

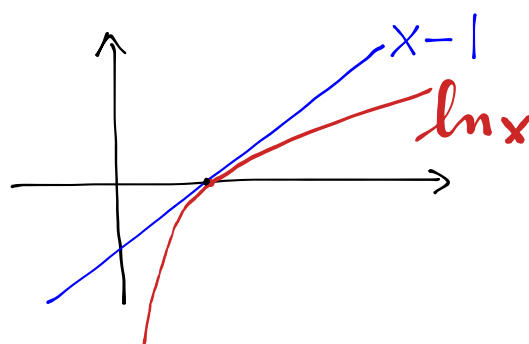
Kullback-Leibler divergence /
relative entropy :

$$D(f|g) \equiv \int f \ln \frac{f}{g} \quad (f, g = \text{normalized probability dist'n})$$

$$D \geq 0 \quad \& \quad D = 0 \text{ iff } f = g$$

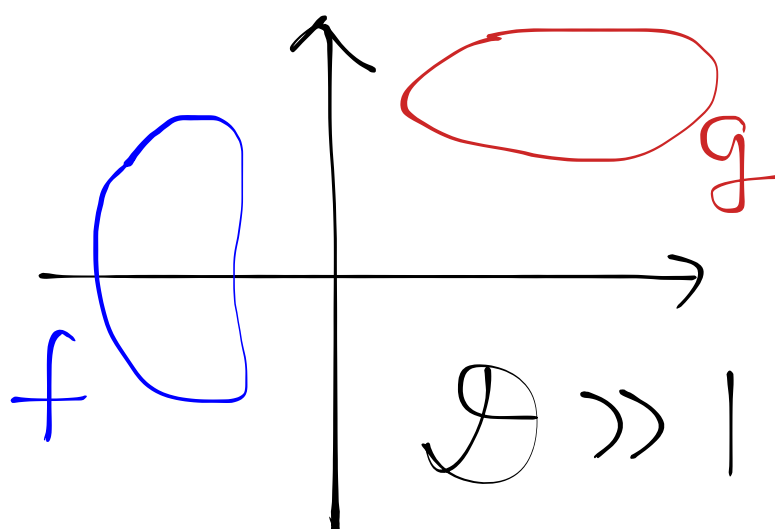
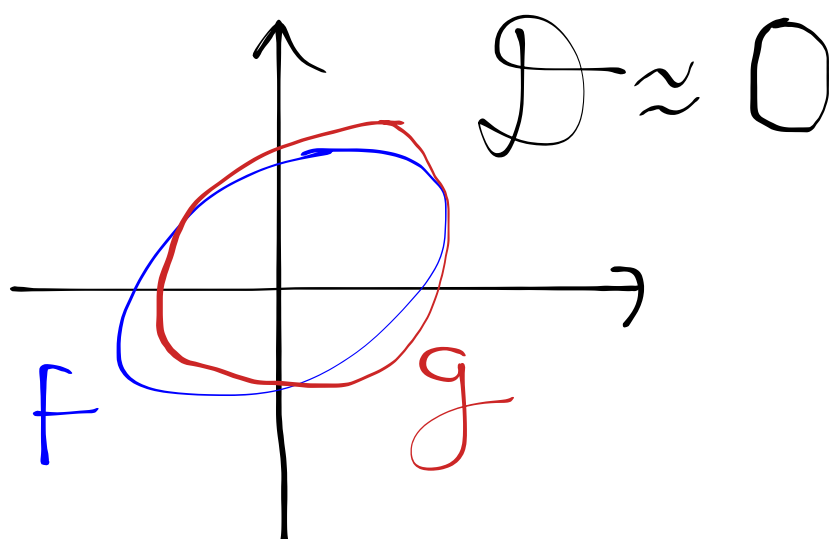
$$\begin{aligned} \int f \ln \frac{f}{g} &= - \int f \ln \frac{g}{f} \\ &\geq - \int f \left(\frac{g}{f} - 1 \right) = 0 \end{aligned}$$

using $\ln x \leq x - 1$:



D is like a "distance" between f & g ...

