Beyond the Second Law of Thermodynamics

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Dissipation: The Phase-Space Perspective

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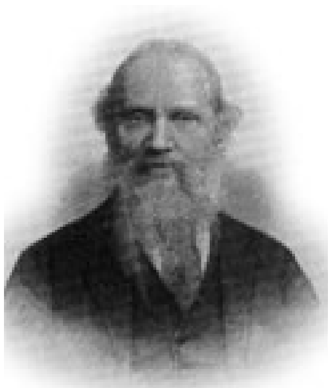
The Second Law of Thermodynamics



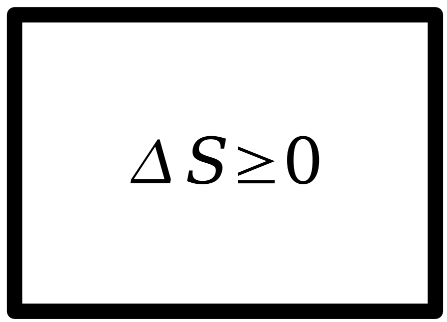
William Thomson
(Lord Kelvin)

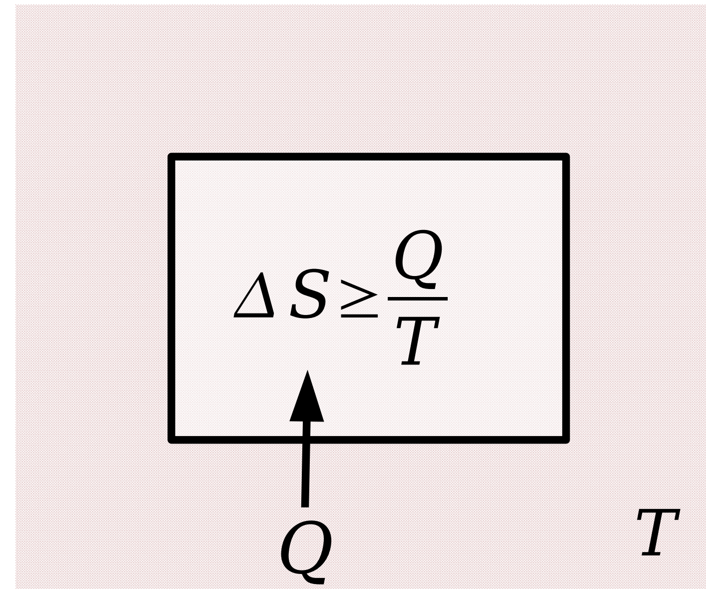
There exists no thermodynamic transformation whose *sole* effect is to extract a quantity of heat from a given heat reservoir and to convert it entirely into work.

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

Entropy and the Second Law





Isolated Systems

No exchange of energy or matter between the system and the environment is allowed.

Closed Systems

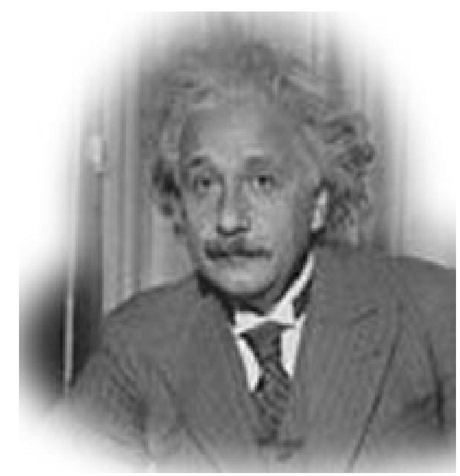
Energy exchange is allowed but not matter exchange.

Second Law → **Time's Arrow!**

Sir Arthur Eddington

“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

Why is the second law an inequality?

$$\Delta S - \frac{Q}{T} = \boxed{\text{Holy Grail of Statistical Mechanics}} \geq 0$$

$$S = S_r + S_i$$

reversible entropy change $\Delta S_r = \frac{Q}{T}$

irreversible entropy production $\Delta S_i \geq 0$

Ludwig E. Boltzmann

(1844-1906)

Second Law with Work

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

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

$$W - \Delta F = T \Delta S - Q = \boxed{\text{Holy Grail}} \geq 0$$

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

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

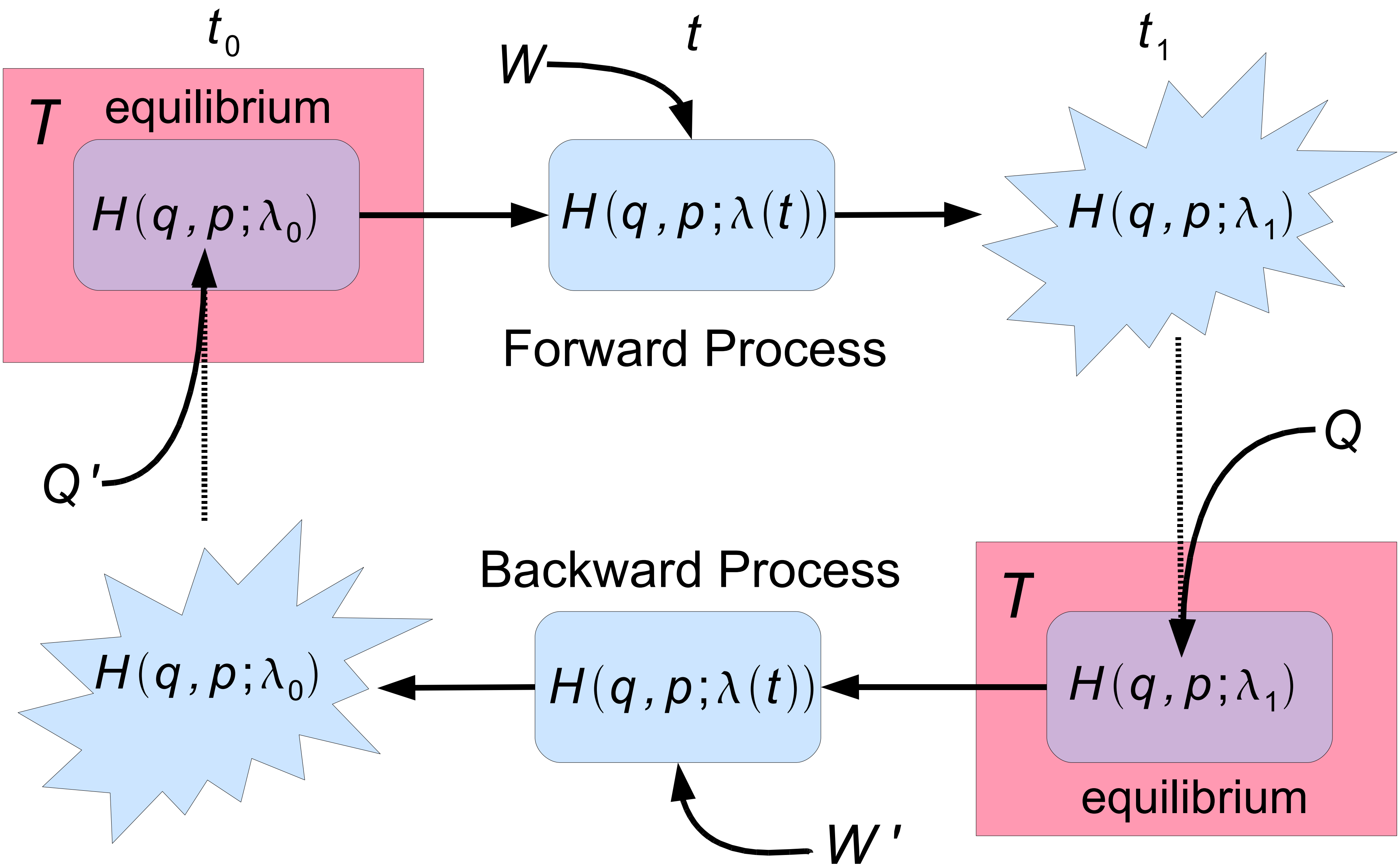
dissipative work $W_{\text{dis}} \geq 0$

