Equilibrium Statistical Mechanics

Ref. <u>Davidson</u>, <u>Statistical Mechanics</u> McGraw-Hill, 1962

We wish to study plasmas in equilibrium for at least two reasons:

(a) Many times real plasmas are near true equilibrium, at least locally and in regard to some of the properties.

(b) For situations outside equilibrium, where <u>rates</u> are important, if the rate of one process is known by measurement or mechanistic calculation, the rate of its <u>inverse</u> process can be deduced from equilibrium properties (micro reversibility).

<u>Statistical Mechanics</u> builds on the quantum mechanical notions of orbital, energy state and exclusion principle, to analyze ensembles of many particles and deduce their macroscopic properties. In the end, Statistical Mechanics deduces the laws of Thermodynamics from those of particle physics. In addition, it provides specific formulae for <u>calculating</u> thermodynamic quantities, which can only be defined and interrelated by Thermodynamics alone.

Instead of solving in detail the multi-particle equations of motion and then taking the pertinent average, Statistical Mechanics uses only a few results from Quantum theory and bridges the transition to the macroscopic world by means of a few simple <u>postulates</u> of a statistical nature. The most important of these is the equi-probability of micro-states, which we will see soon. The plausibility of this postulate arises from a property of <u>classical</u> dynamical systems, namely, that many-degree of freedom systems evolve in time in a quasi-random manner, such that over the long run they spend equal time in <u>any</u> dynamical state compatible with the constraints.[1] A similar situation occurs in interacting multi scale quantum systems, where perturbations of single-particle states ensure over the long run that all possible multi-particle states are occupied the same fraction of the time.

Despite this plausible foundation, it is startling to see the power and quantity of the deductions which can be obtained from such simple statements. Their ability to re-create the well established empirical science of thermodynamics is the best check of the validity of the statistical postulates. On the other hand, their rigorous logical justification is a difficult and subtle task which has kept mathematicians busy for over a century.

Definitions for Quantum Statistical Mechanics:

<u>Single-particle orbital</u>: Set of values of all quantum numbers for a single particle in a given volume and field.

<u>Many-particle orbital</u>: Set of values of all quantum numbers for a given number of particles in a given volume and field.

<u>Microstate</u>: Same thing as a many-particle orbital.

<u>Energy level</u>: Physically allowed value of <u>1-particle</u> energy.

<u>Degeneracy of an energy level</u>: Number of <u>single-particle orbitals</u> which all have the same energy.

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[1] More precisely, in any (small) volume in 6-D phase space $(\vec{x}, \vec{w})$

Energy distribution: Specification of the number of particles which have each energy level.

Macrostate: Same as energy distribution.

Statistical weight of a macro state: Number of micro states in it, i.e., number of ways in which the given number of particles can occupy the available orbitals for a given energy distribution.

System energy: Sum total of the particle energies.

Fermi-Dirac statistics: Specifications that no more than one particle can exist per single-particle orbital. Also called Pauli exclusion principle.

Bose-Einstein Statistics: Specification that any number of particles may have the same quantum numbers, i.e. the same single-particle orbital.

Postulates of Quantum Statistical Mechanics

1. All micro states corresponding to prescribed system energy, number of particles, volume and field, are equally probable.

2. Particles are indistinguishable (but microstates are not).

3. The macroscopically observed value of a quantity Φ can be calculated by equal-weight averaging over all accessible microstates. As the number of particles increases, one macrostate becomes much more probable (more micro states in it) than any other; thus, an alternative way of calculating Φ as to assume that only the most probable macrostate exists.

Example 1:
Three energy levels: $\epsilon_o = 0$ $\epsilon_1 = 1$ $\epsilon_2 = 2$
Doubly degenerate: $g_o = g_1 = g_2 = 2$
Fermi-Dirac statistics (exclusion)
4 particles

Level 0	orbital 1	1	1	1	1	1	1	1	1	0	0	1	1	0	0	0
	orbital 2	1	1	1	1	1	1	0	0	1	1	0	0	1	1	0
Level 1	orbital 1	1	1	1	0	0	0	1	1	1	1	1	0	1	0	1
	orbital 2	1	0	0	1	1	0	1	1	1	1	0	1	0	1	1
Level 2	orbital 1	0	1	0	1	0	1	1	0	1	0	1	1	1	1	1
	orbital 2	0	0	1	0	1	1	0	1	0	1	1	1	1	1	1
		E=2, W=1	E=3, W=4				E=4, W=1	E=4, W=4				E=5, W=4				E=6,W=1

$$
\begin{array}{cccll}
N_0 & N_1 & N_2 & & \\
2 & 2 & 0 & W = 1 \;,\; E = 2 & (\to \tfrac{2!}{2!0!} \times \tfrac{2!}{2!0!} \times \tfrac{2!}{0!2!} = 1 \times 1 \times 1 = 1) \\
2 & 1 & 1 & W = 4 \;,\; E = 3 & (\to \tfrac{2!}{2!0!} \times \tfrac{2!}{1!1!} \times \tfrac{2!}{1!1!} = 1 \times 2 \times 2 = 4) \\
2 & 0 & 2 & W = 1 \;,\; E = 4 & \\
1 & 2 & 1 & W = 4 \;,\; E = 4 & \\
1 & 1 & 2 & W = 4 \;,\; E = 5 & \\
0 & 2 & 2 & W = 1 \;,\; E = 6 & (\to \tfrac{2!}{2!0!} \times \tfrac{2!}{0!2!} \times \tfrac{2!}{0!2!} = 1)
\end{array}
$$