but asymmetric: $D(f|g) \neq D(g|f)$

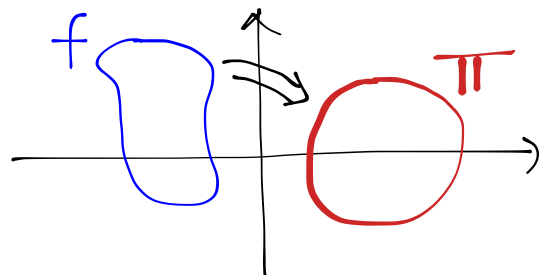


Suppose $f(x,t)$ obeys the Smoluchowski eqn:

$$\frac{\partial f}{\partial t} = \beta D \frac{\partial}{\partial x} \left(\frac{\partial V}{\partial x} f \right) + D \frac{\partial^2 f}{\partial x^2} \equiv \hat{\mathcal{L}} f$$

$$\pi(x) = \frac{1}{Z} e^{-\beta V(x)} = e^{\beta[F - V(x)]}$$

Claim: $\frac{d}{dt} \mathcal{D}(f|\pi) \leq 0$



f evolves "toward π "

$$\mathcal{D}(f|\pi) = \int f \ln \frac{f}{\pi}$$

$$\dot{\mathcal{D}} = \int \frac{\partial f}{\partial t} \ln \frac{f}{\pi} + \int f \cdot \frac{1}{f} \frac{\partial f}{\partial t}$$

$$= \int (\hat{\mathcal{L}} f) \ln \frac{f}{\pi} + \cancel{\frac{\partial}{\partial t} \int f} \rightarrow 0$$

$$= \int f \hat{\mathcal{L}}^+ \left(\ln \frac{f}{\pi} \right) = \int f \hat{\mathcal{L}}^+ \ln f - \int f \hat{\mathcal{L}}^+ \ln \pi$$

$$\hat{\mathcal{L}}^+ = -\beta D V' \frac{\partial}{\partial x} + D \frac{\partial^2}{\partial x^2}$$

$$\left\{ \begin{array}{l} \hat{\mathcal{L}}^+ \ln f = -\beta D V' \frac{f'}{f} + D (\ln f)'' \\ \hat{\mathcal{L}}^+ \ln \pi = \beta \hat{\mathcal{L}}^+ [F - V(x)] = \beta^2 D (V')^2 - \beta D V'' \end{array} \right.$$

$$\begin{aligned}
 \dot{\mathcal{Q}} &= -\beta \mathcal{D} \int v' f' + \underbrace{\mathcal{D} \int f (\ln f)''}_{= -\mathcal{D} \int f' (\ln f)'} - \beta^2 \mathcal{D} \int f (v')^2 + \underbrace{\beta \mathcal{D} \int f v''}_{= -\beta \mathcal{D} \int f' v'} \\
 &= -\mathcal{D} \int (f')^2 / f
 \end{aligned}$$

$$= -\mathcal{D} \int \frac{(f')^2}{f} - \mathcal{D} \int 2\beta f' v' - \mathcal{D} \int \beta^2 f (v')^2$$

$$= -\mathcal{D} \int \frac{1}{f} \left[(f')^2 + 2\beta f' f v' + \beta^2 f^2 (v')^2 \right]$$

$$= -\mathcal{D} \int \frac{1}{f} \underbrace{(f' + \beta f v')^2}_{\geq 0} \leq 0 \quad \checkmark$$

$$= e^{-\beta v} \frac{\partial}{\partial x} (e^{\beta v} f)$$

hence $\dot{\mathcal{Q}} = 0$ iff $f = \pi$.

$\mathcal{D}(f|\pi)$ provides a natural measure of the extent to which a system is out of equilibrium.

Historically, introduced by Boltzmann in the context of dilute gases - the Boltzmann eqn.

↳ Boltzmann's H-theorem

$\dot{S} \leq 0 \rightarrow$ Clausius inequality.

1st we must understand the First Law, for diffuse processes. Heat & Work.

Langevin eqn: $\dot{x} = -\frac{1}{\gamma} \frac{\partial V}{\partial x} + \xi$, $\gamma = \frac{1}{\beta D}$

take $V = V(x; \lambda)$, $\lambda = \lambda(t)$

$$\frac{d}{dt} V(x(t); \lambda(t)) = \dot{x} \frac{\partial V}{\partial x} + \dot{\lambda} \frac{\partial V}{\partial \lambda}$$

$$\Delta V \equiv V(x(\tau); \lambda(\tau)) - V(x(0); \lambda(0))$$

$$= \underbrace{\int_0^\tau dt \dot{x} \frac{\partial V}{\partial x}}_{\text{heat absorbed by system}} + \underbrace{\int_0^\tau \dot{\lambda} \frac{\partial V}{\partial \lambda}}_{\text{work performed on system}}$$