Holy Grail Revealed in Phase Space

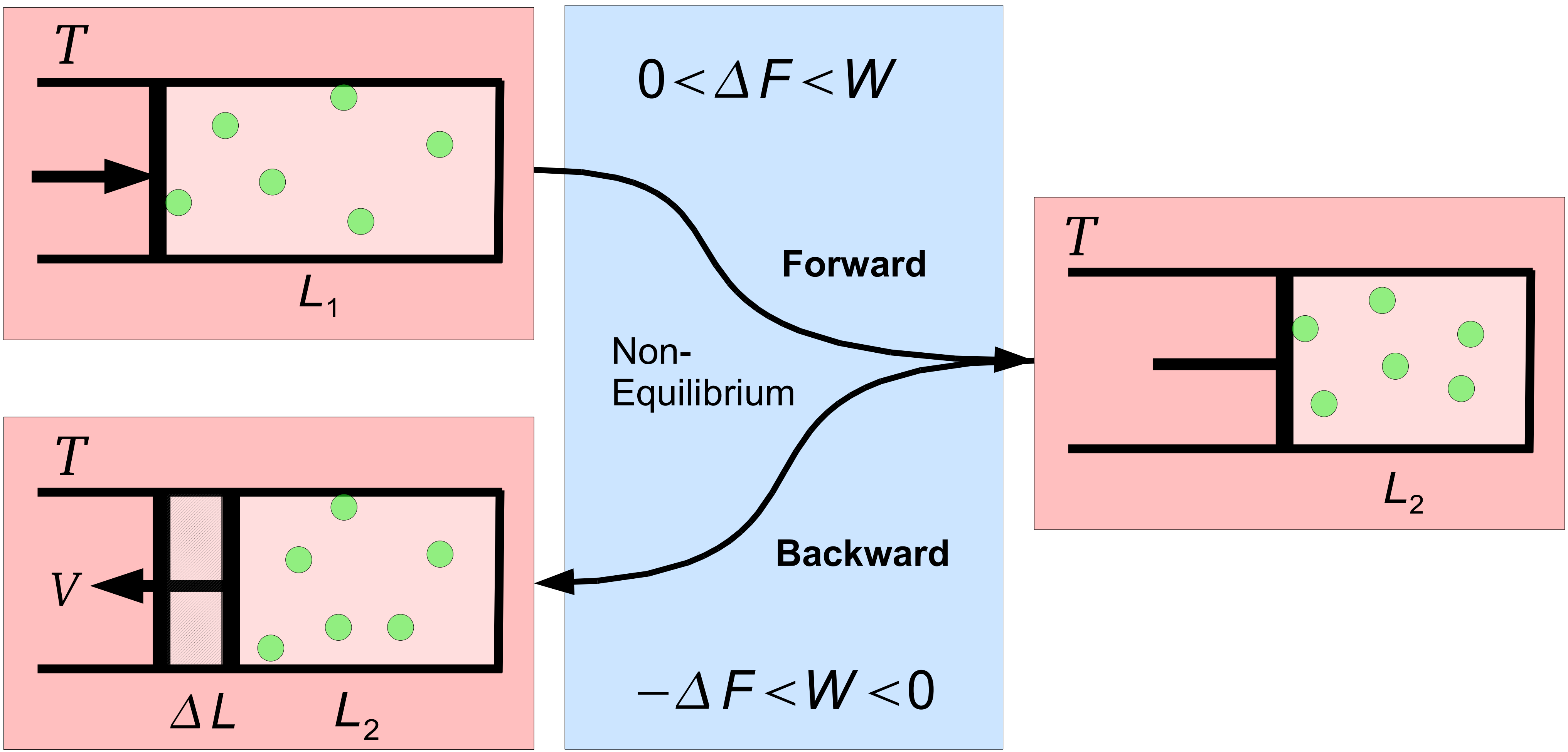
$$\langle W \rangle - \Delta F = k_B T \int \rho_F(q,p,t) \ln \frac{\rho_F(q,p,t)}{\rho_B(q,-p,t)}\, dq\, dp$$

$$= k_B T\, D(\rho_F \| \rho_B)$$

A Non-Equilibrium Process: Time-Dependent Hamiltonian



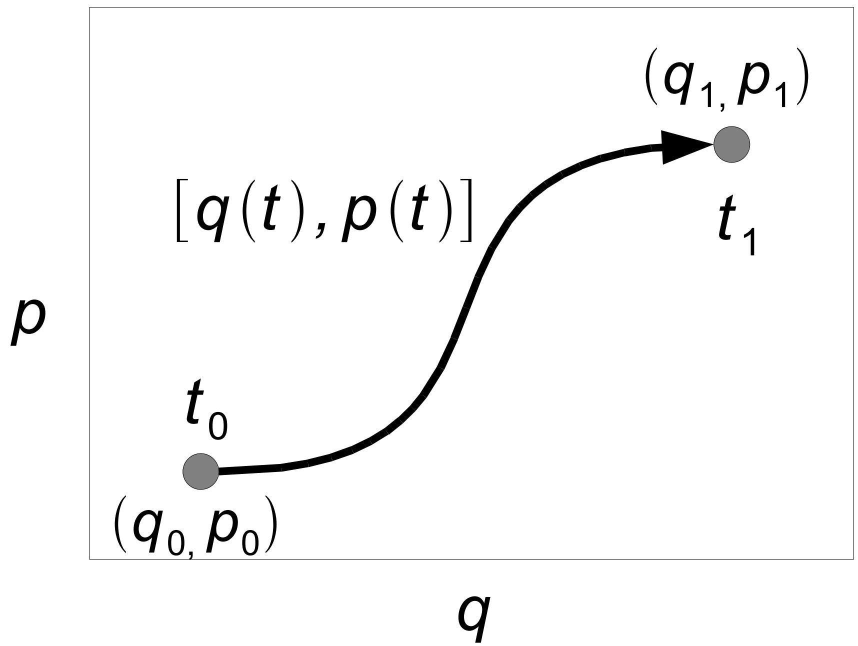
Example



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

Microscopic Time Reversibility $(q_{0,} p_0) \rightarrow (q_{1,} p_1)$

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

Joseph Liouville

(1809-1882)

Thermal Equilibrium and Gibbs Entropy

Equilibrium Density

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

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

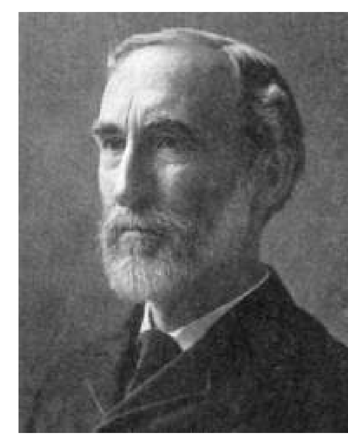
$$\rho_{eq}(q,p)=\rho_{eq}(q-p) \quad \text{(detailed balance)}$$

