

# Systems of Independent Particles

Until now, we have ignored the nature of the particles composing our systems and concentrated on the nature of the systems themselves. We now ask if it is possible to describe the system P.f. in terms of a 'particle P.f.'

## General Comments:

Each system is assumed composed of  $N$  particles that interact at most weakly i.e., strongly enough to maintain thermal equilb. in the ensemble but not so strongly as to influence the energy level spectrum of each particle. Note however that the particle states are continually changing due to collisions etc.

For weakly interacting particles we can write

$$\hat{H} = \sum_{i=1}^N \hat{H}_i$$

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \prod_{i=1}^N \psi_i(\vec{r}_i)$$

$$E = \sum_{i=1}^N E_i$$

$$\hat{H}_i \psi_i = E_i \psi_i \quad i = 1, 2, \dots, N$$

From the viewpoint of the system we have:

$$\hat{H}_{\text{system}} \Psi_{\text{sys}} = E_{\text{sys}} \Psi_{\text{sys}}$$

where

$$E_{\text{sys}} = \sum_{i=1}^N \epsilon_i \quad \epsilon_i - i^{\text{th}} \text{ particle state}$$

and the system P.F. is

$$Q = \sum_j e^{-E_j/kT} = e^{-E_1/kT} + e^{-E_2/kT} + \dots$$

where the sum includes all possible system states available to every system in the ensemble consistent with whatever constraints exist for the particles, eg, Fermion or Boson. Furthermore, the system  $E_j$  are each composed of some combination of particle states and the nature of that combination depends on whether the particles are distinguishable.

For example, for the  $k^{\text{th}}$  system state,  $E_k$  we have:

$$E_k = \underbrace{\epsilon_{a,i}^k + \epsilon_{b,i}^k + \epsilon_{c,i}^k + \dots}_{\text{impossible for Fermions if the particles are indistinguishable}} = \sum_i n_i \epsilon_i^k$$

where  $n_i$  - no. of particles in the  $i^{\text{th}}$  particle state

$\epsilon_{a,i}^k$  - energy of particle a in the  $i^{\text{th}}$  particle state of the  $k^{\text{th}}$  system state

Note that particle state 'i' contains two particles a & b which would not be allowed for Fermions whose occupation number is 0 or 1.

On the other hand, for distinguishable particles, permutation of labels between states leads to new system states but not new energies. Thus for system states  $k$  &  $k+1$

$$E_k = E_{a,i}^k + E_{b,j}^k \quad ; \quad E_{k+1} = E_{b,i}^{k+1} + E_{a,j}^{k+1}$$

Here  $E_k$  &  $E_{k+1}$  are different system states but the energies are the same, i.e. they both belong to the same energy level and this is okay for dist. particles.

We now consider these two cases in more detail by distinguishing between distinguishable and indistinguishable particles.

I) Distinguishable Particles - MAXWELL BOLTZMANN STATISTICS

Label the particles as a, b, c ... etc., ie distinguishable.

Define the 'single particle p.f.' as, for particle P

$q_{P,particle} \equiv \sum_i e^{-\epsilon_{P,i}/KT}$ 
 where the sum is over all possible particle states  $i$ ;  $\epsilon_{P,i}$  is the  $i^{th}$  particle state for particle P.

We now contend that the product

$q_a \cdot q_b \cdot q_c \dots etc.$

will generate all acceptable system states corresponding to the system p.f. Q, ie (Distinguishable particles)

$Q = \sum_{\text{system states}} e^{-E_i/KT} \stackrel{!}{=} \prod_{j=1}^N q_j \equiv q_a \cdot q_b \cdot \dots etc = \sum_{\text{particle states}} e^{-\epsilon_{a,i}/KT} \cdot \sum_{\text{particle states}} e^{-\epsilon_{b,i}/KT} \dots$ 
  
(ie, prod. over particle P.f.'s)

Example

Consider just two particles, a & b w two particles states  $\epsilon_1, \epsilon_2$  available to each. The system states then include

Particle state / system state	$\epsilon_1$	$\epsilon_2$	Deg
$E_1$	a	b	} $\Omega = 2$
$E_2$	b	a	
$E_3$	a, b	$\emptyset$	$\Omega = 1$
$E_4$	$\emptyset$	a, b	$\Omega = 1$

Note: Here we generate sys. states from particle state exactly as we formed ensemble states from system states. In both cases only weak interactions are assumed and the deg. of each system state is given by  $\frac{N!}{\prod n_i!}$  eg,  $\frac{2!}{1!1!}$  for single occupation

Thus

$Q = \sum_{i=1}^4 e^{-E_i/KT} = e^{-E_1/KT} + e^{-E_2/KT} + e^{-E_3/KT} + e^{-E_4/KT}$

where

$$E_1 = \epsilon_{a,1}^1 + \epsilon_{b,2}^1$$

$$E_2 = \epsilon_{a,2}^2 + \epsilon_{b,1}^2$$

$$E_3 = \epsilon_{a,1}^3 + \epsilon_{b,1}^3 + \epsilon_{\phi,2}^3 \text{ (empty)}$$

$$E_4 = \epsilon_{a,2}^4 + \epsilon_{b,2}^4 + \epsilon_{\phi,1}^4 \text{ (empty)}$$

where  $\epsilon_{a,2}^4$  - particle a in particle state 2 of system state 4

Hence

$$Q = c \cdot e^{-\frac{\epsilon_{a,1}^1 + \epsilon_{b,2}^1}{kT}} + e^{-\frac{\epsilon_{a,2}^2 + \epsilon_{b,1}^2}{kT}} + e^{-\frac{\epsilon_{a,1}^3 + \epsilon_{b,1}^3}{kT}} + e^{-\frac{\epsilon_{a,2}^4 + \epsilon_{b,2}^4}{kT}}$$

