Dissipation and Time's Arrow

Beyond the Second Law of Thermodynamics

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Dissipation: The Phase-Space Perspective

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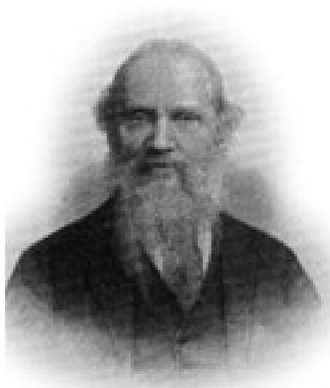
The Second Law of Thermodynamics



William Thomson
(Lord Kelvin)

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.

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

Why is the second law an inequality?

$$\Delta S \geq \frac{Q}{T}$$

$$\Delta S - \frac{Q}{T} = \quad ? \quad \geq 0$$

Holy Grail of Thermodynamics

Second Law with Work

$\Delta U = W + Q$ (First Law of Thermodynamics)

$\Delta F = \Delta U - T \Delta S$ (Helmholtz Free Energy)

$W - \Delta F = T \Delta S - Q =$ Holy Grail ≥ 0

$W = W_{\text{rev}} + W_{\text{dis}}$

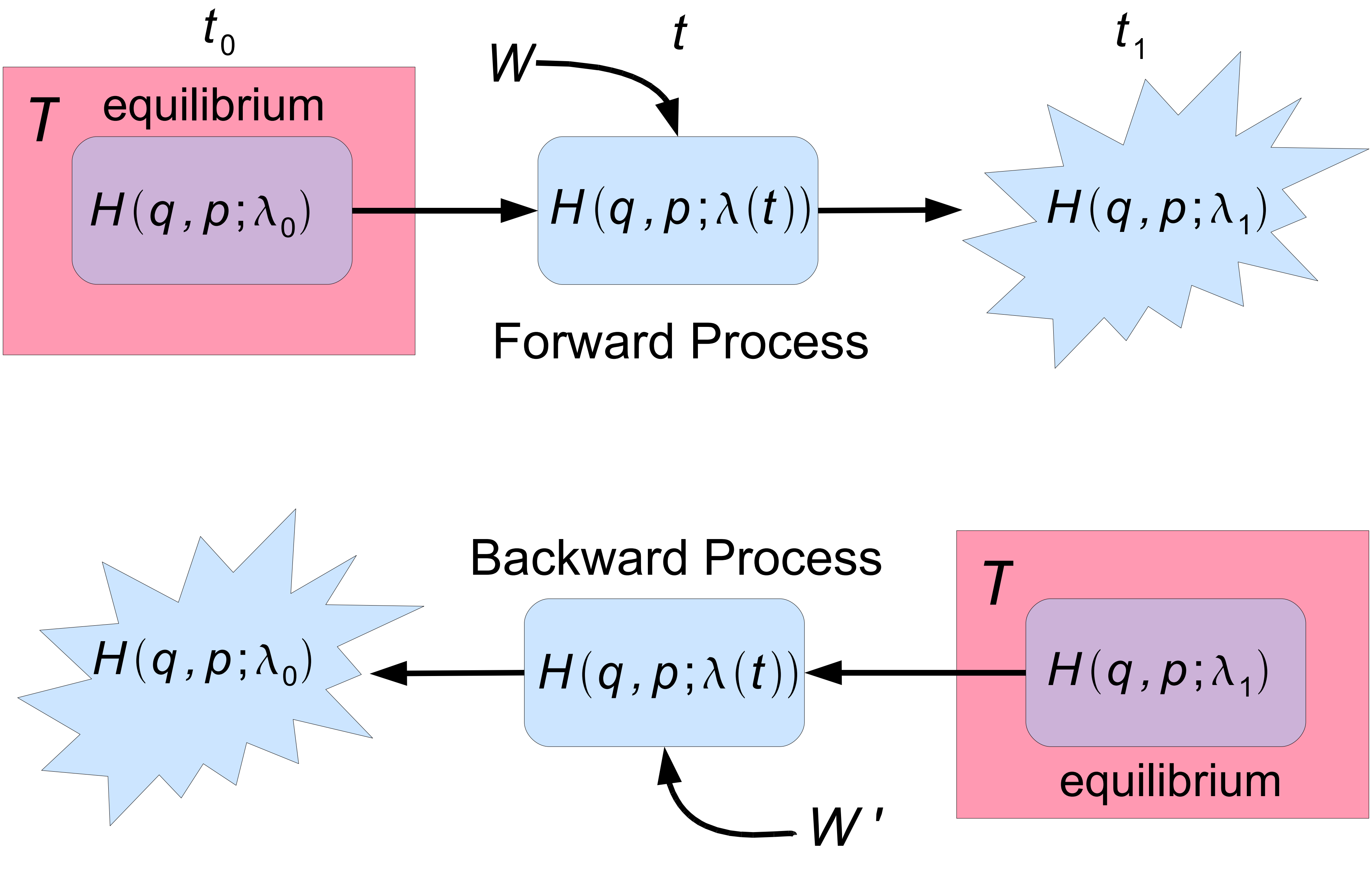
reversible work $W_{\text{rev}} = \Delta F$