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

Gibbs Entropy

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

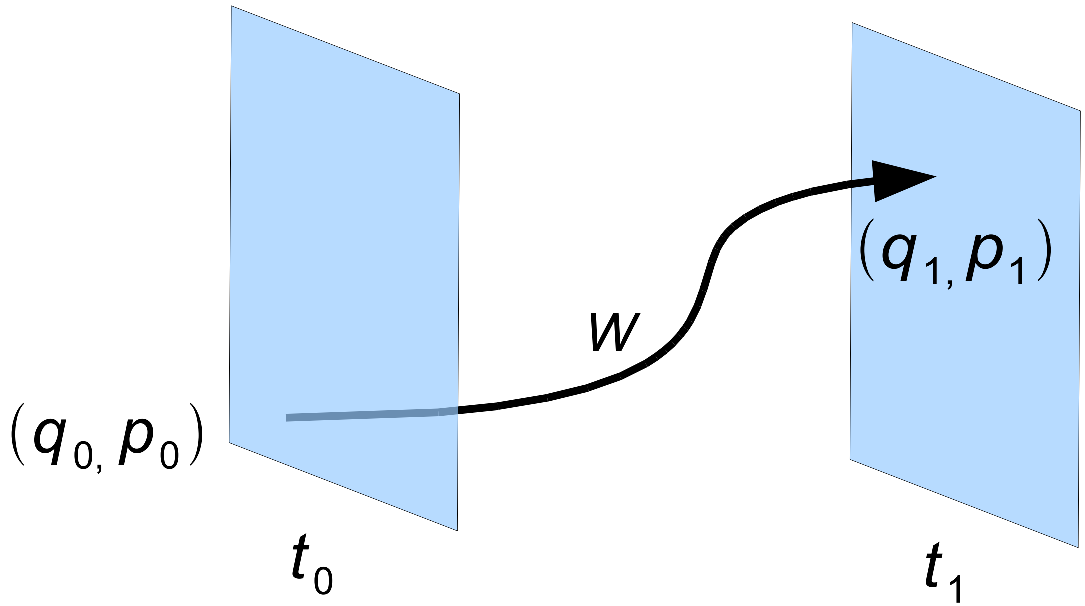
$$S(t_0)=S(t)=S(t_1)$$



J. Willard Gibbs

(1839-1903)

Definition of Work



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

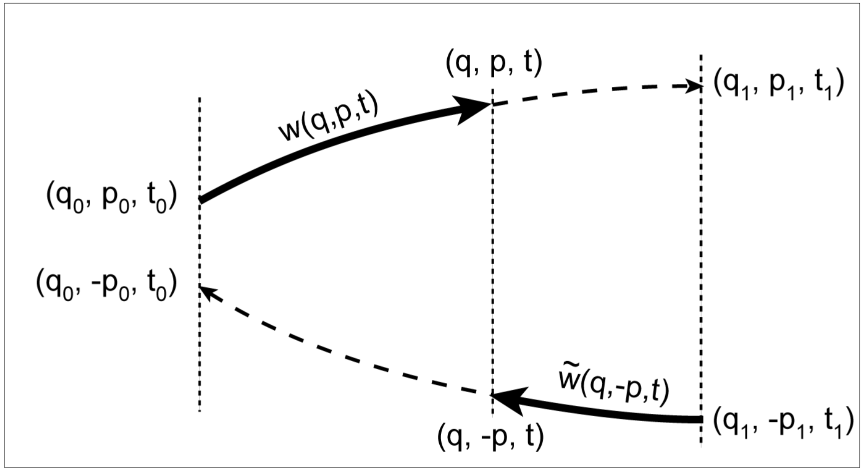
Statistical Average

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

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 difficulity to statistically distinguish two densities. (Stein's lemma)

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

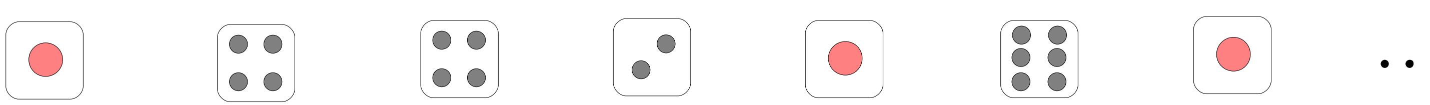
if $\tilde{\rho}$ and $\tilde{\eta}$ have less information than ρ and η

