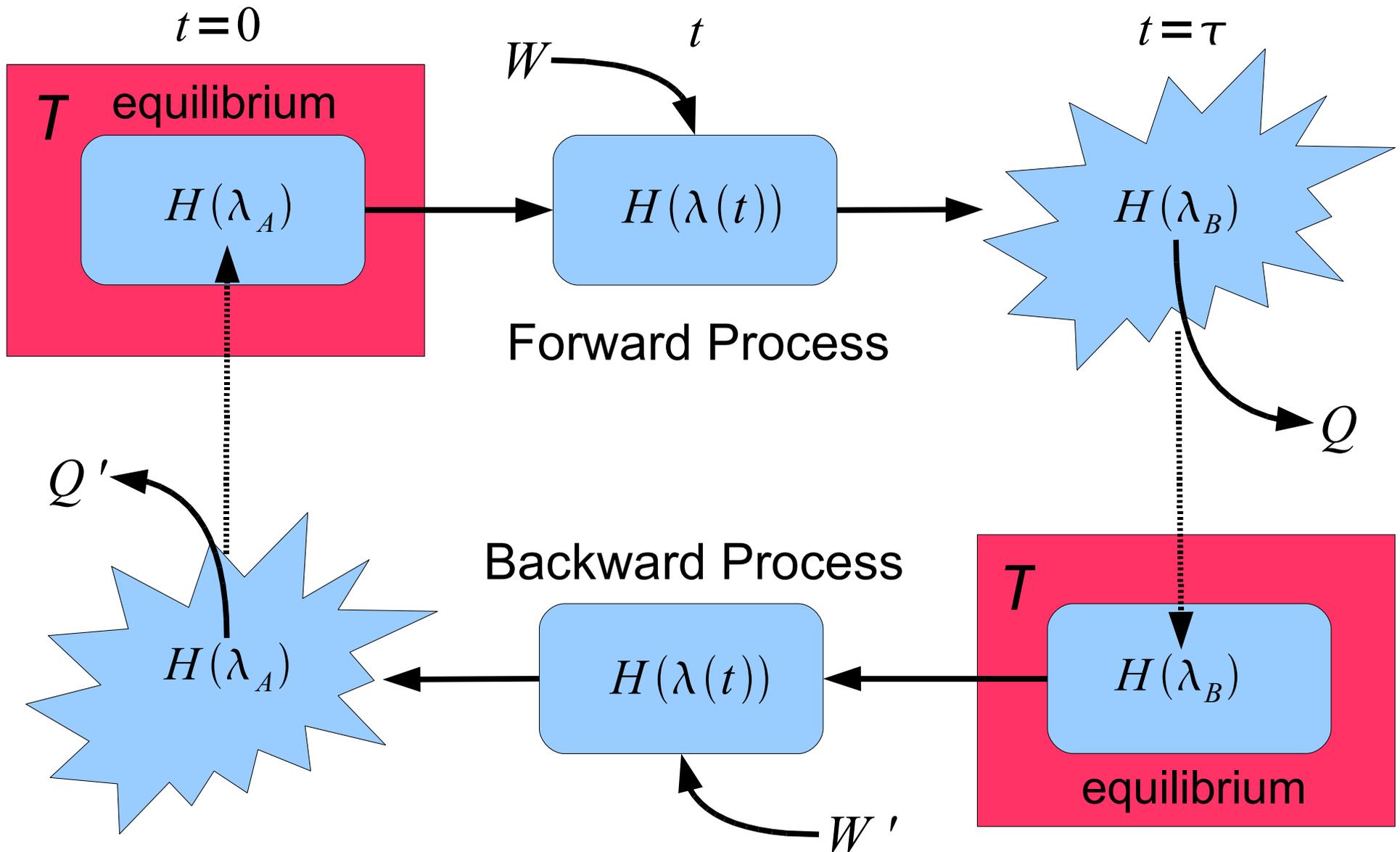
$-v$ $-v$

$\Theta x \Theta^{-1} = x$

$\Theta H \Theta^{-1} = H$
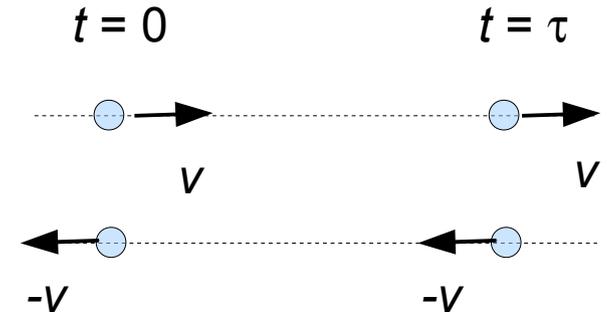
> Time reversed density $\tilde{\rho} \equiv \Theta \rho \Theta^{-1}$ satisfies the same equation of motion.
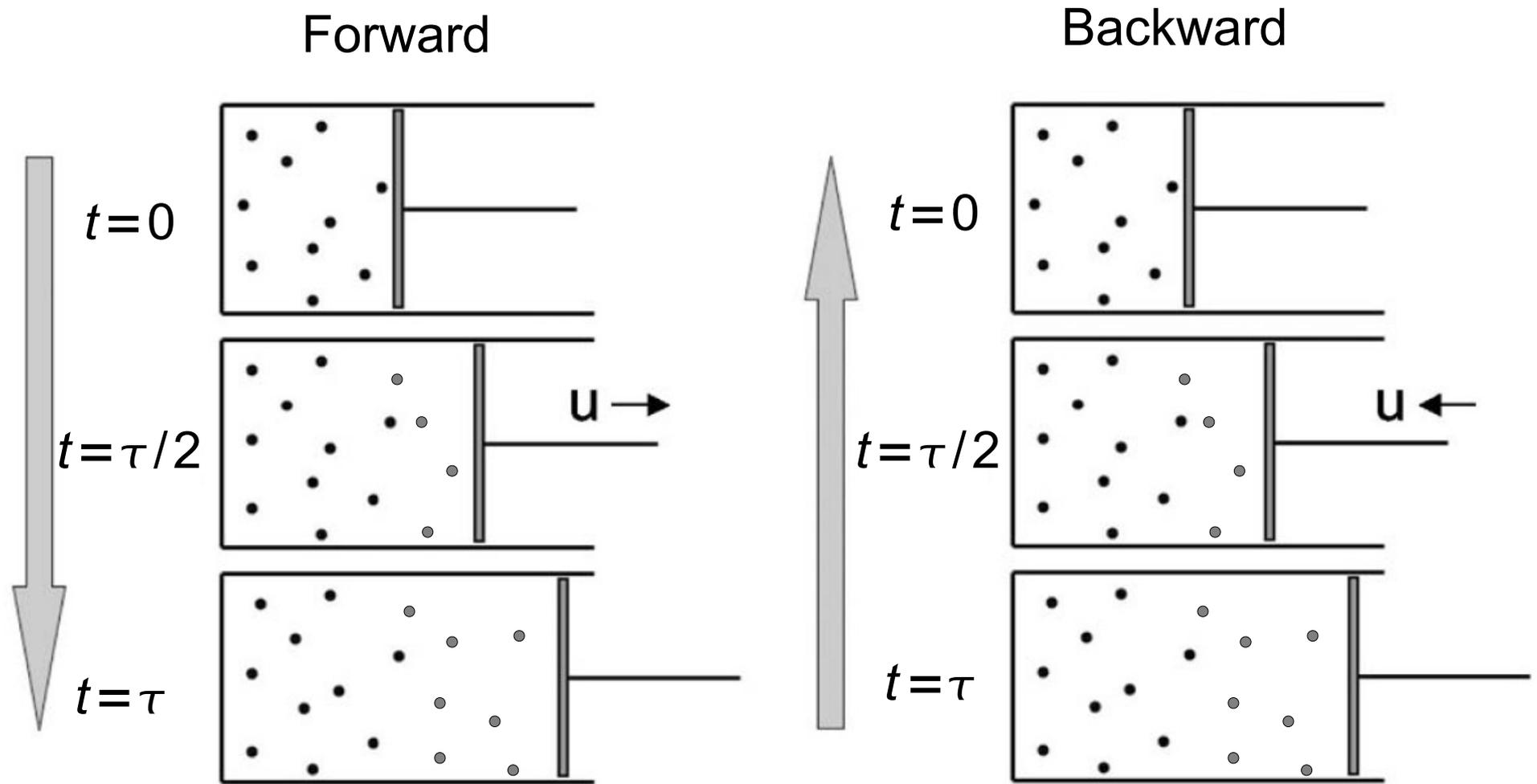
$i\hbar \dfrac{\mathrm{d}}{\mathrm{d}t} \rho = [H, \rho]$

