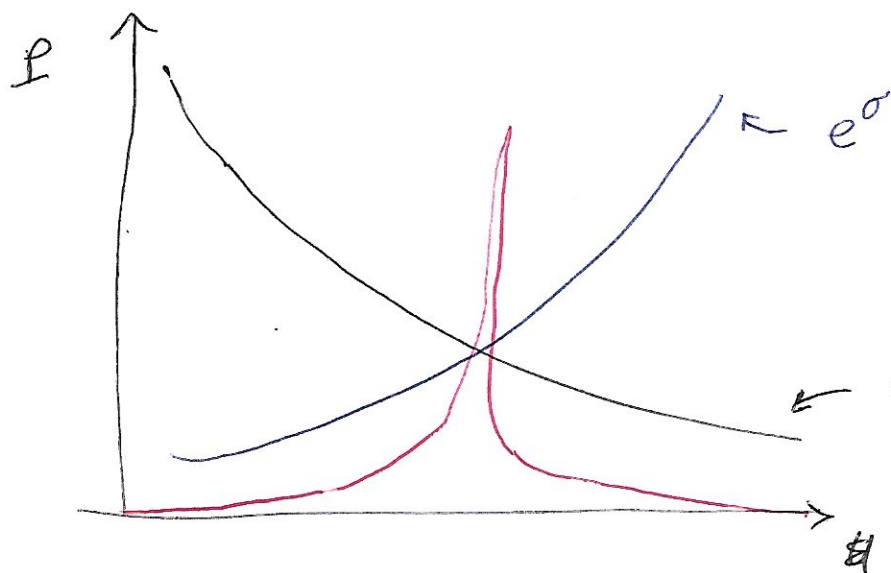


Helmholtz Free Energy pg. 68 KK

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Consider a system S that is large, but R is larger
The probability that ~~the state~~ S has energy ϵ at temperature τ is the Boltzmann distribution $P(\epsilon) = \frac{1}{Z} e^{-\epsilon/\tau}$



The system tries to go to the highest energy possible (maximize entropy)

The system tries to go to the lowest energy possible (minimize energy)

The multiplicity is larger for higher energies $e^{\text{eng}} = e^{\sigma}$, the total probability is

$$P(\epsilon) \propto e^{-\epsilon/\tau} e^{\sigma} = \exp \left[-\frac{1}{\tau} (U - \sigma\tau) \right]$$

To find the maximum, maximize $-\frac{1}{\tau} (U - \sigma\tau)$ or minimize $U - \sigma\tau$

In closed systems in thermal equilibrium, the state that maximizes entropy is when the temperatures are equal. In an open system,

$$\frac{d}{dU} [U - \sigma\tau] = 0 \Rightarrow 1 - \tau \frac{d\sigma}{dU} = 0 \Rightarrow \boxed{\frac{d\sigma}{dU} = 1/\tau}$$

the temp is the trace between energy minimization and entropy maximization

The quantity $\boxed{F = U - \tau\sigma}$ is called the free energy.

KK Eq. 3.35

↑ This quantity is what nature actually minimizes.

Consider reversible changes when the temp τ and volume V change.

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

$$\Rightarrow dF = d(U - \tau\sigma) = dU - \tau d\sigma - \sigma d\tau$$

First, the temp changes but V remains constant

$$\text{Thermodynamic Identity: } \tau d\sigma = dU + p dV$$

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

$$\text{since } dV = 0, \quad 0 = dU - \tau d\sigma$$

$$\text{So } dF|_V = -\sigma d\tau \Rightarrow \boxed{\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma} \quad \text{KK Eq. 49}$$

Then, the volume changes but τ remains constant

$$\text{Thermodynamic Identity: } \tau d\sigma = dU + p dV$$

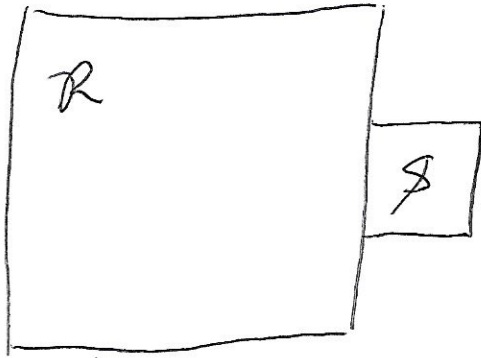
$$\Rightarrow -p dV = dU - \tau d\sigma$$

$$\text{So } dF|_\tau = -p dV \Rightarrow \boxed{\left(\frac{\partial F}{\partial V}\right)_\tau = -p} \quad \text{KK Eq. 49}$$