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

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

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

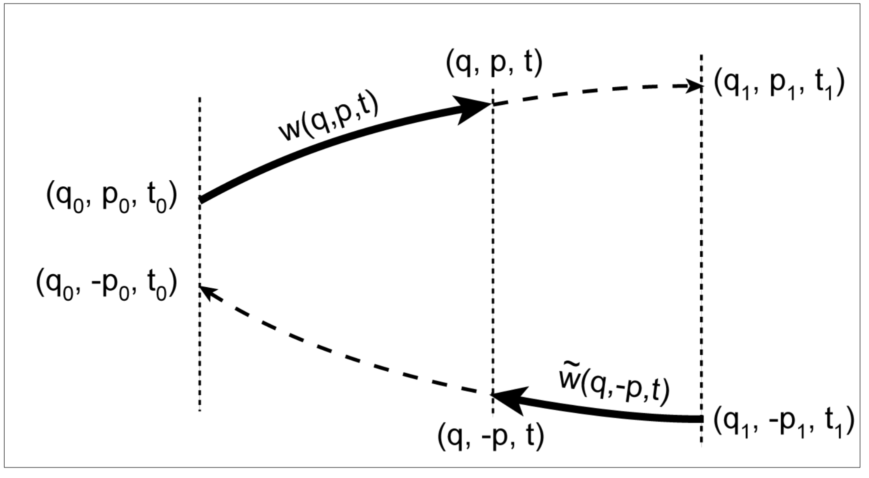
Dissipation and Time's Arrow

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

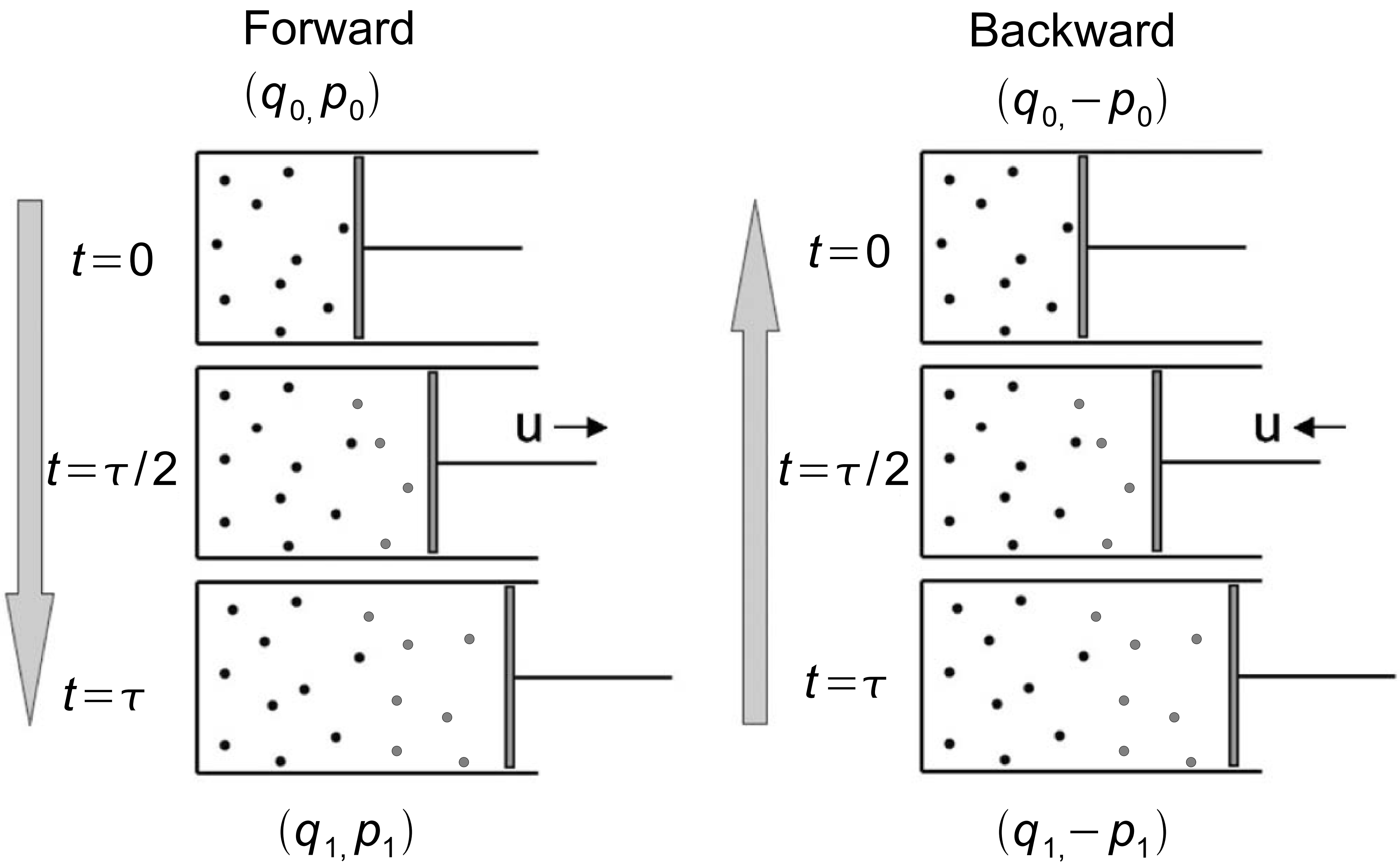
$D(\rho_F \| \rho_B) \geq 0 \quad \rightarrow \quad$ Second Law

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)!.