$\Theta i\hbar \dfrac{\mathrm{d}}{\mathrm{d}t} \rho \Theta^{-1} = \Theta [H, \rho] \Theta^{-1} \;\rightarrow\; i\hbar \dfrac{\mathrm{d}}{\mathrm{d}t} \Theta \rho \Theta^{-1} = [H, \Theta \rho \Theta^{-1}] \;\rightarrow\; i\hbar \dfrac{\mathrm{d}}{\mathrm{d}t} \tilde{\rho} = [H, \tilde{\rho}]$

A Non-Equilibrium Process: Time-Dependent Hamiltonian

$$H[\lambda(t)], \ t \in [0, \tau]; \ \lambda(0) = \lambda_A \ \rightarrow \ \lambda(\tau) = \lambda_B$$

$t = 0$

T

equilibrium

$H(\lambda_A)$

W

t

$H(\lambda(t))$

Forward Process

$t = \tau$

$H(\lambda_B)$

Q

Q'

$H(\lambda_A)$

Backward Process

$H(\lambda(t))$

$H(\lambda_B)$

T

equilibrium

W'

Example: Expansion and Compression of Gas

Forward

Backward

$t=0$

$t=\tau/2$ u →

$t=\tau$

$t=0$

$t=\tau/2$ u ←

$t=\tau$

Claim

$$\Delta S = k\, D\big(\rho_F(t)\|\tilde{\rho}_B(t)\big) = k\, \mathrm{Tr}\big[\rho_F(t)\ln\rho_F(t)\big] - k\, \mathrm{Tr}\big[\rho_F(t)\ln\tilde{\rho}_B(t)\big] \qquad t\in[0,\tau]$$

$$D(\rho\|\sigma) \equiv \mathrm{Tr}\,\rho\ln\rho - \mathrm{Tr}\,\rho\ln\sigma \qquad \text{Quantum Relative Entropy}$$

ρ_F Density of the forward process

$\tilde{\rho}_B$ Time reversed density of the backward process

$$\rho_F(0) \qquad\qquad \rho_F(t) \qquad\qquad \rho_F(\tau)$$

$$\tilde{\rho}_B(0) \qquad\qquad \tilde{\rho}_B(t) \qquad\qquad \tilde{\rho}_B(\tau)$$
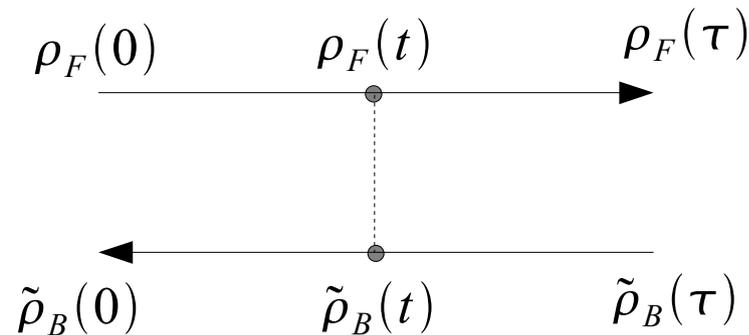
Initial states = thermal equilibrium