Example 2:

Three energy levels: $\epsilon_o = 0$ $\quad \epsilon_1 = 1$ $\quad \epsilon_2 = 2$

Doubly degenerate: $\quad g_o = g_1 = g_2 = 2$

Bose-Einstein statistics (no exclusion principle)

4 particles

Level	orbital																																										
Level 0	orbital 1	4	3	2	1	0	3	3	2	2	1	1	0	0	3	3	2	2	1	1	0	0	2	2	2	2	1	1	1	1	0	0	0	0	2	2	2	1	1	1	0	0	0
	orbital 2	0	1	2	3	4	0	0	1	1	2	2	3	3	0	0	1	1	2	2	3	3	0	0	0	0	1	1	1	1	2	2	2	2	0	0	0	1	1	1	2	2	2
Level 1	orbital 1	0	0	0	0	0	1	0	1	0	1	0	1	0	0	0	0	0	0	0	0	0	1	1	0	0	1	1	0	0	1	1	0	0	2	1	0	2	1	0	2	1	0
	orbital 2	0	0	0	0	0	0	1	0	1	0	1	0	1	0	0	0	0	0	0	0	0	0	0	1	1	0	0	1	1	0	0	1	1	0	1	2	0	1	2	0	1	2
Level 2	orbital 1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	0	0	0	0	0	0	0	0	0
	orbital 2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	0	0	0	0	0	0	0	0
		E=0, W=5					E=1, W=8								E=2, W=8								E=3, W=12												E=2, W=9								

etc

$$
macrostate \begin{cases}
\begin{array}{ccc}
N_0 & N_1 & N_2 \\
4 & 0 & 0 \\
3 & 1 & 0 \\
3 & 0 & 1 \\
2 & 1 & 1 \\
2 & 2 & 0 \\
2 & 0 & 2 \\
1 & 3 & 0 \\
1 & 2 & 1 \\
1 & 1 & 2 \\
1 & 0 & 3 \\
0 & 4 & 0 \\
0 & 3 & 1 \\
0 & 2 & 2 \\
0 & 1 & 3 \\
0 & 0 & 4
\end{array}
\end{cases}
$$

- $4 \ 0 \ 0 \ - \ E=0 \ , W=5 \quad (\rightarrow \frac{5!}{4!1!} \times \frac{1!}{0!1!} \times \frac{1!}{0!1!} = 5\times1\times1 = 5)$
- $3 \ 1 \ 0 \ - \ E=1 \ , W=8 \quad (\rightarrow \frac{4!}{3!1!} \times \frac{2!}{1!1!} \times \frac{0!}{0!1!} = 4\times2\times1 = 8)$
- $3 \ 0 \ 1 \ - \ E=2 \ , W=8$
- $2 \ 1 \ 1 \ - \ E=3 \ , W=12 \quad (\rightarrow \frac{3!}{2!\times1!} \times \frac{2!}{1!\times1!} \times \frac{2!}{1!\times1!} = 3\times2\times2 = 12)$
- $2 \ 2 \ 0 \ - \ E=2 \ , W=9 \quad (\rightarrow \frac{3!}{2!\times1!} \times \frac{3!}{2!\times1!} \times \frac{1!}{0!\times1!} = 3\times3\times1 = 9)$
- $2 \ 0 \ 2 \ - \ E=4 \ , W=9$
- $1 \ 3 \ 0 \ - \ E=3 \ , W=8$
- $1 \ 2 \ 1 \ - \ E=4 \ , W=12$
- $1 \ 1 \ 2 \ - \ E=5 \ , W=12$
- $1 \ 0 \ 3 \ - \ E=6 \ , W=8$
- $0 \ 4 \ 0 \ - \ E=4 \ , W=5$
- $0 \ 3 \ 1 \ - \ E=5 \ , W=8$
- $0 \ 2 \ 2 \ - \ E=6 \ , W=9$
- $0 \ 1 \ 3 \ - \ E=7 \ , W=8$
- $0 \ 0 \ 4 \ - \ E=8 \ , W=5$

Quantum statistics of independent particles: Given an external field, suppose we have N particles with a total energy E prescribed. We can (from Quantum mechanics) find the 1-particle energy levels, ϵ_i, each containing g_i orbitals (degeneracy $= g_i$). A macrostate is a specification of the number of particles N_i per energy level, within in the constraints,

$$N = \sum_{\text{levels}} N_i$$

$$E = \sum_{\text{levels}} N_i \epsilon_i$$

These are two kinds of Q.M. systems of many particles:

(a) Those for which no two particles can share an orbital (Fermi-Dirac statistics)

(b) Those where any number of particles can occupy the same orbital (Bose-Einstein statistics)

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Electrons, protons and neutrons (and many atoms, as long as they hold fractional spin) obey F.D.; photons (and many atoms and even species composed by fermions, as long as their spin is integer) obey B.E..

