UNIVERSITY OF
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IPST

# Connecting thermodynamics to statistical mechanics for strong system-environment coupling

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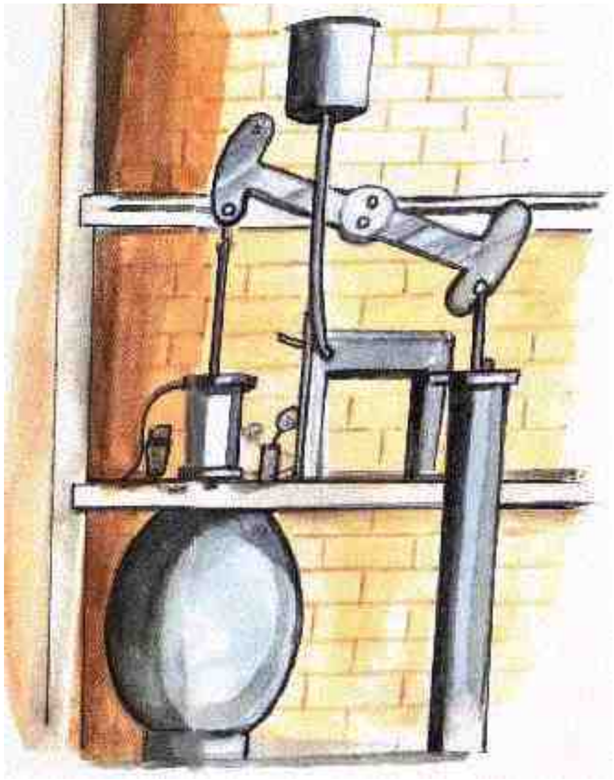
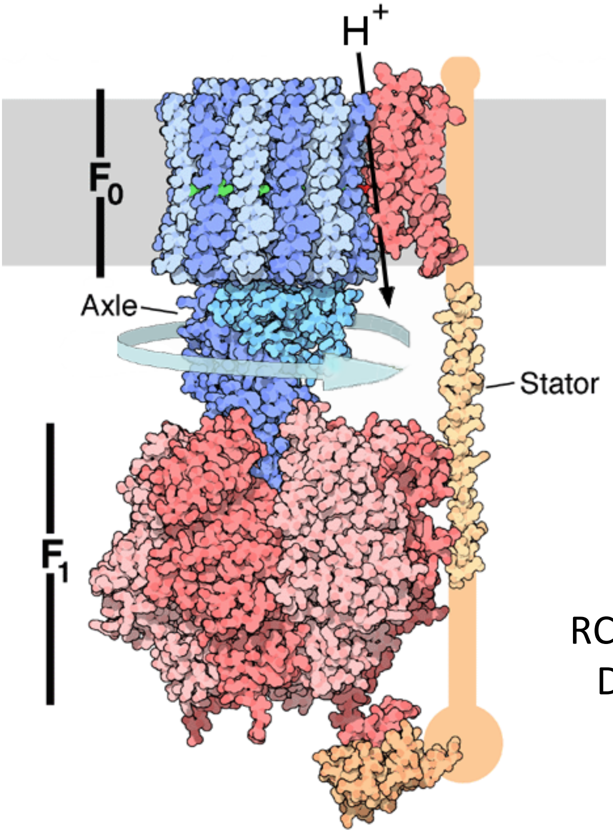
# Macroscopic and microscopic machines

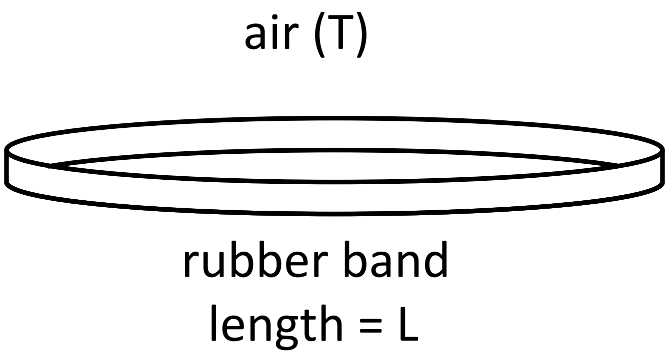
steam engine

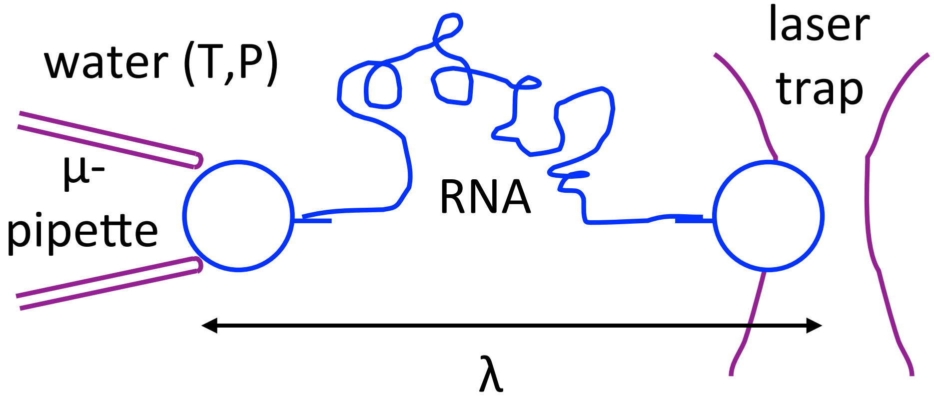


ATP synthase



RCSB Protein
Data Bank





$$U_{S+E} = U_{sys} + U_{env}$$

neglect interaction energy

➔ heat, work, entropy …
1st & 2nd Laws of Thermodynamics

$$U_{S+E} = u_{sys} + U_{env} + u_{\mathrm{int}}$$

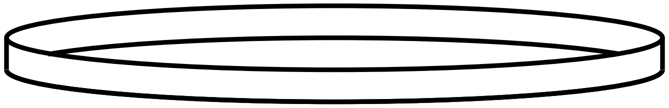
***can't*** neglect interaction energy !