$$\rho_F(0) = \frac{1}{Z_A}e^{-\beta H(\lambda_A)} \qquad\qquad \tilde{\rho}_B(\tau) = \frac{1}{Z_B}e^{-\beta H(\lambda_B)}$$

$$\beta = \frac{1}{kT}$$

$$Z = \mathrm{Tr}\,e^{-\beta H}$$

Lemma

$$D\big(\rho_F(t)\|\tilde{\rho}_B(t)\big)=\mathrm{Tr}\big[\rho_F(0)\ln\rho_F(0)\big]-\mathrm{Tr}\big[\rho_F(\tau)\ln\tilde{\rho}_B(\tau)\big]$$

1. $\mathrm{Tr}\big(\rho_F(t)\ln\rho_F(t)\big)$ is constant of motion (independent of time)

$$\rho_F(t)=U_t\,\rho_F(0)\,U_t^{-1}$$

$$\mathrm{Tr}\big[\rho_F(t)\ln\rho_F(t)\big]=\mathrm{Tr}\big[U_t\rho_F(0)U_t^{-1}\ln\big(U_t\rho_F(0)U_t^{-1}\big)\big]=\mathrm{Tr}\big[U_t\rho(0)\ln\rho(0)U_t^{-1}\big]$$
$$=\mathrm{Tr}\big[\rho(0)\ln\rho(0)\big]$$

2. $\mathrm{Tr}\big(\rho_F(t)\ln\tilde{\rho}_B(t)\big)$ is constant of motion (independent of time)

$$\tilde{\rho}_B(t)=U_t\,\tilde{\rho}_B(0)\,U_t^{-1}$$

$$\mathrm{Tr}\big[\rho_F(t)\ln\tilde{\rho}_B(t)\big]=\mathrm{Tr}\big[U_t\rho_F(0)U_t^{-1}\ln\big(U_t\tilde{\rho}_B(\tau)U_t^{-1}\big)\big]=\mathrm{Tr}\big[U_t\rho_F(0)\ln\tilde{\rho}_B(0)U_t^{-1}\big]$$
$$=\mathrm{Tr}\big[\rho_F(0)\ln\tilde{\rho}_B(0)\big]$$

3. Shift the measurement time separately in each term

$$D\big(\rho_F(t)\|\tilde{\rho}_B(t)\big)=\mathrm{Tr}\big[\rho_F(t)\ln\rho_F(t)\big]\ -\ \mathrm{Tr}\big[\rho_F(t)\ln\tilde{\rho}_B(t)\big]$$

$$\mathrm{Tr}\big[\rho_F(0)\ln\rho_F(0)\big]\ -\ \mathrm{Tr}\big[\rho_F(\tau)\ln\tilde{\rho}_B(\tau)\big]$$

Derivation of Holy Grail

$$D\left(\rho_F(t)\|\tilde{\rho}_B(t)\right)=\mathrm{Tr}\left[\rho_F(0)\ln\rho_F(0)\right]-\mathrm{Tr}\left[\rho_F(\tau)\ln\tilde{\rho}_B(\tau)\right]$$

$$\rho_F(0)=\frac{1}{Z_A}e^{-\beta H(\lambda_A)} \qquad \tilde{\rho}_B(\tau)=\frac{1}{Z_B}e^{-\beta H(\lambda_B)}$$

$$D\left(\rho_F\|\tilde{\rho}_B\right)=-\mathrm{Tr}\left[\rho_F(0)\right]\ln Z_A-\beta\,\mathrm{Tr}\left[H(\lambda_A)\rho_F(0)\right]+\mathrm{Tr}\left[\rho_F(\tau)\right]\ln Z_B+\beta\,\mathrm{Tr}\left[H(\lambda_B)\rho_F(\tau)\right]$$