Let us calculate the statistical weight of a macrostate in both cases. For F.D., the number of ways of selecting N_i orbitals for occupancy out of the $g_i > N_i$ in level ϵ_i is,

$$\binom{g_i}{N_i} = \frac{g_i!}{N_i!(g_i - N_i)!}$$

Then, for any given choice in level ϵ_i, there are a similar number of choices in other levels, and altogether,

$$\boxed{W_{F.D.} = \Pi_i \frac{g_i!}{N_i!(g_i - N_i)!}} \qquad (\text{and } g_i \geq N_i, \text{of course})$$

For B.E. statistics, in each level of ϵ_i the number of ways of distributing N_i particles over g_i orbitals without restriction as to how many per orbital is the number of combinations with repetition of N_i objects taken from a group of g_i; that number is,

$$\binom{N_i + g_i - 1}{N_i} = \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}$$

This can be demonstrated with a simple example having $N_i = 4 \quad g_i = 2$.

Pick one realization: $\underbrace{XXX}_{\text{Box 1}} | \underbrace{X}_{\text{Box 2}}$

Rearrange: $XX|XX \quad ; \quad X|XXX$

Number of (objects+partitions)$= N_i + (g_i - 1)$
Number of ways to scramble these "entities" $= (N_i + (g_i - 1))!$
But objects (N_i) can be separately rearranged without affecting the count, so divide by $N_i!$.
Also, partitions can be rearranged, so divide by $(g_i - 1)!$:

$$W_i = \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}$$

Altogether then,

$$\boxed{W_{B.E.} = \Pi_i \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}}$$

The most probable macrostate is that set of numbers N_i which maximizes W (or better $\ln W$) subject to given N, E. Using Lagrange multipliers, and the approximation (Stirling's),

$$N! \simeq \sqrt{2\pi N}\left(\frac{N}{e}\right)^N \rightarrow \ln N! = \frac{\ln(2\pi)}{2} + \frac{\ln N}{2} + N \ln N - N \approx N \ln N - N \qquad (\text{for large } N)$$

For B.E. statistics:
$$\phi = \ln W - \alpha N - \beta E =$$

$$\sum_i \left[(N_i+g_i-1)\ln(N_i+g_i-1)-(N_i+g_i-1)-N_i\ln N_i+N_i-(g_i-1)\ln(g_i-1)+g_i-1-\alpha N_i-\beta\epsilon_i N_i \right]$$

$$\frac{\partial\phi}{\partial N_i} = 0 \to \ln(N_i+g_i-1)+\cancel{1}-\cancel{1}-\ln N_i-\cancel{1}+\cancel{1}-\alpha-\beta\epsilon_i = 0$$

$$\ln\left(1+\frac{g_i-1}{N_i}\right) = \alpha+\beta\epsilon_i \qquad \to \qquad \ln\left(1+\frac{g_i}{N_i}\right) = \alpha+\beta\epsilon_i$$

since both g_i and N_i are large numbers. Then we have,

$$\boxed{N_i = \frac{g_i}{e^\alpha e^{+\beta\epsilon_i}-1}} \quad \text{B.E.}$$

For F.D. statistics:

$$\phi = \sum_i [g_i\ln g_i-g_i-N_i\ln N_i+N_i-(g_i-N_i)\ln(g_i-N_i)+g_i-N_i-\alpha N_i-\beta\epsilon_i N_i]$$

$$\frac{\partial\phi}{\partial N_i} = -\ln N_i-\cancel{1}+\cancel{1}+\ln(g_i-N_i)+\cancel{1}-\cancel{1}-\alpha-\beta\epsilon_i = 0$$

$$\ln\left(\frac{g_i}{N_i}-1\right) = \alpha+\beta\epsilon_i$$

Therefore we have (and is easy to see that $N_i < g_i$),

$$\boxed{N_i = \frac{g_i}{e^\alpha e^{+\beta\epsilon_i}+1}} \quad \text{F.D}$$

The <u>classical limit</u> or <u>Dilute systems</u> are those for which $g_i \gg N_i$, so that only a few of the orbitals in each level are actually occupied. Then, regardless of the kind of statistics (F.D. or B.E.), only single occupancy of orbitals is probable, and one should get a common limit from the above two cases. Since $g_i \gg N_i$ it must be true that $e^{\alpha+\beta\epsilon_i} \gg 1$, or $\alpha + \beta\epsilon_i$ is a positive, large number. Then,

$$\boxed{N_i \simeq g_i e^{-\alpha}e^{-\beta\epsilon_i}} \quad \text{both F.D. and B.E.}$$

This is called corrected Boltzmann statistics since it is similar (but not identical) to the result in classical mechanics (worked out by Boltzmann), where particles are distinguishable. Mainly due to their large <u>translational</u> degeneracy, gases are in this category most of the time. It is shown in Quantum Mechanics that the number of possible states for a given energy is $\sim (L/\lambda_{DB})^3$, where L is the "box" size (or the "potential well" size), and $\lambda_{DB} = \frac{h}{mv}$ is the DeBroglie wavelength. For a plasma at 3000°K, λ_{DB}(electrons)$\sim 25\mathring{A}$, so the degeneracy is large indeed.

