

## Lecture 9

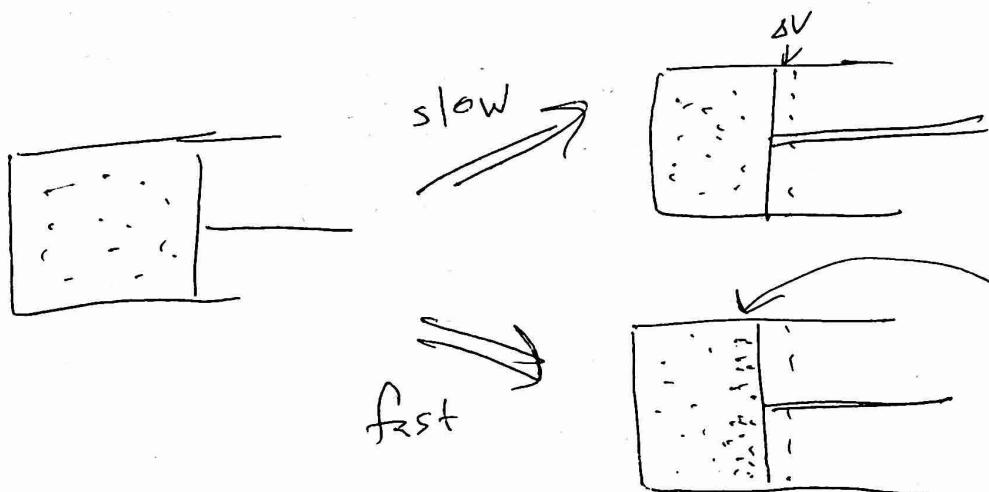
Recap: Work: Energy change in the system due to manipulated variables  
 $X = \{V, N, \dots\}$

$$dW = f_{ext} \cdot dX, \text{ e.g., } dW = -pdV = -p_{ext} dV$$

Heat: Everything else  $dQ = Tds$

So the first law is  $\boxed{dE = dQ + dW}$

We then talked about two possible compressions of a gas, one fast, one slow.



The gas particles don't look like their typical random state after the fast compression

The fast compression forces the system to sample configurations that do not look like the typical equilibrium configurations for  $T, V, N$ .

⇒ The effective pressure pushing up against the plunger is not the equilibrium value for that volume  $V - \Delta V$ .

It actually must push harder than equilibrium model predict.

After both compressors, allow the gas to re-equilibrate.

Now  $E(N, V, S)$  is a state function, so the final  $E$  must be the same in both processes (likewise for the initial  $E$ )

$$\Rightarrow \int_{\text{fast}} dt \frac{dE(t)}{dt}, \text{ which cl will write as } \int_{\text{fast}} dE = E_f - E_i$$

Similarly.  $\int_{\text{slow}} dE = \int_{\text{fast}} dE = E_f - E_i$

But the fast process effectively pushes against more molecules

$$\Rightarrow \int_{\text{fast}} dW > \int_{\text{slow}} dW \quad \left\{ \begin{array}{l} \text{Work done on the system} \\ \text{is greater in the fast process} \end{array} \right.$$

The first law then implies

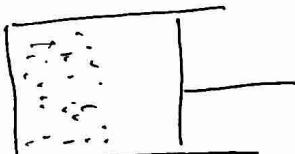
$$\int_{\text{fast}} dQ < \int_{\text{slow}} dQ$$

$dQ$  is the heat flow into the system but heat will flow out, so  $dQ$  is negative for the compression

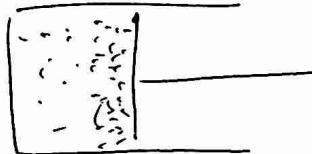
$\Rightarrow$  fast process has more heat flow out of the system

The best we'll ever be able to do is to go slowly (reversibly) so that the gas gets to re-equilibrate before cl pushing more.

What does "reversible" have to do with slow/fast protocols?



A fast expansion visits microstates like this



A fast compression visits microstates like this

If I quickly expand and compress, cl visit different microstates in the two directions. If I go slowly, I am always traveling through the typical equilibrium microstates.

$$\delta W \geq \delta W_{rev}$$

Reversible transformation requires the least amount of work at fixed  $T$ .