$$=\frac{1}{kT}\left[-kT\ln Z_A-E_A+kT\ln Z_B+E^*(\tau)\right]=\frac{1}{kT}\left[(F_A-E_A)-(F_B-E_B)+E^*(\tau)-E_B\right]$$

$$=\frac{1}{kT}\left[-S_A T+S_B T+Q\right]=\frac{1}{k}\left[S_B-S_A+\frac{Q}{T}\right]=\frac{\Delta S}{k}$$

$$\boxed{\Delta S=k\,D\left(\rho_F(t)\|\tilde{\rho}_B(t)\right)}$$

Property I: Measurement Time

Math

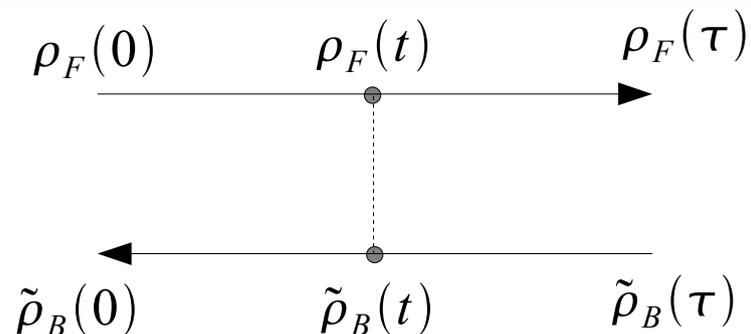Relative entropy is invariant under unitary transformation U.

$$D(\rho\|\sigma) = D(U\rho U^{-1}\|U\sigma U^{-1}) \quad \text{for every } U$$

Physics

$$D(\rho_F(t)\|\tilde{\rho}_B(t)) = D(\rho_F(t')\|\tilde{\rho}_B(t')) \quad \forall\, t,t' \in [0,\tau]$$

$$\rho(t') = U_{t',t}\,\rho(t)\,U_{t',t}^{-1}$$

We can measure entropy production at any time during the process.

$$\rho_F(0) \qquad \rho_F(t) \qquad \rho_F(\tau)$$

$$\tilde{\rho}_B(0) \qquad \tilde{\rho}_B(t) \qquad \tilde{\rho}_B(\tau)$$

Property II: Second Law

Math

Klein inequality

$$D(\rho\|\sigma)\geq 0 \quad \forall\, \rho,\sigma\in\Sigma$$

$$D(\rho\|\sigma)=0 \;\; \text{iff}\;\; \rho=\sigma$$

Physics

$$\Delta S=kD(\rho_F\|\tilde{\rho}_B)\geq 0 \qquad \text{(second law!)}$$

We don't have to know the actual form of $\rho_F(t)$ nor $\tilde{\rho}_B(t)$.

$$\Delta S=0 \;\; \text{iff}\;\; \rho_F(t)=\tilde{\rho}_B(t)$$

Entropy production vanishes when the forward and backward processes are indistinguishable. (Ex. quasi static processes)

The second law of thermodynamics is the best possible statement without knowing any information about the process.

Property III: Bipartite Systems

Math

Monotonicity $\quad D(\rho\|\sigma) \geq D(\mathcal{E}(\rho)\|\mathcal{E}(\sigma)) \quad \mathcal{E}:\text{CPT map}$

$$D(\rho_{12}\|\sigma_{12}) \geq D(\rho_1\|\sigma_1) \quad \rho_1 = \text{Tr}_2\,\rho_{12},\ \sigma_1 = \text{Tr}_2\,\sigma_{12}$$

Physics

Hilbert Space: $\quad \mathcal{H}_{ab} = \mathcal{H}_a \otimes \mathcal{H}_b$

$$\Delta S = D(\rho_{ab}\|\tilde{\rho}_{ab}) \geq D(\rho_a\|\tilde{\rho}_a), \quad \rho_a = \text{Tr}_b\,\rho_{ab}$$

Since information in $\mathcal{H}_b$ is lost, we have only the lower bound of entropy production. (Still better than the second law.)