dissipative work $W_{\text{dis}} \geq 0$

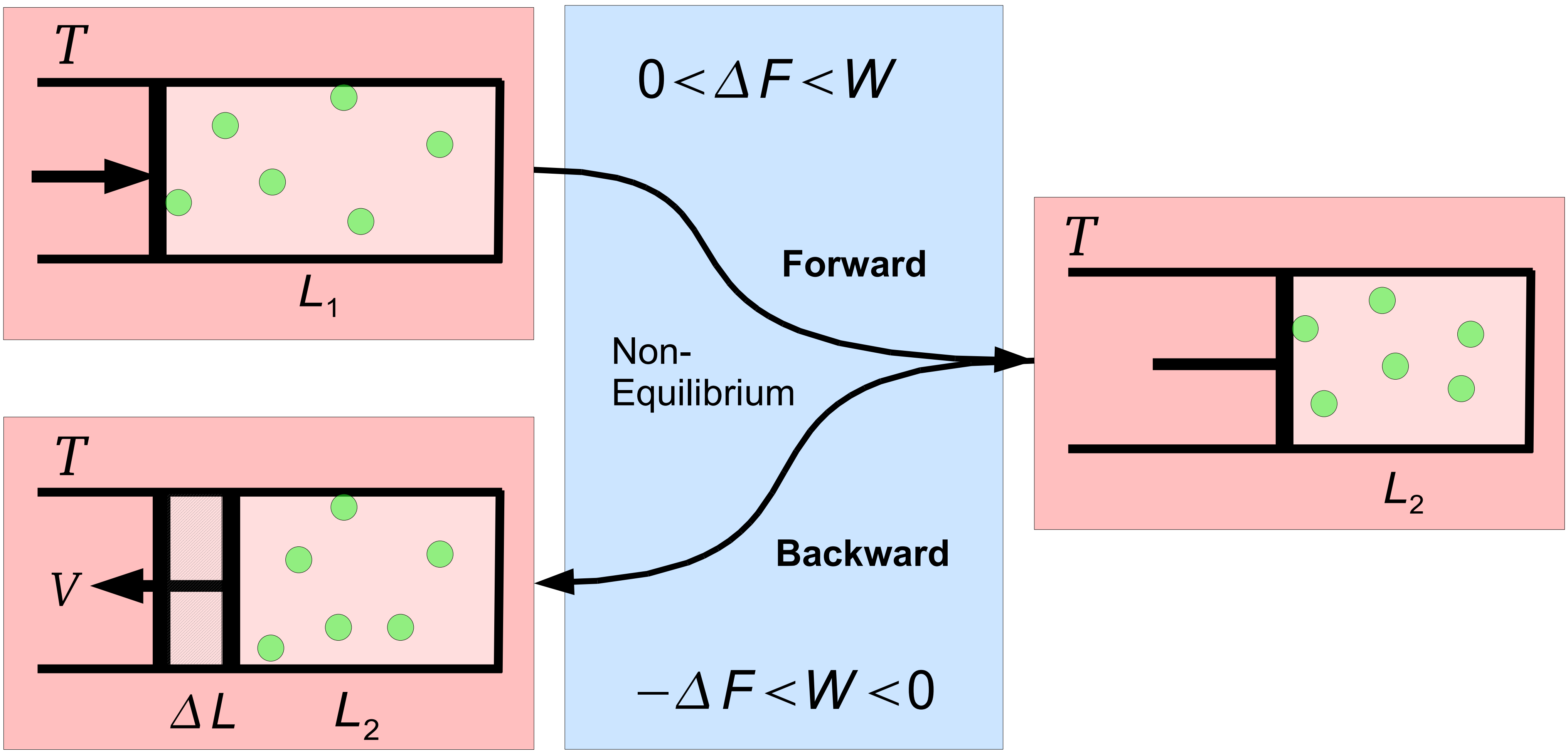
Holy Grail Revealed in Phase Space

$$\langle W \rangle - \Delta F = k_B T \int \rho_F(q,p,t) \ln \frac{\rho_F(q,p,t)}{\rho_B(q,-p,t)} \, dq \, dp$$
$$= k_B T \, D(\rho_F || \rho_B)$$

A Non-Equilibrium Process: Time-Dependent Hamiltonian



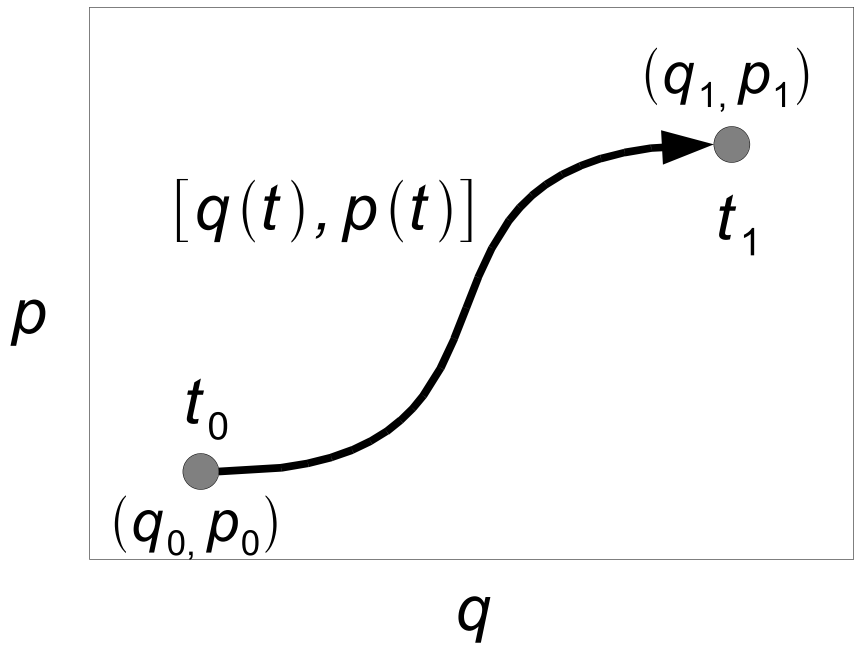
Example



T
L_1
$0 < \Delta F < W$
Forward
Non-
Equilibrium
Backward
$-\Delta F < W < 0$
T
L_2
T
V
ΔL
L_2

Phase Space Trajectory and Density

$6N$-dimension phase space



$q = (q_{1,} q_{2,} \cdots, q_{3N})$ position

$p = (p_{1,} p_{2,} \cdots, p_{3N})$ momentum

$[q(t), p(t)] =$ phase trajectory

$\rho(q, p, t) =$ probability density

Liouville Theorem $\quad \rho(q_{0,} p_{0,} t) = \rho(q(t), p(t), t) = \rho(q_{1,} p_{1,} t_1)$

Microscopic Time Reversibility

$$(q_{0,} p_0) \rightarrow (q_{1,} p_1)$$
$$(q_{1,} - p_1) \rightarrow (q_{0,} - p_0)$$

Conservation of Gibbs Entropy

$$S(t) = -k_B \int \rho(q, p, t) \ln \rho(q, p, t) \, dq \, dp$$
$$S(t_0) = S(t) = S(t_1)$$

Joseph Liouville

(1809-1882)

Equilibrium Density

$$\rho_{\mathrm{eq}}(q,p)=\frac{1}{Z}\exp[-\beta H(q,p)]$$

$$Z=\int \exp[-\beta H(q,p)]\,dq\,dp \quad \text{(partition function)}$$

$$\rho_{eq}(q,p)=\rho_{eq}(q-p) \quad \text{(detailed balance)}$$

$$H(q,p)=-k_B T\ln Z-k_B T\ln\rho_{\mathrm{eq}}(q,p)$$

Definition of Work

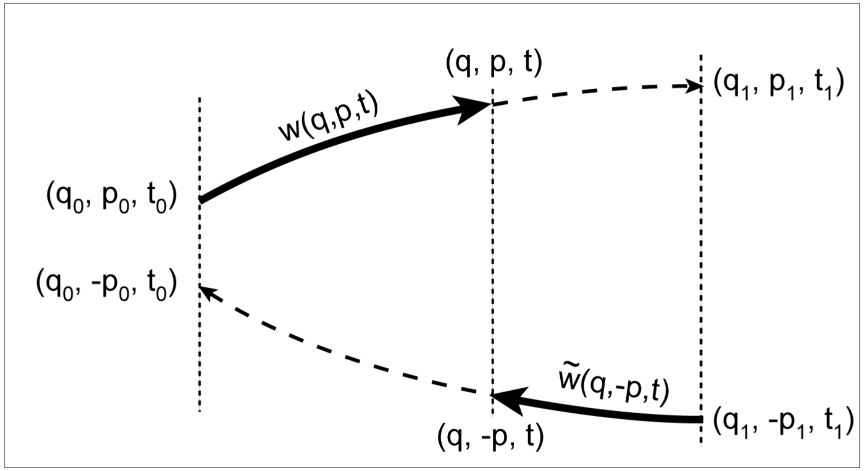
$$W(q_{0,}\,p_0)=H(q_1,p_1;\lambda_1)-H(q_0,p_0;\lambda_0)$$

$$\begin{aligned}\langle W\rangle &=\int \rho(q_{0,}\,p_0;t_0)W(q_o,p_0)\,dq_0\,dp_0\\ &=\int \rho(q_0,p_0;t_0)[H(q_1,p_1;\lambda_1)-H(q_{0,}\,p_0;\lambda_0)]\end{aligned}$$