Putting both of them together, $dF = -\sigma d\tau - p dV$

KK Eq. 48

Let's analyze $\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma$; $dF|_V = -\sigma d\tau$ (43)



1. Change the temperature of the reservoir. Since R and the system are in thermal equilibrium, the temperature of S changes as well.

2. In order for the temperature to change, S must take energy from R or give energy to R , but the volume is constant, so no work is done.

INSIGHT: ~~Some~~ The energy is used to maintain thermal equilibrium. Even in situations in which "some" work is done, we must pay this energy tax. The heat dead of the Universe will occur when "all" the energy of the Universe is locked in this situation.

$$\left(\frac{\partial F}{\partial V}\right)_\tau = -p = \frac{\partial}{\partial V} [U - \tau \sigma - \sigma \tau]_\tau$$

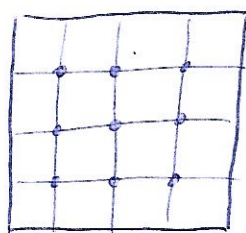
$$\Rightarrow p = -\left(\frac{\partial U}{\partial V}\right)_\tau + \tau \left(\frac{\partial \sigma}{\partial V}\right)_\tau \quad \text{KK Eq. 3.50}$$

1. Change the volume of S . Since R and S are in thermal equilibrium, heat flows in or out to keep temp.

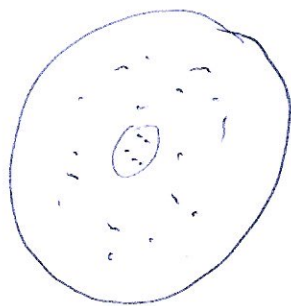
and the pressure changes.

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INSIGHT: There are 2 sources of pressure: the energy pressure and the entropy pressure. Compare this to pressure in classical mechanics $p = -\left(\frac{\partial U}{\partial V}\right)_\sigma$



↖ In solids, the positions of the atoms are pretty constrained, so the entropy does not change as much, so most of the ~~ent~~ pressure change comes from the energy of the particles, kinetic and potential.



↖ In gases, the particles are not very constrained, so most of the pressure change will come from the change in entropy.

Notice that $-pdV|_\sigma = dU|_\sigma$

$$-pdV|_\tau = dF|_\tau$$

↖ In an open system, ~~the Helmholtz free energy~~ the Helmholtz free energy is the "effective" ~~free~~ energy when work is done at constant temperature (isothermal).

Also, remember that partial derivatives commute, so $\frac{\partial^2 F}{\partial V \partial \tau} = \frac{\partial^2 F}{\partial \tau \partial V}$

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

Take home message is that every thermodynamic variable is related to every other one.

Yes, that Maxwell

→ One of Maxwell's relations →

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

KK Eq. 3.51

Since $F \equiv U - \tau \sigma$ and $\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma$, (45)

$$F = U + \tau \left(\frac{\partial F}{\partial \tau}\right)_V \Rightarrow U = F - \tau \left(\frac{\partial F}{\partial \tau}\right)_V$$

Remember that $\frac{d(u/v)}{dx} = \frac{1}{v} \frac{du}{dx} - \frac{u}{v^2} \frac{dv}{dx}$

with $u = F$ and $v = \tau$ and $x = \tau \Rightarrow dx = d\tau$,

$$\frac{d}{d\tau} (F/\tau) = \frac{1}{\tau} \frac{dF}{d\tau} - \frac{F}{\tau^2} \frac{d\tau}{d\tau}$$

$$-\tau^2 \frac{\partial (F/\tau)}{\partial \tau} = -\frac{\tau^2}{\tau} \left(\frac{\partial F}{\partial \tau}\right)_V + \frac{\tau^2 F}{\tau^2} = F - \tau \left(\frac{\partial F}{\partial \tau}\right)_V$$

$$U = -\tau^2 \frac{\partial (F/\tau)}{\partial \tau} \quad \text{KK Eq. 3.52}$$

Assume $F/\tau = -\ln Z$, then $-\frac{U}{\tau^2} = -\frac{\partial}{\partial \tau} \ln Z$

