Lecture 2

Last lecture...

$$P(\nu) = \begin{cases} \dfrac{1}{\Omega(E,V,N)} , & \text{if } E_\nu = E,\ N_\nu = N,\ V_\nu = V \\ 0 , & \text{otherwise} \end{cases}$$

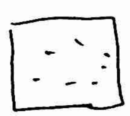
and $$\Omega = \sum_{\substack{\text{allowed} \\ \nu}} (1)$$

discrete

Remember, I am not being careful about distinguishing between discrete probability distributions and continuous probability densities. If ν is a continuous degree of freedom, $\Omega = \underbrace{\int d\nu\ (1)}$

like an area/volume

Dilute Sol'n:

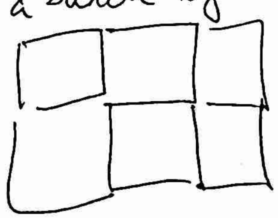


large building blocks of volume v, density ρ, and energy per particle ϵ

$$\underline{\tilde{\omega}(v, \rho, \epsilon)}$$

"number of microstates" (but we really mean something like that volume integral)

Take a bunch together



M independent blocks

$$\Rightarrow \Omega = \tilde{\omega}^M = \omega(v,\rho,\epsilon)^N$$

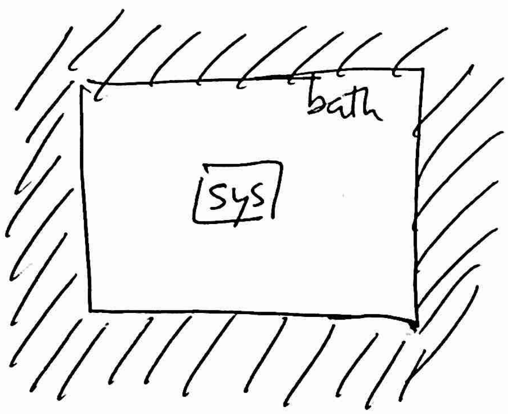
Last lecture we only wrote in the ϵ dependence because of what is to come...

$$\Omega = [\omega(\epsilon)]^N = \exp(N \ln \omega(\epsilon)).$$

Who has ever done an experiment on a closed isolated system? Me neither.

Perhaps you've done experiments with a fixed V and fixed N though.

Usually energy can be exchanged with a (much larger) bath/environment/reservoir/surroundings



Total energy E_T fixed.

System microstate: ν energy: $E(\nu)$

bath microstate: ν_B energy: $E_B(\nu_B)$

total microstate: $\{\nu, \nu_B\}$ energy: E_T

Suppose we only specify the state of the system ν.
The bath could be in <u>many</u> possible microstates —
any ν_B satisfying $E_B(\nu_B) = E_T - E(\nu)$
The number of these bath states is $\Omega_B(E_T - E(\nu))$.

The likelihood of a system microstate ν is entirely determined by how many bath states are compatible.

$$P(\nu) = \sum_{\text{allowed } \nu_B} P(\nu, \nu_B) \boxed{=} \sum_{\substack{\nu_B \text{ with} \\ E_B(\nu_B) = E_T - E(\nu)}} \frac{1}{\Omega(E_T)} = \frac{1}{\Omega(E_T)} \sum_{\substack{\nu_B \text{ with} \\ E_B(\nu_B) = E_T - E(\nu)}} 1$$

The joint system + bath is microcanonical

$$= \frac{1}{\Omega(E_T)} \Omega_B(E_T - E(\nu))$$

$$\propto \Omega_B(E_T - E)$$

energy of sys

How does E_T compare to E?

A) $E_T \approx E$ B) $\underline{\underline{E_T \gg E}}$ C) $E_T \ll E$

$$P(\nu) \propto \Omega_B(E_T - \underbrace{E}_{\text{a small parameter}})$$

$\Rightarrow$ Taylor Expand!