Significance of α, β, W

In general, a Lagrange multiplier is the sensitivity of the maximized function to the corresponding constraint. To see this, consider,

$$\left.\begin{array}{ll} \text{Maximize} & f(x_i) \quad i = 1, 2, \ldots n \\ \text{Subject to} & g_j(x_i) = c_j \quad j = 1, 2, \ldots m < n \end{array}\right\} \phi = f(x_i) - \sum_j \lambda_j(g_j - c_j)$$

For maximization, we impose,

$$\frac{\partial \phi}{\partial x_i} = \frac{\partial f}{\partial x_i} - \sum_j \lambda_j \frac{\partial g_j}{\partial x_i} = 0$$

$$g_j = c_j$$

and calculate the corresponding $x_i = x_i^M$ and $\lambda_i = \lambda_i^M$.

Suppose we now perturb one of the c_j's, say c_n, and solve again. The maximum $f = f(x_i^M)$ will change by $\sum_i \frac{\partial f}{\partial x_i}\left(\frac{\partial x_i^M}{\partial dc_n}\right)_{c_j \neq n} dc_n$, or

$$df = \sum_i \left(\sum_j \lambda_j \frac{\partial g_j}{\partial x_i}\right)\left(\frac{\partial x_i}{\partial c_n}\right)_{c_j \neq n} dc_n = \sum_j \lambda_j \underbrace{\left(\sum_i \frac{\partial g_j}{\partial x_i}\left(\frac{\partial x_i}{\partial c_n}\right)_{c_j \neq n}\right)}_{(\frac{\partial g_j}{\partial c_n})_{c_j \neq n}} dc_n$$

But, since $g_i = c_j$, $\frac{\partial g_j}{\partial c_n} = \delta_{jn}$, so $df = dc_n \sum_j \lambda_j \delta_{jn} = \lambda_n dc_n$

$$\text{i.e.,} \quad \boxed{\lambda_n = \left(\frac{\partial f}{\partial c_n}\right)_{c_j \neq n}} \quad \text{q.e.d.}$$

Suppose now the constraints c_j are allowed to vary along a certain direction in their own m-space, i.e.,

$$\frac{dc_1}{\nu_1} = \frac{dc_2}{\nu_2} = \cdots = \frac{dc_m}{\nu_m} = dt$$

where dt is an arbitrary parameter.

and we want to maximize f <u>also</u> with respect to such changes. Clearly, we first must assume that for any set of c_j's the x_i's are chosen such as to maximize f for those fixed c_j's. Then the change of f_{MAX} due to the dc_j's is

$$df_{MAX} = \sum_j \left(\frac{\partial f_{MAX}}{\partial c_j}\right)_{c_i \neq j} dc_j = dt \sum_j \lambda_j \nu_j$$

and since dt is arbitrary, we must have the linear relation among the λ's:

$$\boxed{\sum_j \nu_j \lambda_j = 0}$$

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(Note this is the equation of the plane normal to $dc_j/\nu_j = dt$ in m-space.)

Applying this to our maximization of $\ln W$ with fixed N (multiplier α), E (multiplier β) and V, we calculate,

$$\alpha = \left(\frac{\partial \ln W}{\partial N}\right)_{V,E}$$

$$\beta = \left(\frac{\partial \ln W}{\partial E}\right)_{V,N}$$

Now, turning to W, it is an aggregate system property which is maximum when the system in equilibrium (maximum likelihood), at fixed N, E. From classical thermodynamics, the same property is possessed by the <u>Entropy</u>, S of the system, so that we must have $S = f(W)$, with f a monotanically increasing function. Now, if we consider two <u>non-interacting</u> systems ① and ② together, we know that $S = S_1 + S_2$. But also, since their probabilities are independent, $W = W_1 W_2$, or $\ln W = \ln W_1 + \ln W_2$. Hence f must be linear, and ignoring any constant shift, $S = k \ln W$ (k still undetermined).

$$\text{Hence} \quad \alpha = \frac{1}{k}\left(\frac{\partial S}{\partial N}\right)_{V,E} \quad ; \quad \beta = \frac{1}{k}\left(\frac{\partial S}{\partial E}\right)_{V,N}$$

$$\text{Now, thermodynamically,} \quad dE = TdS - pdV + \mu dN$$

$$\text{Where } \mu \text{ is by definition } \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} \quad \text{(chemical potential), from here,}$$

$$\left(\frac{\partial S}{\partial N}\right)_{V,E} = -\frac{\mu}{T} \quad ; \quad \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$$

$$\text{and so} \quad \boxed{\alpha = -\frac{\mu}{kT}} \quad \boxed{\beta = \frac{1}{kT}} \quad \text{(any statistics)}$$

This relates α and β to known thermodynamic functions (μ, T). We still need to identify the constant k.