Proof

$$\langle W\rangle = \int \rho(q_0, p_0; t_0)[H(q_1, p_1; \lambda_1) - H(q_0, p_0; \lambda_0)]$$

$$= -kT \int \rho_F(q_1, p_1, t_1) \ln \rho_B(q_1, -p_1, t_1)\, dq_1 dp_1$$
$$+ kT \int \rho_F(q_0, p_0, t_0) \ln \rho_F(q_0, p_0, t_0)\, dq_0 dp_0$$
$$+ kT \ln(Z_0/Z_1)$$



$$= -kT \int \rho_F(q, p, t) \ln \rho_B(q, -p, t)\, dq\, dp$$
$$+ kT \int \rho_F(q, p, t) \ln \rho_F(q, p, t)\, dq\, dp$$
$$+ \Delta F$$

$$\langle W\rangle - \Delta F = kT \int \rho_F(q, p, t) \ln\left[\frac{\rho_F(q, p, t)}{\rho_B(q, -p, t)}\right] dq\, dp = kT\, D(\rho_F \| \rho_B)$$

Relative Entropy (Kullback-Leibler distance)

$$D(\rho\|\eta) = \int \rho(x) \ln \frac{\rho(x)}{\eta(x)} dx$$

$$\rho(x) \geq 0, \eta(x) \geq 0 ; \int \rho(x) dx = \int \eta(x) dx = 1$$

$D(\rho\|\eta)$ is a `distance` between two densities.

$$D(\rho\|\eta) \geq 0, \quad D(\rho\|\eta) = 0 \text{ iff } \rho(x) = \eta(x)$$

$\exp[-D(\rho\|\eta)]$ is a measure of the difficulty to statistically distinguish two densities. (Stein's lemma)

$$D(\rho\|\eta) \geq D(\tilde{\rho}\|\tilde{\eta})$$

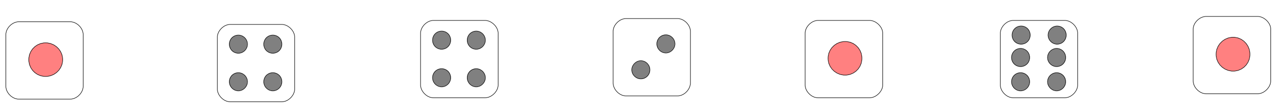
if $\tilde{\rho}$ and $\tilde{\eta}$ have less information than ρ and η

Relative Entropy: Exercise with Dice

normal	$p_1=\frac{1}{6}$	$p_2=\frac{1}{6}$	$p_3=\frac{1}{6}$	$p_4=\frac{1}{6}$	$p_5=\frac{1}{6}$	$p_6=\frac{1}{6}$
biased	$q_1=\frac{1}{3}$	$q_2=\frac{1}{12}$	$q_3=\frac{1}{12}$	$q_4=\frac{1}{12}$	$q_5=\frac{1}{6}$	$q_6=\frac{1}{4}$

$$D(p\|q)=\sum_{i=1}^{6} p_i \ln\frac{p_i}{q_i}=0.163\cdots$$

Find which dice you have by rolling it N times.



…

If you guess it is the normal one the probability that you are wrong is

$$P_{err}(N)=e^{-N D(p\|q)},\quad P_{err}(10)=0.196,\quad P_{err}(20)=0.04,\quad p_{err}(50)=0.00028$$

Relative Entropy and Reduced Information

normal dice $\tilde{p}_{odd}=p_1+p_3+p_5=\frac{1}{2}, \quad \tilde{p}_{even}=p_2+p_4+p_6=\frac{1}{2}$

biased dice $\tilde{q}_{odd}=q_1+q_3+q_5=\frac{7}{12}, \quad \tilde{q}_{even}=q_2+q_4+q_6=\frac{5}{12}$

$$D(\tilde{p}\|\tilde{q})=\tilde{p}_{odd}\ln\frac{\tilde{p}_{odd}}{\tilde{q}_{odd}}+\tilde{p}_{even}\ln\frac{\tilde{p}_{even}}{\tilde{q}_{even}}=0.014$$

$$D(p\|q)>D(\tilde{p}\|\tilde{q})$$

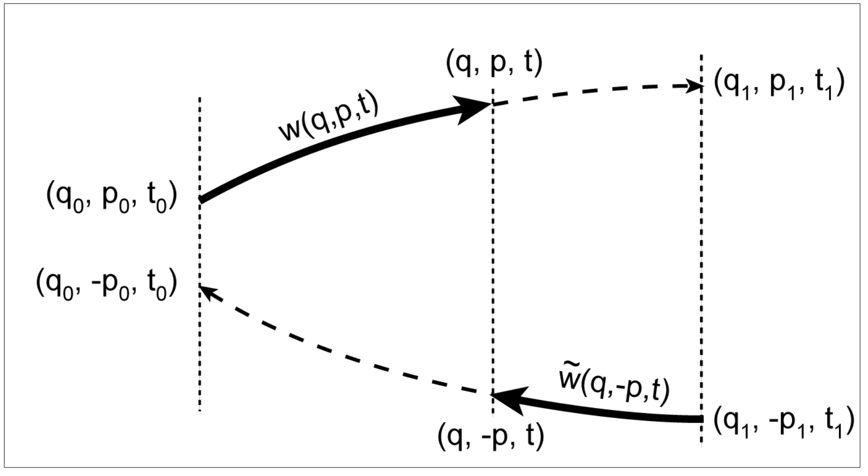
Dissipation and Time's Arrow

$$\langle W \rangle - \Delta F = kT \int \rho_F(q,p,t) \ln\left[\frac{\rho_F(q,p,t)}{\rho_B(q,-p,t)}\right] dq\,dp = kT\, D(\rho_F \| \rho_B)$$

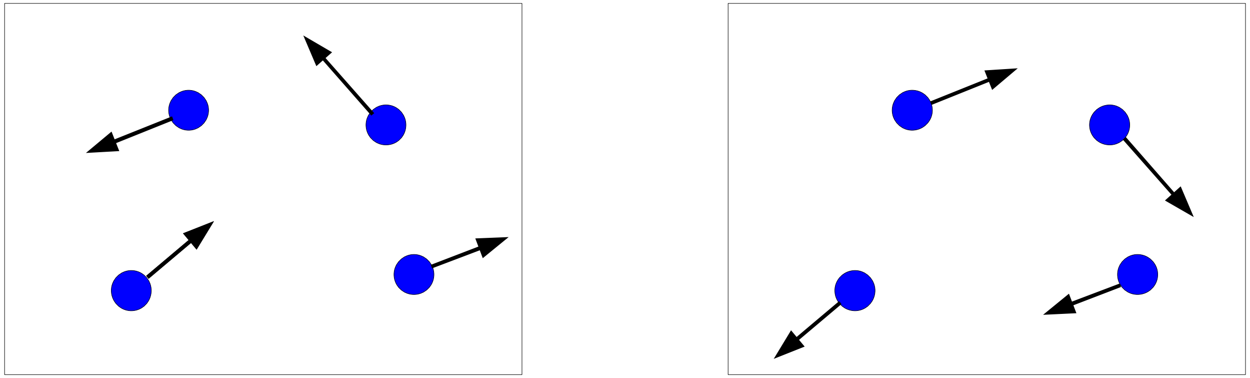
$D(\rho_F \| \rho_B) \geq 0 \quad \rightarrow \quad$ Second Law