Actually, we're going to Taylor expand $\ln \Omega$ rather than Ω. How would you know that is a good idea?

$$\frac{\partial \Omega_B}{\partial E} \sim \frac{e^{N \ln \omega(\epsilon)} \Leftarrow \text{exponential}}{E \Leftarrow \text{extensive}}$$ $\Leftarrow$ ratio grows as the bath gets bigger

$$\frac{\partial \ln \Omega_B}{\partial E} \sim \frac{N \ln \omega(\epsilon) \Leftarrow \text{extensive}}{E \Leftarrow \text{extensive}}$$ $\Leftarrow$ ratio is intensive!

You will explore more on your next homework.

$$\ln \Omega_B(E_T - E)\ \cancel{\ln \Omega_B(E_T) - E\left(\frac{\partial \ln \Omega_B}{\partial E_B}\right)}$$

$$= \ln \Omega_B(E_T - E)\Big|_{E=0} + E\left(\frac{\partial \ln \Omega_B}{\partial E}\right)\Big|_{E=0} + \ldots$$

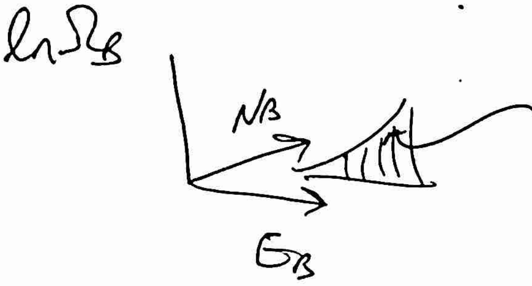
What to do with $\left(\frac{\partial \ln \Omega_B}{\partial E}\right)\Big|_{E=0}$?

Remember $E_T - E = E_B$, so the chain rule gives

$$\frac{\partial \ln \Omega_B}{\partial E} = \frac{\partial \ln \Omega_B}{\partial E_B}\frac{\partial E_B}{\partial E} = \frac{\partial \ln \Omega_B}{\partial E_B}(-1) = -\left(\frac{\partial \ln \Omega_B}{\partial E_B}\right)$$

(1) Why have I written partial derivatives everywhere?

$\Omega_B(N_B, V_B, E_B)$; a multivariable function



We write this as

$$\left(\frac{\partial \ln \Omega_B}{\partial E_B}\right)_{N_B, V_B}$$

Subscript indicates these variables are held fixed.

(2) What is so special about $\left(\frac{\partial \ln \Omega_B}{\partial E_B}\right)$?

It is entirely a property of the <u>bath</u>. The system has dropped out. For now we just give this bath property a name

$$\beta = \left(\frac{\partial \ln \Omega_B}{\partial E_B}\right)$$

Then the Taylor expansion reads:

$$\ln \Omega_B(E_T - E) = \ln \Omega_B(E_T) - E\left(\frac{\partial \ln \Omega_B}{\partial E_B}\right)_{N_B, V_B}$$

$$= \ln \Omega_B(E_T) - \beta E$$

$$\Rightarrow \boxed{P(\nu) \propto e^{-\beta E(\nu)}}$$

Boltzmann distribution Wow!

Q: Why did I discard $\Omega_B(E_T)$?

A: It doesn't have to do with the system energy E, so it is just a constant which will not vary from one ν to the next.

CANONICAL ENSEMBLE. All system microstates are no longer equally probable! (All system+bath microstates still are equally probable)

In the microcanonical (NVE) ensemble, two microstates ν_1 and ν_2 had the same probability

$$P(\nu_1) = P(\nu_2)$$

(ν_1 + ν_2 had to have equal energy due to the constraint)

Has that changed now that we allow energy to flow between system and bath?

Provided ν_1 + ν_2 have the same energy, $P(\nu) \propto e^{-\beta E(\nu)}$ still says $P(\nu_1) = P(\nu_2)$.

Why the $\propto$ sign?