Example: Stochastic processes

Property IV: Coarse graining

Math

Joint convexity.

$$\lambda\, D(\rho_1\|\rho_2)+(1-\lambda)\, D(\sigma_1\|\sigma_2)\geq D(\lambda\,\rho_1+(1-\lambda)\,\sigma_1\|\lambda\,\rho_2+(1-\lambda)\,\sigma_2)$$

$$D(\rho\|\sigma)\geq\sum_i \rho_{ii}\ln\frac{\rho_{ii}}{\sigma_{ii}}=D_c(\rho\|\sigma)$$

Physics

Physical Observable $\qquad \Omega=\sum_i \omega_i\,\mathcal{P}_i, \qquad \mathcal{P}_i^2=\mathcal{P}_i, \qquad \sum_i \mathcal{P}_i=I$

Probability to obtain ω_i in forward process $\qquad p_i=\mathrm{Tr}(\mathcal{P}_i\rho_F)$

Probability to obtain ω_i in backward process $\qquad \tilde{p}_i=\mathrm{Tr}(\mathcal{P}_i\tilde{\rho}_B)$

$$\Delta S=D(\rho_F\|\tilde{\rho}_B)\geq D_c(p\|\tilde{p})$$

Measurement of an physical quantity does not provide full information of the state.
Due to the loss of information, we have only a lower bound.

Property V: Hypothesis Testing

Math

Quantum Stein Lemma

$$\lim_{n \to \infty} \frac{1}{n} \log \beta_n(\rho \| \sigma) = -D(\rho \| \sigma)$$