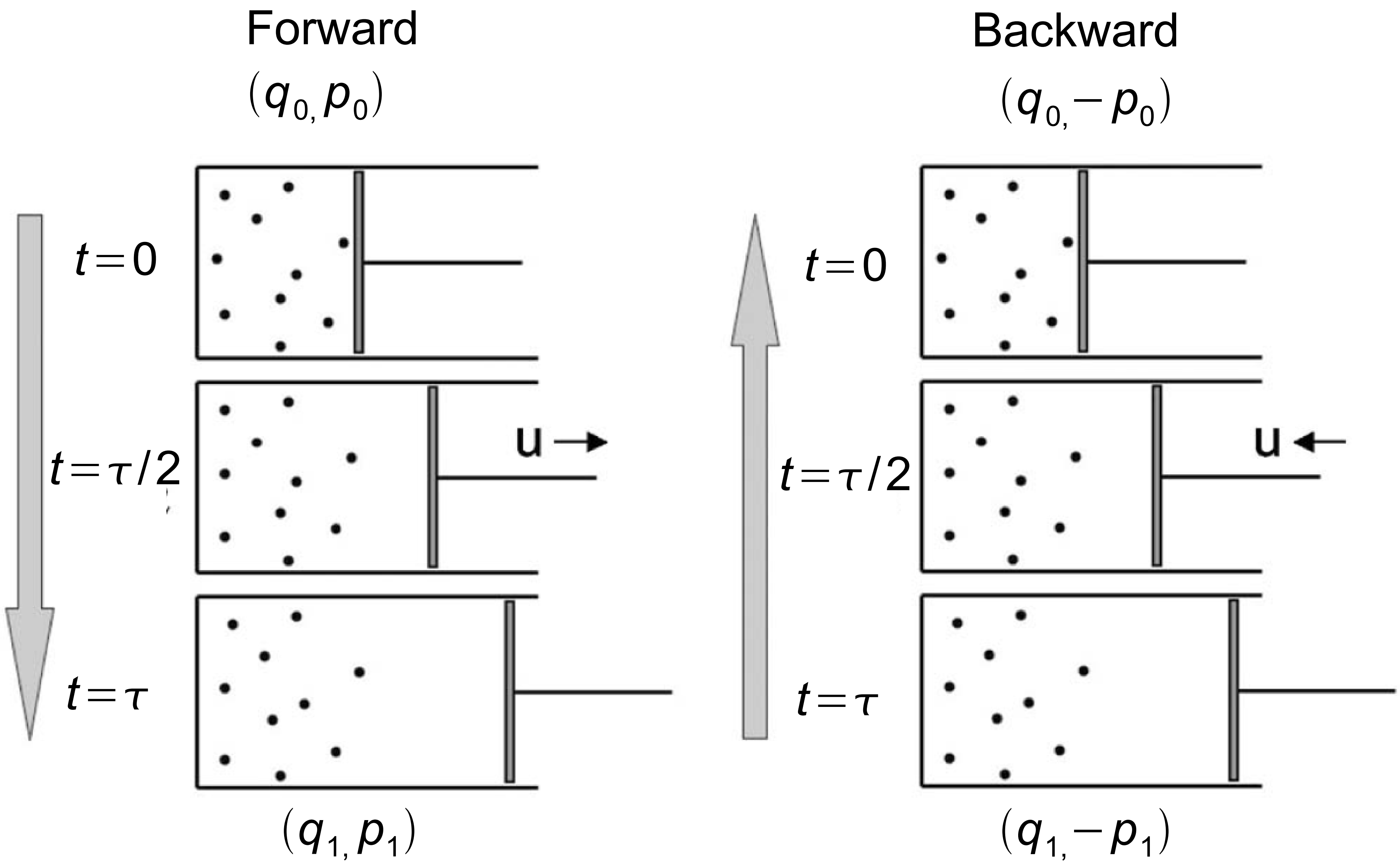


Slow Expansion

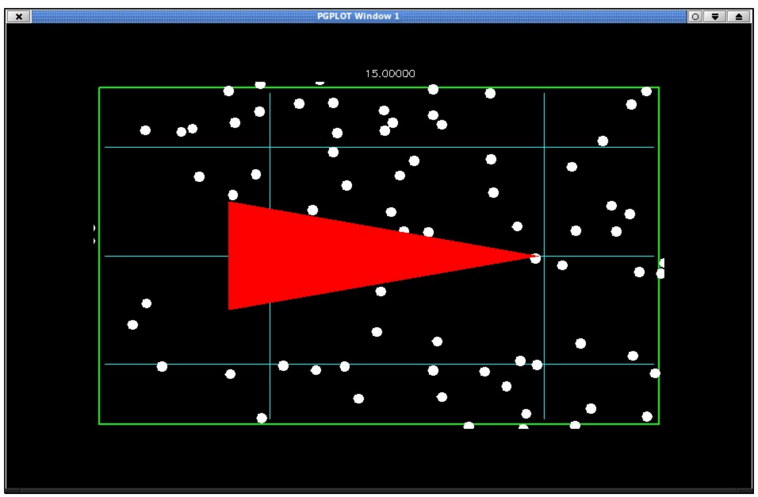


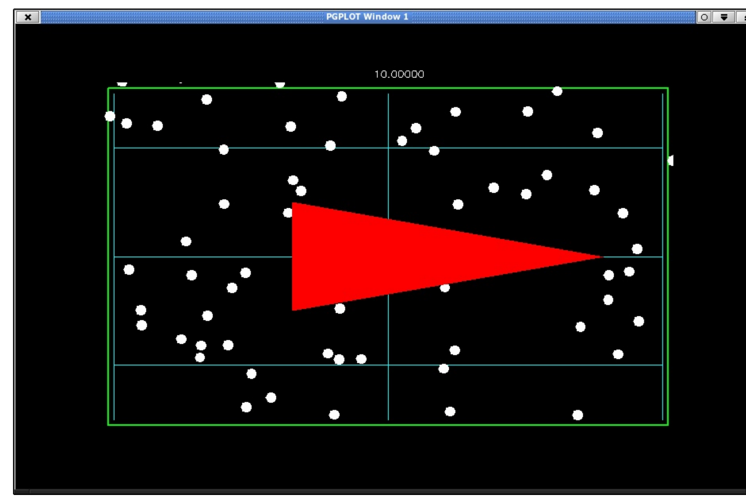
No Dissipation

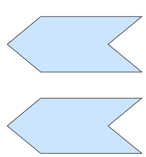
Rapid Expansion

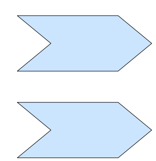


Which direction is the triangle moving?









Jarzinski equality and Crooks Theorem

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

Work at a phase point

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

(can be negative)

Crooks theorem

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

Jarzynski equality

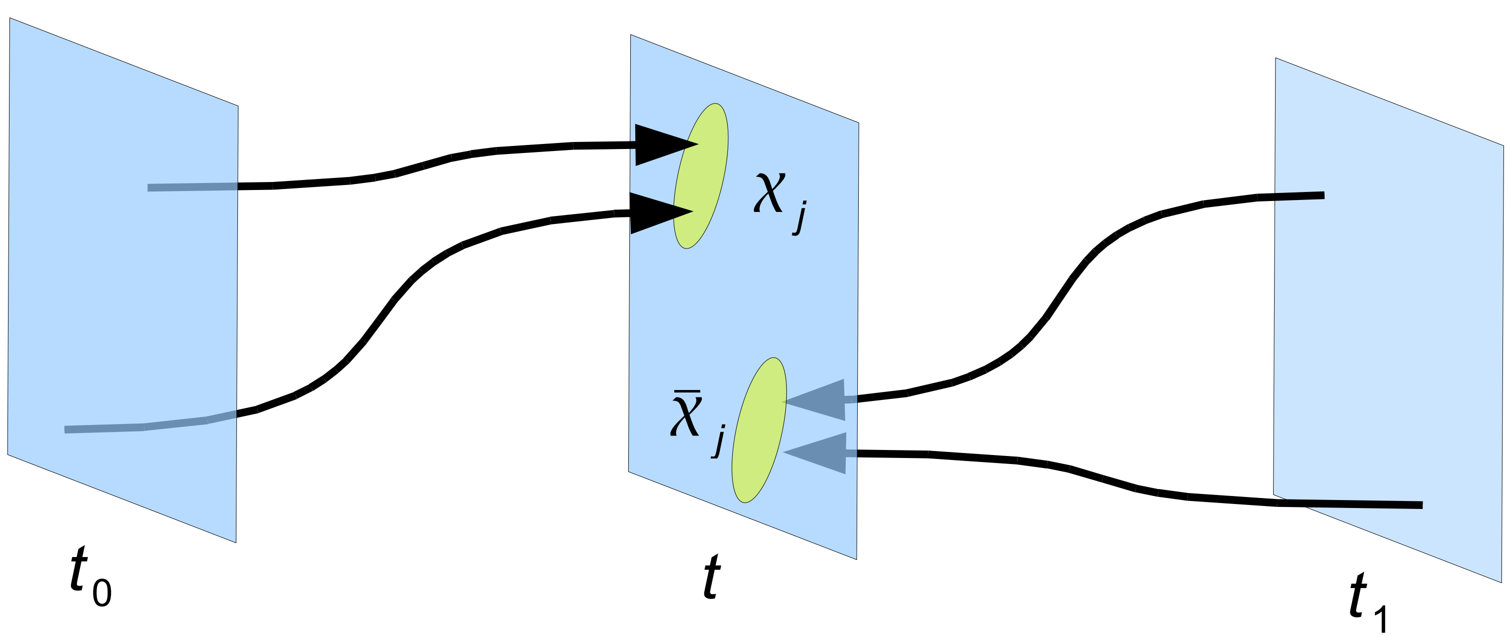
$$\langle \exp[-\beta W_{\mathrm{dis}}] \rangle = \int \rho_F(q,p,t) \exp[-\beta W_{\mathrm{dis}}(q,p,t)]\, dq\,dp = 1$$

Coarse Graining

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

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

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



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

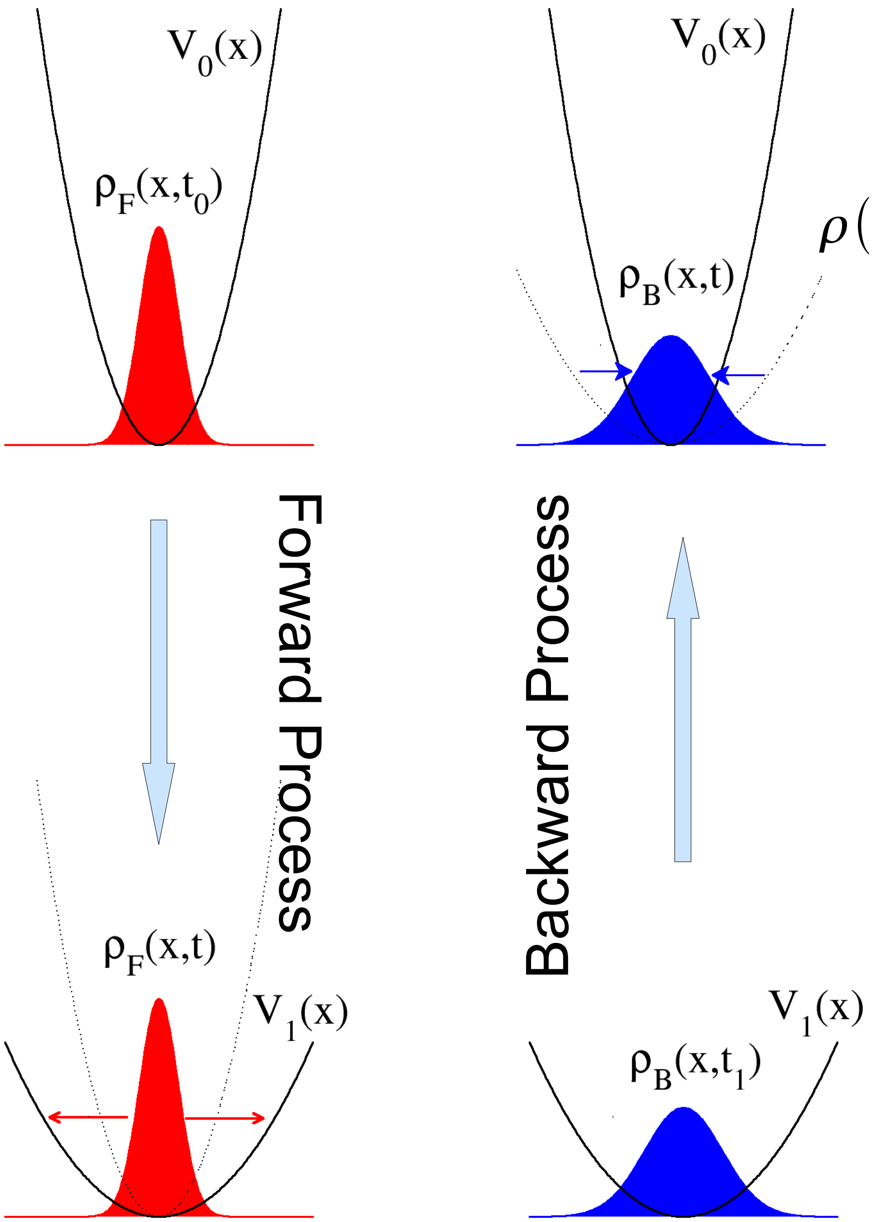
where $D(\rho_F^j \,||\, \rho_B^j) = \sum_{j=1}^{N} \rho_F^j \ln \frac{\rho_F^j}{\rho_B^j}$

