Lecture 8

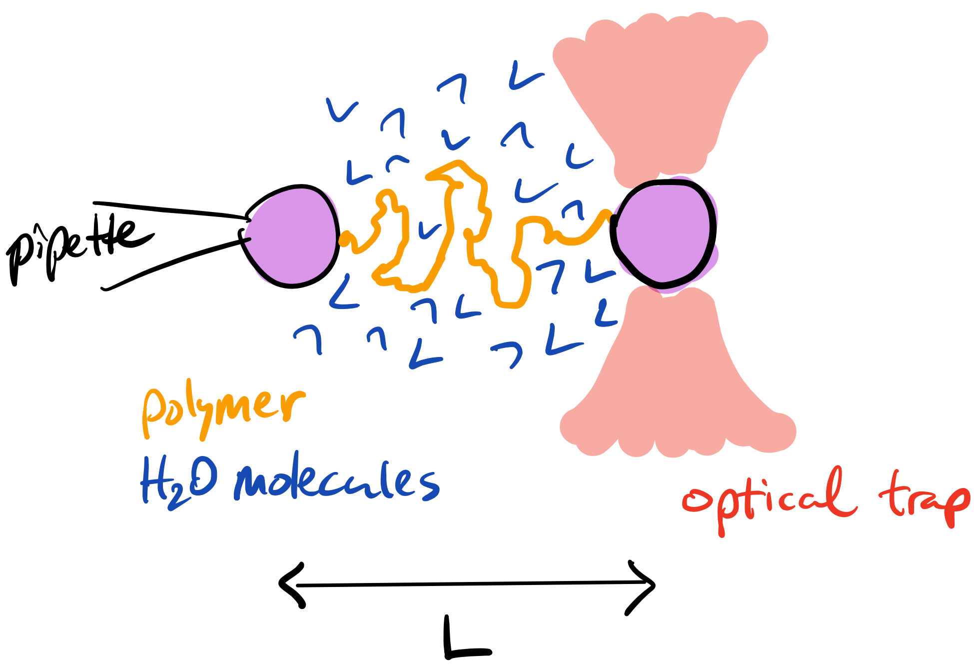
Recall from last lecture...

$$\boxed{đW \geq (dA)_T}$$

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

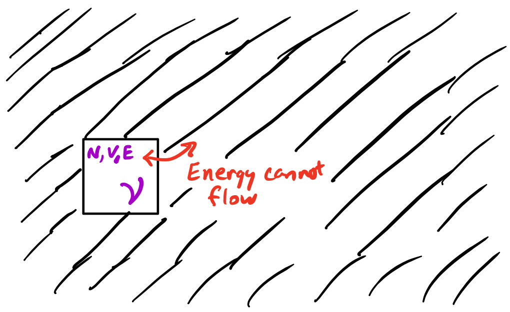
Why was the free energy an A (Helmholtz)?

- Controlling extent of the problem through a 1d L, not a 3d volume

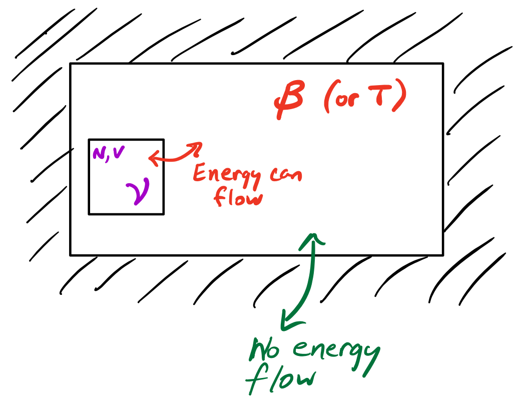
Ensembles or how do I replace a rigid constraint by a "softened" exponential bias?

