Lecture 8

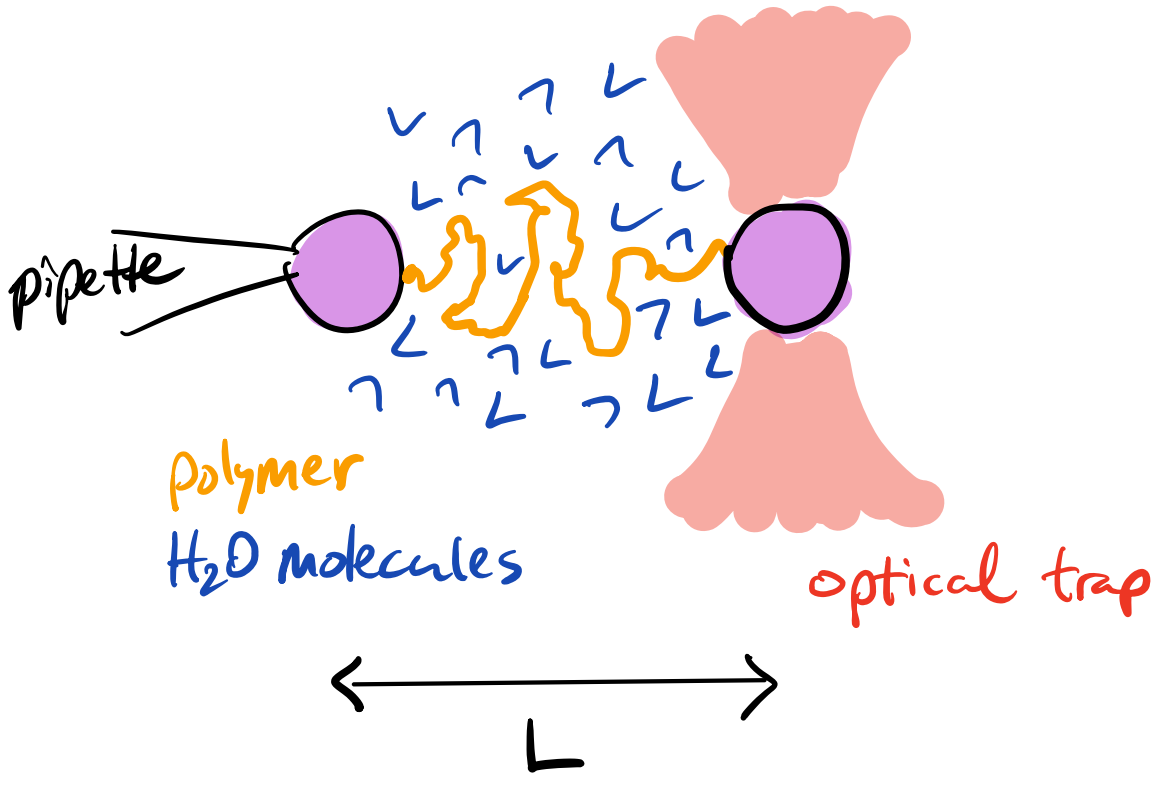
Recall from last lecture...

$$dW \geq (dA)_T$$

The most work that can be extracted comes from a reversible transformation, in which case

$$W = \Delta A = A(N, V_f, T) - A(N, V_i, T)$$

These ideas extend beyond gasses and pistons. They also apply to microscopic systems...



Reversible Work Theorem:

$$\frac{P(L_f)}{P(L_i)} = e^{-\beta W_{rev}(L_i \to L_f)}$$

$$= e^{-\beta[A(L_f) - A(L_i)]}$$

Spontaneous fluctuations

Doing work to stretch the polymer

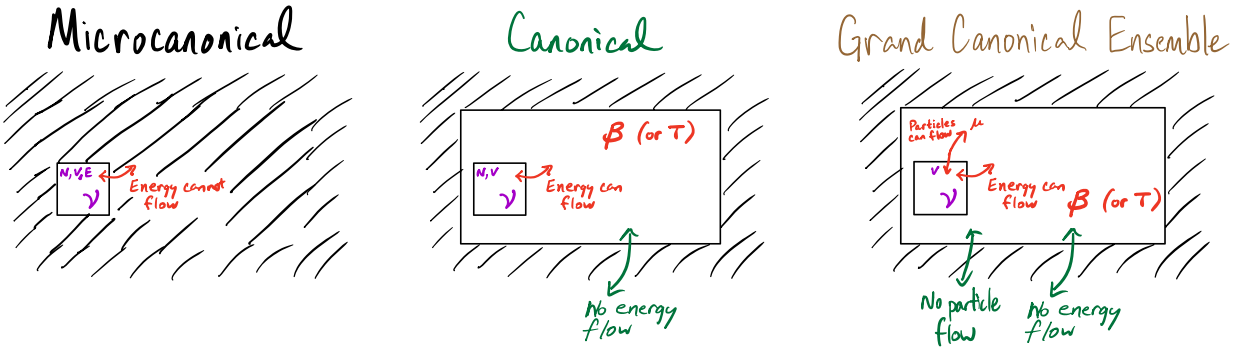
Why was this free energy an A (Helmholtz)?