If we go reversibly, then we are dealing with the actual equilibrium pressure, e.g.,  $\delta W_{rev} = -pdV$ , so

$$dE = TdS + \delta W_{rev}$$

$$\Rightarrow \delta W_{rev} = dE - TdS$$

With a heat bath at fixed  $T$

$$\Rightarrow \delta W_{rev} = d(E - TS) = (dA)_T$$

Hence

$$\boxed{\delta W \geq (dA)_T}$$

(plugging into the box above)

The most work that can be extracted by letting the piston expand would be obtained from a reversible transformation. Then you would get out  $\Delta A = A(N, V_f, T) - A(N, V_i, T)$

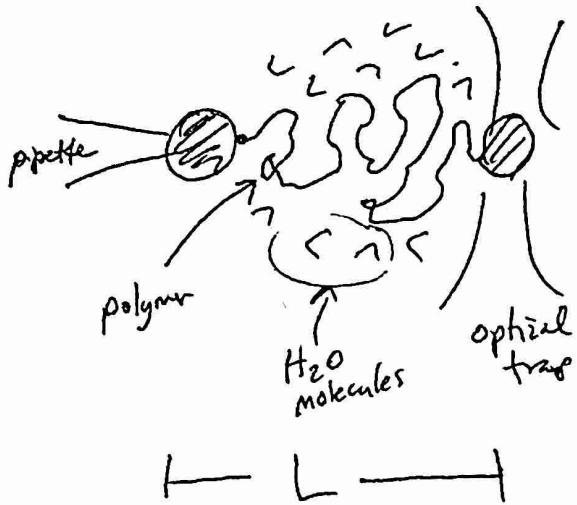


The energy  
which was  
free to be  
extracted.

Notice this energy you could get out is not

$$\Delta E = E(N, V_f, S_f) - E(N, V_i, S_i)$$

Yesterday we discussed heat and work in the context of gasses and pistons. These concepts are also important for microscopic systems.



I am going to measure  $L$   
but not the  $H_2O$  molecules ←  
nor the internal monomer positions  
(These constitute the bath)  
at temperature  $T$ .

My microstates  $\nu$  are given by the polymer configurations

$$\nu = (L, \{x_i\})$$

↑                      ↑  
 end-to-end      everything  
 distance          else

$$P(\nu) = \frac{e^{-\beta E(\nu)}}{Q}$$

What is  $P(L)$ ?

Free polymer at  
this point - free  
to fluctuate that is.

$$P(L) \propto \sum_{\{x_i\}} e^{-\beta E(L, \{x_i\})}$$

average over the degrees  
of freedom I'm not measuring.

$$\Rightarrow \ln P(L) = \ln(\text{constant}) + \ln \left( \sum_i e^{-\beta E(L, \{x_i\})} \right)$$

Differentiate w.r.t  $L$

$$\frac{d \ln P(L)}{dL} = \frac{\beta \sum_i \left( -\frac{dE(L, \{x_i\})}{dL} \right) e^{-\beta E(L, \{x_i\})}}{\left( \sum_i e^{-\beta E(L, \{x_i\})} \right)}$$

← This is the  
statistical  
weight for  
microstate  $\{x_i\}$   
when  $L$  is fixed

Therefore

$$\frac{d \ln P(L)}{d L} = \beta < -\frac{d E(L, \bar{\xi}_i \bar{\beta})}{d L}$$

$\bar{\xi}_i \bar{\beta}$

average over  
all the  $\xi_i \beta$ 's

$= \beta$  (mean force by polymer on coordinate L)

= -  $\beta$  (mean force applied to system to fix L)

Integrate wrt  $L$  from some initial  $L_i$  to final  $L_f$  ...

$$\ln P(L_f) - \ln P(L_i) = -\beta \int_{L_i}^{L_f} dL \left[ -\frac{\delta E(L, \xi_{i3})}{dL} \right] \xi_{i3}$$

distance      mean force

$$= -\beta \text{W}_{\text{rev}}$$

Why does this give the reversible work? If you pull L very slowly, the dynamics naturally averages over all the  $\epsilon_i$ ; at every length L, so the force you're pulling against will be the mean force.

$$\frac{P(L_f)}{P(L_i)} = e^{-\beta W_{\text{rev}}(L_i \rightarrow L_f)} = e^{-\beta [A(L_f) - A(L_i)]}$$

Reversible work

## Helmholtz free energy

Remember  $\ln Q = -\beta A$ , so we also could have

Considered

$$\frac{P(L_f)}{P(L_i)} = \frac{Q(L_f)}{Q(L_i)} = \frac{e^{-\beta A(L_f)}}{e^{-\beta A(L_i)}} = e^{-\beta \Delta_{\text{ref}}(L_i \rightarrow L_f)}$$

ratio of partition functions