- the energy to do the work comes from two sources -- the internal energy of the system, <u>and</u> the flow of heat from the reservoir. Change in free energy reflects the amount of work we can extract as the system is maintained at constant temperature. (<u>Different</u> from adiabatic situation.)

Note that partial derivatives commute

$$\frac{\partial}{\partial V}\frac{\partial}{\partial \tau}F = \frac{\partial}{\partial \tau}\frac{\partial}{\partial V}F$$

Hence $$\boxed{\left(\frac{\partial}{\partial V}\sigma\right)_\tau = \left(\frac{\partial}{\partial \tau}p\right)_V}$$

An example of a <u>Maxwell Relation</u>

- one of many we will encounter...

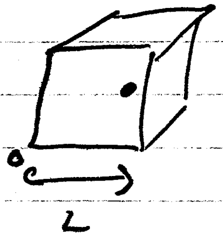
<u>Note</u>: assuming $Z = \sum_s e^{-\varepsilon_s/\tau}$ is <u>dominated</u> by the most probable configuration, as will be the case for a large system, we have

$$Z \sim e^{-F/\tau}$$ or

$$\boxed{F = -\tau \log Z}$$

Example: The ideal gas

An application of the partition function. Start with the case of a single atom in a cubic 3-dimensional box with side L.



We suppose the particle is completely confined to the box, so we impose the boundary condition $\psi = 0$ on the faces of the cube. The stationary states are

$$\psi(x,y,z) = C \sin(\pi n_x x/L) \sin(\pi n_y y/L) \sin(\pi n_z z/L)$$

where $n_{x,y,z}$ are positive integers. The energy is

$$H = \frac{-\hbar^2 \nabla^2}{2m} \Rightarrow \varepsilon(n_x, n_y, n_z) = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \left[n_x^2 + n_y^2 + n_z^2\right]$$

For a single particle, the partition function is

$$Z_1 = \sum_{n_x, n_y, n_z} e^{-\varepsilon/\tau}$$

$$= \sum_{n_x, n_y, n_z = 1}^{\infty} \exp\left[-\frac{\hbar^2}{2m\tau}\left(\frac{\pi}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right)\right]$$

Now assume $\alpha = \frac{\hbar^2}{2m\tau}\left(\frac{\pi}{L}\right)^2 \ll 1$ -- i.e. Temperature is large compared to spacing between successive energy levels (which is always true at $\tau > 0$ for a sufficiently large box $L \to \infty$). Then the sum may be well approximated by an integral --

$$Z_1 = \int_0^{\infty} dn_x dn_y dn_z \exp\left[-\alpha\left(n_x^2 + n_y^2 + n_z^2\right)\right]; \quad \alpha = \frac{\hbar^2 \pi^2}{2m\tau L^2}$$

And $\int_0^\infty dz\, e^{-\alpha z^2} = \frac{1}{\sqrt{\alpha}}\int_0^\infty dx\, e^{-x^2} = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$

so $Z_1 = \left(\frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\right)^3 = \left(\frac{m\tau L^2}{2\pi\hbar^2}\right)^{3/2}$

$\boxed{Z_1 = n_Q V}$ $\qquad n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}, \; V = L^3$

So V is the volume of the gas, and n_Q is called the "quantum concentration"

It has the dimensions of $\frac{1}{\text{volume}}$, or

$n_Q = \frac{1}{L_Q^3}$ where $L_Q^2 \sim \frac{\hbar^2}{m\tau}$ (aside from numerical factors of order 1.)

L_Q is the typical wavelength of a particle ~~[illegible]~~ with an energy of order the temperature τ

$\tau \sim \frac{\hbar^2 k^2}{2m}$ In converting the sum to an integral in the above derivation, we assumed $L \gg L_Q$. Under these condition, quantum effect are not important in determining the equilibrium properties of the particle in the ~~[illegible]~~ box.

For $L \gg L_Q(\tau)$ — we say that we are in the classical regime.

Now we can use Z_1 to compute the most probable configuration -- i.e. $\langle U \rangle$ when the particle is in contact with a reservoir at temperature τ:

$$\langle U \rangle_1 = \tau^2 \frac{\partial}{\partial \tau}(\log Z_1)$$

$$Z_1 = (\text{const}) \cdot \tau^{3/2} \Rightarrow \log Z_1 = \tfrac{3}{2} \log \tau + (\tau\text{-independent})$$

$$\langle U \rangle = \tfrac{3}{2} \tau^2 \frac{\partial}{\partial \tau} \log \tau = \tfrac{3}{2} \tau = \tfrac{3}{2} k_B T$$

For a single particle in a box, we won't have very sharp peaking of the probability distribution about the most probable configuration. But suppose there are N particles with $N \gg 1$. And suppose the particles do not interact with one another: they form an ideal gas.