Now

$$q_a = \sum_{i=1}^2 e^{-\epsilon_{a,i}/kT} = e^{-\epsilon_{a,1}/kT} + e^{-\epsilon_{a,2}/kT}$$

$$q_b = \sum_{i=1}^2 e^{-\epsilon_{b,i}/kT} = e^{-\epsilon_{b,1}/kT} + e^{-\epsilon_{b,2}/kT}$$

QUERY: Does  $Q = q_a \cdot q_b$ ?

$$\begin{aligned} q_a \cdot q_b &= \sum_{i=1}^2 e^{-\epsilon_{a,i}/kT} \cdot \sum_{j=1}^2 e^{-\epsilon_{b,j}/kT} \\ &= \left( e^{-\epsilon_{a,1}/kT} + e^{-\epsilon_{a,2}/kT} \right) \left( e^{-\epsilon_{b,1}/kT} + e^{-\epsilon_{b,2}/kT} \right) \\ &= e^{-\frac{\epsilon_{a,1} + \epsilon_{b,1}}{kT}} + e^{-\frac{\epsilon_{a,2} + \epsilon_{b,1}}{kT}} + e^{-\frac{\epsilon_{a,1} + \epsilon_{b,2}}{kT}} + e^{-\frac{\epsilon_{a,2} + \epsilon_{b,2}}{kT}} \end{aligned}$$

Thus we see that the product

$$Q = q_a \cdot q_b = \sum_i e^{-\epsilon_{a,i}/kT} \cdot \sum_j e^{-\epsilon_{b,j}/kT} = \sum_{ij} e^{-\frac{\epsilon_{a,i} + \epsilon_{b,j}}{kT}}$$

is really valid & more generally, the system P.f. is just the product of particle P.f., i.e.

$$\rightarrow Q(\text{system}) = \prod_{\text{all particles } i} q_i \quad \left. \begin{array}{l} \text{Distinguishable} \\ \text{PARTICLES ONLY} \end{array} \right\} \begin{array}{l} \text{MAXWELL} \\ \text{BOLTZMANN} \end{array}$$

## II) IDENTICAL PARTICLES

If the particles are identical, as is almost always the case (except for lattice models where the lattice sites are labelled) we find:

$$Q_{\text{identical}}(\text{system}) \neq \prod_{i=1}^N q_i$$

Because the nature of the natural particle symmetry must be accounted for. There are three cases that apply to identical particles:

- a) Fermi-Dirac Statistics
  - b) Bose-Einstein " " }
  - c) Corrected Maxwell Boltzmann Statistics
- } exact

Note that all particles are either FD or BE. CMB<sup>\*</sup> statistics are therefore approximate but usually with negligible error. The great advantage of CMB is computational since BE & FD can't be written as products over the individual particles.

### Correction of MB Statistics for Indistinguishability

We have seen that, provided our particles are distinguishable MB statistics are exact, i.e.

$$Q(\text{system}) = \prod_{\substack{\text{all} \\ \text{particle} \\ \text{labels}}} q_{\text{label}}$$

i.e.,  $Q$  can be written as a product over individual particle P.F.'s.

\* CMB - Corrected Maxwell Boltzmann

## Correction of $Q$ Statistics for Indistinguishability

Starting with the exact MB statistics where

$$Q = \prod_{\text{labels}} q_{\text{label}} = q_a q_b \dots$$

and removing the labels i.e.,  $a = b = c = \dots$

We have

$$Q = \prod_{\text{label}} q_{\text{label}} = q^N$$

for  $N$  particles. However this presents problems for indistinguishable particles due to overcounts, since a permutation of labels do not lead to new system states when the particles are identical.

### Example

Consider 3 identical particles  $a, b$  &  $c$  for moment labelled and 3 available states  $e_1, e_2$  &  $e_3$ . Then

$$Q = q_a q_b q_c = \sum_{i=1}^3 e^{-E_{a,i}/kT} \sum_{i=1}^3 e^{-E_{b,i}/kT} \sum_{i=1}^3 e^{-E_{c,i}/kT}$$

This leads to  $3^3 = 27$  terms that can be classified as follows:

Classification

Occurrence

$\pm_3 Q = g^N$  OK  
if particles are identical?

The Fix

1) Each particle in a different state eg,  
 $e^{-[\epsilon_{a1} + \epsilon_{b2} + \epsilon_{c3}]}$

$\frac{3!}{1!1!1!} = 6$

{	ABC
	ACB
	BAC
	BCA
	CAB
	CBA

No. All 6 terms lead to the same system energy states.  
We have an  $N!$  overcount.

Divide by  $N!$

2) Two particles in the same state, eg,  
 $e^{-[\epsilon_{a1} + \epsilon_{b2} + \epsilon_{c2}]}$

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$\epsilon_1$	$\epsilon_2$	$\epsilon_3$	$\Omega$
2(a,b)	1(c)	-	3
-	2	1	3
1	2	-	3
1	-	2	3
2	-	1	3
-	1	2	3

No - FD: forbids it and BE allows classification 1.