If $\rho_F = \rho_B, \quad D(\rho_F \| \rho_B) = 0 \quad \rightarrow \quad$ No Dissipation

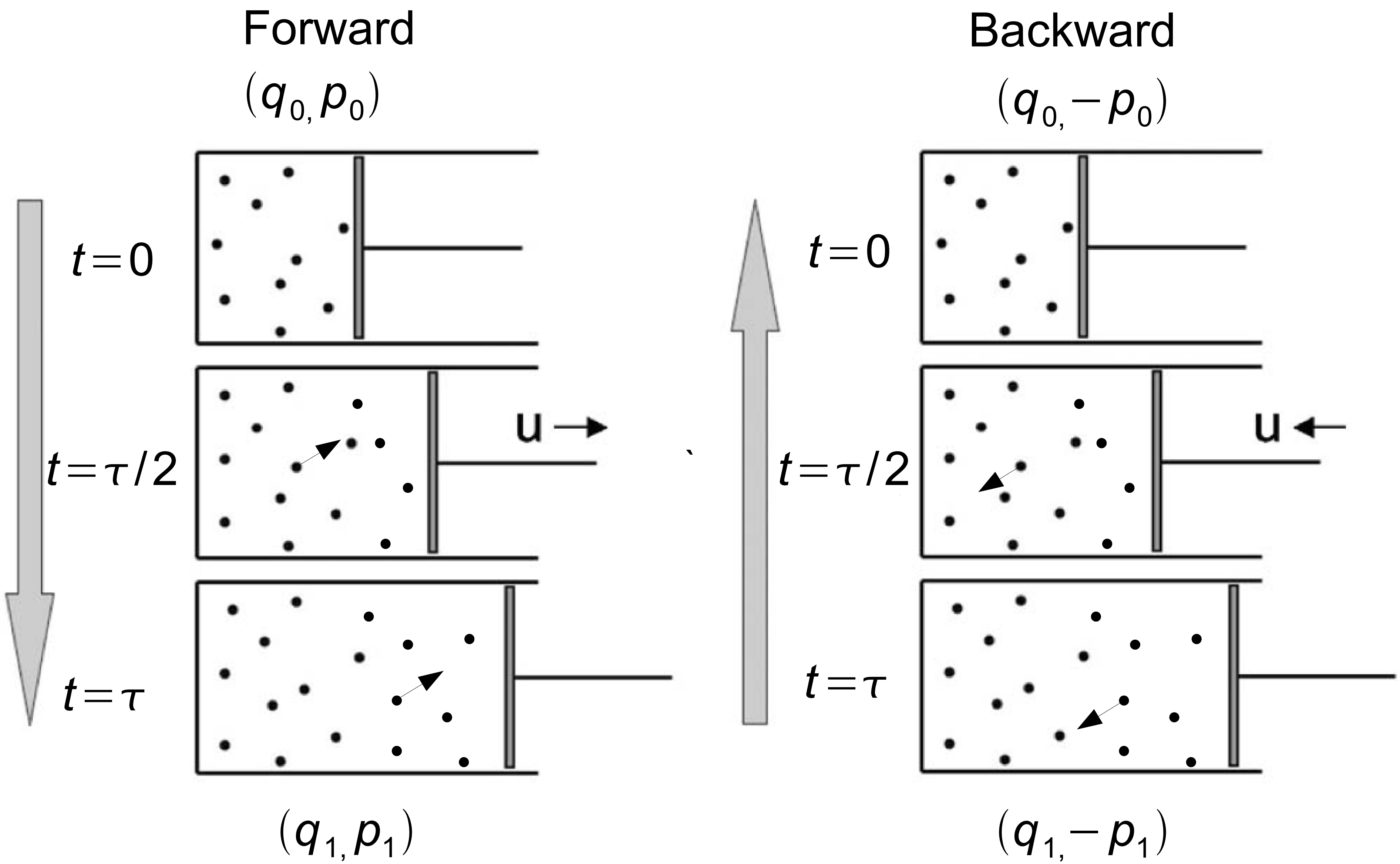
Dissipation is a quantitative measure of Irreversibility (time's arrow)!.