➔ ??

Goal: *microscopic* definitions that preserve the structure of thermodynamic laws

# Macroscopic thermodynamics

air (T)



rubber band
length = L

variables: (L,T) … *equilibrium state*

state functions:

| | |
|---|---|
| U | internal energy |
| S | entropy |
| Ψ | tension |

thermodynamic potential: $F = U - ST$ Helmholtz free energy

First Law: $\Delta U = Q + W$ $$W = \int \Psi \cdot dL$$

Second Law: $Q \leq T\Delta S$ Clausius inequality

$W \geq \Delta F$

… all about equilibrium states and thermodynamic processes

# Statistical mechanics

x = (**q**,**p**) = microstate of system

$U_{sys}(x;\lambda)$ = Hamiltonian (energy function)

*equilibrium states* (λ,T)

⟷ statistical ensembles

$$p^{eq}(x;\lambda,T) = \frac{1}{Z}\exp\left[-\beta U_{sys}(x;\lambda)\right] \qquad \beta = \frac{1}{k_B T}$$

fluctuating observable

state functions

$$U = \int p^{eq} U_{sys}$$

$$S = -\int p^{eq} \ln p^{eq}$$

$$F = -k_B T \ln Z$$

→ $F = U - ST$

# Statistical mechanics

x = (**q**,**p**) = microstate of system

$U_{sys}(x;\lambda)$ = Hamiltonian (energy function)

*thermodynamic processes*

$$\lambda : A \to B\,,\ \ 0 \le t \le \tau$$

λ(t) = *protocol* - how we act on the system
x(t) = *trajectory* - how the system responds

$$U_{sys}\left(x_\tau;B\right)-U_{sys}\left(x_0;A\right)=\int_0^\tau dt\,\dot{x}\,\frac{\partial U_{sys}}{\partial x}+\int_0^\tau dt\,\dot{\lambda}\,\frac{\partial U_{sys}}{\partial \lambda}=Q+W$$

Average over realizations:
$A \to B$

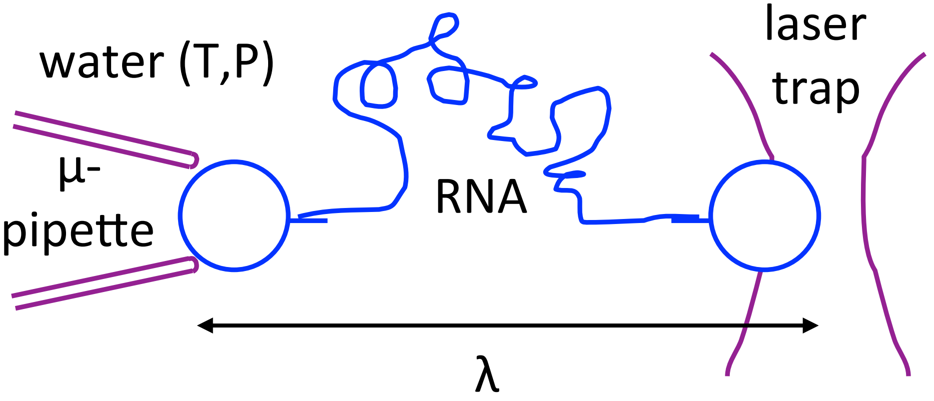
$$\Delta U = \left\langle Q \right\rangle + \left\langle W \right\rangle$$ First Law

$$\left\langle W \right\rangle \ge \Delta F$$ Second Law

$$F = U - ST$$

# *Nanoscale* statistical mechanics

x = microstate of system
y = microstate of environment
λ = work parameter

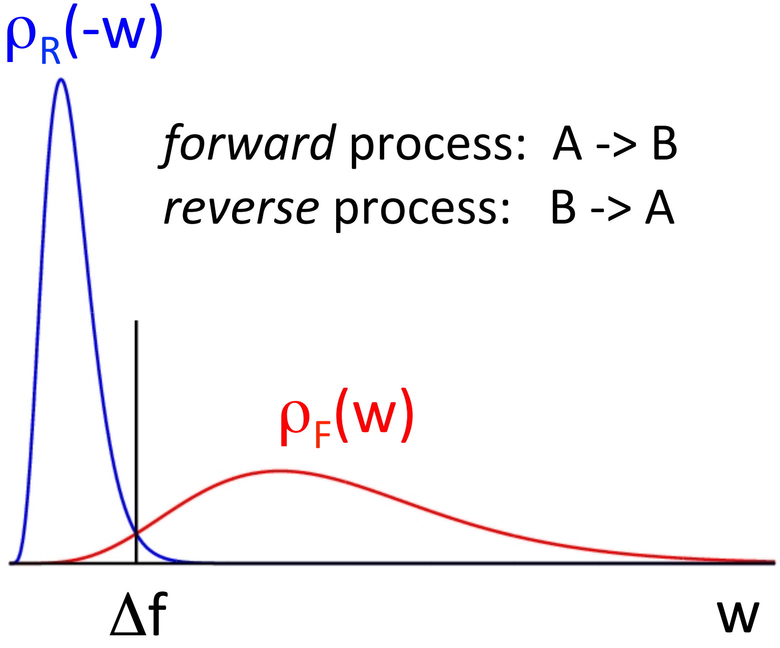


## *Fluctuation Theorems*

$$\left\langle e^{-\beta w}\right\rangle = e^{-\beta\Delta f}$$

$$\frac{\rho_F(+w)}{\rho_R(-w)} = \exp\left[\beta\left(w-\Delta f\right)\right]$$