See Below

3) All particles in the same state eg  
 $e^{-[\epsilon_{a1} + \epsilon_{b1} + \epsilon_{c1}]}$

3

$\epsilon_1$	$\epsilon_2$	$\epsilon_3$
abc	abc	abc

No - same reason as 2. See Below

The Fix: For classification 1 we can divide by  $N!$ . For classifications 2 & 3 we obviate the possibility of multiple occupancy by using Corrected Maxwell Boltzmann Statistics only when the degeneracy so overwhelms the number of particles that multiple occupancy is very unlikely.



# CMB: Corrected Maxwell Boltzmann Statistics

Classification 1 required us to divide by  $N!$  whereas classifications 2 & 3 required we use CMB statistics when the no. of particle states  $\gg$  the no. of particles.

Define  $\bar{c}_j$  as the avg. particle density of particle state  $j$ .

Thus the conditions for the use of CMB statistics is then:

$$Q_{\text{CMB}} = \sum e^{-E_j/kT} = \frac{q^N}{N!} \text{ and } \bar{c}_j \ll 1 \text{ for all } j.$$

which hold for indistinguishable particles, the condition that  $\bar{c}_j \ll 1$  is ensured by translation alone (usually).

In the event that the requirement  $\bar{c}_j \ll 1$  fails one must turn to the FD or BE statistics.

Conversely, one can show that at high temperatures and/or low densities  $n_j/w_j \rightarrow 0$  i.e.  $\bar{c}_j \ll 1$  and one finds that FD/BE  $\rightarrow$  CMB statistics.

## Summary

Distinguishable Particles:  $Q = q_a \cdot q_b \cdot q_c \dots$  MBS (exact)

Indistinguishable " :  $Q = q^N / N!$  and  $\bar{c}_j \ll 1$

Use FD or BE statistics for indistinguishable particles if  $\bar{c}_j \not\ll 1$ .

## Comments Regarding the Condition that $\bar{C}_j \ll 1$

The question that arises is 'when does the restriction that  $\bar{C}_j \ll 1$  apply?'

The density of states computation we did for a particle in a three dimensional box showed that the density of states  $\phi(\epsilon) \leq \epsilon$  was given

by

$$\phi(\epsilon) = \frac{\pi}{6} \left( \frac{8ma^2\epsilon}{h^2} \right)^{3/2} \approx 10^{30} \text{ for } \epsilon = \frac{3}{2} kT$$

and  $T \approx 300 \text{ K}$ . For  $N$  particles,  $\phi(\epsilon) \approx 10^{10}$ ,

Since  $\bar{C}_j \ll 1$  is equivalent to  $\phi(\epsilon) \gg N$  we have, using  $\epsilon = \frac{3}{2} kT$  &  $(a^2)^{3/2} = V$  that

$$\frac{\pi}{6} \left( \frac{12m kT}{h^2} \right)^{3/2} \gg \frac{N}{V} = \rho$$

which favors low densities, large mass & high  $T$ .

Thus particles like He liquid at  $4^\circ \text{K}$  are a problem but gaseous He at  $20^\circ \text{K}$  is amenable to CMB statistics. See table 4-1 in your text.

# Molecular Probability Function, $n_i$

In the same way we define  $P_j$  that a system selected at random is in the  $j^{\text{th}}$  system energy state, we can define the prob. that a specific particle (distinguishable particles) or a particle picked at random (indistinguishable particles) by a relationship of the same form as  $P_j = \frac{e^{-E_j/kT}}{Q}$ .

Thus we can write, totally w.o. justification

Prob. of a particle picked at random will be in the  $i^{\text{th}}$  particle state

$$n_i = \frac{e^{-E_i/kT}}{q} \begin{cases} \text{Dist. particles - no restrictions} \\ \text{Indist. particles - } \bar{q}_i \ll 1 \end{cases}$$

## Separation of Degrees of Freedom or Modes

By 'Deg. of Freedom' we mean modes like

Rotation, Vibration, Translation, Electronic, Nuclear.

Provided the modes are independent we can write,

$$\hat{H}_{\text{particle}} = \sum \hat{H}_{\text{modes}} = \hat{H}_T + \hat{H}_V + \hat{H}_R + \hat{H}_e + \hat{H}_n$$

in which case

$$E_{\text{TOTAL}} = E_T + E_V + E_R + E_e + E_n \text{ and}$$

$$q = \sum_{\text{states}} e^{-E_{\text{TOTAL}}/kT} = \sum_{T,V,R,e,n} e^{-E_{\text{TOTAL}}/kT} = q_T q_V q_R q_e q_n$$

## Summary

In terms of molecular partition functions, we have

$$Q(\text{dist}) = \prod_{\text{labels}} (g_T g_v g_r g_e g_n) \quad \text{exact}$$

$$Q(\text{indist.}) = (g_T g_v g_r g_e g_n)^N \cdot \frac{1}{N!} \quad \bar{c}_j \ll 1$$

Note: In terms of 'levels' we have:

$$g = \sum_{\text{levels}} w_j e^{-\epsilon_j / kT} = \sum_T \sum_V \sum_R \sum_E \sum_N \underbrace{w_T w_V w_R w_E w_N}_{w_j} e^{-\sum_{\text{modes}} \epsilon_{\text{mode}} / kT}$$

## Multicomponent Systems

$$Q_{\text{cmB}} = \frac{\prod_j g_j^{N_j}}{\prod_j N_j!} \quad \text{for } j \text{ components}$$

## Probability of a Specific Mode

Again we can write assuming modes are separable,

$$\eta_j(\text{mode } k) = \frac{e^{-\epsilon_{kj} / kT}}{g_k}$$

where  $\eta_j$  is the prob. of a particle being in the  $k^{\text{th}}$  mode of the  $j^{\text{th}}$  particle state.