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

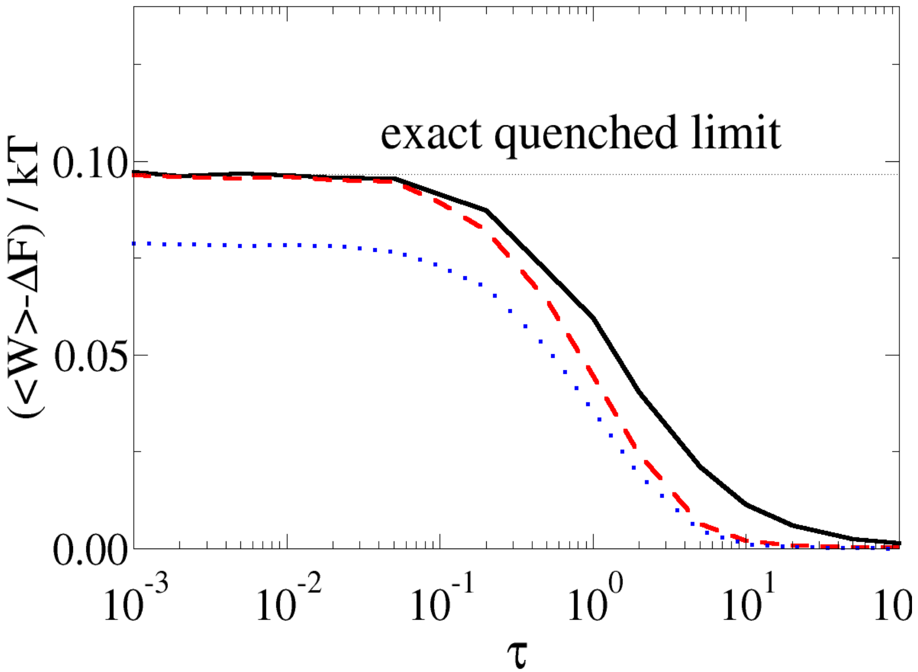
$$D(\rho_F \,||\, \rho_B) = 0 \ \rightarrow \ \langle W \rangle \geq \Delta F$$ **2nd law!**

Overdumped Brownian Particle in a Harmonic Potential



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

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

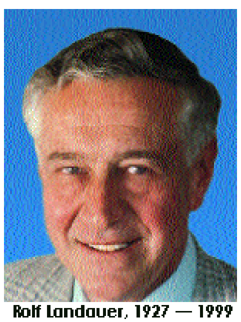


Application: Physics and Information

Leó Szilárd
(1898-1964)

Szilard found a relation between physics and information.

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

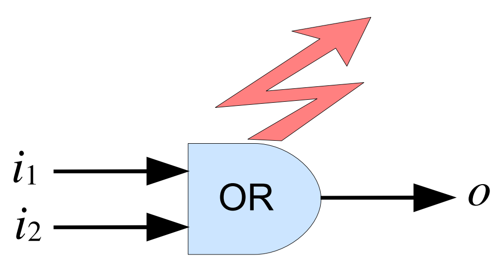


Ralf Landauer
(1929-1999)

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.