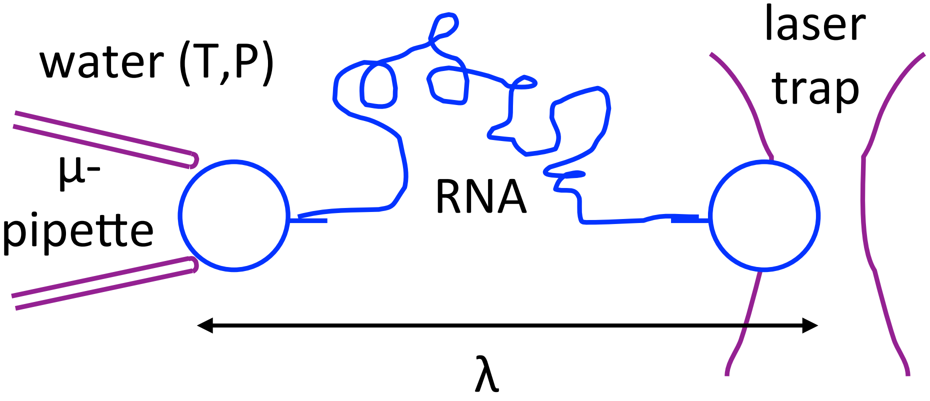
… & others



*forward* process: A -> B
*reverse* process: B -> A

# *Nanoscale* statistical mechanics

x = microstate of system
y = microstate of environment
λ = work parameter



## *Fluctuation Theorems*

$$\left\langle e^{-\beta w} \right\rangle = e^{-\beta \Delta f}$$

$$\frac{\rho_F(+w)}{\rho_R(-w)} = \exp\left[\beta\left(w - \Delta f\right)\right]$$

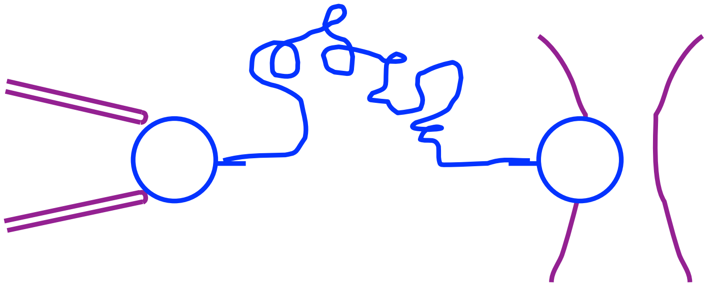
… & others

$\Delta f$ or $\Delta g$ ?

| Thermodynamics | Statistical Mechanics |
|---|---|
| equilibrium states | ensembles $p^{eq} \propto e^{-\beta U_{sys}}$ |
| thermodynamic processes | trajectories |
| F = U - ST | F = U - ST |
| Q + W = ΔU | <Q> + <W> = ΔU |
| W ≥ ΔF | <W> ≥ ΔF |
|  | + *fluctuation theorems* |

$$U_{S+E}(x,y;\lambda) = u_{sys}(x;\lambda) + U_{env}(y) + \boxed{u_{\text{int}}(x,y)}$$

can't be neglected !



## Thermodynamics

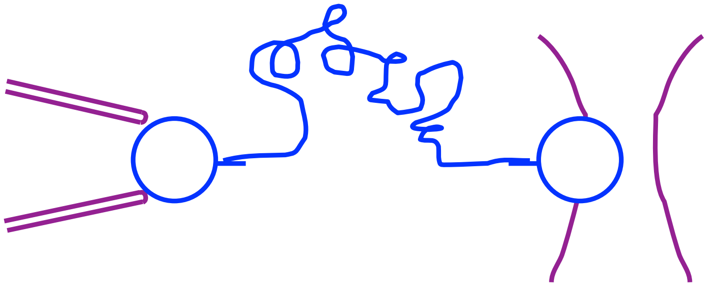
## Statistical Mechanics

Develop a statistical mechanical framework that:

- [correctly describes the equilibrium state of a nanoscale system]
- provides precise microscopic definition of relevant state functions (internal energy, entropy, free energy, etc.), heat & work
- includes statements of first & second laws, fluctuation theorems
- scales up to macroscopic thermodynamics, when the system is large

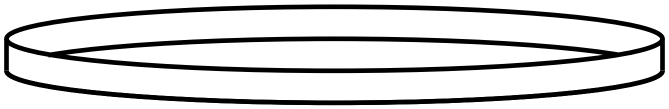
$$U_{S+E}(x,y;\lambda) = u_{sys}(x;\lambda) + U_{env}(y) + u_{\text{int}}(x,y)$$

can’t be neglected !



# Macroscopic thermodynamics revisited

air (T,P)



rubber band
length = L

variables: (L,T,P)

state functions:

| | |
|---|---|
| U | internal energy |
| S | entropy |
| Ψ | tension |
| V | volume |

thermodynamic potentials:

$F = U - ST$ Helmholtz free energy

$H = U + PV$ enthalpy

$G = H - ST$ Gibbs free energy

First Law:

$\Delta U = Q + W - P\Delta V$

$\Delta H = Q + W$

$$W = \int \Psi \cdot dL$$

"non-PdV work"

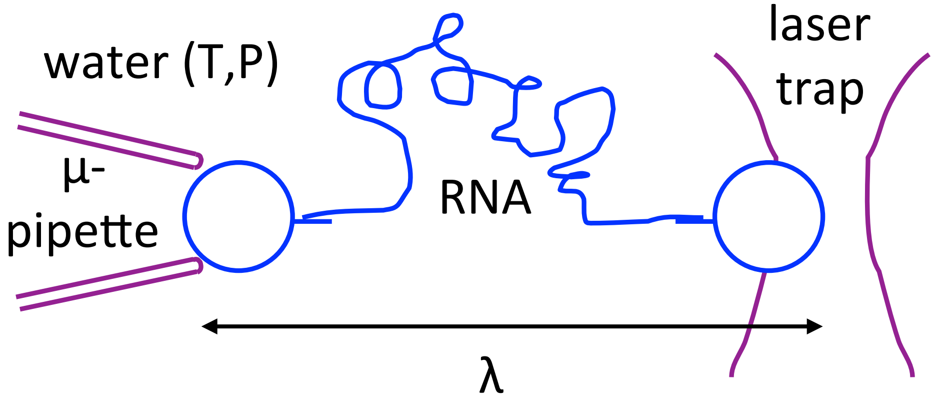
Second Law:

$Q \le T\Delta S$ Clausius inequality

$W \ge \Delta G$

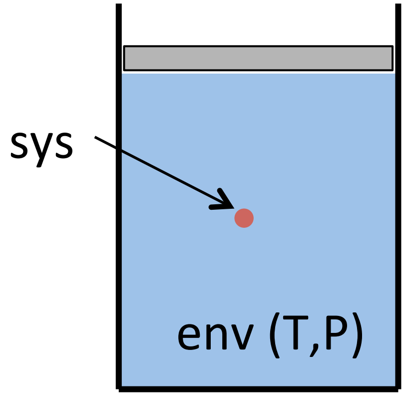
# Nanoscale statistical mechanics - setup

x = microstate of system
y = microstate of environment
λ = work parameter



$$U_{S+E}(x,y;\lambda) = u_{sys}(x;\lambda) + U_{env}(y) + u_{\text{int}}(x,y)$$

<u>fluctuating observable</u>



$$p^{eq}(x,y;\lambda) = \frac{1}{Z_{S+E}} \exp(-\beta U_{S+E})$$

Define <u>state functions</u> *u, s, v, h, g* that describe the thermodynamic state of the *system of interest*.

# Equilibrium state of the system of interest

$$p^{eq}(x,y;\lambda) = \frac{1}{Z_{S+E}} \exp\left(-\beta U_{S+E}\right) \qquad U_{S+E} = u_{sys} + U_{env} + u_{\mathrm{int}}$$

$$\begin{aligned} p^{eq}(x;\lambda) &= \int dy\, p^{eq}(x,y;\lambda) \\ &= \frac{1}{Z_{S+E}} \exp\left(-\beta u_{sys}\right) \int dy \exp\left[-\beta\left(U_{env} + u_{\mathrm{int}}\right)\right] \\ &\propto \boxed{e^{-\beta\left(u_{sys}+\phi\right)}} \end{aligned}$$

$$\phi \to 0 \;\; as \;\; u_{\mathrm{int}} \to 0$$

$$\phi(x) = -\frac{1}{\beta} \ln \frac{\int dy \exp\left[-\beta\left(U_{env} + u_{\mathrm{int}}\right)\right]}{\int dy \exp\left(-\beta U_{env}\right)}$$

# Equilibrium state of the system of interest

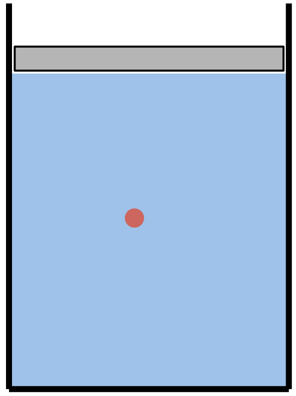
$$p^{eq}(x;\lambda) \propto \exp\left[-\beta\left(u_{sys}+\phi\right)\right] \overset{?}{=} \exp\left(-\beta \overline{u}_{sys}\right)$$

U. Seifert, Phys Rev Lett **116**, 020601 (2016)

$$\phi(x) = -\frac{1}{\beta}\ln\frac{\int dy\, \exp\left[-\beta\left(U_{env}+u_{\text{int}}\right)\right]}{\int dy\, \exp\left(-\beta U_{env}\right)}$$

= *solvation free energy* for system in “frozen” microstate x

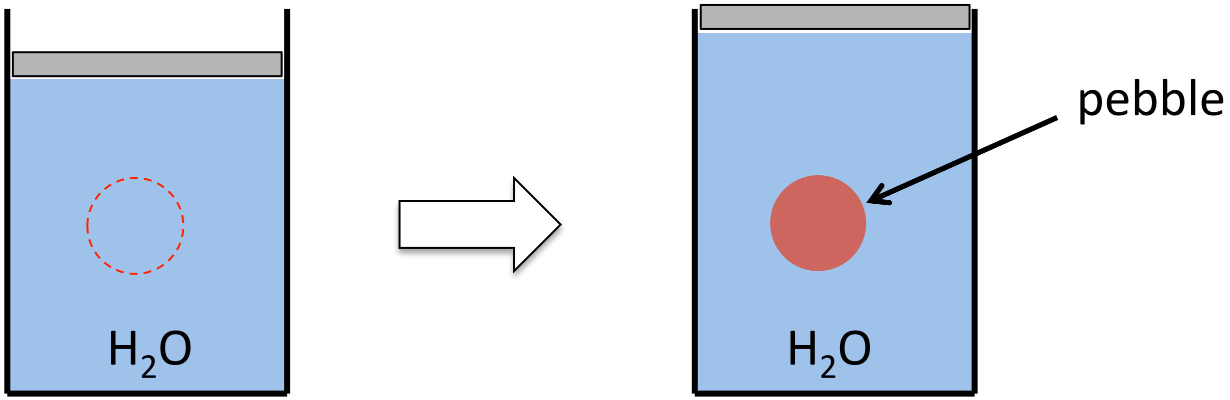
= *reversible work* required to insert system into environment



J.G. Kirkwood, *J Chem Phys* **3**, 300 (1935)

# Solvation free energy and volume

Macroscopic system:



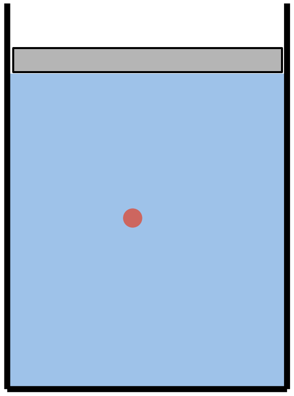
$\phi$ = solvation free energy = reversible work of insertion = P $V_{peb}$

$$V_{peb} = \phi / P$$

“thermodynamic” definition of $V_{peb}$

Use this relation to *define* the volume of our microscopic system:

$$\boxed{v_{sys}\left(x\right) \equiv \phi\left(x\right) / P}$$



# Fluctuating observables and state functions

$$\begin{aligned} p^{eq}(x;\lambda) &\propto \exp\left[-\beta\left(u_{sys}+\phi\right)\right] \\ &= \exp\left[-\beta\left(u_{sys}+P\,v_{sys}\right)\right] \\ &\equiv \exp\left(-\beta h_{sys}\right) \end{aligned}$$