<u>Dilute Systems The Partition Function</u>. The following applies <u>only</u> to corrected Boltzmann statistics, i.e.,

$$N_i = g_i e^{-\alpha - \beta \epsilon_i} = g_i e^{-\frac{\epsilon_i - \mu}{kT}}$$

We can now relate α, β (i.e., μ, T) to the actual constraints N, E:

$$\begin{cases} N = \sum N_i = e^{-\alpha} \sum_i g_i e^{-\beta \epsilon_i} \\ E = \sum \epsilon_i N_i = e^{-\alpha} \sum_i g_i \epsilon_i e^{-\beta \epsilon_i} \end{cases}$$

The group $\boxed{Q(\beta) = \sum_i g_i e^{-\beta \epsilon_i} = \sum_{\text{orbitals}} e^{-\beta \epsilon_i}}$ can be calculated a priori, once the quantum mechanics problem of one particle in the given volume and field has been solved. It is called

the <u>Partition Function</u>, and it plays an important role in chemical equilibrium and other statistical mechanics derivations. In terms of Q,

$$N = e^{-\alpha}Q(\beta) \quad \text{and then} \quad \frac{N_i}{N} = g_i\frac{e^{-\beta\epsilon_i}}{Q(\beta)}$$

therefore, we can write,

$$\boxed{\mu = -kT\ln\frac{Q}{N}}$$

Also, since,

$$E \;=\; e^{-\alpha}\sum_i g_i\epsilon_i e^{-\beta\epsilon_i} \;=\; -e^{-\alpha}\frac{\partial Q}{\partial\beta}$$

then,

$$\frac{E}{N} = -\frac{1}{Q}\frac{\partial Q}{\partial\beta} = -\frac{\partial\ln Q}{\partial\beta}$$

which can be written as,

$$\boxed{E \;=\; NkT^2\frac{\partial\ln Q}{\partial T}}$$

<u>Systems with non-interacting degrees of freedom.</u> In many dilute systems, translation, rotation, vibration, excitation, etc. interact very weakly with each other, so that the quantum mechanics problems can be solved separately, leading to independent sets of translational, rotational, etc. energy levels and degeneracies, and to a total energy,

$$\epsilon = \epsilon_{\text{tr.}} + \epsilon_{\text{rot.}} + \epsilon_{\text{vib.}} + \epsilon_{\text{exc.}} + \cdots$$

Then,

$$Q \;=\; \sum_{\text{levels}} g_i e^{-\beta\epsilon_i} \;=\; \sum_{\text{orbitals}} e^{-\beta\epsilon_i} \;=\; \sum_{\text{tr.}}\sum_{\text{rot.}}\sum_{\text{vib.}}\sum_{\text{exc.}}\cdots e^{-\beta e_i}$$

$$=\; \left(\sum_{\text{tr.}} e^{\beta\epsilon_{i.tr.}}\right)\left(\sum_{\text{rot.}} e^{-\beta\epsilon_{i.rot.}}\right)\cdots$$

and so we can calculate separately the various partition functions, and then multiply them,

$$\boxed{Q = Q_{tr.}Q_{rot.}Q_{vib.}Q_{exc.}\cdots}$$

Also then, since $\mu = -kT\ln Q/N$

$$\boxed{\mu \;=\; \mu_{tr.} + \mu_{rot.} + \cdots} \;=\; -kT\ln\frac{Q_{tr.}}{N} - \underbrace{kT\ln Q_{rot.}\cdots}_{\text{all others have no N}}$$

$$\text{and}\quad \frac{E}{N} \;=\; -\frac{\partial}{\partial\beta}\ln(Q_{tr.}Q_{rot}\cdots) \;=\; \frac{E_{tr.} + E_{rot.}\cdots}{N} \quad \left(\frac{E_{tr.}}{N} = -\frac{\partial\ln Q_{tr.}}{\partial\beta}, \text{etc.}\right)$$

<u>Entropy of a dilute system.</u> We have $S = k \ln W$, $\ln W = \lim\limits_{N_i << g_i} (\ln W_{FD})$ and $N_i = g_i e^{-\alpha - \beta \epsilon_i}$.

$$\ln W_{FD} = \sum_i \left[g_i \ln g_i - \cancel{g_i} - N_i \ln N_i + \cancel{N_i} - (g_i - N_i) \ln(g_i - N_i) + \cancel{g_i} - \cancel{N_i} \right]$$

$$\ln(g_i - N_i) = \ln g_i + \ln\left(1 - \frac{N_i}{g_i}\right) \underset{N_i \ll g_i}{\simeq} \ln g_i - \frac{N_i}{g_i}$$

$$\ln W = \sum_i \left[\cancel{g_i \ln g_i} - N_i \ln N_i - (g_i - N_i)\left(\ln g_i - \frac{N_i}{g_i}\right) \right] = \sum_i N_i \left(-\ln N_i + 1 + \ln g_i - \underset{\ll 1}{\cancel{\frac{N_i}{g_i}}} \right)$$

$$S = k \sum_i N_i \left(1 - \ln \frac{N_i}{g_i}\right) = k \sum_i N_i (1 + \alpha + \beta \epsilon_i) = k[N(1 + \alpha) + \beta E]$$

$$\boxed{S = k\left(1 - \frac{\mu}{kT}\right)N + \frac{E}{T}}$$

or

$$\boxed{\mu N = E + NkT - TS}$$

<u>The Gibbs free energy.</u> By definition, the Gibbs free energy G is $\boxed{G \equiv E + PV - TS}$