I thought Helmholtz was $A(N, V, T)$

Here, we have a fixed number (of monomers) N, a fixed temperature T, but the extent of our system is measured in terms of the 1d L, not the 3d V.

Ensembles or how do I replace a rigid constraint by a "softened" exponential bias?

(probability distribution for microstate ν)



	Microcanonical	Canonical	Grand Canonical Ensemble
What is held fixed?	N, V, E	N, V, T	μ, V, T
$P(\nu)$?	$P(\nu) \propto \begin{cases} 1, & \text{Rigid constraints are met} \\ 0, & \text{Otherwise} \end{cases}$	$P(\nu) \propto \begin{cases} e^{-\beta E(\nu)}, & \text{Rigid constraints are met} \\ 0, & \text{Otherwise} \end{cases}$	$P(\nu) \propto \begin{cases} e^{+\beta\mu N(\nu) - \beta E(\nu)}, & \text{Rigid constraint (only } V\text{!) met} \\ 0, & \text{Otherwise} \end{cases}$
Partition Function? (Normalization)	$\Omega(N,V,E) = \sum_{\nu \text{ meeting rigid constraints}} 1$	$Q(N,V,T) = \sum_{\nu \text{ meeting rigid constraints}} e^{-\beta E(\nu)}$	$\mathcal{Z}(\mu,V,T) = \sum_{\nu \text{ meeting rigid constraints}} e^{+\beta\mu N(\nu) - \beta E(\nu)}$
Thermodynamic Potential? (Effective Energy)	$S(N,V,E) = k_B \ln \Omega(N,V,E)$ Entropy	$A(N,V,T) = -k_B T \ln Q(N,V,T)$ Helmholtz Free Energy	$\Phi(\mu,V,T) = -k_B T \ln \mathcal{Z}(\mu,V,T)$ Grand Potential

$$\mathcal{Z}(\mu,V,T) \approx e^{-\beta\left(E^* - TS(N^*,V,E^*) - \mu N^*\right)}$$

$$\Phi = E - TS - \mu N$$

like how we would write $A = E - TS$ in a thermo class.

What exactly is μ? μ is like β, a bath property

$$-\beta\mu = \left(\frac{\partial \ln \Omega_B}{\partial N_B}\right) \qquad \beta = \left(\frac{\partial \ln \Omega_B}{\partial E_B}\right)$$

Aside:

$$\frac{\partial \ln \Omega}{\partial N} = \frac{1}{k_B}\frac{\partial S}{\partial N}$$

$$dE = TdS - pdV + \mu dN$$

$$dS = \frac{dE + pdV - \mu dN}{T}$$

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}$$

$$\frac{\partial \ln \Omega}{\partial N} = -\frac{\mu}{k_B T} = -\beta\mu$$

Let's check that things are consistent w/ thermo manipulations... $\Phi = E - TS - \mu N$

$$d\Phi = dE - d(TS) - d(\mu N)$$
$$= dE - TdS - SdT - \mu dN - Nd\mu$$
$$= TdS - pdV + \mu dN - TdS - SdT - \mu dN - Nd\mu$$
$$= -pdV - SdT - Nd\mu$$

$\Rightarrow \Phi$ is a "natural function" of V, T, and μ

so Φ, generated from 2 Legendre transforms of S is indeed a function of .

How are the various partition functions related to each other?

$$\mathcal{Z}(\mu, V, T) = \sum_N \sum_E e^{\beta\mu N - \beta E} \Omega(N, V, E)$$

$$\mathcal{Z}(\mu, V, T) = \sum_{\nu \text{ meeting rigid constraints}} e^{+\beta\mu N(\nu) - \beta E(\nu)}$$

$$= \sum_N e^{\beta\mu N} \underbrace{\left(\sum_E e^{-\beta E} \Omega(N, V, E) \right)}_{Q(N, V, T)}$$

$$\mathcal{Z}(\mu, V, T) = \sum_N e^{\beta\mu N} Q(N, V, T)$$

$$Q(N, V, T) = \sum_E e^{-\beta E} \Omega(N, V, E)$$

By the Laplace transform!

What's up with Gibbs?

