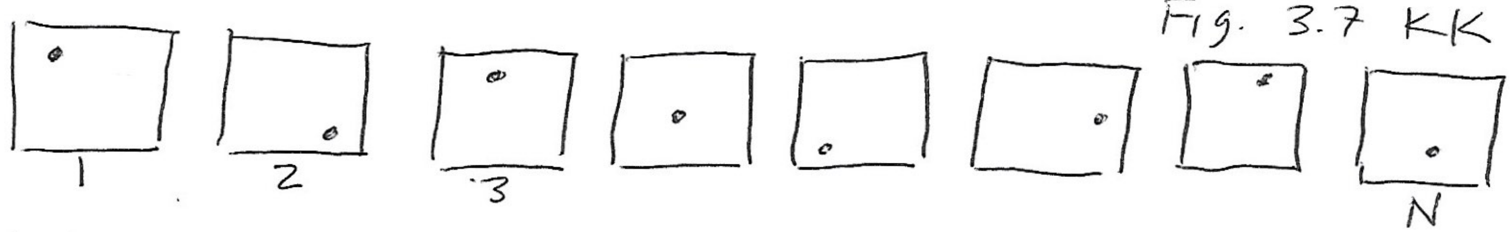
We just saw the case for 1 particle in a box.
What about N boxes with 1 particle each?

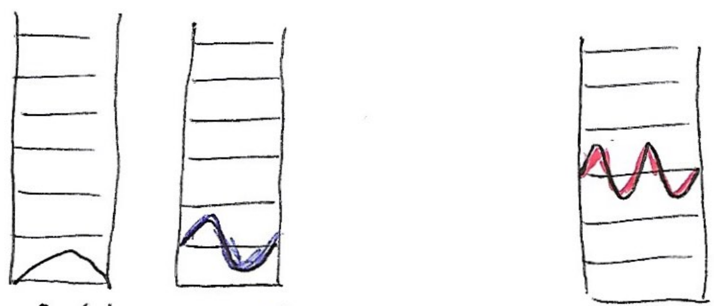
Fig. 3.7 KK



well, $Z_{N\ boxes} = Z_1(1)\, Z_1(2)\, Z_1(3) \cdots Z_1(N)$ KK 3.66

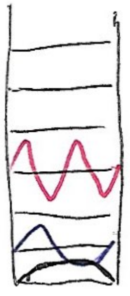
The number of states gets multiplied, each has the same partition function Z_1.

The product on the right hand side includes every independent state, for example the state of energy



$\varepsilon_\alpha(1) + \varepsilon_\beta(2) + \ldots + \varepsilon_\zeta(N)$ KK 3.67

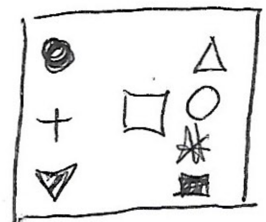
Consider the case for N particles in 1 box, $N > 1$, that are distinguishable and noninteracting. The box



↑ so  and are different

looks like Fig. 3.8 KK

can be in the same state



Notice that the partition function is the same as for N boxes!

In both cases, $Z_N = Z_1^{\,N} = \left(\frac{n_Q}{n}\right)^N$ $\quad n_Q =$

Remember that $U = \tau^2 \frac{\partial}{\partial \tau} \ln Z$ and $F = -\tau \ln Z$

$V = 1/n$

$$U_N = \tau^2 \frac{\partial}{\partial \tau} \ln Z_N = \tau^2 \frac{\partial}{\partial \tau}\left[N \ln Z_1\right] = \tau^2 \frac{\partial}{\partial \tau}\left[N \ln (n_Q \cancel{V})\right]$$

$$U_N = \tau^2 \frac{\partial}{\partial \tau} \ln \left[\frac{3}{2} N \left(\frac{M\tau}{2\pi\hbar}\right)\right] = \tau^2 \frac{\partial}{\partial \tau}\left[\frac{3}{2} N \ln(\gamma\tau)\right]$$

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

$$U_N = \tau^2 \frac{3}{2} N \frac{\partial}{\partial \tau}\left[\cancel{\ln\gamma} + \ln\tau\right] = \frac{3\tau^2 N}{2} \frac{\partial}{\partial \tau} \ln\tau = \frac{3N\tau^{\cancel{2}}}{2\cancel{\tau}}$$

$$\boxed{U_N = \frac{3}{2} N\tau = \frac{3}{2} N k_B T}$$ KK 3.69

$$F_N = -\tau \ln Z_N = -\tau N \ln Z_1 = -\tau N \ln(n_Q/n)$$

$$\cancel{= -\tau N\left[\ln n_Q - \ln n\right] = -\tau N \ln(\gamma\tau) = -\tau N \ln}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_\tau = +\frac{\partial}{\partial V}\left[+\tau N \ln(n_Q \cdot V)\right] = \frac{\partial}{\partial V}\left[\tau N(\ln n_Q + \ln V)\right]$$

n_Q is independent of volume, so

$$p = \frac{\partial}{\partial V}\left[\tau N \ln V\right] = \frac{\tau N}{V} \Rightarrow \boxed{pV = N\tau = N k_B T}$$ KK Eq. 3.73