Temperature Dependence of  $\eta_i$  (particle states)

- a) Limit  $\eta_0 \rightarrow 1$  since only the g.s.  $\epsilon_0$  is populated  
 $T \rightarrow 0$
- b) Limit  $\eta_i \rightarrow$  constant, i.e. all energy states within a level are equally populated but the levels are populated in proportion to their degeneracy.  
 $T \rightarrow \infty$

States vs Levels

Here

$$\eta_j(\text{levels}) = w_j \cdot \eta_j(\text{states}) = \frac{w_j \cdot e^{-\epsilon_j/kT}}{q}$$

$$q = \sum_{\text{states}} e^{-\epsilon_j/kT} = \sum_{\text{levels}} w_j \cdot e^{-\epsilon_j/kT}$$

Avg. Energy/Particle

$$\bar{\epsilon} = \sum \eta_i \epsilon_i = \frac{1}{q} \sum \epsilon_i e^{-\epsilon_i/kT}$$

$$\bar{E}(\text{system}) = N \bar{\epsilon}(\text{particle}) = E_T / N_T$$

OR

$$\bar{E}_{\text{system}} = N \bar{\epsilon}_{\text{particle}} = \sum N \eta_i \epsilon_i \text{ but } \bar{c}_i = N \eta_i$$

$$\bar{E}_{\text{system}} = \sum \bar{c}_i \epsilon_i \text{ where again,}$$

$\eta_i$  - prob. of the  $i^{\text{th}}$  particle state

$N$  - total particles in a system

$\bar{c}_i$  - avg no. of particles in  $i^{\text{th}}$  particle state

Note that  $\sum \bar{c}_i = N \sum \eta_i = N$  as  $\sum_{\text{all } i} \eta_i = 1$

Also  $\bar{c}_j \ll 1 \Rightarrow \eta_j \ll 1/N$

## Fluctuations in $\epsilon_j$

$$\bar{\epsilon} = \frac{1}{g} \sum \epsilon_j e^{-\epsilon_j/kT}$$

Diff. w.r.t T & using  $\bar{\epsilon}_{\text{system}} = N\bar{\epsilon}$  in the same way we did when we studied fluctuations in a system we arrive at the conclusion that

$$\sigma_{\epsilon} = \left[ \frac{kT^2 C_v}{N} \right]^{\frac{1}{2}} \approx O(\bar{\epsilon}) \approx O(kT) \text{ for } C_v \sim Nk$$

instead of  $\frac{1}{\sqrt{N}}$  ie, the dispersion is broad showing that sharp distributions are typical of a  $N$  body problem when  $N$  is very large.

# IDEAL MONOATOMIC GAS

We assume a monoatomic gas which is basically ideal. Since the particles are indistinguishable and  $\bar{\epsilon} \ll 1$  (translation), we can thus write:

$$Q = \frac{q^N}{N!}$$

Assuming further that, at least to a first approx., all modes are independent we have:

$$q = q_T q_C q_n$$

so

$$Q = (q_T q_C q_n)^N \frac{1}{N!}$$

## Translational Partition Function, $q_T$

Our model of the gas is the particle in a 3 dim. cubic box of side  $L$ . Then

$$\epsilon_{n_x, n_y, n_z} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z = 1, 2, \dots$$

Our energy zero is all particles at rest, i.e.  $\epsilon = 0$ , which violates the UCP but causes no problems.

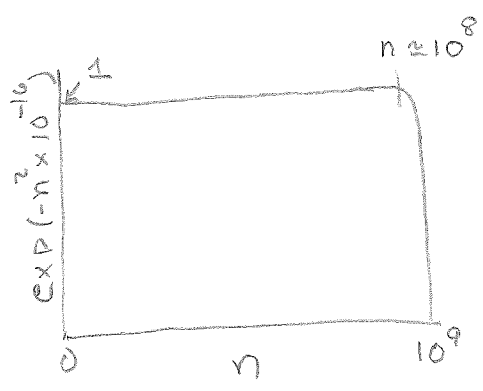
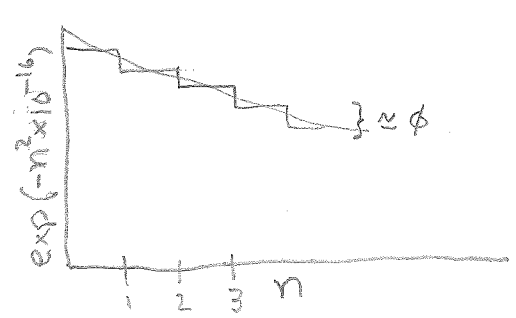
Then

$Q_T = \sum_{n_x, n_y, n_z} e^{-\beta \epsilon_{n_x, n_y, n_z}}$  single particle P.f.

$$= \sum_{n_x=1}^{\infty} \exp\left(-\frac{\beta h^2 n_x^2}{8mL^2}\right) \sum_{n_y=1}^{\infty} \exp\left(-\frac{\beta h^2 n_y^2}{8mL^2}\right) \sum_{n_z=1}^{\infty} \exp\left(-\frac{\beta h^2 n_z^2}{8mL^2}\right)$$

$$= \left[ \sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8mL^2}\right) \right]^3 \text{ since all 3 sums are identical}$$

There is no closed form evaluation possible for this sum so the alternative is to replace the sum by an integral. This is justified by the fact that the individual terms in the sum are all essentially 1 until  $n \approx 10^8$  after which the exponential drops to zero as the following graph shows.