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau}$$

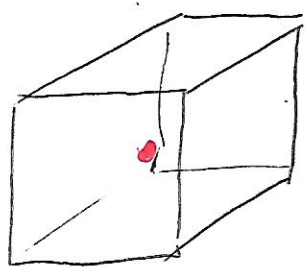
The average energy of system with the Boltzmann distribution is $U = \tau^2 \frac{\partial \ln Z}{\partial \tau}$ (KK Eq 3.12). Hence

$$\boxed{F = -\tau \ln Z} \quad \text{KK Eq. 3.55}$$

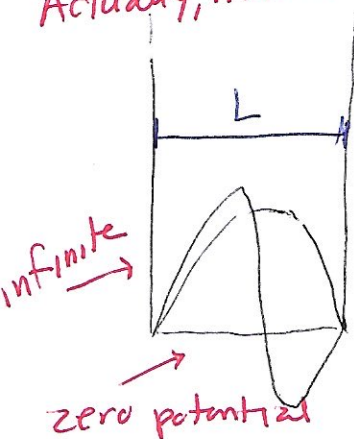
Ideal Gas: A first look (of many)

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Let's compute the partition function (so an enumeration of all the states and probabilities) of 1 atom of mass M that is free to move in a cubical box of volume $V = L^3$.



Looks like that.
Actually, more like this



Actually, this is a quantum mechanical particle, so what we know is its wavefunction. The particle is "free," so it has no potential energy.

The wavefunction is given by the Schrödinger Equation

$$-\frac{\hbar^2}{2M} \nabla^2 \psi = \epsilon \psi$$

we are not going to solve this differential equation, but we know the solutions

$$\Psi(x, y, z) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \quad \text{KK. Eq. 58}$$

Boundary conditions require that $\Psi(x, y, z) = 0$ if:

$$x=0$$

$$x=L$$

$$y=0$$

$$y=L$$

$$y=0$$

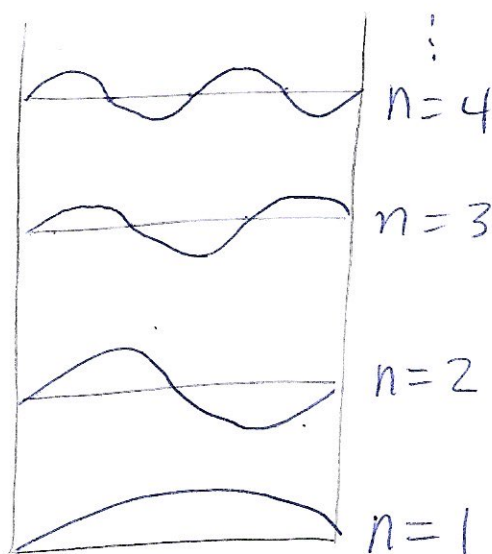
$$y=L$$

which holds with the sine function and if n is integer.

the energy levels are given by

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$$\epsilon_n = \frac{\hbar^2}{2M} \left(\frac{\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2) \quad \text{KK Eq. 3.59}$$



Notice that the more nodes the wavefunction has, the higher the energy (particle accommodates more energy by increasing its frequency)

This particular particle has no more structure than this (so no spin, etc.) State of the system is completely specified by the values n_x, n_y, n_z . (not all zero)

~~★~~ WHAT IS THE PARTITION FUNCTION??