$\beta_n(\rho \| \sigma)$ Minimum value of second kind error probability

Physics

Probability that after *n* measurements you are still confused between *F* and *B* processes.
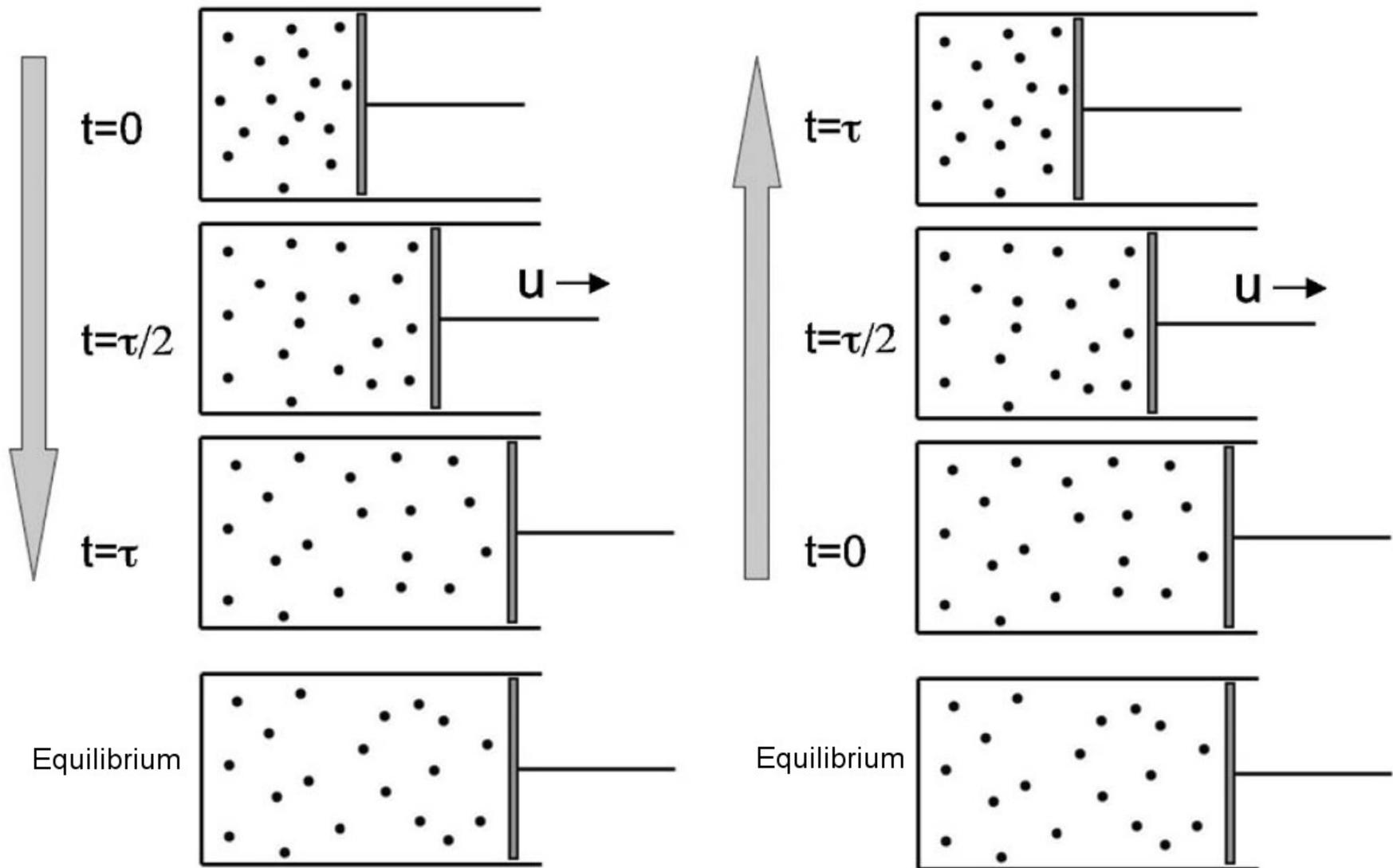
$$\beta_n(\rho_F \| \tilde{\rho}_B) \approx e^{-nD(\rho_F \| \tilde{\rho}_B)} = e^{-n \Delta S / k}$$

When ΔS is small, it is difficult to distinguish the forward and backward processes.