$n$	$\frac{\exp(-n^2 \times 10^{-16})}{1}$
0	1
$10^6$	0.999999
$10^7$	0.989...
$10^8$	$6 \times 10^{-2}$
$10^9$	$10^{-79}$

Thus the sum  $\sum \exp(-\alpha^2 n^2)$  where  $\alpha^2 = \frac{h^2}{8mL^2 kT} \approx 10^{-16}$

can be replaced by an integral, i.e.

$$\sum_{n=1}^{\infty} e^{-n^2 \alpha^2} \approx \sum_{n=1}^{\infty} e^{-n^2 \alpha^2} \Delta n \approx \int_0^{\infty} e^{-n^2 \alpha^2} dn = \frac{\sqrt{\pi}}{2\alpha} = \frac{a}{h} \sqrt{2\pi m kT}$$



Note:  $e^{-\frac{n^2 h^2}{8ma^2 kT}} \sim e^{-10^{-16} n^2}$  for a Helium at  $n \sim 300k$   
 ie,  $\frac{h^2}{8ma^2 kT} \sim 10^{-16}$

```

10 ! CALC. OF EXP(-N^2*10^-16)
    VS N^2 TO JUSTIFY REPLACING
    THE TRANS.P.F. BY AN INTEGRA
    L.
20 PRINT TAB(5); "N"; TAB(13); "EX
    P(-N^2)*10^-16"
30 PRINT
40 FOR N=0 TO 1000000000 STEP 1
    0
50 N=2*N
60 Q=EXP((-N^2)*1.E-16)
70 PRINT N; TAB(13); Q
80 NEXT N
90 END
    
```

N	EXP(-N^2)*10^-16
0	1
20	1
60	1
10 <sup>2</sup> 140	.999999999999998
300	.999999999999991
620	.999999999999962
10 <sup>3</sup> 1260	.99999999999841
2540	.99999999999355
5100	.9999999997399
10 <sup>4</sup> 10220	.9999999989555
20460	.9999999958139
40940	.9999999832392
81900	.9999999329239
10 <sup>5</sup> 163820	.9999997316304
327660	.99998926395
655340	.999957053871
10 <sup>6</sup> 1310700	.999828221307
2621420	.999313051775
5242860	.997255016279
10 <sup>7</sup> 10485740	.989065150567
20971500	.956972731922
41943020	.838683655842
83886060	.494757712355
10 <sup>8</sup> 167772140	5.99197509582E-2
335544300	1.28907865049E-5
671088620	2.76131846557E-20
10 <sup>9</sup> 1342177260	5.81384778213E-79

Note:  $\sum_{n=0}^{\infty} e^{-10^{-16} n^2} \sim 10^8$  because all terms in the p.f. for  $n \gtrsim 10^8$  contribute

unity, hence  $g_T(\text{dim}) = \sum_{n=0}^{\infty} e^{-10^{-16} n^2} \sim 1 \times N_{\text{effective}} \sim 1 \times 10^8 = 10^8$ . We

may compare this w/ the integrated result, ie  $g_T(\text{int.}) = \frac{\sqrt{2\pi m a^2 kT}}{h}$ .

From above,  $\frac{8ma^2 kT}{h^2} \sim 10^{+16}$  so  $\sqrt{\frac{8ma^2 kT}{h^2}} \sim 10^8$

OR  $\frac{\sqrt{8ma^2 kT}}{h} = \frac{2}{\sqrt{\pi}} \times \frac{\sqrt{2\pi m kT a^2}}{h}$  so  $\frac{2}{\sqrt{\pi}} \cdot g_T(\text{int.}) \sim 10^8$  OR  $g_T \sim \frac{\sqrt{\pi} \cdot 10^8}{2} \sim 10^8$

Thus we see that the int. form & the direct sum give essentially the same result, which of course, they must.

Thus,  $g_{\text{translational}} = \left( \frac{2\pi m kT}{h^2} \right)^{3/2} V$  and defining

$$\Delta \text{ (lambda)} = \frac{h}{(2\pi m kT)^{1/2}} \text{ we often write}$$

$$g_{\text{trans}} = \frac{V}{\Delta^3} \text{ for a single particle}$$

where  $\Delta$  has the units of length.

### Alternative Derivation of $g_T$

We have from chapter, the density of states for a single particle in a box

$$w(\epsilon, \Delta\epsilon) = \Phi(\epsilon + \Delta\epsilon) - \Phi(\epsilon) \approx \frac{\pi}{4} \left( \frac{2mL^2}{h^2} \right)^{3/2} \epsilon^{1/2} \Delta\epsilon$$

$$g_T = \left[ \sum e^{-n^2 \alpha^2} \right]^3 = \sum_{\epsilon} w(\epsilon) e^{-\epsilon/kT} \rightarrow \int_0^{\infty} \phi(\epsilon) e^{-\epsilon/kT} d\epsilon$$

$$= \left( \frac{2\pi m kT}{h^2} \right)^{3/2} V \text{ as before}$$

# Energy References in General

It is usually convenient to reference energy levels to the ground state  $\epsilon_1$ , which we typically set to  $\phi$ , i.e.  $\epsilon_1 \equiv \phi$ . Then  $q$  can be written

$$\begin{aligned}
 q &= \sum_{\text{levels}} w_i e^{-\epsilon_i/kT} = e^{\epsilon_1/kT} \cdot e^{-\epsilon_1/kT} \sum_{i=1}^{\infty} w_i e^{-\epsilon_i/kT} \\
 &= e^{-\epsilon_1/kT} \sum_{i=1}^{\infty} w_i e^{-(\epsilon_i - \epsilon_1)/kT} \\
 &= e^{-\epsilon_1/kT} \sum_{i=1}^{\infty} w_i e^{-\Delta\epsilon_i/kT} \quad \text{so we have}
 \end{aligned}$$

$$q_T = \sum_i w_i e^{-\Delta\epsilon_i/kT} = w_1 + w_2 e^{-\Delta\epsilon_2/kT} + \dots$$