$$v_{sys}(x) \equiv \phi(x)/P$$

fluctuating observables

Now define state functions (of λ,T,P):

$$u \equiv \int dx\, p^{eq}\, u_{sys}(x;\lambda)$$

$$v \equiv \int dx\, p^{eq}\, v_{sys}(x)$$

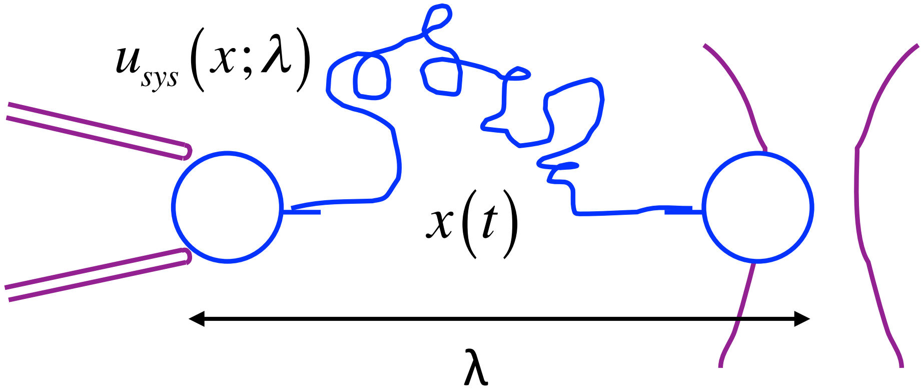
$$h \equiv \int dx\, p^{eq}\, h_{sys}(x;\lambda)$$

$$s \equiv -\int dx\, p^{eq} \ln p^{eq}$$

$$g \equiv -\frac{1}{\beta}\ln\int dx \exp\left[-\beta\left(u_{sys}+P\,v_{sys}\right)\right]$$

$$\longrightarrow \quad \boxed{\begin{aligned} h &= u + Pv \\ g &= h - sT \end{aligned}}$$

# First Law of Thermodynamics , ΔU = Q – PΔV + W



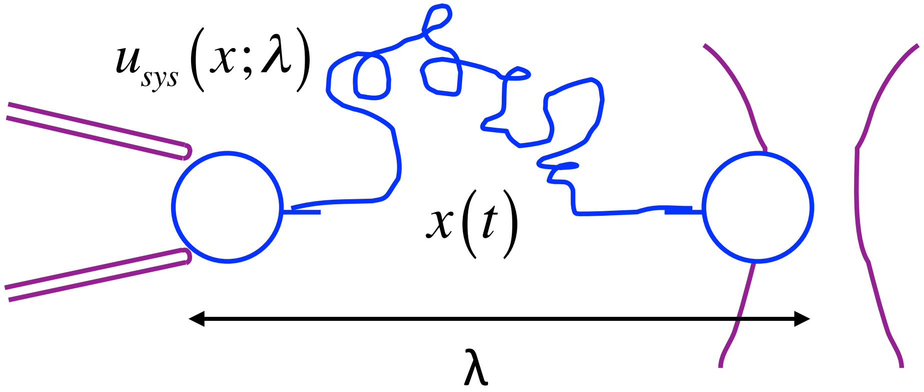
$$\lambda : A \rightarrow B$$

$$h_{sys}(x;\lambda) \equiv u_{sys}(x;\lambda) + Pv_{sys}(x)$$

$$\Delta u_{sys} = \int dt \left( \dot{x}\frac{\partial u_{sys}}{\partial x} + \dot{\lambda}\frac{\partial u_{sys}}{\partial \lambda} \right) = \underbrace{\int dt\, \dot{x}\frac{\partial h_{sys}}{\partial x}}_{\text{heat (Q)}} - \underbrace{\int P\, dv_{sys}}_{\text{PdV work (-P ΔV)}} + \underbrace{\int dt\, \dot{\lambda}\frac{\partial u_{sys}}{\partial \lambda}}_{\text{non-PdV work (W)}}$$

$$\boxed{q \equiv \int dt\, \dot{x}\frac{\partial h_{sys}}{\partial x}} \qquad \boxed{w \equiv \int dt\, \dot{\lambda}\frac{\partial u_{sys}}{\partial \lambda}}$$

# First Law of Thermodynamics , ΔU = Q – PΔV + W



$$\lambda : A \rightarrow B$$

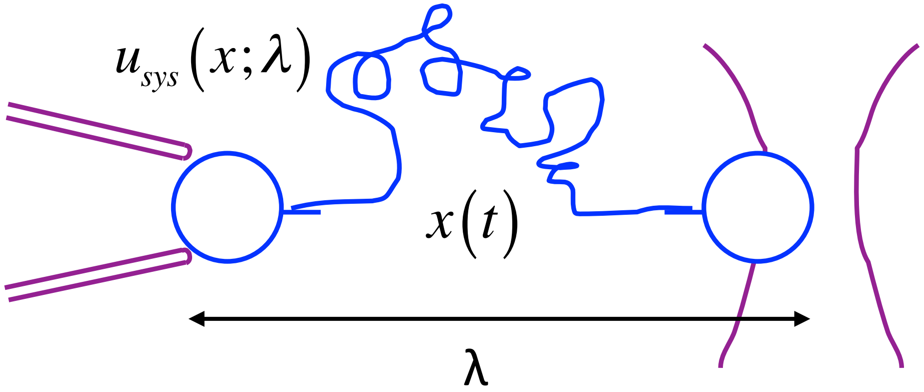
$$h_{sys}(x;\lambda) = u_{sys}(x;\lambda) + Pv_{sys}(x)$$

$$\Delta u_{sys} = \int dt\left(\dot{x}\frac{\partial u_{sys}}{\partial x} + \dot{\lambda}\frac{\partial u_{sys}}{\partial \lambda}\right) = \int dt\,\dot{x}\frac{\partial h_{sys}}{\partial x} - \int P\,dv_{sys} + \int dt\,\dot{\lambda}\frac{\partial u_{sys}}{\partial \lambda}$$

$$= q - P\Delta v_{sys} + w$$

$$\boxed{q \equiv \int dt\,\dot{x}\frac{\partial h_{sys}}{\partial x}} \qquad \boxed{w \equiv \int dt\,\dot{\lambda}\frac{\partial u_{sys}}{\partial \lambda}} = \int dt\,\dot{\lambda}\frac{\partial h_{sys}}{\partial \lambda}$$