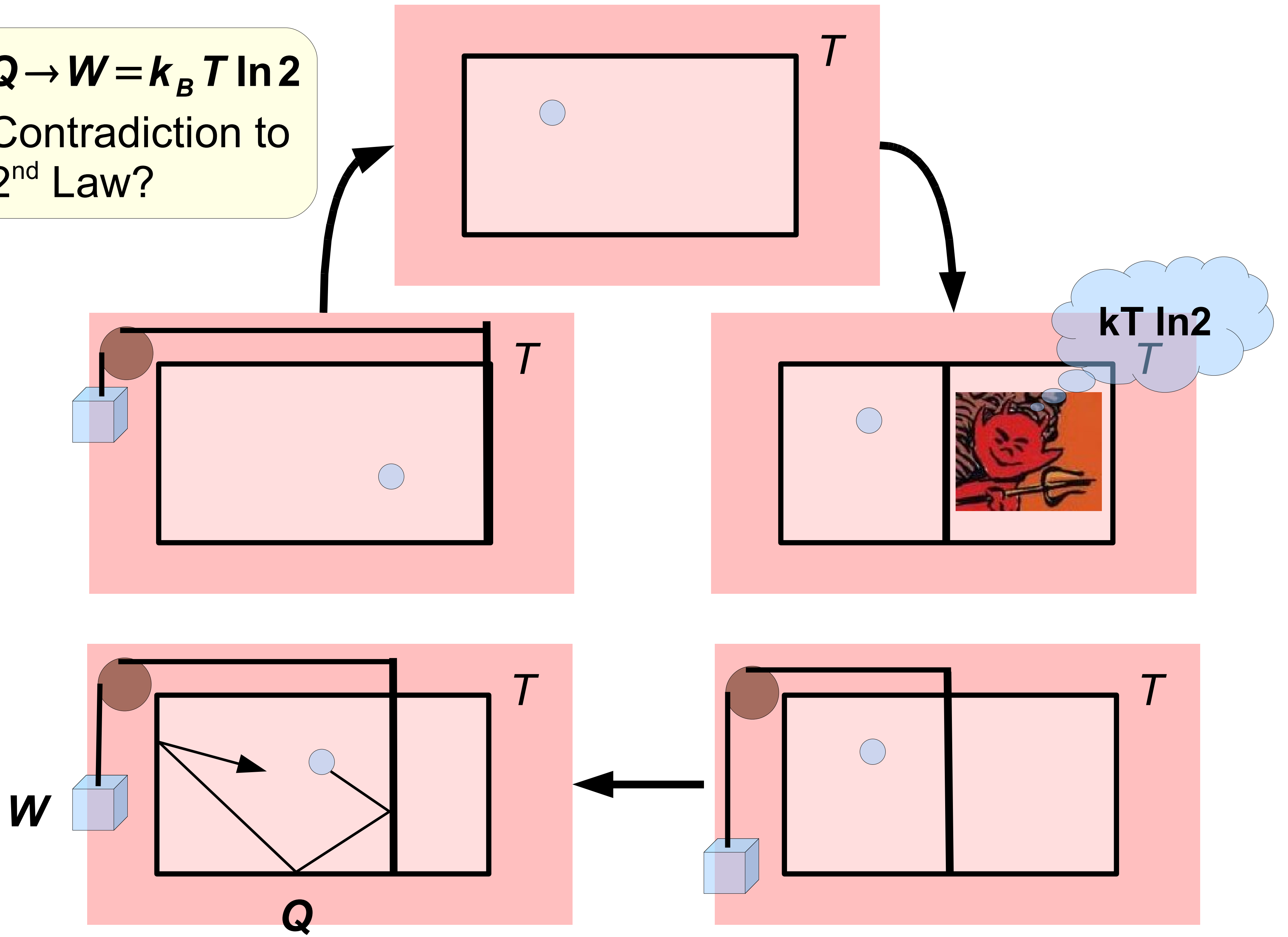
$$Q \geq k_B T \log 2$$



Szilard's Engine

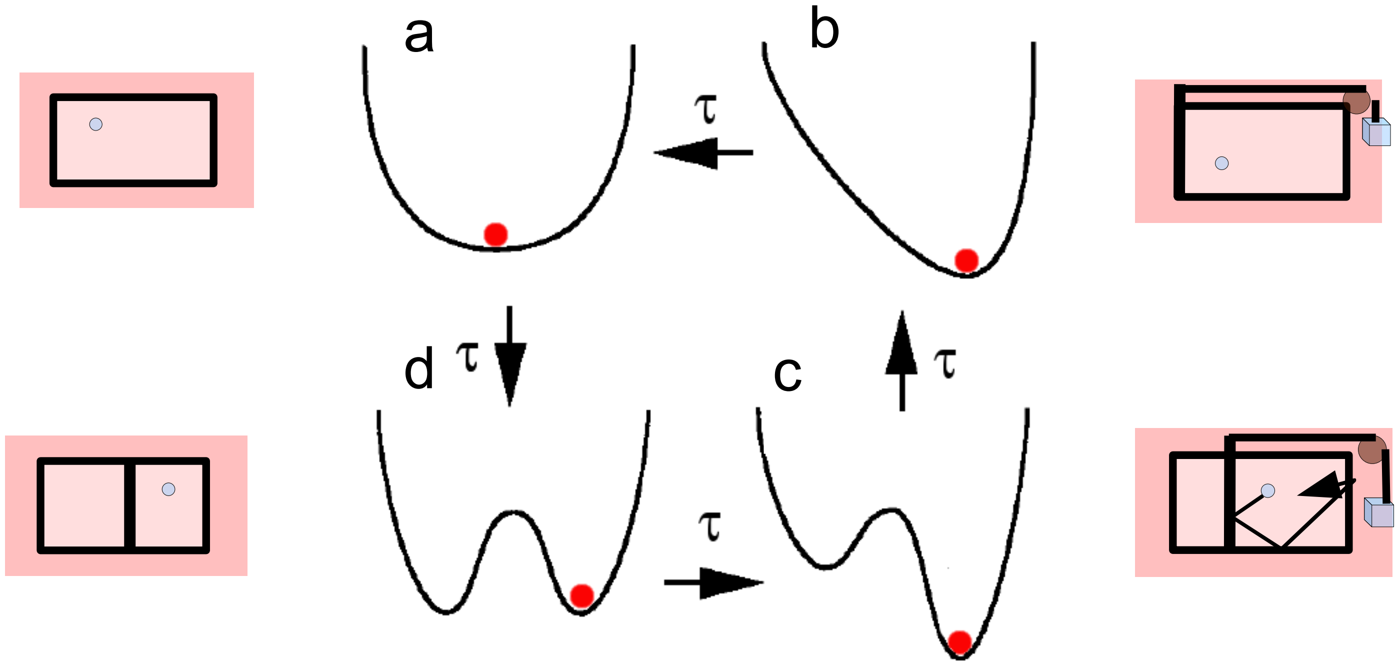
$Q \rightarrow W = k_B T \ln 2$

Contradiction to 2^{nd} Law?

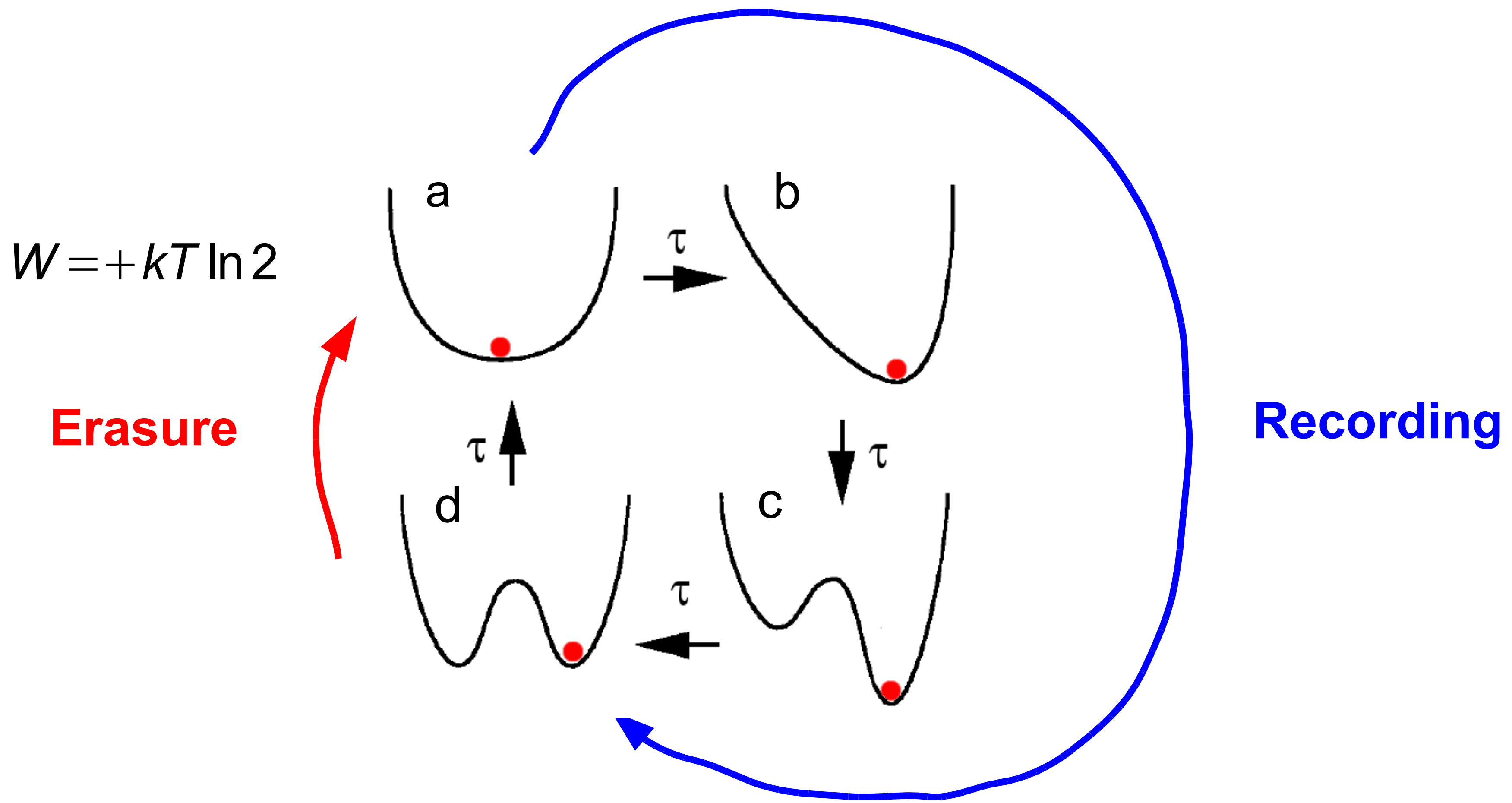


Brownian Engine (Backword Process)