Since  $\epsilon_1 \equiv \phi$  & where  $\Delta\epsilon_2 \equiv \epsilon_{i2} = \epsilon_2 - \epsilon_1 = \epsilon_2$

## Internal Modes

The internal modes, nuclear and electronic are rigorously separable from translation.

### 1) Nuclear Partition Function

$$q_n = \sum_{\text{levels } s,j} w_{n,j} e^{-\epsilon_j/kT} = w_{n,1} + w_{n,2} e^{-\Delta\epsilon_2/kT} + \dots$$

where again  $\Delta\epsilon_2 = \epsilon_2 - \epsilon_1$ . Now  $\epsilon_2 - \epsilon_1 \sim 0(10^{-6} \text{ ergs or } @ 1 \text{ meV})$ . Thus for  $\Delta\epsilon_2 \sim 0(kT) \sim 10^{-6}$  so

$T = \frac{10^{-6}}{10^{-16}} \sim 10^{10} \text{ K}^*$  so it take  $T \sim 10^{10} \text{ K}$  to promote from  $\epsilon_1 \equiv \phi$  to  $\epsilon_2$ .

\*  $k \approx 10^{-16} \text{ erg/k or } 10^{-23} \text{ J/k}$

Percentage of each electronic level occupied in atomic Oxygen as a function of temperature. Energies and weights from McQuarrie, p 84.

39.2

Temperature = 1E-300 K  
Energy Level( 0 )= 100  
Energy Level( 1 )= 0  
Energy Level( 2 )= 0  
Energy Level( 3 )= 0  
Energy Level( 4 )= 0

Temperature = 0.00001 K  
Energy Level( 0 )= 100  
Energy Level( 1 )= 0  
Energy Level( 2 )= 0  
Energy Level( 3 )= 0  
Energy Level( 4 )= 0

Temperature = 0.1 K  
Energy Level( 0 )= 100  
Energy Level( 1 )= 0  
Energy Level( 2 )= 0  
Energy Level( 3 )= 0  
Energy Level( 4 )= 0

Temperature = 10 K  
Energy Level( 0 )= 99.999999950088  
Energy Level( 1 )= 4.99120092644484E-09  
Energy Level( 2 )= 1.51743710690186E-14  
Energy Level( 3 )= 0  
Energy Level( 4 )= 0

Temperature = 100 K  
Energy Level( 0 )= 93.8916078256494  
Energy Level( 1 )= 5.53074208853659  
Energy Level( 2 )= 0.577650085814036  
Energy Level( 3 )= 4.84347134153904E-98  
Energy Level( 4 )= 1.25540525415E-210

Temperature = 298.15 K  
Energy Level( 0 )= 74.756149104292  
Energy Level( 1 )= 20.5927866431876  
Energy Level( 2 )= 4.65106425252043  
Energy Level( 3 )= 3.73651124672633E-32  
Energy Level( 4 )= 2.21961428383793E-70

} room T

Temperature = 1000 K  
Energy Level( 0 )= 61.8460113490636  
Energy Level( 1 )= 29.4214101403125  
Energy Level( 2 )= 8.73257850333659  
Energy Level( 3 )= 7.2872671609089E-09  
Energy Level( 4 )= 9.43744445326195E-21

Temperature = 10000 K  
Energy Level( 0 )= 53.1182627521461  
Energy Level( 1 )= 31.1397532599407  
Energy Level( 2 )= 10.2601554141681  
Energy Level( 3 )= 5.39969416593261  
Energy Level( 4 )= 8.21344078125132E-02

Temperature = 100000 K  
Energy Level( 0 )= 33.6961692662939  
Energy Level( 1 )= 20.2130095891407  
Energy Level( 2 )= 6.73688800405582  
Energy Level( 3 )= 32.9345538107517  
Energy Level( 4 )= 6.41937932975794

Temperature = 1E+100 K  
Energy Level( 0 )= 33.3333333333333  
Energy Level( 1 )= 20  
Energy Level( 2 )= 6.66666666666667  
Energy Level( 3 )= 33.3333333333333  
Energy Level( 4 )= 6.66666666666667

10<sup>100</sup> K

Temperature = 1E+300 K  
Energy Level( 0 )= 33.3333333333333  
Energy Level( 1 )= 20  
Energy Level( 2 )= 6.66666666666667  
Energy Level( 3 )= 33.3333333333333  
Energy Level( 4 )= 6.66666666666667

10<sup>300</sup> K

We have then

$$g_n = w_1$$

which can be ignored as  $w_1$  does not change in the course of normal thermodynamic processes.

### Electronic Partition Function

$$g_e = \sum_{\text{levels}} w_{e,i} e^{-\epsilon_i/kT} = w_{e,1} + w_{e,2} e^{-\Delta\epsilon_2/kT} + \dots$$

where again  $\epsilon_1 \equiv \phi$ .

