Quiz 5 today

Quiz 6 Thursday, April 21

Today: finish Chapter 6, start Chapter 7 "Quantum Statistics"

At end of last lecture:

$$Z_{\text{total}} = Z_1 Z_2 \cdots Z_N$$

for distinguishable weakly interacting particles

$$Z_{\text{total}} = Z_1^N$$

distinguishable, identical, weakly interacting particles

"distinguishable" arises in two ways:

particles large, made of many atoms but not exactly the same

particles localized in space, e.g. nuclei or magnetic dipoles in a crystal

so possible to be identical but distinguishable for crystal

Case 2: identical weakly-interacting undistinguishable particles in some system.

Claim: $Z_{total} \simeq \frac{1}{N!} Z_1^N$ low-density high-T

Z_{total} is only approximately equal to right side, holds when system has many more energy levels than there are particles so unlikely that two particles will have same energy state. This corresponds to low-density and high-temperature gases.

To see what is going on, assume quantum system such as particle in impenetrable box (one of simplest examples discussed in QM, see pages 368–369 of Appendix A in Schroeder), that has discrete energy levels, $\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$. If particles weakly interact, each particle can have its own energy value from these four choices. If we have two distinguishable particles, possible states $s = (s_1, s_2)$ can be listed like this

	ϵ_1	ϵ_2	ϵ_3	ϵ_4	E
4	AB	0	0	0	$2\epsilon_1$
	0	AB	0	0	$2\epsilon_2$
	0	0	AB	0	$2\epsilon_3$
	0	0	0	AB	$2\epsilon_4$
12	A	B	0	0	$\epsilon_1+\epsilon_2$
	B	A	0	0	$\epsilon_1+\epsilon_2$
	A	0	B	0	$\epsilon_1+\epsilon_3$
	B	0	A	0	$\epsilon_1+\epsilon_3$

and so on. Other states would be:

A 0 B 0	A 0 0 B
B 0	B 0 0 A
	0 A B 0
	0 B A 0
	0 A 0 B
	0 B 0 A
	0 0 A B
	0 0 B A

16 states total

$$Z = \sum_{s_1=1}^{4} \sum_{s_2=1}^{4} e^{-\beta E_1} e^{-\beta E_2} = Z_1 Z_2$$

If particles are <u>indistinguishable</u> weakly-interacting, possible states are

6 states instead of 12	1100	2000
	1010	0200
	1001	0020
	0110	0002
	0101	
	0011	

these are double counted in sum

these should not be double counted in sum

$$\frac{1}{2!}\sum_{s_1}^{\prime}\sum_{s_2}^{\prime} e^{-\beta E_{s_1}} e^{-\beta E_{s_2}} = \frac{1}{2!}\left(\overbrace{\sum_{s_1=s_2}^{\prime} e^{-\beta 2E_{s_1}}}^{\text{trouble}} + \sum_{s_1\neq s_2}^{\prime} e^{-\beta(E_{s_1}+E_{s_2})}\right)$$

For this case, $Z_{total} \neq \frac{1}{2} Z_1^2$ because of the states that have two (or more) particles. But note how if there are many levels N and few particles K, number of states that have distinct levels grows rapidly with N compared to number of states with 2 or more in same state, so for low-density gases, for which $N \gg K$, most states have at most one particle and it is acceptable error to include states with two or more particles in same energy level. So

$$Z_{total} \approx \frac{1}{N!} Z_1^N$$

↳ what you get if particles are distinguishable

↑ corrects for states that have identical particles with different energies, but wrong for states w/ 2 or more particles

Example of identical weakly-interacting indistinguishable particles: what is Helmholtz free energy F in terms of partition f^n Z_1 for single particle?

Problem 6.44 on p. 257 of Schroeder

$$Z_N \cong \frac{1}{N!} Z_1^N$$

$$F_N = -kT \ln Z_N = -kT \ln\left[\frac{Z_1^N}{N!}\right]$$

$$\cong -kT\left[N \ln Z_1 - N \ln N + N\right] \quad \text{use Stirling}$$

$$\boxed{F = -NkT\left[1 + \ln\left(Z_1/N\right)\right]} \quad (*)$$

Quite useful, we will use for ideal gas

Subtlety: F extensive requires Z_1/N to be intensive which requires Z_1 to be extensive since N is extensive.

Not all obvious $Z_1 = \sum_{s_1} e^{-\beta E_s}$ is extensive object.

F extensive since $F = U - TS$ (ext, ext)

For ideal gas, we will see

$$Z_1 = \frac{V}{V_Q} Z_{int} \propto V$$

and so is indeed extensive quantity

From $(*)$, $\boxed{\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT \ln\left(\frac{Z_1}{N}\right)}$ simple form

Ideal gas with molecules: Section 6.7

Will leave most details for you to read in Schroeder, I have little to add and there are so many equations, gets confusing. So let me outline steps and issues.