Prob. dist. for ν

Microcanonical



Canonical



What is held fixed? N,V,E $\quad$ N,V,T

$P(\nu)$?

$$P(\nu) \propto \begin{cases} 1, & \text{Rigid constraints are met} \\ 0, & \text{Otherwise} \end{cases} \qquad P(\nu) \propto \begin{cases} e^{-\beta E(\nu)}, & \text{Rigid constraints are met} \\ 0, & \text{Otherwise} \end{cases}$$

Partition Function? (Normalization)

$$\Omega(N,V,E) = \sum_{\substack{\nu \text{ meeting} \\ \text{rigid constraints}}} 1 \qquad Q(N,V,T) = \sum_{\substack{\nu \text{ meeting} \\ \text{rigid constraints}}} e^{-\beta E(\nu)}$$

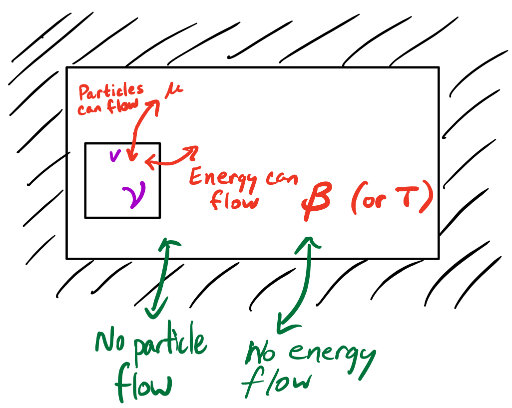
Thermodynamic Potential? (Effective Energy)

$$S(N,V,E) = k_B \ln \Omega(N,V,E) \qquad A(N,V,T) = -k_B T \ln Q(N,V,T)$$

$$Q(N,V,T) \approx e^{-\beta(E^* - TS(N,V,E^*))} = e^{-\beta A(N,V,T)}$$

thermodynamic limit
(large system)

What if particles can fluctuate too?



Grand Canonical Ensemble

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

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

What is held fixed? μ, V, T

$P(\nu)$? $P(\nu) \propto \begin{cases} e^{+\beta\mu N(\nu) - \beta E(\nu)}, & \text{Rigid constraint (only } V!) \text{ met} \\ 0, & \text{Otherwise} \end{cases}$

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

Thermodynamic Potential? (Effective Energy) Grand potential

$$\Phi(\mu, V, T) = -k_B T \ln \mathcal{Z}(\mu, V, T)$$

$$\mathcal{Z}(\mu, V, T) \approx e^{-\beta \underbrace{(E^* - TS(N^*, V, E^*) - \mu N^*)}_{\Phi = E - TS - \mu N}}$$

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

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

$$d\Phi = dE - d(TS) - d(\mu N)$$
$$= \cancel{TdS} - pdV + \cancel{\mu dN} - \cancel{TdS} - SdT - \cancel{\mu dN} - Nd\mu$$
$$= -pd\underline{V} - Sd\underline{T} - Nd\underline{\mu}$$

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

How are the various partition functions related to each other?

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

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

By the Laplace transform!

What's up with Gibbs?

Isothermal-Isobaric Ensemble $\quad N, p, T$

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

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...

$$\begin{tikzcd}
 & & \begin{array}{c} N,p,T \\ \text{isothermal-isobaric} \end{array} \arrow[dd, bend left, "\begin{array}{c}\text{softened}\\ N\end{array}"] \\
 & \begin{array}{c} N,V,T \\ \text{canonical} \end{array} \arrow[ur, "\begin{array}{c}\text{softened}\\ V\end{array}"] \arrow[d, "\begin{array}{c}\text{softened}\\ N\end{array}"'] & \\
\begin{array}{c} N,V,E \\ \text{microcanonical} \end{array} \arrow[ur, "\begin{array}{c}\text{softened}\\ E\end{array}"] & \begin{array}{c} \mu,V,T \\ \text{grand canonical} \end{array} \arrow[r, "\begin{array}{c}\text{softened}\\ V\end{array}"'] & \cancel{\mu,p,T}
\end{tikzcd}$$

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?

$$dE = T\,dS - p\,dV + \mu\,dN$$

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

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.

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

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

$$\cancel{TdS} - \cancel{pdV} + \cancel{\mu dN} - \cancel{TdS} - SdT - \cancel{\mu dN} - Nd\mu$$
$$+ \cancel{pdV} + Vdp$$

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

(Gibbs-Duhem)