Usually  $\Delta\epsilon_2 \approx 10^{-12}$  ergs or 0.1 eV in which case  $T \approx 10^4$  to effect a transition from  $\epsilon_1$  to  $\epsilon_2$ . Again we find

that usually  $g_e \approx w_{e,1} = 1$ . Exceptions include the alkali metals ( $w_{e,1} = 2$ ), Halogens  $g_e = w_1 + w_2 e^{-\Delta\epsilon_2/kT}$  and oxygen requires three terms. See Handout, P 39.2

### Thermodynamic Functions

We have:

$$Q = \frac{g^N}{N!} = \frac{(g + g_e g_n)^N}{N!} = \frac{1}{N!} \frac{V}{\Lambda^3} (g_e g_n)^N \text{ and } \Lambda = \frac{h}{(2\pi m k T)^{1/2}}$$

And

$$A = -kT \log Q \text{ or}$$

$$A(N, V, T) = -NkT \log \left[ \left( \frac{2\pi m k T}{h^2} \right)^{3/2} \frac{V e^*}{N} \right] - NkT \log g_{elec}$$

$$\text{where } g_{elec} = -NkT \log (w_{e,1} + w_{e,2} e^{-\beta \Delta\epsilon_2})$$

\* Note:  $\log N! = N \log \frac{N}{e} = N(\log N - \log e) = N \log N - N$

From  $dA = -SdT - PdV + \sum \mu_i dn_i$  we have:

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = \frac{NkT}{V} = \frac{RT}{V}$$

$$E = -T^2 \left(\frac{\partial A/T}{\partial T}\right)_{V,N} = \frac{3}{2} NkT + \frac{Nw_{e2} \Delta E_{12} e^{-\beta \Delta E_{12}}}{g_e}$$

$$S = Nk \log \left[ \left(\frac{2\pi m k T}{h^2}\right)^{3/2} \frac{V e^{5/2}}{N} \right] + S_e \quad \text{where}$$

$$S_e = Nk \log(w_{e1} + w_{e2} e^{-\beta \Delta E_{12}}) + \frac{Nk w_{e2} \beta \Delta E_{12} e^{-\beta \Delta E_{12}}}{g_e}$$

$$\begin{aligned} \mu(T,P) &= -kT \left(\frac{\partial \log Q}{\partial N}\right)_{V,T} = -kT \log \frac{q}{N} \\ &= \mu^\ominus(T) + kT \log P \quad \text{where} \end{aligned}$$

$$\mu^\ominus(T) = -kT \log \left[ \left(\frac{2\pi m k T}{h^2}\right)^{3/2} kT \right] - kT \log(g_e g_n)$$

### Summary - Monoatomic IDEAL GAS

$$Q = \frac{(q_{\text{trans}} q_{\text{elec}} q_{\text{nuc1}})^N}{N!} \quad \bar{c}_j \ll 1$$

$$q_{\text{trans}} = \left(\frac{2\pi m k T}{h^2}\right)^{3/2} V = \frac{V}{\Lambda^3} \quad \text{where } \Lambda = \left[\frac{h^2}{2\pi m k T}\right]^{1/2}$$

$$q_{\text{elec}} = w_{e1} + w_{e2} e^{-\Delta E_{12}/kT} + \dots$$

$$q_{\text{nuc1}} = w_{n,1} + \dots$$

### Computational Accuracy

See Table S.3 P86 for comparison between  $S_{\text{sim}}^\ominus$  vs  $S_{\text{meas}}^\ominus$  for 10 different elements.

## Binary Mixture of Ideal Gases

It is easy to show that the equivalent of  $Q = \frac{g^N}{N!}$  for a binary gas mixture is given by:

$$Q = \frac{g_1^{N_1} g_2^{N_2}}{N_1! N_2!} \quad \text{where } g_1 = \frac{V}{\Delta_1^3} \quad \text{and} \quad g_2 = \frac{V}{\Delta_2^3}$$

where  $g_1$  &  $g_2$  differ through  $m_1$  &  $m_2$ .

Then:

It follows that:

$$PV = (N_1 + N_2)kT$$

$$E = \frac{3}{2}(N_1 + N_2)kT$$

$$S = N_1 k \log \left( \frac{V e^{5/2}}{\Delta_1^3 N_1} \right) + N_2 k \log \left( \frac{V e^{5/2}}{\Delta_2^3 N_2} \right)$$

## Other Ensembles:

Grand Ensemble:  $\lambda = e^{-\mu/kT}$

$$\Xi = \sum_{N \geq 0} Q(N, V, T) \lambda^N = \sum_{N \geq 0} \frac{[g_T(V, T) \lambda]^N}{N!} = e^{g_T \lambda} = e^{PV/kT}$$

Series expansion  $PV = -kT \log \Xi$

$$\text{So } \bar{N} = \left( \frac{\partial \lambda}{\partial \mu} \right) \left[ \frac{\partial (PV)}{\partial \lambda} \right] = \lambda \left[ \frac{\partial \log \Xi}{\partial \lambda} \right]_{V, T} = \frac{PV}{kT}$$

See prob. 3-8 homework.

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

## Conditions for the use of Classical Statistics

The usual condition for the use of classical statistics is,

$$\bar{C}_j = \eta_j N = \frac{N e^{-\epsilon_j / kT}}{g_T}$$

↑ prob. of the  $j^{\text{th}}$  particle state

TOTAL PARTS

where generally translational alone ensures its validity.