# First Law of Thermodynamics ,  ΔU = Q – PΔV + W



$$\lambda : A \rightarrow B$$

$$h_{sys}(x;\lambda) = u_{sys}(x;\lambda) + Pv_{sys}(x)$$

$\Delta u_{sys} = q - P\Delta v_{sys} + w$   for one realization of the process

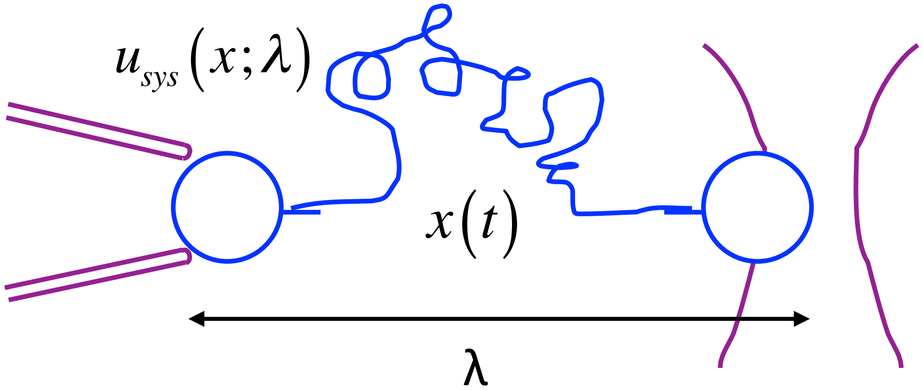
Averaging over an ensemble of realizations from one equilibrium state to another gives:

$$\Delta u = \langle q \rangle - P\Delta v + \langle w \rangle$$

$$\Delta h = \langle q \rangle + \langle w \rangle$$

$$q \equiv \int dt\, \dot{x} \frac{\partial h_{sys}}{\partial x} \qquad w \equiv \int dt\, \dot{\lambda} \frac{\partial u_{sys}}{\partial \lambda} = \int dt\, \dot{\lambda} \frac{\partial h_{sys}}{\partial \lambda}$$

# Second Law of Thermodynamics , W ≥ ΔG



$$\lambda : A \rightarrow B$$

$$h_{sys}(x;\lambda) = u_{sys}(x;\lambda) + Pv_{sys}(x)$$

$$w \equiv \int dt\, \dot{\lambda} \frac{\partial u_{sys}}{\partial \lambda} \Rightarrow \left\{ \begin{array}{l} \left\langle e^{-\beta w} \right\rangle = e^{-\beta \Delta g} \\ \\ \dfrac{\rho_F(+w)}{\rho_R(-w)} = e^{\beta(w-\Delta g)} \end{array} \right. \Rightarrow \boxed{\langle w \rangle \geq \Delta g}$$

$$g \equiv -\frac{1}{\beta} \ln \int dx \exp\left[-\beta\left(u_{sys} + P\, v_{sys}\right)\right] = u + Pv - sT$$

# Summary to this point

$$p^{eq}(x;\lambda) = \frac{1}{Z}\exp\left[-\beta\left(u_{sys}+\phi\right)\right]$$

| | | |
|---|---|---|
| Internal energy | $u_{sys}(x;\lambda)$ | $u = \langle u_{sys}\rangle^{eq}$ |
| Volume | $v_{sys}(x) = \phi / P$ | $v = \langle v_{sys}\rangle^{eq}$ |
| Enthalpy | $h_{sys} = u_{sys} + Pv_{sys}$ | $h = \langle h_{sys}\rangle^{eq}$ |
| Entropy | | $s = -\langle \ln p^{eq}\rangle^{eq}$ |
| Gibbs free energy | | $g = -\beta^{-1}\ln Z$ |
| Heat , Work | $\dot{q} = \dot{x}\,\partial_x h_{sys}$ , $\dot{w} = \dot{\lambda}\,\partial_\lambda u_{sys}$ | |

$$h = u + Pv \qquad \Delta h = \langle q\rangle + \langle w\rangle$$

$$g = h - sT \qquad \langle w\rangle \geq \Delta g$$

&

$$\left\langle e^{-\beta w}\right\rangle = e^{-\beta\Delta g}$$

$$\frac{\rho_F(+w)}{\rho_R(-w)} = e^{\beta(w-\Delta g)}$$

# Summary to this point

$$p^{eq}(x;\lambda) = \frac{1}{Z}\exp\left[-\beta\left(u_{sys} + \phi\right)\right]$$

| | | |
|---|---|---|
| Internal energy | $u_{sys}(x;\lambda)$ | $u = \langle u_{sys} \rangle^{eq}$ |
| Volume | $v_{sys}(x) = \phi / P$ | $v = \langle v_{sys} \rangle^{eq}$ |
| Enthalpy | $h_{sys} = u_{sys} + P v_{sys}$ | $h = \langle h_{sys} \rangle^{eq}$ |
| Entropy | | $s = -\langle \ln p^{eq} \rangle^{eq}$ |
| Gibbs free energy | | $g = -\beta^{-1} \ln Z$ |
| Heat , Work | $\dot{q} = \dot{x}\,\partial_x h_{sys}$ , $\dot{w} = \dot{\lambda}\,\partial_\lambda u_{sys}$ | |

Also: *u,v,h,s,g -> U,V,H,S,G for a macroscopic system of interest*.