First suppose that all N particles are distinguishable -- they all carry colors or labels so we can tell them apart. For the ideal gas, the energy is the sum of the energies of the particles:

$$E = E(1) + E(2) + \cdots + E(N)$$

So the Boltzman factor factorizes

$$e^{-E/\tau} = \prod_{i=1}^{N} e^{-E(i)/\tau}$$

And the sum over states is performed by summing over the quantum states of each particle independently

$$Z_N = \prod_i \left(\sum_s e^{-E_s(i)/\tau} \right) = Z_1^N = (n_Q V)^N$$

From the partition function, we may compute U, pressure P and entropy σ

$$U = \tau^2 \frac{\partial}{\partial \tau} \log Z \qquad\qquad F = -\tau \log Z$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_\tau \qquad \sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$$

Here we have $\log Z = N \log(n_Q V)$

$$F = -N\tau \log(n_Q V)$$

where $n_Q \propto \tau^{3/2}$

Hence $\boxed{U_N = \frac{3}{2} N\tau}$ (all the particles contribute $\frac{3}{2}\tau$ to the energy)

$$p = -\frac{\partial}{\partial V}\left(-N\tau \log V\right)_\tau = \frac{N\tau}{V}$$

$\Rightarrow \boxed{pV = N\tau = N k_B T}$ the familiar ideal gas law

Entropy:

$$\sigma_N = -\frac{\partial}{\partial \tau}\left[-N\tau \log(n_Q V)\right]_V$$

$\boxed{\sigma_N = N \log(n_Q V) + \frac{3}{2} N}$ (from $n_Q \propto \tau^{3/2}$)

- This is a strange and interesting formula.
- First of all, while formulas for U and p are entirely classical, and can be understood with classical reasoning, our formula for σ depends on ħ, since $n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$. In fact n_Q and σ → ∞ in the ħ → 0 limit

- So this entropy is incomprehensible to a classical physicist. We need quantum mechanics to make sense of "counting" the microscopic states of a system.

- Secondly -- this formula scales with the number of particles N in a peculiar way:

~~that~~ Let $n = N/V$ denote the concentration - the number of particles per unit volume. Then our formula is

$$(\sigma_N)_{\text{disting}} = N\log\left(\frac{n_Q}{n}\right) + \frac{3}{2}N + \underbrace{N\log N}_{?}$$

this term is puzzling — it does not scale linearly with N (or V) when the concentration is held fixed — entropy does not appear to be extensive in the usual sense. In fact, the $N\log N$ term eventually dominates for a large box

- Our formula does not agree with experiment for real gases...

How do you measure the entropy?

Recall

$$dU = \tau\, d\sigma - p\,dV$$

- thermodynamic identity

Heat capacity at constant volume is

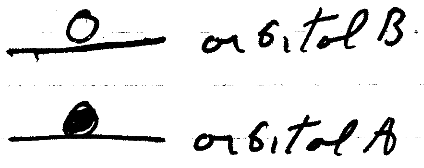
$$C_V \equiv \left(\frac{\partial U}{\partial \tau}\right)_V = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_V$$

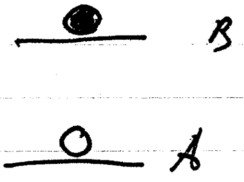
— How much heat do we need to add to raise the temp. of the box?

But this won't tell us the $N\log N$ term — consider e.g. entropy of mixing?

(we can test the formula by considering C_p instead see p 167 ff of text)

It was Gibbs who realized how to fix the formula... we need to regard the atoms as indistinguishable -- they carry no labels





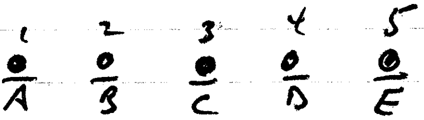
— these two states are really the same

How do we fix the counting? In the classical regime it is pretty easy. Suppose $n \lll n_Q$, so $\sigma_1 \gg 1$ — a very dilute one particle gas $\Rightarrow$ # of states $\gg 1$ — and with N particles, no. of states per particle is large — this means it is not likely that the occupation number of a state is > 1. So we ignore multiple occupancy in our state counting

# of orbitals $= e^{\sigma_1} \sim n_Q V = \frac{n_Q}{n} \cdot N$

So $n \ll n_Q$ means # of orbitals $\gg$ # of particles

Then our counting for distinguishable particles over counts by a factor of $N!$ -- all the permutations of the particles leave the state of indistinguishable particles unchanged -- but change the state if particles are distinguishable



(assuming no double occupancy)

Then $$(Z_N)_{\text{indist}} = \frac{1}{N!} Z_1^{\,N}$$

or $$(\log Z_N)_{\text{indis}} = (\log Z_N)_{\text{dist}} - \log N!$$

$$(F_N)_{\text{indist}} = (F_N)_{\text{dist}} + \tau \log N!$$

This does not modify $\tau^2 \frac{\partial}{\partial \tau} \log Z$ or $\left(-\frac{\partial}{\partial V} F\right)_\tau$ so our (successful) predictions for U and p are unmodified — but

$$(\sigma_N)_{\text{indist}} = (\sigma_N)_{\text{dist}} - \log(N!)$$

And using Stirling: $\log N! \sim N \log N - N + O(\log N)$ — the crazy $N \log N$ cancels

$$\boxed{(\sigma_N)_{\text{indist}} = N\left[\log\left(\frac{n_Q}{n}\right) + 5/2\right]_{n \ll n_Q} \quad \text{(Classical Regime)}}$$

— the Sackur-Tetrode equation

This formula does agree with experiment, and now we obtain σ_N that is extensive (linear in N at fixed concentration) -- the $\hbar$ dependence remains even in the classical regime.