Slow Expansion

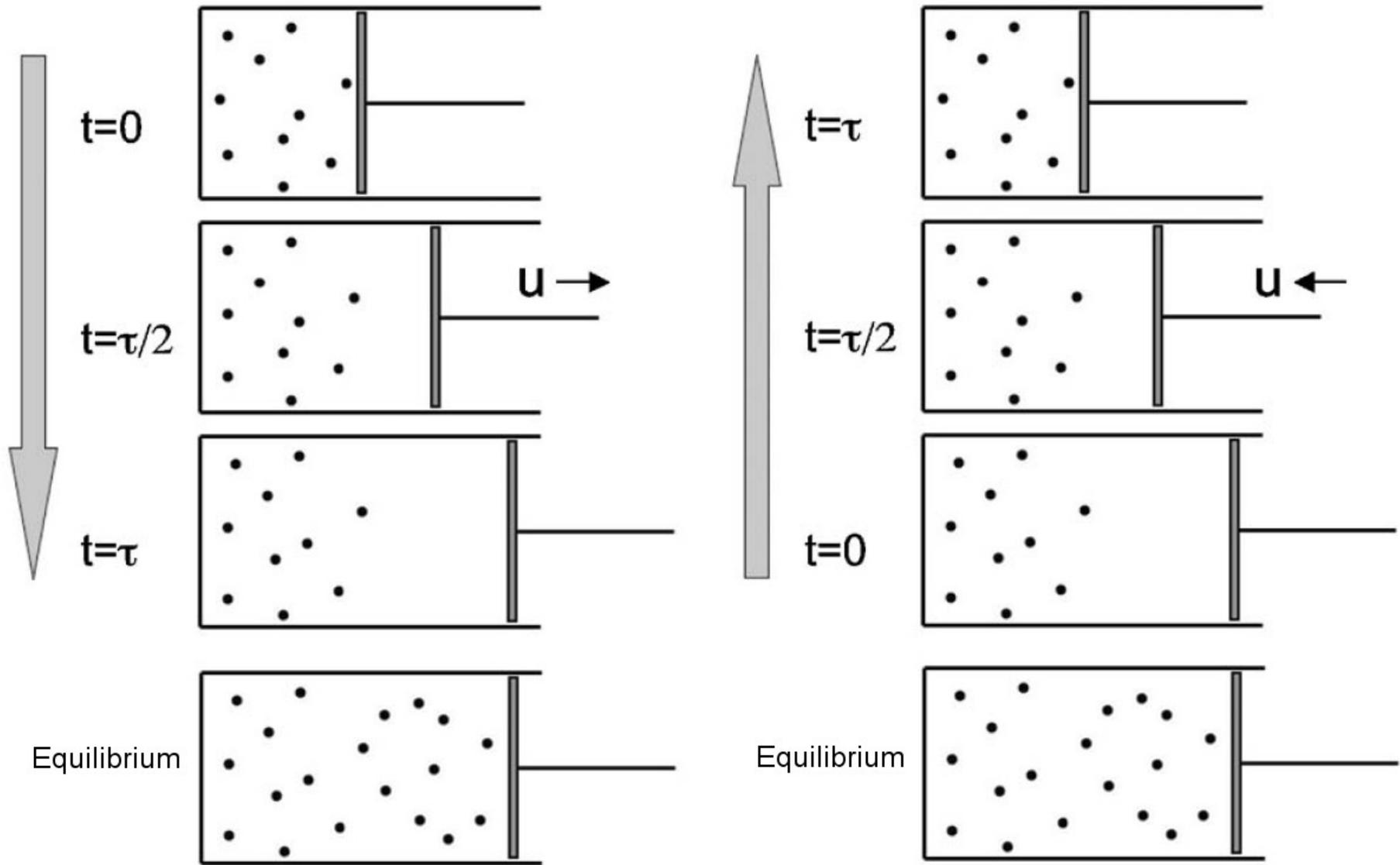Small entropy production

Rapid Expansion

Forward

Backward

$t=0$

$t=\tau/2$

$t=\tau$

Equilibrium

$t=\tau$

$t=\tau/2$

$t=0$

Equilibrium

$u \rightarrow$

$u \leftarrow$

Large entropy production

Did we really find the Holy Grail?

Holy Grail

We found the microscopic expression of entropy production.

Does that mean we proved the second law from the first principle?

Not really. In the derivation, we used the part of the second law.

We grabbed its tail but the body of the Holy Gail is still in the smoke!

$$D(\rho_F\|\tilde{\rho}_B)=-\mathrm{Tr}[\rho_F(0)]\ln Z_A-\beta\,\mathrm{Tr}[H(\lambda_A)\rho_F(0)]+\mathrm{Tr}[\rho_F(\tau)]\ln Z_B+\beta\,\mathrm{Tr}[H(\lambda_B)\rho_F(\tau)]$$

$$=\frac{1}{kT}[-kT\ln Z_A-E_A+kT\ln Z_B+E^*(\tau)]=\frac{1}{kT}[(F_A-E_A)-(F_B-E_B)+E^*(\tau)-E_B]$$

$$=\frac{1}{kT}[-S_AT+S_BT+Q]=\frac{1}{k}[S_B-S_A+\frac{Q}{T}]=\frac{\Delta S}{k}$$

Conclusion

$$\Delta S = k\, D(\rho_F \| \tilde{\rho}_B)$$

- An exact expression of entropy production is obtained.
- Now the second law of thermodynamics is an equality!
- Entropy production is a direct measure of irreversibility (time's arrow).
- Even when full information is not available, the formula provides a lower bound of the entropy production.