Ideal gas law

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = +\frac{\partial}{\partial \tau}\left[+\tau N \ln(n_Q/n)\right]_V = \frac{\partial}{\partial \tau}\left[\tau N \ln(n_Q V)\right]_V$$

$$\sigma = N\frac{\partial}{\partial \tau}\left[\tau(\ln n_Q + \ln V)\right]_V = N\frac{\partial}{\partial \tau}\left[\tau \ln n_Q + \tau \ln V\right]_V$$

$$\sigma = N\left[\tau\frac{\partial}{\partial \tau}\ln n_Q + \ln n_Q \frac{\partial \tau}{\partial \tau} + \cancel{\tau\frac{\partial}{\partial \tau}\ln V} + \ln V\frac{\partial \tau}{\partial \tau}\right]_V$$

$$\sigma = N\left[\tau\frac{\partial}{\partial \tau}\frac{3}{2}\ln(\gamma\tau) + \ln n_Q + \ln V\right]_V$$

$$\sigma = N\left\{\ln(n_Q V) + \frac{3}{2}\tau\frac{\partial}{\partial \tau}\left[\cancel{\ln\gamma} + \ln\tau\right]\right\}_V$$

$$\sigma = N\ln(n_Q V) + \frac{3}{2}N\cancel{\frac{\tau}{\tau}}$$

Let $n = \frac{N}{V}$, then $V = \frac{N}{n}$ and

$$\sigma = N\ln\left(\frac{n_Q N}{n}\right) + \frac{3}{2}N = N\ln(n_Q/n) + N\ln N + \frac{3}{2}N$$

$$\sigma = N\left[\ln(n_Q/n) + \frac{3}{2} + \ln N\right]$$

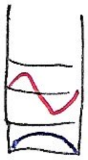
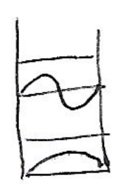
Notice that it looks like KK Eq. 3.76, but not quite

We were able to derive the energy and pressure of an ideal gas assuming noninteracting distinguishable particles, but the entropy can't be correct because the equation above does not produce an extensive quantity (it should increase linearly with size of the system, so the number of particles. Energy is also an extensive quantity and we got $U_N = \frac{3}{2} N\tau \Rightarrow \frac{U_N}{N} = \frac{3}{2}\tau$ (constant with N)

Volume is an extensive quantity and we got $pV = N\tau \Rightarrow \frac{V}{N} = \frac{\tau}{p}$ (constant with N)

but the entropy $\frac{\sigma}{N} = \ln(n_Q/n) + \frac{3}{2} + \ln N$ Not constant with N!

There is a problem with our assumptions. If the particles have the same energy levels, then they are <u>NOT</u> distinguishable. Later we will see more ~~deta~~ details about why they are indistinguishable, maybe you have seen this in QM. For now keep two things in mind: Indistinguishability is required by thermodynamics and satisfied by quantum physics AND the fact that matter occupies a volume in space is because of this.

 and  can't be different ~~are~~ ~~[illegible]~~ in fact, it is the same state 

If the order matters: distinguishable permutation

order does not matter indistinguishable

~~possible orbitals~~ ~~occupied orbitals~~

$$\frac{O!}{(O-N)!}$$

Notice that the difference is the $N!$

# of particles, possible # of orbitals

$$\frac{O!}{N!(O-N)!}$$

So the real partition function is the one for indistinguishable particles, given by

$$\boxed{Z_N = \frac{1}{N!} Z_1^N = \frac{1}{N!}(n_Q V)^N}$$

KK Eq. 3.68

$$U = \tau^2 \frac{\partial}{\partial \tau} \ln Z = \tau^2 \frac{\partial}{\partial \tau}\left[\ln Z_1^N - \cancel{\ln N!}\right]$$

$U = \frac{3}{2} N\tau$ so we get the same as before

$$F = -\tau N \ln Z = -\tau N\left[\ln Z_1^N - \ln N!\right]$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_\tau = \frac{\partial}{\partial V}\left[\tau N \ln Z_1 - \cancel{\tau N \ln N!}\right]$$

$pV = N\tau$ as before

but

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = -\frac{\partial}{\partial \tau}\left[-\tau N \ln Z_1 + \tau N \ln N!\right]$$

Additional term

Additional term $\quad \ln N! \approx N \ln N - N \quad$ Stirling's

$$\sigma = N\left[\ln(n_Q/n) + \frac{3}{2} + \ln N\right] - N\left[\ln N - N\right]$$

$$\sigma = N\left[\ln(n_Q/n) + \frac{3}{2} + \cancel{\ln N} - \cancel{\ln N} + 1\right]$$

$$\boxed{\sigma = N\left[\ln(n_Q/n) + \frac{5}{2}\right]}$$

KK Eq. 3.76. Now it is correct.

Sackur-Tetrode equation

$$\frac{\sigma}{N} = \ln(n_Q/n) + \frac{5}{2}$$

is constant as needed.

Notice that n_Q includes $\hbar$!