Now, then,

$$dG = dE + PdV + VdP - TdS - SdT$$

and since,

$$dE = TdS - PdV + \mu dN$$

Then,

$$dG = -SdT + VdP + \mu dN$$

Hence, an alternative definition of the chemical potential is

$$\mu \equiv \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

This has the advantage that (T, P) are <u>intensive</u> variables. We can "build" up the G of a system by adding new molecules (dN) while maintaining the same T and P. Since μ is also intensive, $\mu = \mu(T, P)$, so μ is constant during this building up, and we obtain simply,

$$\boxed{G = \mu N}$$

Notice we <u>cannot</u> go from $\mu = (\partial E / \partial N)_{V,S}$ to $E = \mu N$, since when we keep V, S constant and vary N, p will also vary, hence μ will too.

<u>Equation of state of dilute systems.</u> We have calculated for a dilute system,

$$\mu N = E + NkT - TS$$

Since $\mu N = G$, we have,

$$G = E + NkT - TS$$

But G in general is $E + PV - TS$, so we conclude,

$$\boxed{PV = NkT}$$

Now, by comparing to the ideal gas law,

$$PV = N\left(\frac{R}{N_A}\right)T$$

we identify Boltzmann's constant,

$$\boxed{k_B = \frac{R}{N_A}} = \frac{8.314 J/(\text{mol.}^\circ K)}{6.022 \times 10^{-23}(\text{Molecules/mol.})} = 1.38 \times 10^{-23}\frac{J}{^\circ K}$$

In retrospect, the reason we arrive at $PV = NkT$ is that we are assuming non-interactive systems, where the energy levels and g_i's are calculated for each particle as if it were alone in the box. Statistical mechanics can also be applied to more complex systems, of course, but the methods are somewhat more difficult (canonical and grand-canonical ensemble, as opposed to out "micro-canonical" ensemble).

Multi-component systems. Suppose there are 3 species A, B, C, non-reacting for now. The total W is the product of $W = W_A W_B W_C$ and then $\ln W = \ln W_A + \ln W_B + \ln W_C$. There are 3 number constraints and one E constraint:

$$N_A = \sum_i N_i^A$$

$$N_B = \sum_j N_j^B$$

$$N_C = \sum_k N_k^C$$

$$E = \sum_i \epsilon_i^A N_i^A + \sum_j \epsilon_j^B N_j^B + \sum_k \epsilon_k^C N_k^C$$

Forming again,

$$\phi = \ln W_A + \ln W_B + \ln W_C - \alpha_A N_A - \alpha_B N_B - \alpha_C N_C - \beta E$$

and we differentiate relative to each N_i^A, each N_j^B, and each N_k^C. We then get for each species a F.D. or B.E. (or corrected Boltzmann) distribution with a different α for each, but with a common β. Following the same steps as before, we can again relate these to the μ's and the T:

$$\alpha_A = -\frac{\mu_A}{kT} \qquad \alpha_B = -\frac{\mu_B}{kT} \qquad \alpha_C = -\frac{\mu_C}{kT} \qquad \beta = -\frac{1}{kT}$$
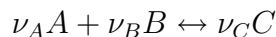
and can also prove that

$$G = N_A \mu_A + N_B \mu_B + N_C \mu_C$$
$$PV = (N_A + N_B + N_C)kT$$

and (for dilute systems)

$$\mu_A = -kT \ln \frac{Q_A}{N_A}, \qquad \mu_B = -kT \ln \frac{Q_B}{N_B}, \qquad \mu_C = -kT \ln \frac{Q_C}{N_C}$$

Reacting Systems. Suppose now that A, B, C can interconvert according to the reaction,

$$\nu_A A + \nu_B B \leftrightarrow \nu_C C$$

This means that N_A, N_B, N_C are not fixed, but that, if they change according to this reaction,

$$\frac{dN_A}{\nu_A} = \frac{dN_B}{\nu_B} = -\frac{dN_C}{\nu_C} \qquad \text{(a direction in } N_A, N_B, N_C \text{ space)}$$

But we have proven before that for the object function ($\ln W$ or S in our case) still to be maximum, there must exist a relationship among the multipliers of the form,

$$\nu_A \alpha_A + \nu_B \alpha_B = \nu_C \alpha_C$$

or, in terms of the $\mu = -kT\alpha$,

$$\boxed{\nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C} \qquad 1^{st} \text{ form of the law of mass action}$$

In terms of the N's and Q's,

$$\nu_A \ln \frac{Q_A}{N_A} + \nu_B \ln \frac{Q_B}{N_B} = \nu_C \ln \frac{Q_C}{N_C} \quad \rightarrow \quad \left(\frac{Q_A}{N_A}\right)^{\nu_A} \left(\frac{Q_B}{N_B}\right)^{\nu_B} = \left(\frac{Q_C}{N_C}\right)^{\nu_C}$$

$$\frac{N_A^{\nu_A} N_B^{\nu_B}}{N_C^{\nu_C}} = \frac{Q_A^{\nu_A} Q_B^{\nu_B}}{Q_C^{\nu_C}} \qquad 2^{nd} \text{ form of the law of mass action}$$

or,

$$\frac{n_A^{\nu_A} n_B^{\nu_B}}{n_C^{\nu_C}} = \frac{q_A^{\nu_A} q_B^{\nu_B}}{q_C^{\nu_C}} \quad \text{with} \quad n_j = \frac{N_j}{V}, q_j = \frac{Q_j}{V}$$