*bare* representation

C.J., Phys Rev X **7**, 011008 (2017)

# Alternative framework

$$\overline{v}_{sys}(x) = \partial\phi / \partial P$$

$$\phi_T \equiv T\frac{\partial\phi}{\partial T} \quad , \quad \phi_P \equiv P\frac{\partial\phi}{\partial P}$$

| | |
|---|---|
| Internal energy | $\overline{u} = u + \langle\phi\rangle^{eq} - \langle\phi_T\rangle^{eq} - \langle\phi_P\rangle^{eq}$ |
| Volume | $\overline{v} = \langle\overline{v}_{sys}\rangle^{eq}$ |
| Enthalpy | $\overline{h} = h - \langle\phi_T\rangle^{eq}$ |
| Entropy | $\overline{s} = s - \frac{\langle\phi_T\rangle^{eq}}{T}$ |
| Gibbs free energy | $\overline{g} = g$ |
| Heat , Work | $\overline{q} = q - \Delta\phi_T \quad , \quad \overline{w} = w$ |

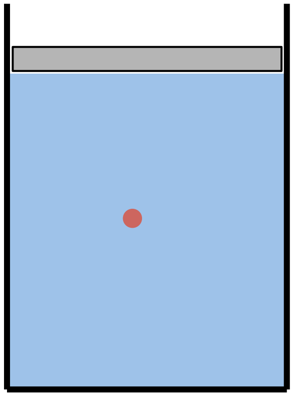
~ Seifert
PRL (2016)

Also: $\overline{u}$,$\overline{v}$,$\overline{h}$,$\overline{s}$,$\overline{g}$ *-> U,V,H,S,G for a macroscopic system of interest*.

*partial molar* representation

C.J., Phys Rev X **7**, 011008 (2017)

# Derivation of $\left\langle e^{-\beta w} \right\rangle = e^{-\beta \Delta g}$



$$p^{eq}(x,y;\lambda) = \frac{1}{Z_{S+E}} \exp(-\beta U_{S+E})$$

$$U_{S+E}(\zeta;\lambda) = u_{sys}(x;\lambda) + \underset{\uparrow}{U_{env}}(y) + u_{\mathrm{int}}(x,y)$$

includes the piston

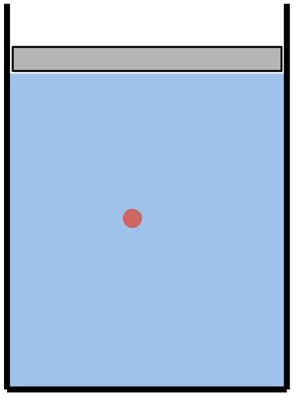
$\zeta=(x,y)$

Assume:

(1) Initial conditions are sampled from $p^{eq}(x,y;\lambda)$.

(2) Evolution is governed by Hamiltonian dynamics, with externally imposed protocol $\lambda(t)$.

# Derivation of $\left\langle e^{-\beta w} \right\rangle = e^{-\beta \Delta g}$

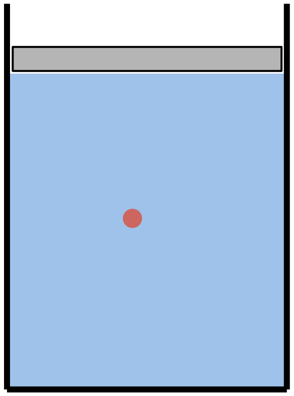


$$p^{eq}(x,y;\lambda) = \frac{1}{Z_{S+E}} \exp\left(-\beta U_{S+E}\right)$$

$$U_{S+E}(\zeta;\lambda) = u_{sys}(x;\lambda) + U_{env}(y) + u_{\text{int}}(x,y)$$

$$w = \int_0^\tau dt\, \dot{\lambda} \frac{\partial u_{sys}}{\partial \lambda} = \int_0^\tau dt\, \dot{\lambda} \frac{\partial U_{S+E}}{\partial \lambda} = U_{S+E}(\zeta_\tau;B) - U_{S+E}(\zeta_0;A)$$

# Derivation of $\left\langle e^{-\beta w} \right\rangle = e^{-\beta \Delta g}$

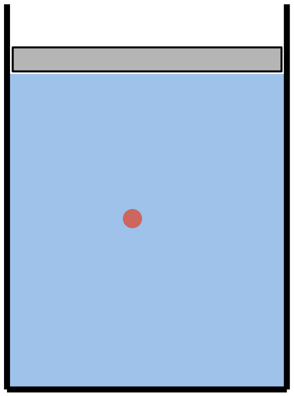


$$p^{eq}(x,y;\lambda) = \frac{1}{Z_{S+E}} \exp\left(-\beta U_{S+E}\right)$$

$$w = U_{S+E}\left(\zeta_\tau; B\right) - U_{S+E}\left(\zeta_0; A\right)$$

$$\begin{aligned} Z_{S+E}(\lambda) &= \int d\zeta \exp\left(-\beta U_{S+E}\right) \\ &= \int dx \exp\left[-\beta\left(u_{sys} + \phi\right)\right] \cdot \int dy \;\; \exp\left(-\beta U_{env}\right) \\ &= \exp\left[-\beta g(\lambda)\right] \cdot Z_{env} \end{aligned}$$

