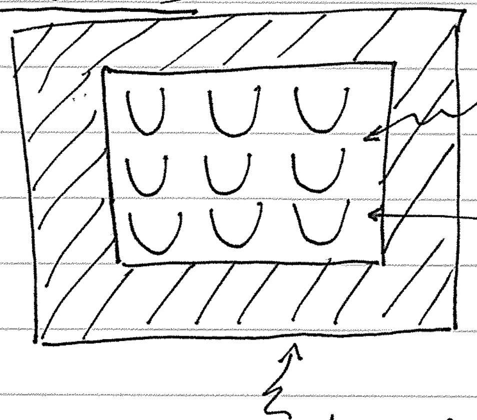
Ensembles



An ensemble of identical harmonic oscillators makes up our system, each with $E_i = (n_i + \frac{1}{2})\hbar\omega$

A thermal reservoir (constant T) can exchange energy between members of the ensemble

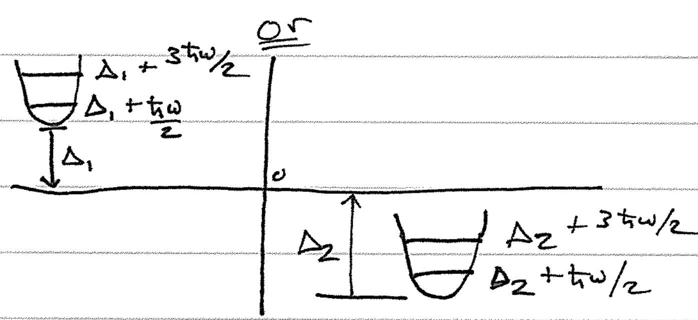
An adiabatic boundary prevents energy from entering or leaving the system.

a_i = # of members of the ensemble with energy E_i

$$\frac{a_2}{a_1} = f(E_1, E_2)$$

relative populations can only depend on the energies as there's nothing else to distinguish the states.

Energy is always measured relative to some fixed energy zero:



If we move the zero-bar up or down the relative fractions between states,

$\frac{a_1}{a_0}$ should not change

$$\therefore \frac{a_1}{a_0} = f(E_0 - E_1)$$

energy difference matters, not absolute values!

We can look at multiple energy states to try to discern the function f:

$$\frac{a_3}{a_2} = f(E_2 - E_3) \qquad \frac{a_2}{a_1} = f(E_1 - E_2)$$

The <u>combined</u> case: $\dfrac{a_3}{a_1} = f(E_1 - E_3)$

Now let's put this together:

$$\frac{a_3}{a_1} = \frac{a_3}{a_2} \cdot \frac{a_2}{a_1} = f(E_2 - E_3) f(E_1 - E_2)$$

$$\|$$

$$f(E_1 - E_3) = f(E_2 - E_3) f(E_1 - E_2)$$

$$\boxed{f(x+y) = f(x) f(y)}$$

What function has this property?

If $f(x) = e^{\beta x}$ and $f(y) = e^{\beta y}$

Then $f(x+y) = e^{\beta(x+y)} = e^{\beta x} e^{\beta y} = f(x) f(y)$

So the exponential function has the correct properties, and

$$f(E) = e^{\beta E}$$

$$\frac{a_2}{a_1} = f(E_1 - E_2) = e^{\beta(E_1 - E_2)}$$

Normalization factor

And, $a_n = C e^{-\beta E_n}$

Probability information

Suppose we have a fixed number of states and we want the probability of observing an oscillator in state n:

$$P_n = \frac{a_n}{\sum_i a_i} = \frac{c\, e^{-\beta E_n}}{\sum_i c\, e^{-\beta E_i}}$$

$$P_n = \frac{e^{-\beta E_n}}{\sum_i e^{-\beta E_i}}$$

← This denominator is something special called the partition function

$$Q(N, V, \beta) = \sum_i e^{-\beta E_i}$$

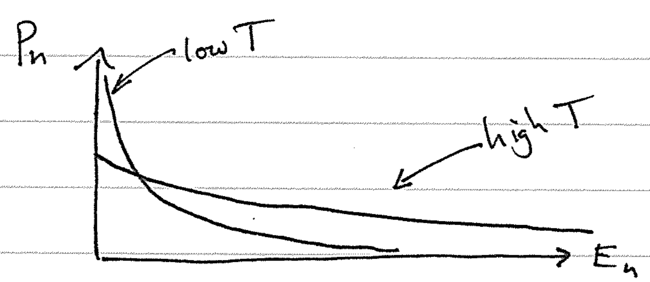
↑ sum over all states for one member of the ensemble!

$$\beta = \frac{1}{k_B T}$$

← can be derived, but we'll just state this now.

$$P_n(N, V, T) = \frac{e^{-E_n/k_B T}}{Q(N, V, T)}$$

← probability of state n depends on temperature (and particle number and volume)



low energy states are always more favored

We can do very powerful things if we know Q:

Consider the average energy, $\langle E \rangle$

$$\langle E \rangle = \sum_i E_i P_i = \frac{\sum_i E_i e^{-E_i/k_B T}}{Q(N,V,T)}$$

$$= \frac{\sum_i E_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}}$$

Let's re write this with $\beta = \frac{1}{k_B T}$

$$\langle E \rangle = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

Remember: $Q(N,V,\beta) = \sum_i e^{-\beta E_i}$

Now let's do: $\frac{\partial \ln Q}{\partial \beta} = \frac{1}{Q} \frac{\partial Q}{\partial \beta}$

$$= \frac{1}{Q} \frac{\partial}{\partial \beta}\left(\sum_i e^{-\beta E_i} \right)$$

$$= \frac{1}{Q} \sum_i \frac{\partial}{\partial \beta}\left(e^{-\beta E_i} \right)$$

$$= \frac{1}{Q} \sum_i -E_i e^{-\beta E_i}$$

$$= - \frac{\sum_i E_i e^{-\beta E_i}}{Q}$$

or:
$$\frac{\partial \ln Q}{\partial \beta} = \frac{-\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

$$= -\langle E \rangle$$

In other <u>words</u>:
$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)$$

If we prefer to use temperature, there's a chain rule to get that as well:
$$\beta = \frac{1}{k_B T}$$

$$\frac{\partial f}{\partial T} = \frac{\partial f}{\partial \beta}\frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}\left(\frac{\partial f}{\partial \beta}\right) \Rightarrow \left(\frac{\partial f}{\partial \beta}\right) = -k_B T^2 \left(\frac{\partial f}{\partial T}\right)$$

So:

microscopic state information

$$\langle E \rangle = +k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

Average energy (macroscopic)

$\boxed{\text{What is } Q\text{?}}$ The partition function is a way of expressing the likelihood of a state in an ensemble of N identical particles in volume V.

Once we know the likelihood of all microscopic states, we can predict macroscopic properties.