In terms of P's,

$$P_A = N_A \frac{kT}{V} \qquad P_B = N_B \frac{kT}{V} \qquad P_C = N_C \frac{kT}{V}$$

$$\boxed{\frac{P_A^{\nu_A} P_B^{\nu_B}}{P_C^{\nu_C}} = \frac{\left(Q_A \frac{kT}{V}\right)^{\nu_A} \left(Q_B \frac{kT}{V}\right)^{\nu_B}}{\left(Q_C \frac{kT}{V}\right)^{\nu_C}}} \qquad 3^{rd} \text{ form of the law of mass action}$$

The importance of this one is that the RHS will be shown to depend on $\underline{T}$ only. It is called the Equilibrium constant $K_P(T)$ for the reaction.

The zero of energy. For a single species, or for non-reacting species, the ϵ_i's can be measured from arbitrary levels; a shift $\epsilon_i' = \epsilon_i - \epsilon_0$ merely makes a new p.f. $Q' = \epsilon^{\epsilon_0/kT} Q$ and a new $\mu' = \mu - \epsilon_0$. However, when species can interconvert, they generally liberate or absorb

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definite amounts of energy in the process. If $A + B + \Delta E \rightarrow C$ then in the state in which $\epsilon_A = 0$ and $\epsilon_B = 0$, we must say that C has an energy ΔE, not arbitrary anymore. In all, we can assign arbitrary zero levels of energy only to a set of non-interconvertible atoms or particles. The zeros of all the others then follow from their energies of formation.

In chemical thermodynamics, the convention is to assign zero enthalpy to the pure species at 298°K, 1 atm, in the <u>natural state</u> (O_2, H_2, C (graphite), ...). Then, for instance, since $O + O \rightarrow O_2 + 59 Kcal$, the enthalpy per mole of O at 298°K, 1atm is,

$$+ \frac{59}{2} \frac{kcal}{mole} (\text{ per atom, } \frac{59 \times 4180}{2 \times 6 \times 10^{23}} J).$$

The Translational Partition Function

Consider a single "particle" in a rectangular box, with sides L_x, L_y, L_z. The first task is to solve the Schrödinger equation in order to obtain the allowable energies and quantum numbers (hence the degeneracies). The general Schrödinger equation is (with $\hbar = h/2\pi$),

$$-\frac{\hbar}{i} \frac{\partial \psi_T}{\partial t} = \mathscr{H}(\psi_T) \quad ; \quad \mathscr{H} = \frac{p^2}{2m} + V \quad ; \quad p = \frac{\hbar}{i} \nabla \tag{2}$$

Assume separation of the time dependence:

$$\psi_T(t, \vec{x}) = \Pi(t)\psi(\vec{x}) \tag{3}$$

Substitute and divide by ψ_T:

$$-\frac{\hbar}{i} \frac{1}{\pi} \frac{d\pi}{dt} = \frac{1}{\psi} \mathscr{H}(\psi) = \epsilon \tag{4}$$

where ϵ is the (so far arbitrary) separation constant. This gives the two equations,

$$\frac{d\pi}{dt} + \frac{i\epsilon}{\hbar}\pi = 0 \tag{4a}$$

$$\mathscr{H}(\psi) = \epsilon\psi \tag{4b}$$

and so,

$$\pi = Ce^{(i\epsilon/\hbar)t} \quad , \quad \psi_T = Ce^{(i\epsilon/\hbar)t}\psi(\vec{x}) \tag{5}$$

For our case, there is no potential energy inside the box: $V(\vec{x}) = 0$ for $(0 < x, y, z < L_{x,y,z})$, so (4b) reduces to,

$$\frac{1}{2m}\left(\frac{\hbar}{i}\nabla\right)^2 \psi = \epsilon\psi$$

or,

$$\frac{\hbar^2}{2m}\nabla^2\psi + \epsilon\psi = 0 \tag{6}$$

Assume next a solution that is also separable in (x, y, z):

$$\psi(x, y, z) = X(x)Y(y)Z(z) \tag{7}$$

Substitute in (6), divide by ψ:

$$\frac{\hbar^2}{2m}\left(\frac{X_{xx}}{X} + \frac{Y_{yy}}{Y} + \frac{Z_{zz}}{Z}\right) + \epsilon = 0 \tag{8}$$

Each of the terms $\frac{X_{xx}}{X}$, etc. must be <u>separately</u> a constant, and we therefore obtain 3 equations,

$$X_{xx} + \frac{2m}{\hbar^2}\epsilon_x X = 0$$

$$Y_{yy} + \frac{2m}{\hbar^2}\epsilon_y Y = 0 \qquad (9)$$

$$Z_{zz} + \frac{2m}{\hbar^2}\epsilon_z Z = 0$$

with,

$$\epsilon_x + \epsilon_y + \epsilon_z = \epsilon \qquad (10)$$

The particle is confined by the box, and so we must have $\psi = 0$ at each wall. This gives the boundary conditions:

$$\begin{cases} X(0) = X(L_x) = 0 \\[2mm] Y(0) = Y(L_y) = 0 \\[2mm] Z(0) = Z(L_z) = 0 \end{cases} \qquad (11)$$