Consider ideal gas of N identical molecules, temp. T. "Ideal" automatically implies weakly interacting, but again need assumption of <u>low density</u> and high-temperature. Then ok to write

$$Z_N \simeq \frac{1}{N!} Z_1^N$$

$$Z_1 = \sum_s e^{-\beta E_s} = \sum_s e^{-\beta\left[\frac{1}{2}mv^2 + E_s\right]}$$

(E_s: quantum levels)

$$= \sum_{x,v} e^{-\beta m v^2/2} \cdot \sum_s e^{-\beta E_s}$$

$e^{-\beta\left[\frac{mv^2}{2} + V(x,y,z)\right]} e^{-\beta E_s}$ is rot. energy V

$$\boxed{Z_1 = Z_{trans} \times Z_{int}}$$

"int" = internal energy structure: rotation, vibration, electronic

Generally can <u>not</u> write Z_{int} in simple form, e.g.

$$Z_{int} \neq Z_{elect.} \times Z_{rot} \times Z_{vibration}$$

(but can often write $Z_{int} = Z_{el} \times Z_{vib\text{-}rot}$)

Reason is vibration mode can modify $I = \mu r^2$ and so affect rotation energy levels, and vice versa.

example: $E_{n,j} = hf\left(n + \frac{1}{2}\right) + j(j+1)\epsilon(n)$

(n: vibration quantum #; $\epsilon(n)$: energy $\frac{\hbar^2}{\mu r^2}$; $f = f(j)$)

rotation can "stretch" molecule and alter vibration, and vice versa

Partition function for translational degrees of freedom in two ways:

$$Z_{trans} = \frac{V}{L_Q^3} = \frac{V}{V_Q} \qquad L_Q = \frac{h}{\sqrt{2\pi m k T}}$$

(1) <u>semiclassical approximation</u>, valid when variables are continuous

$$Z_{trans} = \sum_s e^{-\beta m v^2/2} = \sum_x \sum_p e^{-\beta p^2/(2m)}$$

$$\simeq \int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} e^{-\beta p^2/(2m)} \frac{d^3\vec{x}\, d^3\vec{p}}{h^3} \qquad d^3\vec{x} = dx\,dy\,dz \quad d^3\vec{p} = dp_x\,dp_y\,dp_z$$

$$\simeq \frac{V}{h^3}\left(2\pi m k T\right)^{3/2} = \frac{V}{L_Q^3}$$

$L_Q = \frac{h}{\sqrt{2\pi m k T}}$ = de Broglie wavelength of particle of mass m and energy kT, not quite $\frac{1}{2}kT$

For N_2 at $T = 300K$, $L_Q \simeq 2\cdot 10^{-11}\,m \simeq \frac{1}{2} r_{Bohr}$

$V_Q \simeq \frac{1}{8}$ volume of H atom, tiny!

$V/N / V_Q$ $\quad L_Q^3 \sim 10^{-33}$ $\quad \times 10^7$

$V/N \simeq 10^{-26}$

(2) quantum mechanics: free particle in box L^3

$$E_n = \frac{h^2 n^2}{8mL^2} \qquad n^2 = n_x^2 + n_y^2 + n_z^2$$

$$Z_{3D,trans} = \sum_{n_x,n_y,n_z} e^{-\beta(n_x^2+n_y^2+n_z^2)\epsilon} = Z_x Z_y Z_z = Z_x^3$$

$$Z_x = \sum_{n=1}^{\infty} e^{-\beta\epsilon n^2} \simeq \int_0^{\infty} e^{-\beta\epsilon n^2} dn = \frac{L}{L_Q} \qquad Z_{3D} = \frac{L^3}{L_Q^3} = \frac{V}{V_Q}$$

provided high-Temp $e^{-\beta\epsilon n^2}$ slowly varying w/ n

For ideal gas of identical indistinguishable weakly-interacting particles

$$F = -kT \ln Z_N = -NkT\left[1 + \ln\left(\frac{Z_1}{N}\right)\right]$$

$$= -NkT\left[1 + \ln\left(\frac{V}{N}\frac{Z_{int}}{V_Q}\right)\right]$$

$$= \underbrace{-NkT\left[1 + \ln\left(\frac{V}{V_Q N}\right)\right]}_{F_{trans}} \underbrace{- NkT \ln Z_{int}}_{F_{internal}}$$

$Z_{int} = 1$ for atom!

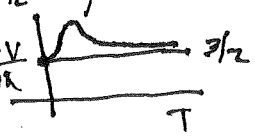
So we see that complexities of molecular structure, all related to Z_{int}, simply adds to result if we had only atoms and so only translational motion. Turn out that this holds also for all thermodynamic quantities.

$$U = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[\frac{F}{kT}\right] = -\frac{\partial}{\partial \beta}[\beta F]$$

$$U = \underbrace{\frac{3}{2}NkT}_{\text{equipartition result}} + \underbrace{U_{int}}_{\text{contribution from molecular structure}} \qquad U_{int} = -N\frac{\partial}{\partial \beta}\ln Z_{int}$$

$$C_V = \frac{dU}{dT} = \frac{3}{2}Nk + \frac{\partial U_{int}}{\partial T}$$

example: gas of spin-1/2 magnetic dipoles



$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V} \quad \text{ideal gas law!}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = \underbrace{Nk\left[\frac{5}{2} + \ln\left(\frac{V}{V_Q}\frac{1}{N}\right)\right]}_{\text{Sackur-Tetrode}} - \underbrace{\frac{\partial F_{int}}{\partial T}}_{\text{molecular correction to entropy}}$$