$$W = -kT \ln 2$$

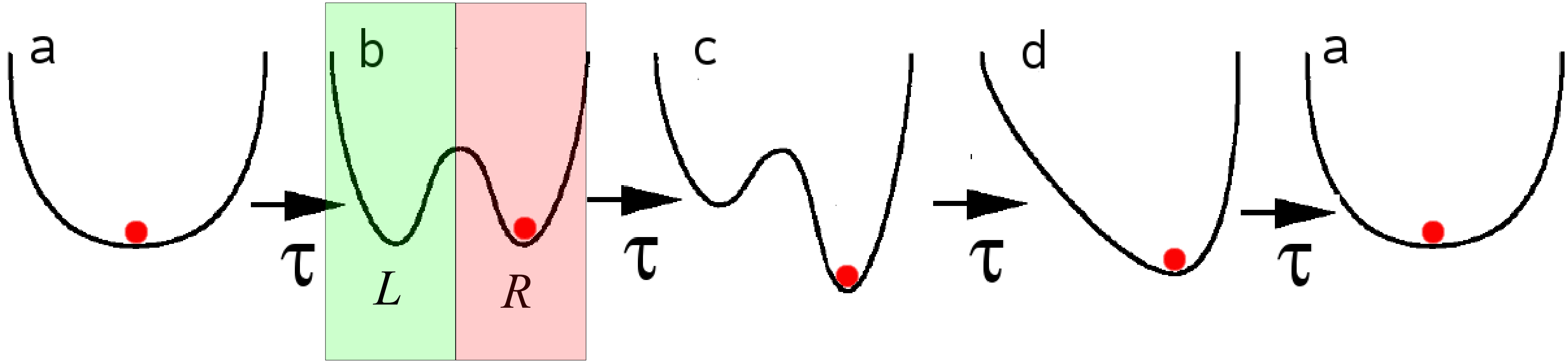


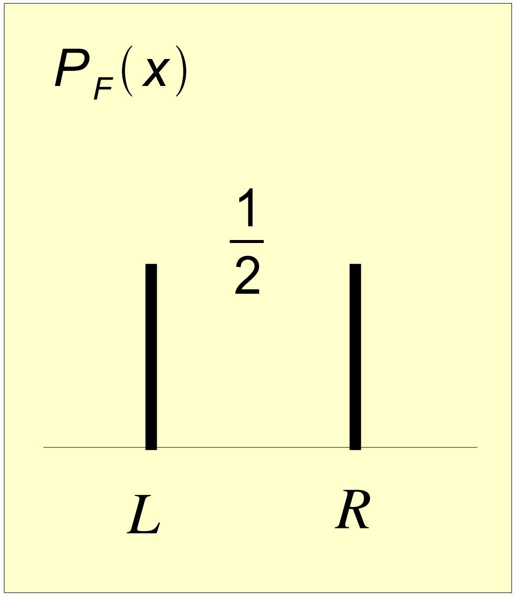
Brownian Computer (Forward Process)

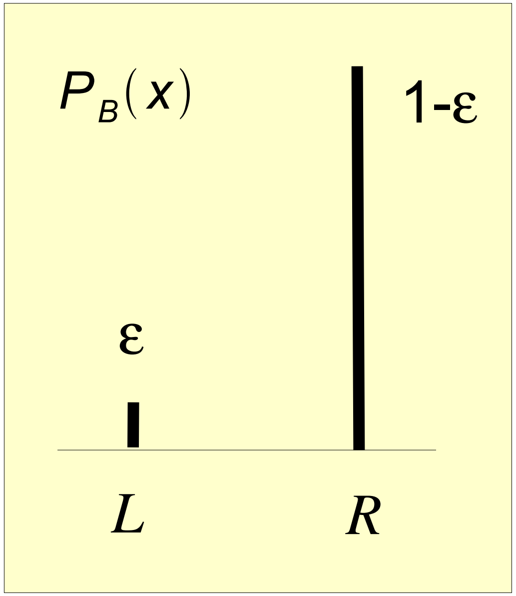


Restore-to-One Procedure: $d \to a \to b \to c \to d$

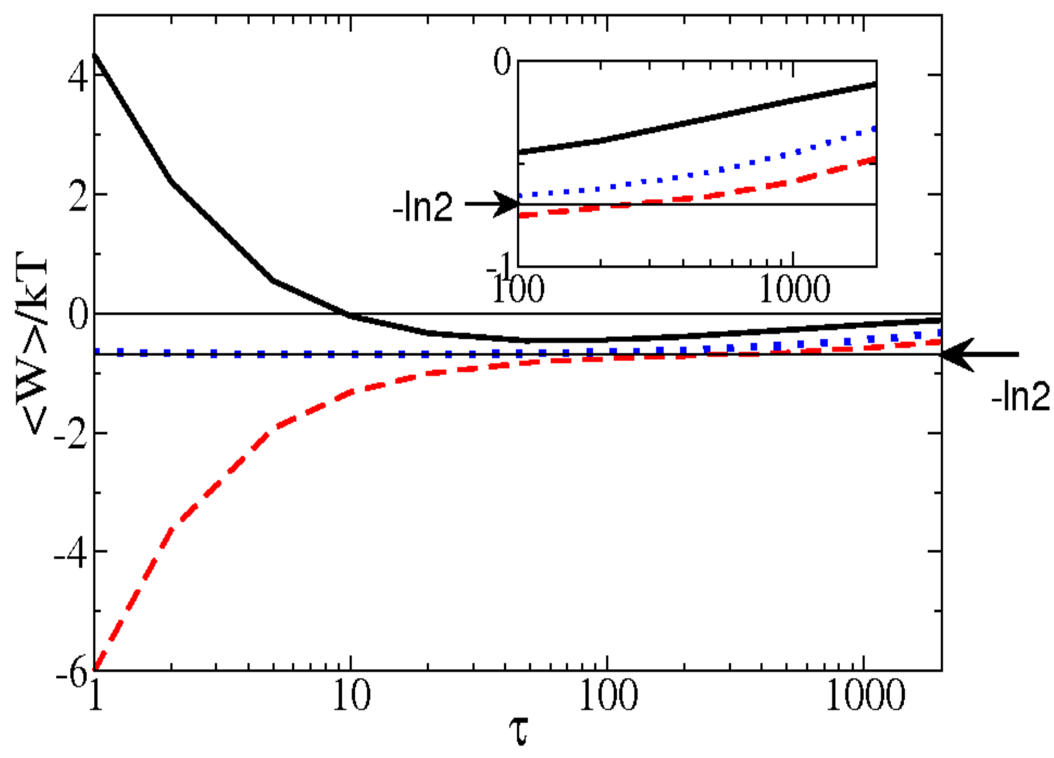
Coarse Grained Measurement







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



<W>/kT
τ
-ln2
-ln2

For quantum systems

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

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

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 of thermodynamics 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.