The solutions that are zero at $x = y = z = 0$ are,

$$X = A_x \sin\sqrt{\frac{2m\epsilon_x}{\hbar^2}}x \quad ; \quad Y = A_y \sin\sqrt{\frac{2m\epsilon_y}{\hbar^2}}y \quad ; \quad Z = A_z \sin\sqrt{\frac{2m\epsilon_z}{\hbar^2}}z \qquad (12)$$

and imposing zero value at $x = L_x, y = L_y, z = L_z$ gives the conditions,

$$\sqrt{\frac{2m\epsilon_x}{\hbar^2}}L_x = n_x\pi \qquad (n_x = 1, 2, 3, \ldots)$$

$$\sqrt{\frac{2m\epsilon_y}{\hbar^2}}L_y = n_y\pi \qquad (n_y = 1, 2, 3, \ldots) \qquad (13)$$

$$\sqrt{\frac{2m\epsilon_z}{\hbar^2}}L_z = n_z\pi \qquad (n_z = 1, 2, 3, \ldots)$$

Where the numbers (n_x, n_y, n_z) identify a <u>quantum state</u>, and are the quantum numbers for this problem. Finally, imposing $\epsilon_x + \epsilon_y + \epsilon_z = \epsilon$ gives,

$$\boxed{\epsilon = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)} \qquad (14)$$

which gives all the possible energy levels of the particle. Clearly, there are many possible combinations of n_x, n_y, n_z giving the same energy ϵ (degenerate states), and the degeneracy will increase with the size of the box. We can now calculate the translational partition function as,

$$Q^{tr.} = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\epsilon/kT} \qquad (15)$$

In this form, since the summation includes all the quantum numbers, the degeneracy factors are not needed. In detail,

$$Q^{tr.} = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\frac{\pi^2\hbar^2}{2mkT}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)} \qquad (16)$$

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The summation can be approximated as an integral, provided $\frac{\pi^2\hbar^2}{2mkTL^2} \ll 1$. Recalling that the DeBroglie wavelength for a particle with average thermal energy is,

$$\lambda_{DB} = \frac{h}{p} = \frac{2\pi\hbar}{m\sqrt{\frac{3kT}{m}}} = \frac{2\pi\hbar}{\sqrt{3mkT}} \tag{17}$$

We see that the condition to go to a continuum view in the (n_x, n_y, n_z) space is $\frac{\lambda_{DB}^2}{L^2} << 1$, or a matter wave much shorter than the container size. Notice this is a weaker condition than that we already assumed for a <u>dilute</u> (Boltzmann) system: $\lambda_{DB} \ll n^{-1/3}$ (distance between particles), and so the continuum approximation is well justified. We then write,

$$Q^{tr.} \simeq \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z e^{-\frac{\pi^2\hbar^2}{2mkT}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)} \tag{18}$$

$$= \left(\int_0^\infty e^{-\frac{\pi^2\hbar^2}{2mkT}\frac{n_x^2}{L_x^2}} dn_x\right)\left(\int_0^\infty e^{-\frac{\pi^2\hbar^2}{2mkT}\frac{n_y^2}{L_y^2}} dn_y\right)\left(\int_0^\infty e^{-\frac{\pi^2\hbar^2}{2mkT}\frac{n_z^2}{L_z^2}} dn_z\right)$$

Change variables to $n_x = \sqrt{2mkT}\frac{L_x}{\pi\hbar}\xi$, $n_y = \sqrt{2mkT}\frac{L_y}{\pi\hbar}\eta$, $n_z = \sqrt{2mkT}\frac{L_z}{\pi\hbar}\zeta$ and use $\int_0^\infty e^{\xi^2} d\xi = \frac{\sqrt{\pi}}{2}$, etc. We obtain,

$$Q^{tr.} = (2mkT)^{3/2}\frac{L_xL_yL_z}{(\pi\hbar)^3}\left(\frac{\sqrt{\pi}}{2}\right)^3$$

Note that $\pi\hbar = \frac{1}{2}h$, and $L_xL_yL_z = V$ (the box volume). So,

$$\boxed{Q^{tr.} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V} \tag{19}$$

This can be written in terms of λ_{DB} as $Q^{tr.} = (2\pi/3)^{3/2}V/\lambda_{DB}^3$, which gives $Q^{tr.}$ an interpretation: (roughly) the number of "DeBroglie boxes" that fit into the volume.

Notice $Q^{tr.}$ is proportional to volume. The other pieces, Q^{rot}, Q^{vib}, etc. are independent of V, and so $Q \sim V$ altogether, and $q = \frac{Q}{V} = q(T)$. This proves that the equilibrium constant K_P, as derived previously, is indeed only a function of temperature.

16.55 Ionized Gases
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