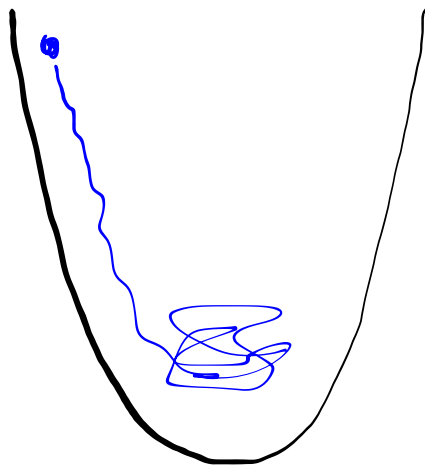
heat
absorbed by
system

work
performed
on system

[K. Sekimoto, "Langevin eqn. & thermodynamics"
Prog. Theor. Phys. Suppl. 130, 17-27 (1998)]
"stochastic energetics"

Plausibility argument:

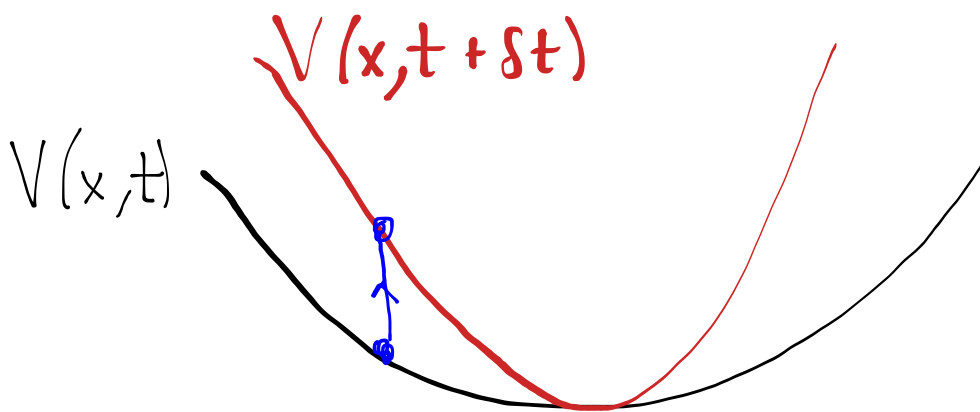
① $\dot{\lambda} = 0$



$$\Delta V = \int \frac{\partial V}{\partial x} \dot{x}$$

System loses energy, which goes into the environment as heat.

② λ is changed suddenly.



$$x(t + \delta t) = x(t)$$
$$\Delta V = \int \frac{\partial V}{\partial \lambda} \dot{\lambda}$$

No time for exchg. of energy w/ surroundings.
Change of energy is due to work.

Ensemble: $\langle V \rangle(t) = \int f(x,t) V(x,\lambda) \quad , \quad \lambda = \lambda(t)$

$$\frac{d}{dt} \langle V \rangle = \int \frac{\partial f}{\partial t} V + \int f \dot{\lambda} \frac{\partial V}{\partial \lambda}$$

$$= \underbrace{\int (\hat{\mathcal{L}} f) V}_{\frac{d}{dt} \langle Q \rangle} + \underbrace{\int \dot{\lambda} f \frac{\partial V}{\partial \lambda}}_{\frac{d}{dt} \langle W \rangle}$$