Likelihood of time-reversed states

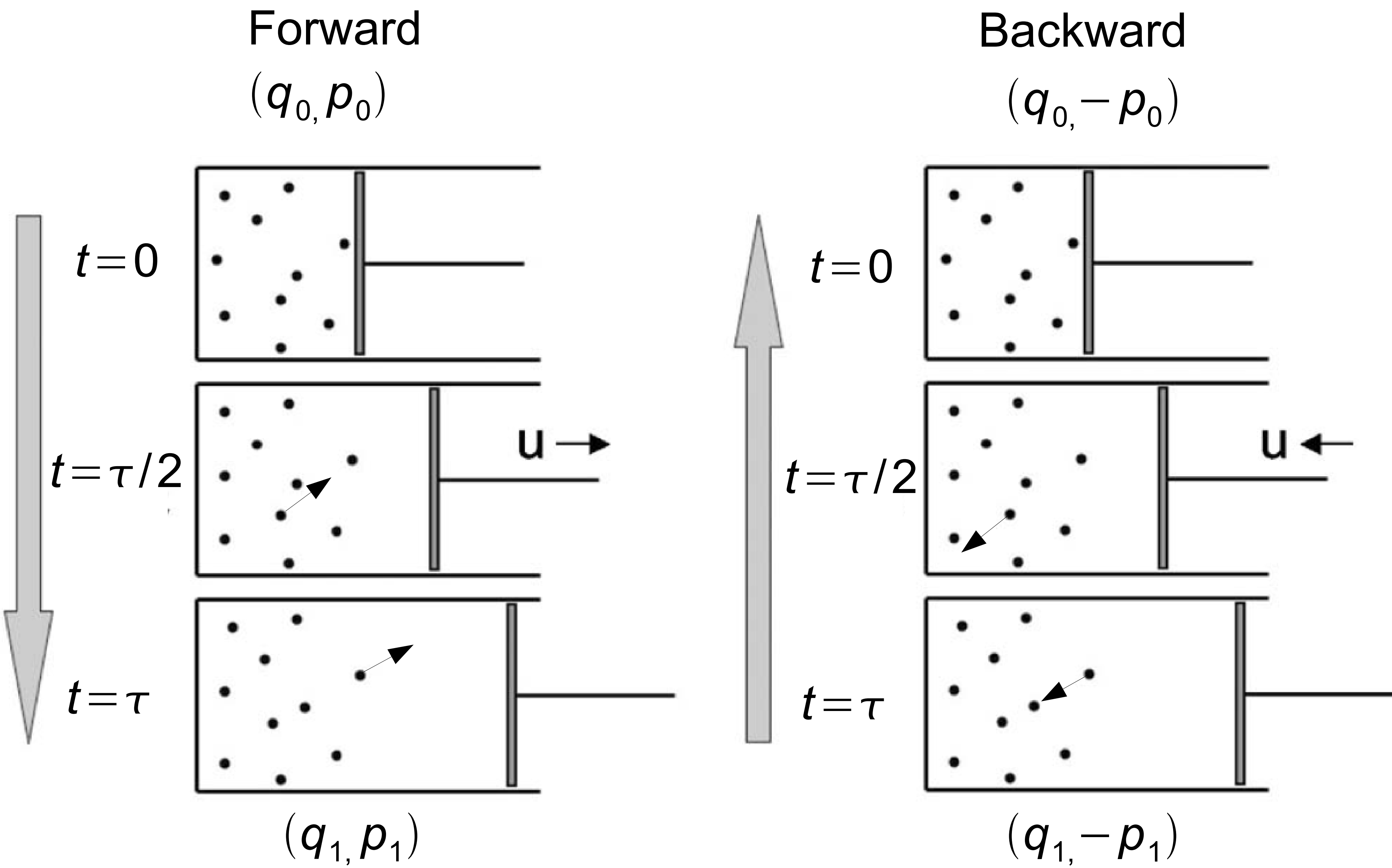


Slow Expansion



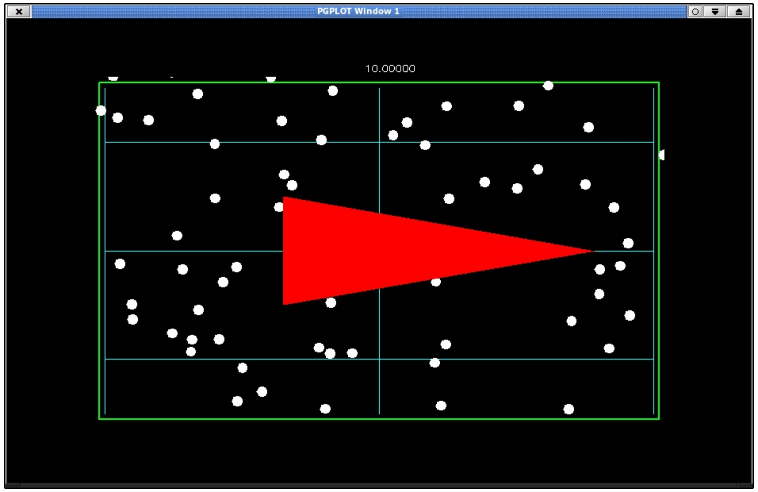
Little Dissipation

Rapid Expansion



Large Dissipation

Which time direction is the triangle moving?



Jarzinski equality and Crooks Theorem

$$\langle W_{\text{dis}} \rangle = kT \int \rho_F(q,p,t) \ln\left[\frac{\rho_F(q,p,t)}{\rho_B(q,-p,t)}\right] dq\,dp$$

Work at a phase point

$$W_{\text{dis}}(q,p,t) = kT \ln\frac{\rho_F(q,p,t)}{\rho_B(q,-p,t)}$$

(can be negative)

Crooks theorem

$$\exp[-\beta W_{\text{dis}}(q,p,t)] = \frac{\rho_B(q,-p,t)}{\rho_F(q,p,t)}$$

Jarzynski equality

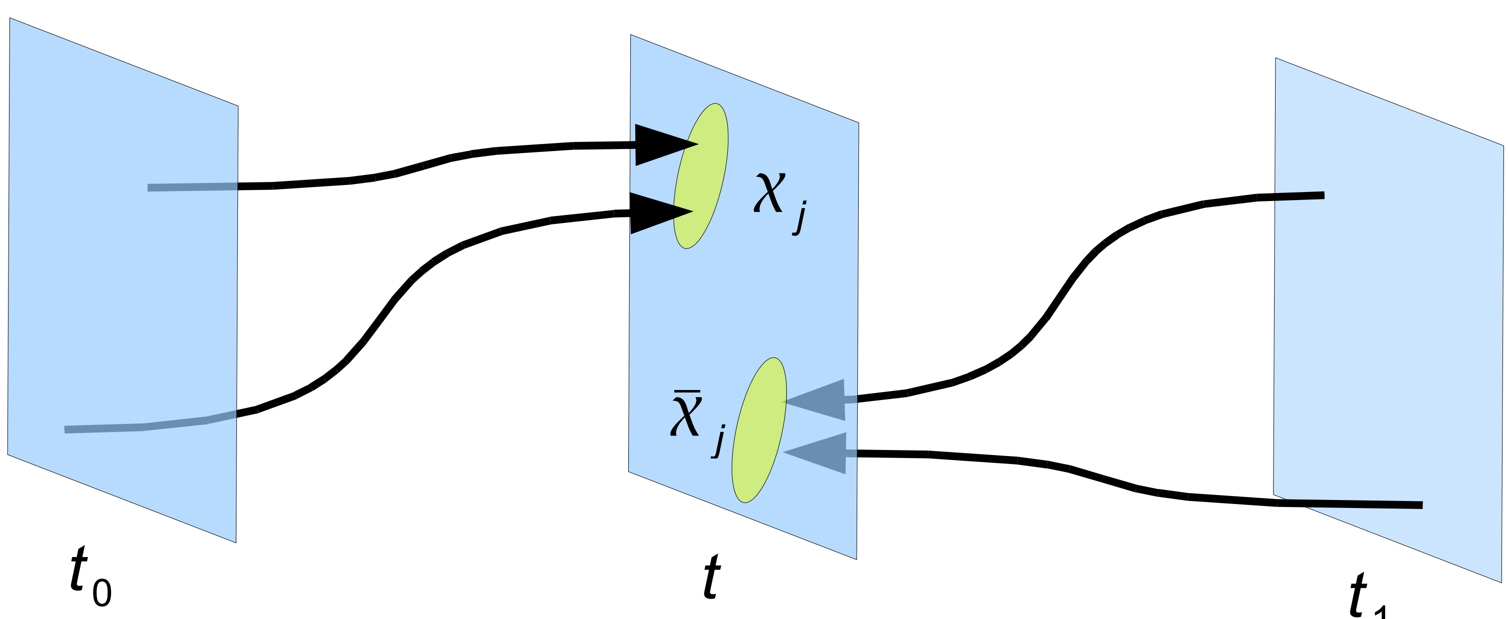
$$\langle \exp[-\beta W_{\text{dis}}] \rangle = \int \rho_F(q,p,t) \exp[-\beta W_{\text{dis}}(q,p,t)]\, dq\,dp = 1$$

