Identical Particles

For a single particle in a box we found $Z_1 = \frac{V}{\lambda_D^3}$ where the de Broglie wavelength

$$\lambda_D = \left(\frac{2\pi\hbar^2}{mk_BT}\right)^{\frac{1}{2}}$$

From this the entropy is calculated as $S = k_B\left[lnV + \frac{3}{2}ln\left(\frac{mk_BT}{2\pi\hbar^2}\right) + \frac{3}{2}\right]$

For N particles $Z_N = Z_1{}^N = \left(\frac{V}{\lambda_D^3}\right)^N$

And for N particles $S_N = Nk_B\left[lnV + \frac{3}{2}ln\left(\frac{mk_BT}{2\pi\hbar^2}\right) + \frac{3}{2}\right]$

$$NlnV = NlnN + Nln\left(\frac{V}{N}\right)$$

For fixed density N/V, S contains $NlnN$

Paradox: S not extensive (should scale as N)

This problem arises because we did not account for properties of identical particles,

Consider wave function $\psi(x_1, x_2)$ for particle 1 at x_1 and particle 2 at x_2

Now exchange particles and the resulting wave function is $\psi(x_2, x_1)$

Meaningful entity are the probabilities $|\psi(x_1, x_2)|^2$

If particles are indistinguishable MUST have $|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2$

And thus $\psi(x_1, x_2) = e^{i\alpha}\psi(x_2, x_1)$ For a second exchange must return to same state thus

$$e^{2i\alpha} = 1$$

TWO CHOICES $e^{i\alpha} = \pm 1$

Wave functions are either symmetric (+1) -- bosons

or antisymmetric (-1) -- fermions

This changes how we are allowed to count available states

If we ignore exchange symmetry,

$\chi_1 = \varphi_i(x_1)\varphi_j(x_2)$ and $\chi_2 = \varphi_i(x_2)\varphi_j(x_1)$ have same Energy $E = \varepsilon_i + \varepsilon_j$

And must not count both states. Need to construct properly symmetrized wave functions and count states using in each energy eigenstate.

$$\psi_i = |n_1, n_1, n_1 \ldots\ldots >$$

Energy $E_i = n_1 e_1 + n_2 e_2 + n_3 e_3 + \cdots$ n an integer but….

Fermi wave functions must be antisymmetric

e.g. for two particles $\Psi = \varphi_i(x_1)\varphi_j(x_2) - \varphi_j(x_2)\varphi_j(x_1)$ is correctly antisymmetric with particle exchange. Note that Ψ vanishes if $i = j$

NO TWO PARTICLES (FERMIONS) CAN OCCUPY THE SAME STATE.

Only possible values are for n = 0 or 1.

Changes how the accessible sates are counted.

General fermion wave function can be expressed as determinant of single particle states

$$\begin{vmatrix} \varphi_i(x_1) & \varphi_j(x_1) & \varphi_k(x_1) \\ \varphi_i(x_2) & \varphi_j(x_2) & \varphi_k(x_2) \\ \varphi_i(x_3) & \varphi_j(x_3) & \varphi_k(x_{13}) \end{vmatrix}$$

For bosons no such restriction can have many particles in same state.

Book Example

Distribute 2 particles over 3 energy levels 0, e, 2e

```
2e   --------   --------   ----x--   --------   -----x---   ---xx--

e     --------   ---x---   -------   ---xx---   ---x----   -------

0    --xx----   ----x--   ----x--   --------   --------   -------
```

Bosons $Z_{boson} = 1 + e^{-\beta\epsilon} + 2e^{-2\beta\epsilon} + e^{-3\beta\epsilon} + e^{-4\beta\epsilon}$

Fermions (no double occupancy)

$$Z_{fermions} = e^{-\beta\epsilon} + e^{-2\beta\epsilon} + e^{-3\beta\epsilon}$$

Have to examine each case in detail to calculate Z

? How to treat case of N particles

Assume can factorize $Z_N = (Z_1)^N$ but this over counts states

e.g. $Z_2 = \left(\sum_i e^{-\beta\varepsilon_i}\right)\left(\sum_i e^{-\beta\varepsilon_i}\right)$ includes terms $e^{-\beta(\varepsilon_1+\varepsilon_2)}$ and $e^{-\beta(\varepsilon_2+\varepsilon_1)}$ i.e. counted same energy state twice

Crude approximation is to divide by N!. Not perfect but OK for independent particles