# Derivation of $\left\langle e^{-\beta w} \right\rangle = e^{-\beta \Delta g}$



$$p^{eq}(x,y;\lambda) = \frac{1}{Z_{S+E}} \exp\left(-\beta U_{S+E}\right)$$

$$w = U_{S+E}(\zeta_\tau;B) - U_{S+E}(\zeta_0;A)$$

$$Z_{S+E}(\lambda) = \exp\left[-\beta g(\lambda)\right] \cdot Z_{env}$$

$$\zeta_\tau = \zeta_\tau(\zeta_0)$$

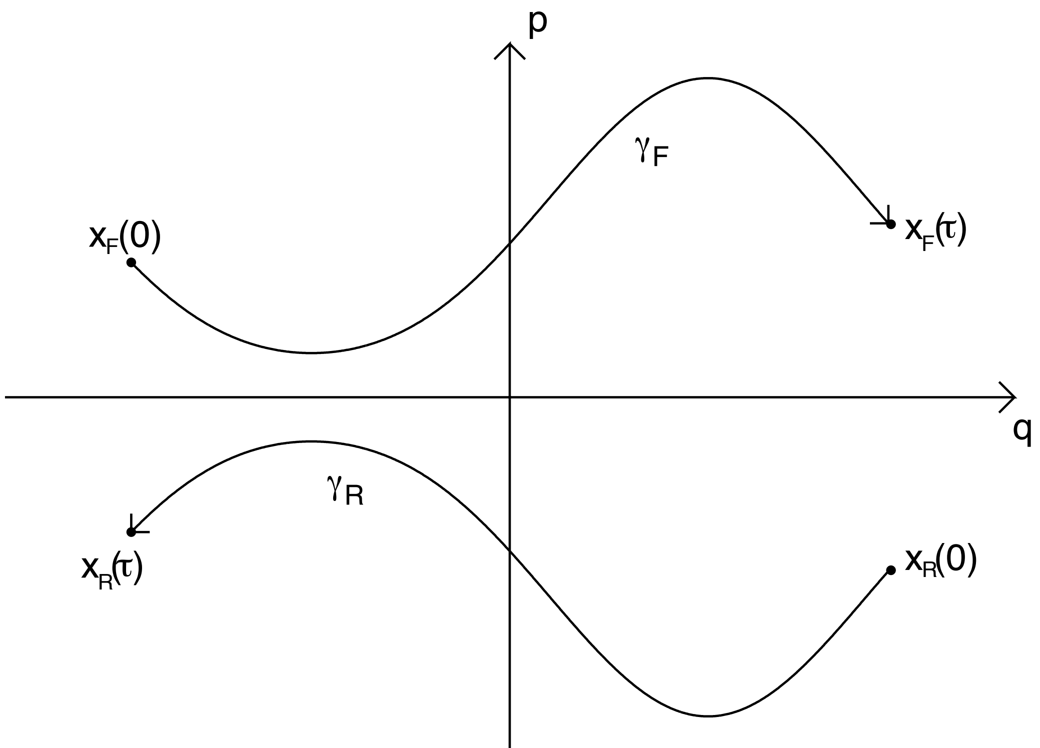
$$\left\langle e^{-\beta w} \right\rangle = \int d\zeta_0 \, \frac{\exp\left[-\beta U_{S+E}(\zeta_0;A)\right]}{Z_{S+E}(A)} \exp(-\beta w)$$

$$= \frac{1}{Z_{S+E}(A)} \int d\zeta_0 \, \exp\left[-\beta U_{S+E}(\zeta_\tau;B)\right] = \frac{Z_{S+E}(B)}{Z_{S+E}(A)} \quad = e^{-\beta \Delta g}$$

# Conjugate (forward & reverse) processes

*Forward* process: A->B
*Reverse* process: A<-B

$$\lambda_t^F = \lambda_{\tau-t}^R$$

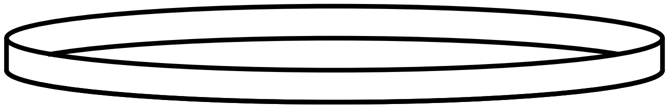


$$\boxed{\frac{P^F[x_t^F \mid x_0^F)}{P^R[x_t^R \mid x_0^R)} = \exp\left(-\beta q\left[x_t^F\right]\right)}$$

compare w/
G.E. Crooks, J Stat Phys
**90**, 1481 (1998)

# Summary

C.J., Phys Rev X **7**, 011008 (2017)



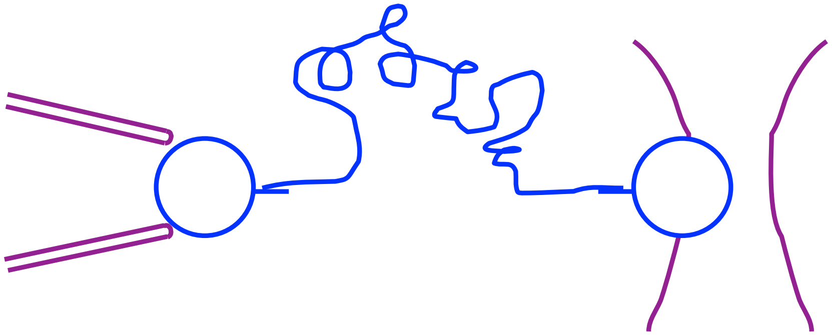
state functions *U*, *V*, *S* …

thermodynamic potentials

$H=U+PV$ , $G=H-ST$

1st Law: $\Delta H = Q+W$

2nd Law: $W \geq \Delta G$



**?**

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$$p^{eq}(x;\lambda)=\frac{1}{Z}\exp\left[-\beta\left(u_{sys}+\phi\right)\right]$$

| | | |
|---|---|---|
| Internal energy | $u_{sys}(x;\lambda)$ | $u=\langle u_{sys}\rangle^{eq}$ |
| Volume | $\boxed{v_{sys}(x)=\phi/P}$ | $v=\langle v_{sys}\rangle^{eq}$ |
| Enthalpy | $h_{sys}=u_{sys}+Pv_{sys}$ | $h=\langle h_{sys}\rangle^{eq}$ |
| Entropy | | $s=-\langle \ln p^{eq}\rangle^{eq}$ |
| Gibbs free energy | | $g=-\beta^{-1}\ln Z$ |
| Heat , Work | $\dot{q}=\dot{x}\,\partial_x h_{sys}$ , $\dot{w}=\dot{\lambda}\,\partial_\lambda u_{sys}$ | |

$$h=u+Pv \qquad \Delta h=\langle q\rangle+\langle w\rangle$$

$$g=h-sT \qquad \langle w\rangle\geq\Delta g$$

&

$$\left\langle e^{-\beta w}\right\rangle=e^{-\beta\Delta g}$$

$$\frac{\rho_F(+w)}{\rho_R(-w)}=e^{\beta(w-\Delta g)}$$