Coarse Graining

Devide the whole phase space into N subsets $\chi_j \ (j=1\cdots N)$

$$\rho_F^j(t)=\int_{x_j}\rho_F(q,p,t)\,dq\,dp\,; \qquad \rho_B^j(t)=\int_{\bar{x}_j}\rho_B(q,-p,t)\,dq\,dp$$

$$\langle W\rangle_j \ \geq\ \Delta F+kT\ln\frac{\rho_F^j}{\rho_B^j}\ \geq\ -\langle\tilde{W}\rangle_j$$



$$\langle W \rangle - \Delta F \;\geq\; kT\, D(\rho_F^j \| \rho_B^j)$$

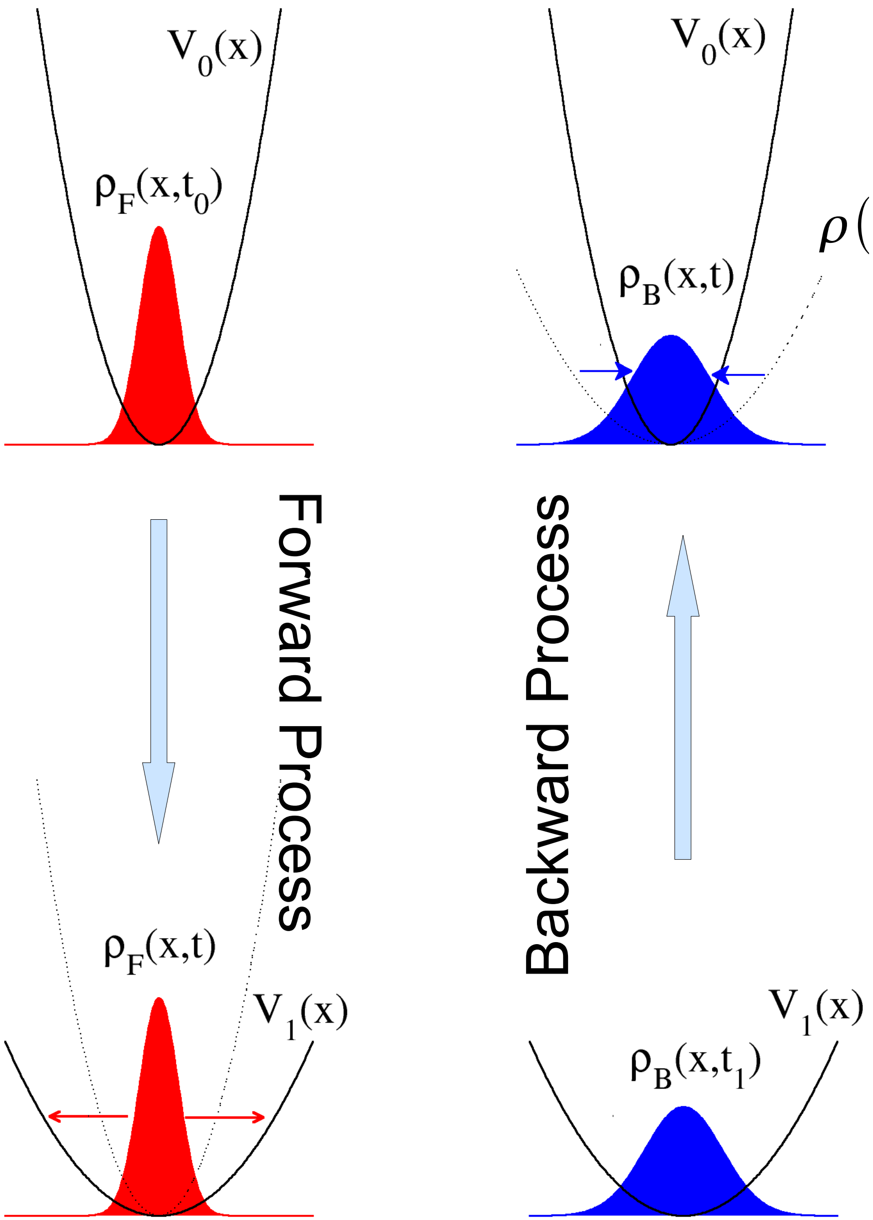
where $D(\rho_F^j \| \rho_B^j) = \sum_{j=1}^{N} \rho_F^j \ln \frac{\rho_F^j}{\rho_B^j}$

Since we don't have full information of the phase densities, we can have only a lower bound.

If we have no information at all (N=1), then

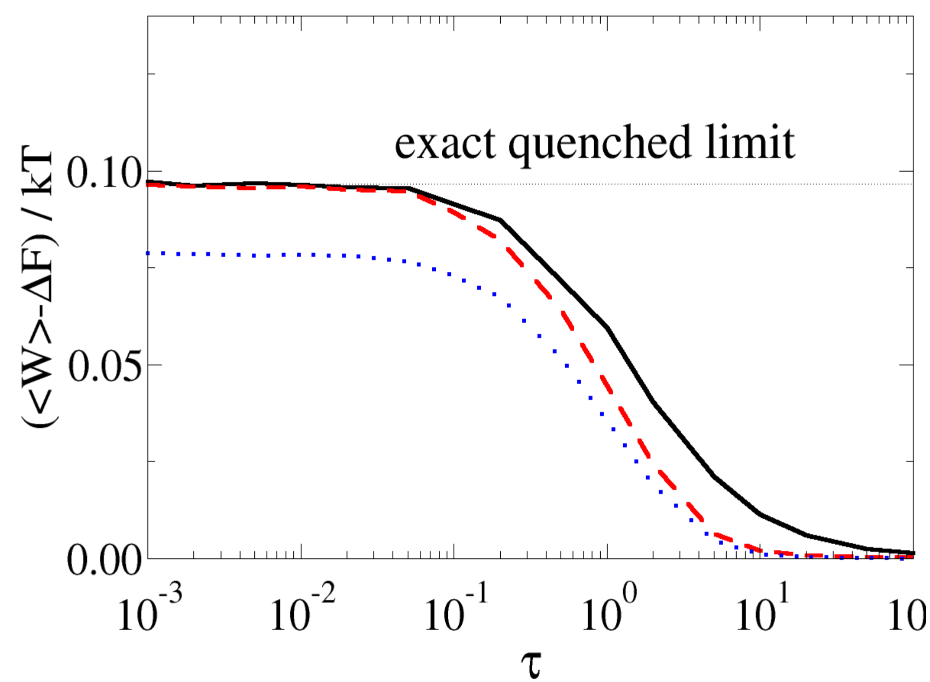
$$D(\rho_F \| \rho_B) = 0 \;\rightarrow\; \langle W \rangle \geq \Delta F$$ **2nd law!**

Overdumped Brownian Particle in a Harmonic Potential



$$\rho(x,t)=\int \rho(x,p,\underbrace{x_{1,}p_{1,}x_{2,}p_{2,}\cdots}_{\text{Heat Bath}},t)\,dp\,dx_1\,dp_1\cdots$$

$$\langle W\rangle-\Delta F\geq D(\rho_F(x,t)\|\rho_B(x,t))$$

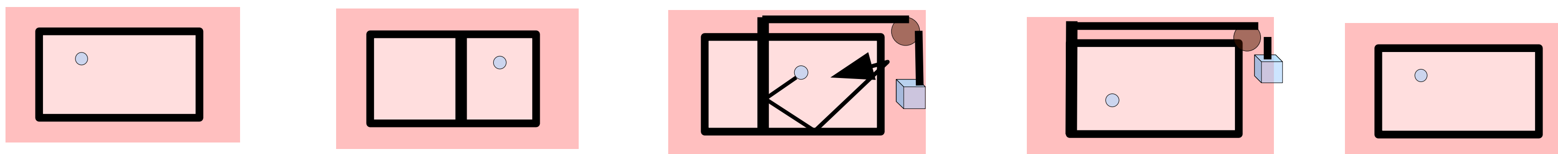


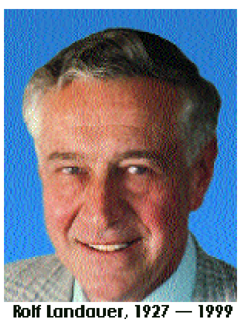
Application: Physics and Information

Leó Szilárd
(1898-1964)