WE JUST NEED TO SUM !

$$Z = \sum_s e^{-\epsilon/\tau}, \text{ so}$$

$$Z_1 = \sum_{n_x} \sum_{n_y} \sum_{n_z} \exp \left[-\hbar^2 \pi^2 (n_x^2 + n_y^2 + n_z^2) / 2ML^2 \tau \right] \quad \text{KK Eq. 3.60}$$

For sufficiently large τ , the spacing between energy levels is small, so we can replace the summations by integrations.

$$Z_1 = \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \exp[-\alpha^2(n_x^2 + n_y^2 + n_z^2)] \quad (48)$$

with $\alpha^2 \equiv h^2 \pi^2 / 2ML^2\tau$

$$\exp[-\alpha^2(n_x^2 + n_y^2 + n_z^2)] = e^{-\alpha^2 n_x^2} e^{-\alpha^2 n_y^2} e^{-\alpha^2 n_z^2}$$

so $Z_1 = \left[\int_0^\infty dn_x \exp(-\alpha^2 n_x^2) \right]^3$

Let $\alpha^2 n_x^2 = x^2$

$\Rightarrow x = \alpha n_x$ so $dx = \alpha dn_x$

$dn_x = \frac{dx}{\alpha}$

$$Z_1 = \left(\frac{1}{\alpha}\right)^3 \left[\int_0^\infty dx \exp(-x^2) \right]^3 \quad \text{KK Eq. A4}$$

$$Z_1 = \left(\frac{1}{\alpha}\right)^3 \left(\frac{1}{2} \pi^{1/2}\right)^3 = \frac{\pi^{3/2}}{8\alpha^3} = \frac{\pi^{3/2}}{8(h^3 \pi^3 / 2^{3/2} M^{3/2} L^3 \tau^{3/2})}$$

$$Z_1 = \frac{2^{3/2} M^{3/2} V \tau^{3/2} \pi^{3/2}}{2^3 h^3 \pi^3} = \frac{M^{3/2} V \tau^{3/2}}{2^{3/2} h^3 \pi^{3/2}} = \frac{V}{(2\pi h^2 / M\tau)^{3/2}}$$

Let $n_Q \equiv \left(\frac{M\tau}{2\pi h^2}\right)^{3/2}$, with concentration $n = \frac{1}{V}$ (particle density)

$Z_1 = \frac{n_Q}{n}$

KK Eq. 3.62

quantum concentration ↑ KK Eq. 3.63

★ WHAT IS THE ENERGY OF AN IDEAL GAS?

Remember that $U = \langle \epsilon \rangle = \tau^2 \frac{d}{d\tau} \ln Z$

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$$U = \tau^2 \frac{d}{d\tau} \ln(n_Q/n) = \tau^2 \frac{d}{d\tau} [\ln n_Q - \ln n]$$

$$U = \tau^2 \frac{d}{d\tau} \ln \left[\left(\frac{M\tau}{2\pi\hbar} \right)^{3/2} \right] = \tau^2 \frac{d}{d\tau} \left[\frac{3}{2} \ln(\gamma\tau) \right]$$

with $\gamma = \frac{M}{2\pi\hbar}$

$$U = \tau^2 \frac{3}{2} \frac{d}{d\tau} [\ln \gamma + \ln \tau] = \frac{3\tau^2}{2} \frac{d}{d\tau} \ln \tau = \frac{3}{2} \tau$$

KK Eq. 3.65

$$U = \frac{3}{2} \tau$$

since $\tau = k_B T$, $U = \frac{3}{2} k_B T$

which is the well know result. (i)

The quantum concentration n_Q is the concentration associated with one atom ~~in a~~ in a cube of side equal to the de Broglie thermal wavelength.

$$\text{Just like } n = \frac{1}{V} = \frac{1}{L^3}, \quad n_Q = \frac{1}{L_Q^3} \Rightarrow L_Q = \left(\frac{2\pi\hbar^2}{M\tau} \right)^{1/2}$$

$$L_Q = \left(\frac{2\pi\hbar^2}{M\tau} \right)^{1/2}$$

since $\lambda_{\text{deBroglie}} = \frac{h}{p} = \frac{2\pi\hbar}{Mv}$

$$L_Q^2 = \lambda_{\text{dB}}^2 \Rightarrow \frac{2\pi\hbar^2}{M\tau} = \frac{(2\pi\hbar)^2}{M^2 v^2} \Rightarrow \frac{Mv^2}{2} = \tau$$

the higher the temperature, the higher the velocity and viceversa