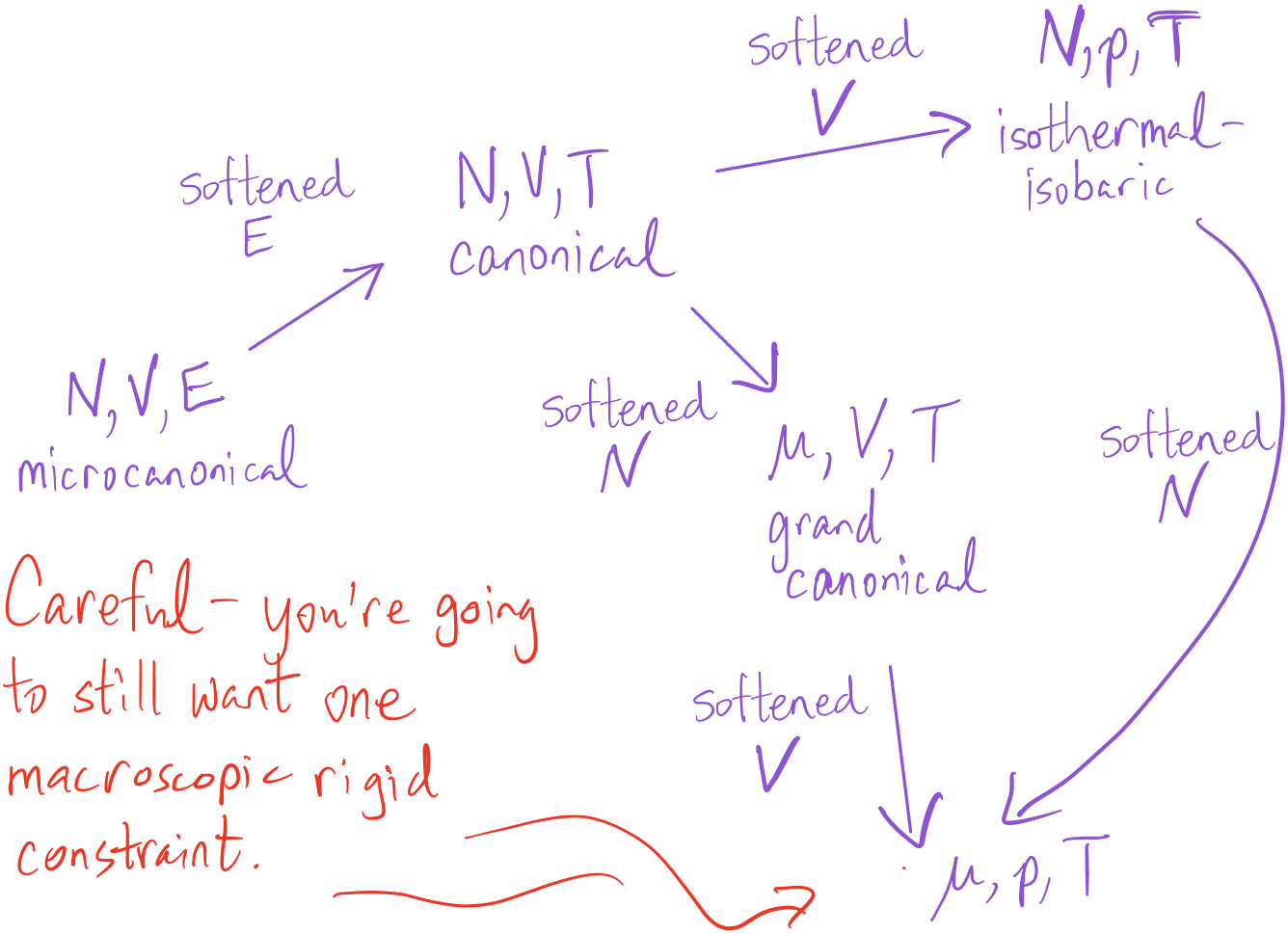
Isothermal-Isobaric Ensemble **N, p, T**

$$\Delta(N, p, T) = \sum_V \sum_E e^{-\beta(E + pV)} = \sum_V e^{-\beta pV} Q(N, V, T)$$

↖ Partition fn. for fixed N, fluctuating E + V

$$G(N, p, T) = -k_B T \ln \Delta(N, p, T)$$

Soft constraints vs. hard constraints...



Careful - you're going to still want one macroscopic rigid constraint.

What is wrong with μ, p, T?

First physical... I want ν to be all microstates for all system sizes?!

Now mathematically... taking three successive Legendre transforms of E gives an free energy for this "μ, p, T ensemble" of

$$E - TS + pV - \mu N$$

But this expression actually equals zero.

Why?

$$dE = TdS - pdV + \mu dN$$

Double the size $\Rightarrow$ $\quad E \to 2E \quad S \to 2S \quad V \to 2V \quad N \to 2N$

Let's parameterize everything by a variable c that counts how many copies of a system are glued together

$$\frac{dE}{dc}dc = T\frac{dS}{dc}dc - p\frac{dV}{dc}dc + \mu\frac{dN}{dc}dc$$

$$\Rightarrow \frac{dE}{dc} = T\frac{dS}{dc} - p\frac{dV}{dc} + \mu\frac{dN}{dc}$$

Intensive (independent of c)

$$\Rightarrow E = TS - pV + \mu N$$

Therefore $E - TS + pV - \mu N$ vanishes.

$$0 = d\left(E - TS - \mu N + pV\right)$$

$$= dE - d(TS) - d(\mu N) + d(pV)$$

$$= TdS - pdV + \mu dN - TdS - SdT - \mu dN - Nd\mu + pdV + Vdp$$

$$= -SdT - Nd\mu + Vdp$$

(Gibbs-Duhem)