For $Z_N = (Z_1)^N/N!$ Helmholtz free energy $F = -Nk_BT\{lnZ_1 - lnN + 1\}$

For single particle in 3D, translation degrees of freedom give

$$Z_1 = V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}$$

Therefore

$$F = -Nk_BT\left\{lnV + \frac{3}{2}ln\left(\frac{mk_BT}{2\pi\hbar^2}\right) + 1 - lnN\right\}$$

$$F = -Nk_BT\left\{ln\frac{V}{N} + \frac{3}{2}ln\left(\frac{mk_BT}{2\pi\hbar^2}\right) + 1\right\}$$

Now we like this because for constant density (N/V) it is extensive

Entropy

$$S = -\frac{\partial F}{\partial T} = Nk_BT\left\{ln\frac{V}{N} + \frac{3}{2}ln\left(\frac{mk_BT}{2\pi\hbar^2}\right) + \frac{5}{2}\right\}$$

Sackur-Tetrode formula

Problems

6.3 Four particle states with energy: 0(doubly degenerate), e, 2e and 3e

Distribute 2 identical particles

(a) fermions

2e ----- ---- --x-- ---- ---x-- -----x---

e ----- --x-- ---- ---x-- ----- ---x--

o --x-- ---- ---- ---x--- ---x- -------

0 --x-- ---x-- --x-- ----- ----- -------

$$Z_F = 1 + 2e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}$$

(b) bosons need to add terms with double occupancy

$$Z_B = Z_F + 2e^0 + e^{-2\beta\varepsilon} + e^{-4\beta\varepsilon} = 3 + 2e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon}$$

6.6 Ortho-para H2

Para: ground state L=0 n molecules

Ortho: excited state e L=1 3-fold degenerate N-n molecules

Number of ways of distributing N with n ortho $W = \frac{N!}{n!(N-n)!}$ If ortho singly degenerate.

But extra multiplicity of n 3-fold degenerate states $=3^n$

$$W_{total} = \frac{N!}{n!\,(N-n)!}3^n$$

Free energy $U = n\varepsilon$

Entropy

$$S = k_B lnW = k_B\{NlnN - nln(n) - (N-n)\ln(N-n) + nln3\}$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial S}{\partial n}\frac{\partial n}{\partial U} = \frac{1}{\varepsilon}\left[k_B\left(ln\left(\frac{N-n}{n}\right) + ln3\right)\right]$$

$$\frac{\varepsilon}{k_B T} = ln\left[3\left(\frac{N}{n} - 1\right)\right]$$

$$e^{\frac{\varepsilon}{k_B T}} = 3\frac{N}{n} - 3$$

$3 + e^{\frac{\varepsilon}{k_B T}} = 3\frac{N}{n}$ $\frac{n}{N} = \frac{3}{3+e^{\frac{\varepsilon}{k_B T}}}$

High temperature (300 K) bottle compressed H_2 is 75% ortho

Low temperature: 0% ortho and 100% para. Note if production of H_2 creates 75% ortho, lose a lot of liquid H_2 in transport because the ortho to para decay releases a lot of heat (comparable to latent heat of evaporation). E(ortho-para) ~ 110 K. After production the liquefiers are constructed to have beds of Fe_3O_4 to convert ortho to para before shipping.

Problem 6.7

Spin ½ particles in magnetic field. Particles have magnetic moment μ. Two spin states with energy $+\mu B$ and $-\mu B$.

Partition function for single particle $Z_1 = e^{-\frac{\mu B}{k_B T}} + e^{+\frac{\mu B}{k_B T}} = 2cosh\frac{\mu B}{k_B T}$

For N particles $Z_N = (Z_1)^N$

Free energy $F = -k_B T ln Z_N = -N k_B T \left\{ \ln 2 + \ln[cosh \frac{\mu B}{k_B T}] \right\}$

Entropy $S = -\frac{\partial F}{\partial T} = N k_B \left\{ \ln 2 + \ln[cosh \frac{\mu B}{k_B T}] \right\} + N k_B T \left(-\frac{\mu B}{k_B T^2} tanh\left(\frac{\mu B}{k_B T}\right) \right)$

S is a function only of B/T.

If isolate a paramagnet, B/T remains constant (no heat leaks). Start at 1K in 10T and demagnetize to 10 gauss, T will decrease to 100μK. Usually keep final field higher to have a larger heat capacity and can stay colder longer in face of inevitable heat leaks (~ nW)