Szilard found a relation between physics and information.

$$1\,\text{bit} = k_B \log 2$$



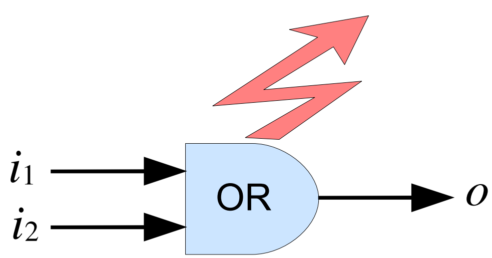


Ralf Landauer
(1929-1999)

Landauer principle

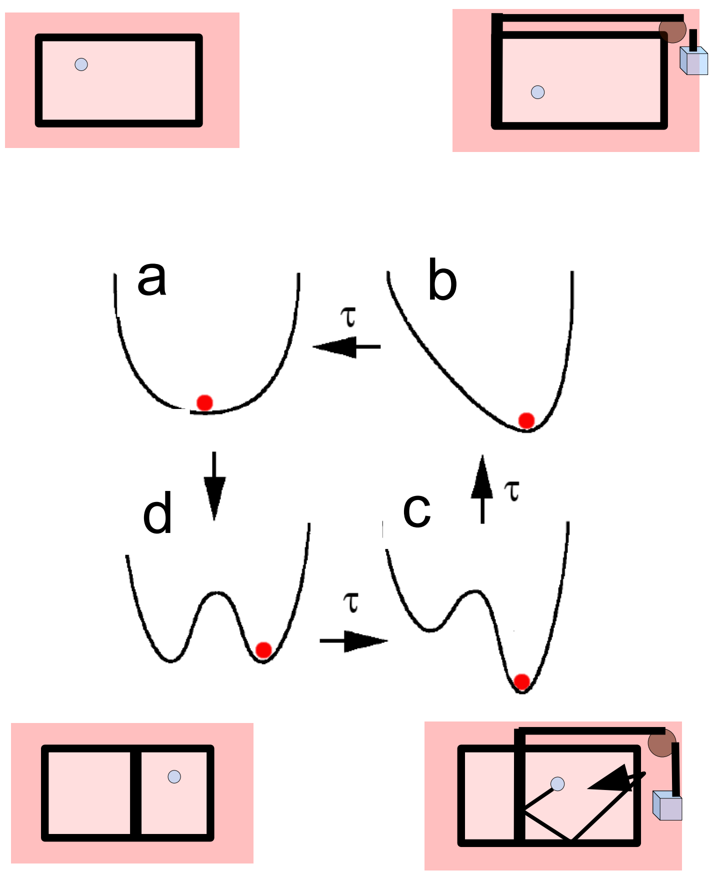
The erasure of one bit of information is necessarily accompanied by a dissipation of at least $k_B T \log 2$ heat.
Information can be obtained without dissipation of heat.