Now for a monoatomic gas we have shown that

$$g_T = \frac{V}{\Lambda^3} \text{ so } \bar{C}_j \text{ can be written}$$

$$\bar{C}_j = \frac{N \Lambda^3 e^{-\epsilon_j / kT}}{V}$$

or since  $e^{-\epsilon_j / kT} \approx 0(1)$  for  $E \approx 0(kT)$

$$\bar{C}_j = \frac{N \Lambda^3}{V} = \frac{N h^3}{V (2\pi m kT)^{3/2}} = \frac{\rho h^3}{(2\pi m kT)^{3/2}} \ll 1$$

Thus the condition that  $\bar{C}_j \ll 1$  is favored when

- i) high temperatures
- ii) large mass
- iii) low densities ( $\rho = \frac{N}{V}$ )

Note: For computational purposes,  
 $\frac{\Lambda^3 N}{V} = \frac{3206 \rho}{M^{3/2} T^{3/2}}$   
 where  $\rho$  = density in  $\text{gm/cm}^3$ ,  
 $m = MW \cdot \rho$  &  $T$  is in  $\text{K}$ 's.

## de Broglie Wave Length, $\lambda$

For translation, classical mechanics says

$$\frac{p^2}{2m} = E \text{ all of which is kinetic, or}$$

$$p = \sqrt{2mE} = \sqrt{2mkT} \text{ since } E \approx 0(kT)$$

Furthermore

$$p = hK = \frac{h}{2\pi} \cdot \frac{2\pi}{\lambda} = \frac{h}{\lambda} \text{ i.e.}$$

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mkT}}$$



In addition,

$$\Lambda = \frac{h}{\sqrt{2\pi m k T}} \approx \frac{h}{\sqrt{2m k T}} = \lambda, \text{ i.e.}$$

$\lambda \approx \Lambda$  since they differ only by  $\sqrt{\pi}$

Thus the condition:

$$\bar{Q}_j = \left(\frac{N}{V}\right) \Lambda^3 \ll 1 \text{ implies}$$

$$\Lambda^3 \ll \frac{V}{N} \text{ OR}$$

$\Lambda \ll \left(\frac{V}{N}\right)^{1/3}$  and, since  $\lambda \approx \Lambda$  we have

$\lambda \ll \left(\frac{V}{N}\right)^{1/3}$  as an alternative statement of the condition  $\bar{Q}_j \ll 1$ .

Now  $\left(\frac{V}{N}\right)^{1/3}$  can be interpreted as the nearest neighbour separation between atoms, since  $V^{1/3} \approx$  dimension of a box on one side and  $(V/N)^{1/3} \approx$  dimensions/particle.

So the use of classical statistics<sup>⊗</sup> is also ensured when

$\lambda \ll$  separation between particles, which also corresponds to no wave function overlap so

Quantum statistics  $\rightarrow$  CMB statistics, thus

See Table 4.1 McQuarrie, P 72.

⊗ i.e., corrected MB where  $Q_{\text{cmB}} = \frac{g^N}{N!} \bar{Q} \ll 1$

# Excitation of Modes and Contributions to the P.F.

Note:

$$\Theta_v = \frac{h\nu}{k}$$

$$\Theta_r = \frac{B}{k} = \frac{h^2}{8\pi^2 I k}$$

## A) Typical Excitation Energies:

$kT$  (300°K)  $\approx$  0.03 eV, - Available energy

$\Delta E$  (electronic)  $\approx$  0 (5 eV) Never classical

$\Delta E$  (vibration)  $\approx$  0 (0.3 eV) Sometimes "

$\Delta E$  (rotation)  $\approx$  0 ( $5 \times 10^{-4}$  eV) Usually " except for  $H_2$  &  $D_2$

$\Delta E$  (translational)  $\approx$  0 ( $10^{-18}$  eV) always "

$\Delta E$  (nuclear)  $\approx$  0 (1 MeV) Never " ,  $T \sim 10^{10}$  K

## B) Criterion for Excitation:

$$0 \leq \exp(-\Delta E/kT) \leq 1$$

$$\Delta E \gg kT \quad \Delta E \approx kT \quad \Delta E \ll kT$$

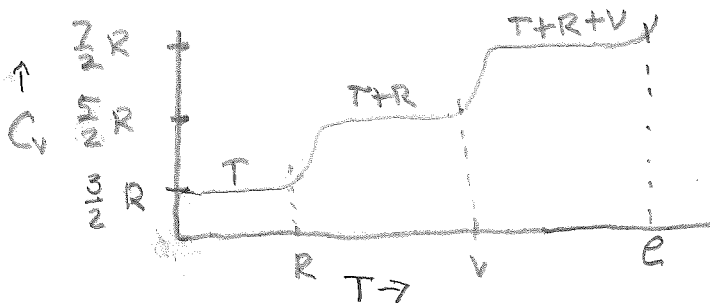
Classical  $\Delta E \ll kT$  or  $\Theta \ll T$ : Replace  $\sum$  by  $\int$

Quantum  $\Delta E \approx 0(kT)$  or  $\Theta \sim 0(T)$ : Use  $\sum$  w multiple terms

Unexcited  $\Delta E \gg kT$  or  $\Theta \gg T$ : Use  $\sum$  w one or two terms

Summary: Only when  $\Delta E \lesssim 0(kT)$  do we get a contribution to the P.f. beyond the g.s.

For example, consider  $C_v$  vs  $T$ :



Note: All modes are partially activated at all temps but only when  $T \gg \Theta_{mode}$  is there a measurable contribution to  $A, E, C_v$  etc.