We'll learn later how to deal with a dense gas, the case in which double occupancy is not unlikely

Gibbs Paradox

$$(\sigma_N)_{dist} = N\log(n_Q V) + \tfrac{3}{2}N$$ – the naive (wrong) formula

Let 2 gases at same concentration mix

$$\Rightarrow \quad \Delta\sigma = (N_1+N_2)\log(V_1+V_2) - N_1\log V_1 - N_2\log V_2$$

$$= N_1\log\frac{V_1+V_2}{V_1} + N_2\log\frac{V_1+V_2}{V_2} = N\log 2$$ for 2 identical boxes (each particle has twice as many states)

Mixing the gases is irreversible (generates entropy)
This is a correct calculation when two species mix, but not for the case when gas 1 and gas 2 are the same

Indistinguishability of the particles is a quantum effect with no classical analog.

(3.22)

Entropy of Mixing

Illustrates the competition between minimizing energy and maximizing entropy (Quantified by $F = U - \tau\sigma$ seeks a minimum at specified temperature τ)

Combine metals A and B by melting them together, and cooling

Will they crystalize with A and B separated, or alloyed together?

Typically energy favors A's together and B's together. So at zero τ, they will separate. But entropy favors that they mix

Suppose N total atoms
xN B atoms $x \ll 1$ (small contamination)
$(1-x)N$ A atoms

At fixed τ, for x sufficiently small, B atoms will dissolve — the entropy always wins as $x \to 0$. So, at finite $\tau > 0$, any metal inevitably contains impurities

Why — because there are many ways of placing the B atoms among A atoms.

Let's be more quantitative:

3.23

$$g(N,x) = \frac{N!}{[N(1-x)]!\,(Nx)!}$$ — same counting as in our spin model

N sites, each either A or B

Now use Stirling

$$\log N! = N\log N - N + \underbrace{O(1)}_{\text{ignore actually } \log N}$$

$$\log g(N,x) \equiv \sigma(N,x)$$

$$= N\log N - N - N(1-x)[\log N + \log(1-x)] + N(1-x) - Nx[\log N + \log x] + Nx$$

$$= -N[(1-x)\log(1-x) + x\log x]$$

(Recall $0 \le x \le 1$, so both terms are positive)

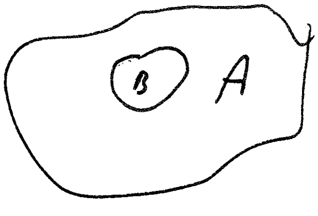
$$x \ll 1 \Rightarrow \sigma(N,x) \sim -Nx\log x$$

Free energy $F = U - \tau\sigma$

$$F = \text{constant} + N(x\underset{\uparrow}{\varepsilon} + \tau x\log x)$$

energetic cost of replacing A atom by a B atom (if surrounded by A atoms)

So — for $\tau \to 0$, atoms want to separate (to minimize U)



But ---
$$\frac{dF}{dx} = N(\epsilon + \tau + \tau \log x) = 0$$
$$\Rightarrow \log x = -1 - \epsilon/\tau$$
or
$$\boxed{x = e^{-1} e^{-\epsilon/\tau}}$$

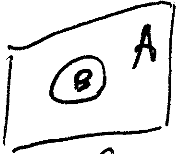
As $\tau \to 0$, an exponentially small fraction of B atoms remain dissolved, in thermal equilibrium.

Our approximation is consistent for x small, or $e^{-\epsilon/\tau} \ll 1$ i.e. sufficiently low temp

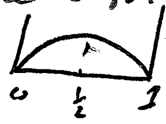
then
$$F_{min} = \text{const} + N x_0 (\epsilon + \tau \log x_0)$$
$$= \text{const} + \underbrace{N x_0 (-\tau)}$$

since this is < 0, the phase with fraction x_0 dissolved will be favored over the differentiated phase

Actually -- differentiation occurs -- but a small amount of B remains dissolved in A (it is hard to make a pure crystal!)



[In fact



$-x \log x - (1-x)\log(1-x)$ achieves its max at $x = \frac{1}{2}$, where it has the value $\log 2$

For $\tau \to \infty$, the energetic cost becomes insignificant and $x \to \frac{1}{2}$ ...]

- To make an alloy, you might need to quench to stay far from equilibrium
- It is hard in practice to make pure materials!