$$Q \geq k_B T \log 2$$



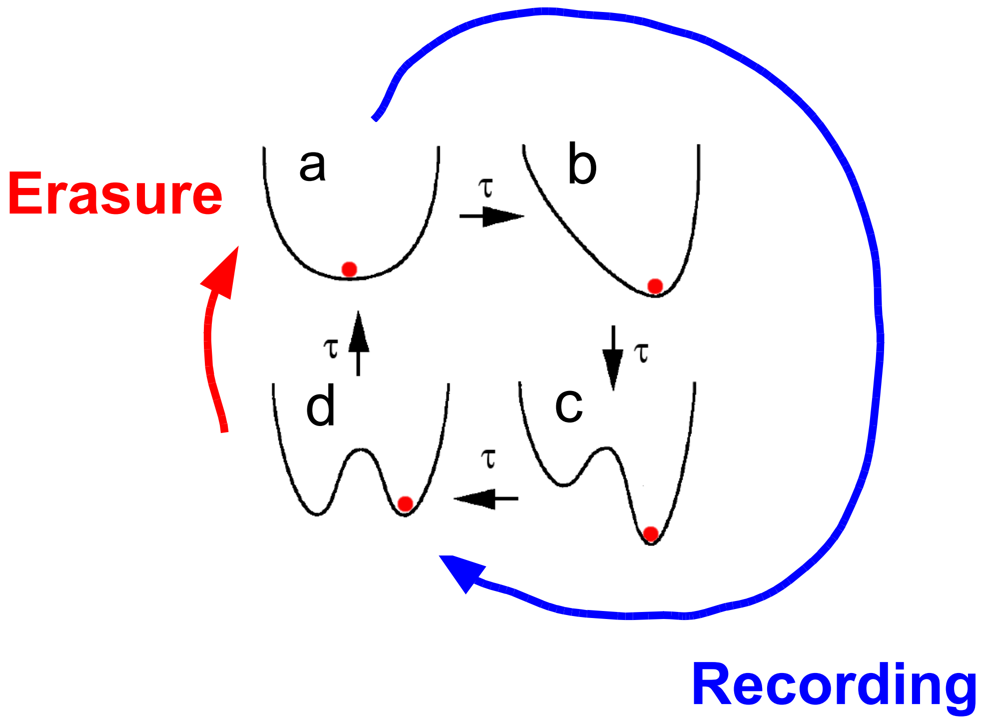
Szilard Engine

$$W \geq -kT\ln 2$$

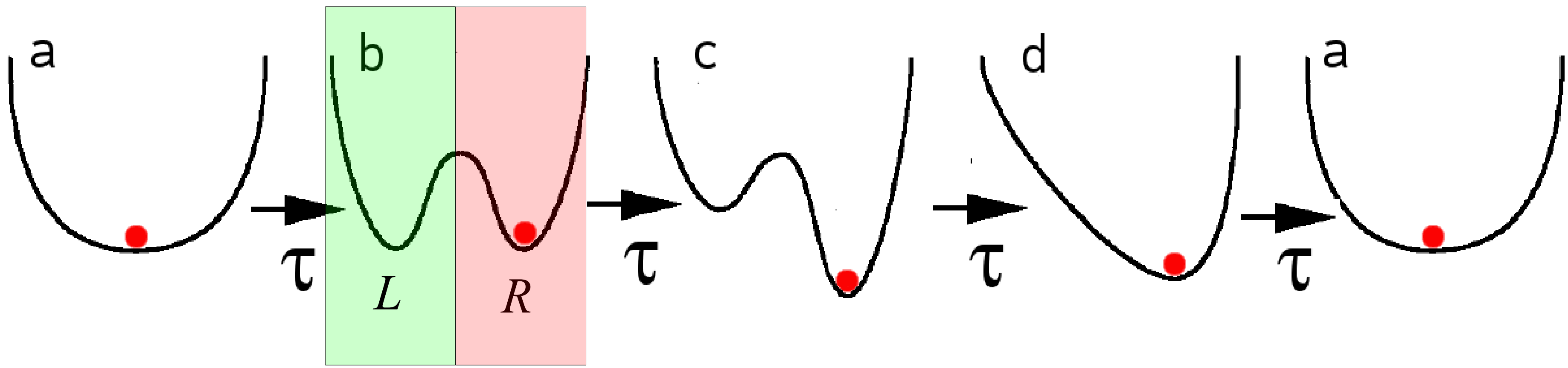


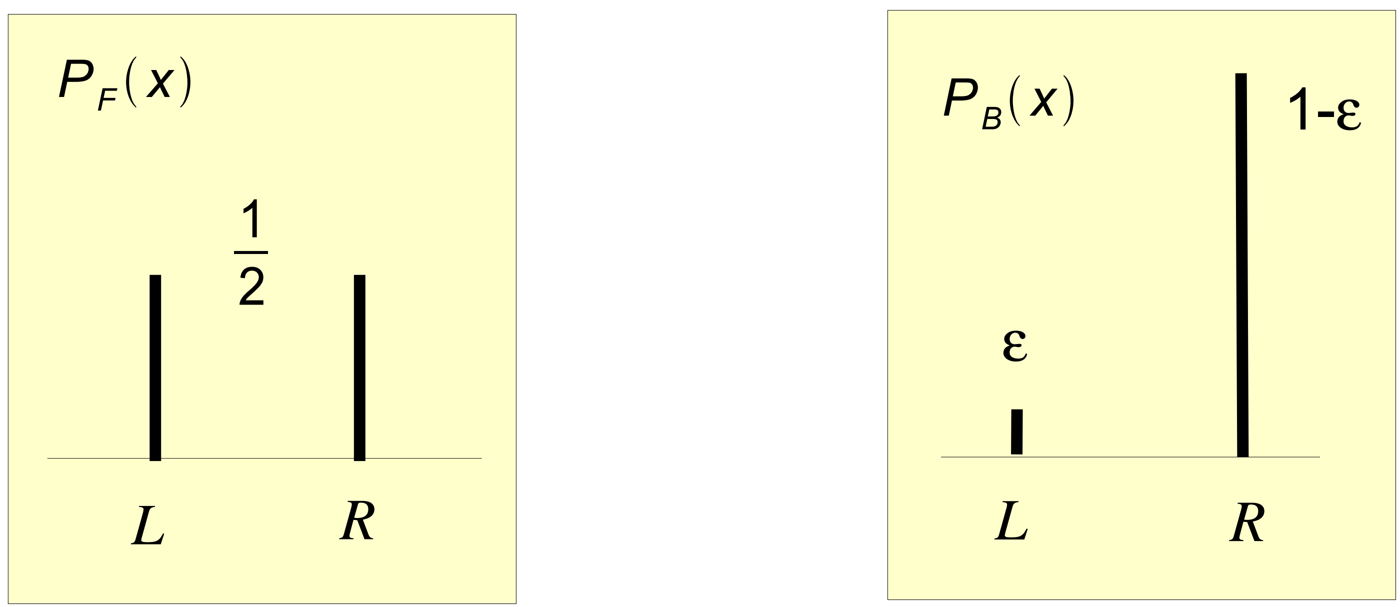
Landauer Principle

$$W \geq +kT\ln 2$$

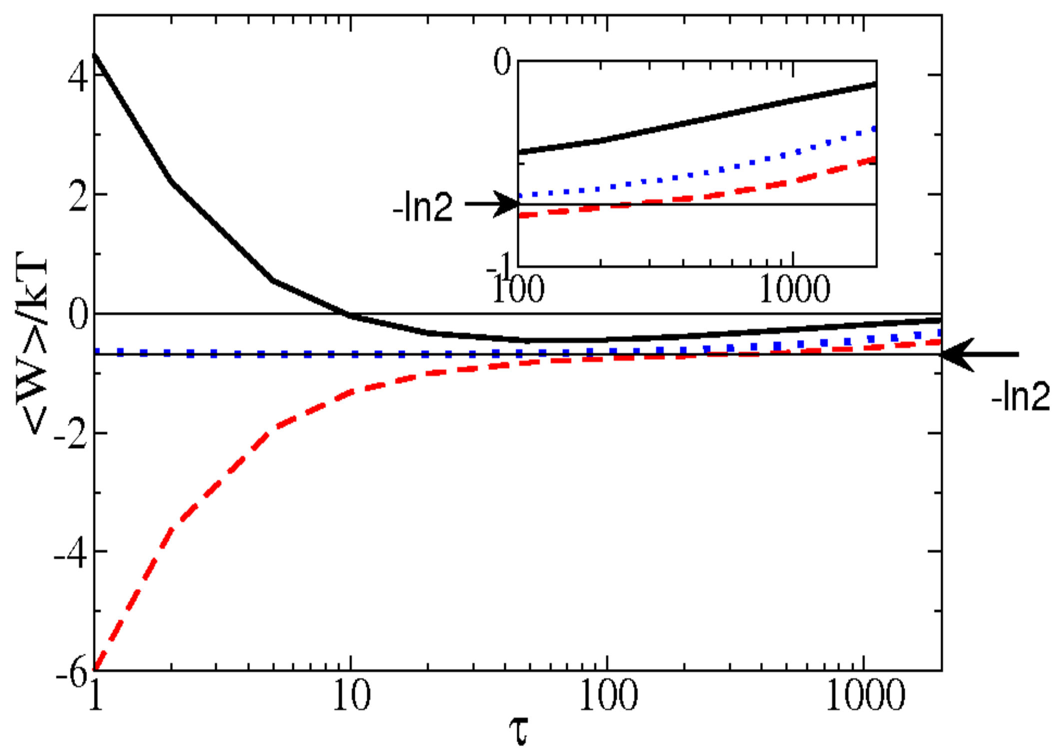


Coarse Grained Measurement





$$\langle W \rangle_R \geq \ln\left[\frac{P_F(R)}{P_B(R)}\right] = -k_B T \ln 2 - k_B T \ln(1-\epsilon)$$



<W>/kT
τ
-ln2
-ln2
4
2
0
-2
-4
-6
1
10
100
1000
0
-1
100
1000

For quantum systems

von Neumann Entropy : $S = -k \, \mathrm{Tr} \, \hat{\rho} \ln \hat{\rho}$

$$\langle W_{\text{dis}} \rangle = kT \left[\mathrm{Tr} \, \hat{\rho}_F \ln \hat{\rho}_F - \mathrm{Tr} \, \hat{\rho}_F \ln (\hat{\rho}_B) \right]$$

Conclusion

$$\langle W \rangle - \Delta F = k_B T \int \rho_F(q,p,t) \ln \frac{\rho_F(q,p,t)}{\rho_B(q,-p,t)} dq\,dp$$
$$= k_B T\, D(\rho_F \| \rho_B)$$

- An exact expression of dissipation is obtained.
  Now the second law is an equality!
- Dissipation is a direct measure of irreversibility (time's arrow).
- Even when full information is not available, the formula provides a lower bound of the dissipation
- The relation between information and physical processes is unambiguously formulated. The Landauer principle is proven.