$\langle Q \rangle = \text{avg. heat absorbed by system}$

$\langle W \rangle = \text{avg. work performed on system}$

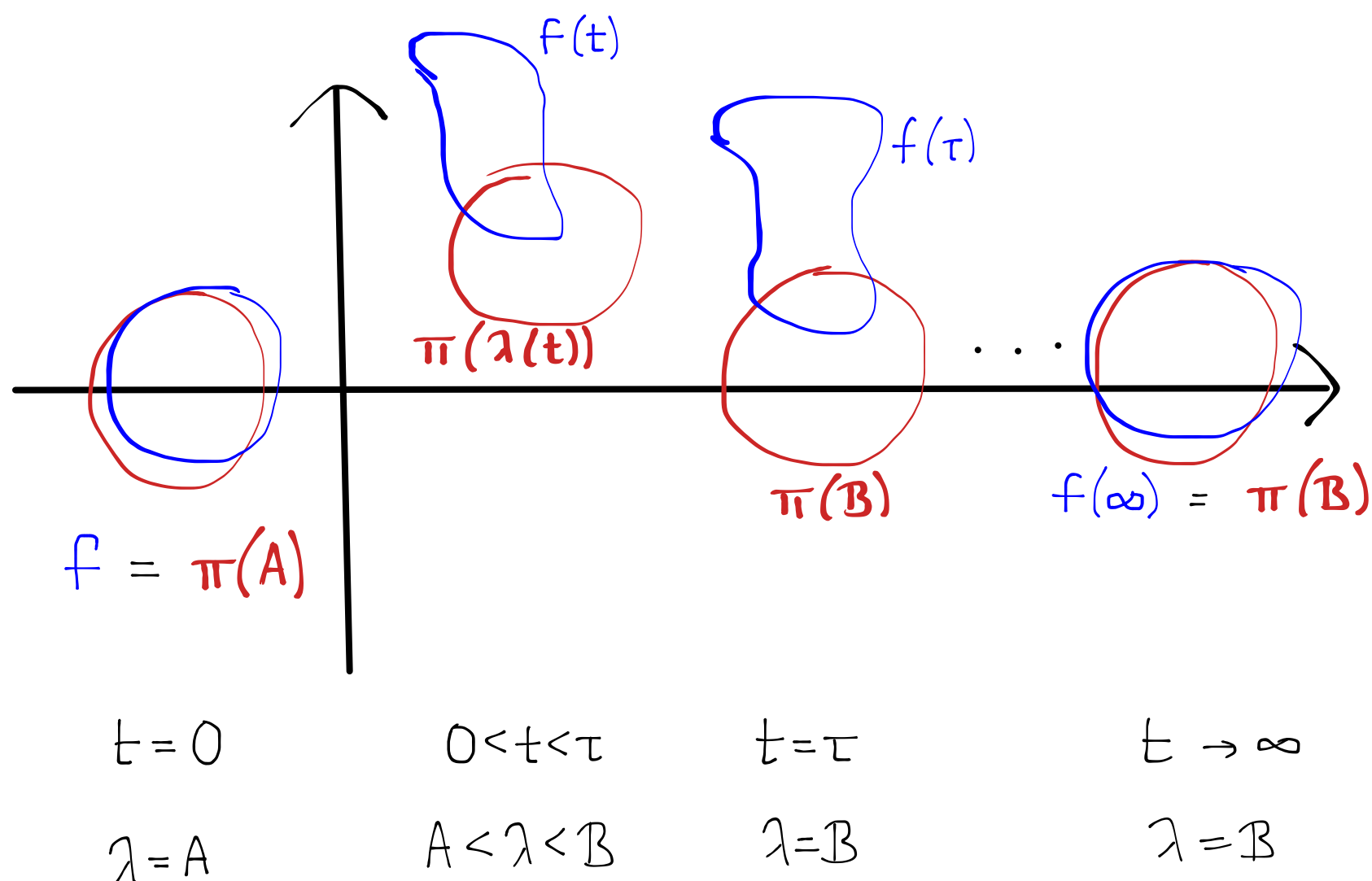
$$\frac{d}{dt} \langle Q \rangle = \int (\hat{\mathcal{L}} f) V = \int f (\hat{\mathcal{L}}^\dagger V)$$

$$= \dots = D \left\langle e^{\beta V} \frac{\partial}{\partial x} (V' e^{-\beta V}) \right\rangle$$

Exercise: fill in the steps!

$$\frac{d}{dt} \langle W \rangle = \dot{\lambda} \left\langle \frac{\partial V}{\partial \lambda} \right\rangle$$

Now consider the following process:



- ① Begin in equilibrium @ $t=0$. $\lambda = A$
- ② Vary $\lambda : A \rightarrow B$ as $t : 0 \rightarrow \tau$.
- ③ $t > \tau$: hold λ fixed @ B . Let system relax.

$f(x,t)$ = current statistical state of system
 $\pi(x;\lambda(t))$ = instantaneous equil. state
 "moving target"

Intuitive picture: $f(x,t)$ chases $\pi(x;\lambda(t))$

$$\mathcal{D}(t) \equiv \mathcal{D}(f(x,t) | \pi(x; \lambda(t))) = \int f \ln \frac{f}{\pi}$$

$$\dot{\mathcal{D}} = \int \left(\dot{f} \ln \frac{f}{\pi} + f \frac{1}{f} \dot{f} - f \frac{1}{\pi} \dot{\lambda} \frac{\partial \pi}{\partial \lambda} \right)$$

same as before

$$= \underbrace{-\mathcal{D} \int \frac{1}{f} (f' + \beta f V')^2}_{\leq 0} - \dot{\lambda} \int f \frac{\partial}{\partial \lambda} \ln \pi$$