We would need to normalize the distribution

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

(Normalization factor)
- depends on β
- Does Q also depend on ν?
  No - dummy variable, summed over

$$\Rightarrow \boxed{P(\nu) = \begin{cases} \dfrac{e^{-\beta E(\nu)}}{Q(\beta; N, V)}, & \text{if } N_\nu = N,\ V_\nu = V \\ 0, & \text{otherwise} \end{cases}}$$

We'll be talking more about $Q(\beta, N, V)$ soon but first

Suppose we will measure the energy but not the complete microstate.

What is $P(E)$? All of those possible ν's with $E_\nu = E$ have the same probability and combine together to give the total probability of E.

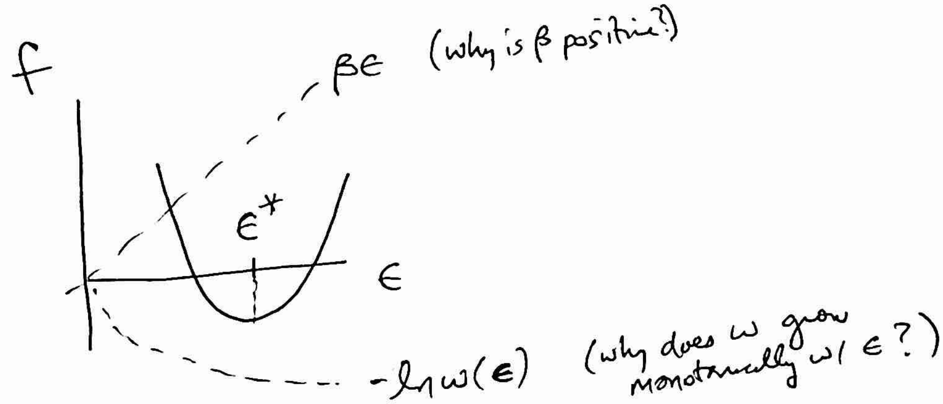
$$P(E) = \sum_{\substack{\nu \text{ with} \\ E_\nu = E}} P(\nu) \;\propto\; e^{-\beta E} \sum_{\substack{\nu \text{ with} \\ E_\nu = E}} (1) = e^{-\beta E} \underbrace{\Omega(\epsilon)}_{e^{-N \ln \omega}}$$

$$= \exp[-\underbrace{N}_{\text{extensive}} (\underbrace{\beta\epsilon - \ln\omega}_{\text{intensive}})]$$

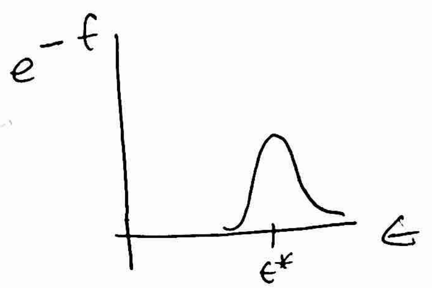
Another large deviation form

Let's study this distribution in the limit of a big system ($N \to \infty$)

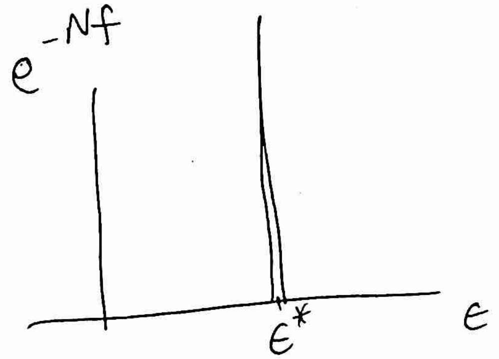
Define $f(\epsilon) = \beta\epsilon - \ln\omega(\epsilon) \implies P(E) \propto e^{-Nf(\epsilon)}$



So



and



Only one value of $\epsilon = \epsilon^*(\beta)$ has non-negligible weight.

Things look boring at macroscopic scale. (Think about the bottle of H_2O.)