$\pi = e^{\beta(F-V)}$

$$\therefore \dot{\mathcal{D}} \leq -\dot{\lambda} \int f \beta \left(\frac{\partial F}{\partial \lambda} - \frac{\partial V}{\partial \lambda} \right) = \beta \dot{\lambda} \left[\left\langle \frac{\partial V}{\partial \lambda} \right\rangle - \frac{\partial F}{\partial \lambda} \right]$$

$$\mathcal{D}(t \rightarrow \infty) - \mathcal{D}(t=0) \leq \beta \int_0^\infty dt \dot{\lambda} \left\langle \frac{\partial V}{\partial \lambda} \right\rangle - \beta \Delta F$$

$$\Delta F = F(B) - F(A)$$

But $\mathcal{D}(0) = \mathcal{D}(\infty) = 0$ (begin & end in equil.)

$$\therefore 0 \leq \beta \langle W \rangle - \beta \Delta F$$

$$\boxed{\langle W \rangle \geq \Delta F}$$

← Clausius inequality
(for isothermal processes)

We can derive a similar result for entropy.

$$\text{Take } \frac{\partial f}{\partial t} = \beta D \frac{\partial}{\partial x} \left(\frac{\partial V}{\partial x} f \right) + D \frac{\partial^2 f}{\partial x^2} \equiv \hat{\mathcal{L}} f$$

For now, assume $V(x)$ has no time-dependence.

$$S[f] = - \int f \ln f \quad \text{entropy}$$

$$\mathcal{Q}(f|\pi) = \int f \ln \frac{f}{\pi}$$

$$\pi = e^{\beta(F-V)}$$

$$S + \mathcal{Q} = - \int f \ln \pi = \beta \langle V \rangle - \beta F$$

$$\dot{S} + \dot{\mathcal{Q}} = \beta \frac{d}{dt} \langle V \rangle = \beta \frac{d}{dt} \langle Q \rangle \quad (W = 0)$$

but $\dot{\mathcal{Q}} \leq 0$ (as already shown)

$$\therefore \frac{d}{dt} S[f(x,t)] \geq \beta \frac{d}{dt} \langle Q \rangle$$

$$\boxed{\frac{\langle Q \rangle}{T} \leq \Delta S} \equiv S[f_{\text{final}}] - S[f_{\text{initial}}]$$

This "generalized" 2nd Law remains valid

even when $f_{\text{in}}, f_{\text{fin}} \neq \pi$.

The above derivation can be extended to the case of time-dependent $V(x,t)$.

(Exercise: fill in the details!)

In that case, if the system begins & ends in equilibrium, i.e. if $f_{\text{in}} = \pi(A)$ & $f_{\text{fin}} = \pi(B)$, then we get the usual Clausius inequality:

$$\frac{\langle Q \rangle}{T} \leq S_B - S_A ,$$

equivalently $\langle W \rangle \geq \Delta F$

Finally, let's return to the intuitive picture of $f(x,t)$ "chasing" $\pi(x; \lambda(t))$.

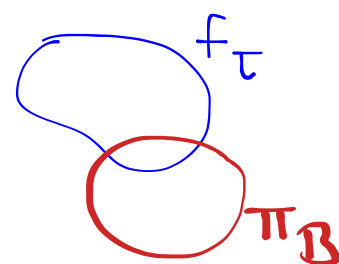
The dissipated work, $\langle W \rangle - \Delta F$, reflects the degree to which the system "lagged behind equilibrium" over the course of the process.

Going back to $\dot{D} \leq \beta \dot{\lambda} \left[\left\langle \frac{\partial V}{\partial \lambda} \right\rangle - \frac{\partial F}{\partial \lambda} \right]$,

let's integrate both sides from $t=0$ to τ .

$$\mathcal{Q}(\tau) - \mathcal{Q}(0) \leq \beta [\langle W \rangle - \Delta F]$$

$$\underbrace{\langle W \rangle \geq \Delta F}_{2^{\text{nd}} \text{ Law}} + \underbrace{\beta^{-1} \mathcal{Q}(f_\tau | \pi_B)}_{\text{"penalty"}}$$



I.e. there is a thermodynamic penalty for ending away from equilibrium. This makes sense intuitively, in view of the natural tendency of the system to relax to equilibrium.

(One can similarly derive a "benefit" associated with starting away from equilibrium.)