

COURSE OUTLINE

- Important introductory principles (revision).
- Diffusion & the Langevin equation.
- Statistical mechanics of random walks/long chain molecules (polymers).
- The Poisson-Boltzmann Equation - screening in plasmas and ionic solutions.
- Phase transitions with examples. Landau Theory. (Fluctuations)

Books

- 1* Statistical Physics, 2nd Ed., Tony Guénault, Chapman & Hall.
- 2* An Introduction to Statistical Physics, W.G.V. Rosser, Ellis Horwood.
- 3* Introduction to Modern Statistical Mechanics, David Chandler, Oxford. (Examples available.)
- 4* Introductory Statistical Mechanics, Bowley & Sánchez, Oxford.
- 5* Introduction to polymer physics, M. Doi; translated by H. See; Oxford: Clarendon Press, 1996.
- 6 A modern course in Statistical Physics, L.E. Reichl, Arnold.
- 7 Statistical Thermodynamics of Surfaces, Interfaces and Membranes, S.A. Safran, Addison Wesley.
- 8 Scaling Concepts in Polymer Physics, P.G. de Gennes, Cornell.
- 9 Statistical Physics, Landau & Lifshitz, Pergamon. (2 vols)

* contents of book should be at a *level* accessible to students of this course (all contain much more volume of material than we will be able to cover).

Handouts etc available at <http://www.warwick.ac.uk/~phscz/teach/>

What is Statistical Mechanics and why do we need it ?

There are two ways of looking at the physics of large objects/systems.

(i) “Classical” thermodynamics. The study of the macroscopic properties of a system using empirical principles derived from experiments. Independent of the microscopic (atomic) details of the system. e.g. heat and work are both forms of energy and are conserved. Fundamental but cannot always be used to predict the properties of physical systems, e.g. phase transitions.

(ii) Statistical mechanics can be used to predict observable physical properties of systems. It can incorporate or describe fluctuations, diffusion and other *dynamic* effects. These are essential in phase transitions (boiling water) and indeed all chemical processes, including life. Divides into **equilibrium** statistical mechanics (phase transition, fluctuations) and **non-equilibrium** statistical mechanics (chemical reactions, diffusion, e.g. dispersion of ink in water).

Background: Review of thermodynamics and some important introductory principles.

Basic concepts:

- A system is in thermodynamics equilibrium if the mechanical variables do not change with time and there are no flow processes present.

It is possible to change from one equilibrium state to another, either:

- reversibly, in which case the system remains infinitesimally close to thermodynamic equilibrium and the change is reversible with no change in the thermodynamic state of the universe. Or,
- by irreversible or spontaneous changes in which the system does not stay infinitesimally close to equilibrium during each step, giving rise to flow or friction effects. The system cannot be brought back to its original state without causing a change in the thermodynamic state of the Universe.

Thermodynamics: the four laws

(o) The zeroth law

If two systems A and B are in thermal equilibrium with a third system C then A and B are also in equilibrium with C. Empirical basis for the concept of a temperature.

(i) The first law

The total increase in internal energy of a system is equal to the sum of the work done on the system and the heat supplied to it. If we permit matter to be added to the system we can also do chemical work

$$dU = dW + dQ + \mu dN \quad (1)$$

This thermodynamic statement doesn't require any specification of the nature of the internal energy but we will often interpret it as a sum of potential and kinetic energies for all particles. The signs of these terms are positive for work done on the system, heat in or particles in (convention).

(ii) The second law

The second law explains why certain processes allowed by the first law don't take place. Two (equivalent) statements

Clausius: No process is possible which *only* results in the transfer of heat from a colder body to a hotter one.

Kelvin: No process is possible which *only* results in the absorption of heat from a reservoir and the conversion of all this heat to work.

Leads to the concept of reversible and irreversible processes. For reversible processes

$$\oint \frac{dQ}{T} = 0$$

Such processes can always be constructed from Carnot engines. This leads to the identification of the new state variable of *Entropy*

$$dS \equiv \frac{dQ_{rev}}{T}$$

Hence global entropy (disorder) doesn't increase in reversible processes, only in irreversible processes. However, for irreversible processes $\oint dQ/T < 0$. For any process, reversible or irreversible, the entropy change can be found by constructing a reversible path and computing the quantity $\Delta S = \int_{rev} dS = \int_{rev} dQ/T$ because the entropy change depends only on the end points (entropy is a state variable, and therefore an

exact differential). For an irreversible process the integral $\int_{rev} dQ/T$ will be larger than $\int_{irr} dQ/T$ hence

$$dS \geq \frac{dQ}{T} \quad (2)$$

with equality only for a reversible process and inequality for a spontaneous or irreversible process (e.f.r.i.f.i/s).

For thermally isolated systems $dQ = 0$ and so

$$\Delta S \geq 0$$

Hence the equilibrium state is the state of maximum entropy.

(iii) The third law

The difference in entropy between states connected by a reversible process goes to zero as $T \rightarrow 0$.

Extensive variables are those that scale \sim mass e.g total internal energy, entropy, volume or number of particles; Intensive variables are the others that don't scale like mass but rather measure its nature, e.g. pressure, chemical potential, temperature. If one puts two similar systems into contact at equilibrium there is no change in T or P but the extensive variables all double.

The entropy is an extensive, additive quantity. If a system is chopped up into independent subsystems then the entropy of the whole system is the sum of the entropies of the subsystems. Combining the first and second laws we can write down a condition for differential changes in S via changes in the other extensive state variables

$$TdS \geq dU + PdV - \mu dN \quad (3)$$

e.f.r.i.f.i/s.

Thermodynamic potentials

In mechanical systems we can store energy in a spring or gravitational potential energy to retrieve later. The same is true for thermodynamic systems. We can store energy in a system most efficiently by doing work on it reversibly. The energy which is stored and can be retrieved in the form of work is called the free energy.

The five most commonly encountered are the internal energy U , enthalpy H , Helmholtz free energy F , Gibbs free energy G and grand potential Ω . These quantities *all* play a role analogous to that of potential energy in a spring and for that reason are also referred to as thermodynamic *potentials*.

1. Helmholtz free energy F

Useful for systems which are closed, mechanically isolated but thermally coupled to the outside world. It is obtained by adding an additional energy due to thermal coupling to the internal energy U

$$F = U - ST$$

This is called a Legendre transform and has the effect of changing the independent variables (of U) from $\{S, V, N\}$ to $\{T, V, N\}$. From (3)

$$dF \leq -SdT - PdV + \mu dN$$

For a reversible process at constant $\{T, V, N\}$, work can be stored as Helmholtz free energy and can be recovered completely. For processes involving no work being done on the system $\Delta F \leq 0$ e.f.r.i.f.i/s. An equilibrium state at fixed $\{T, V, N\}$ is a state of minimum Helmholtz free energy F . This is an extremely important identification.

2. Internal energy U

From (3)

$$dU \leq TdS - PdV + \mu dN$$

e.f.r.i.f.i/s. Thus $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$ etc. For a reversible process at constant $\{S, V, N\}$, work is stored as internal energy and can be recovered completely. For processes involving no work being done on the system $\Delta U \leq 0$ e.f.r.i.f.i/s. An equilibrium state at fixed $\{S, V, N\}$ is a state of minimum internal energy U .

3. Enthalpy H

Useful for systems which are thermally isolated and closed but mechanically coupled to the outside world. It is obtained by adding an additional energy due to the mechanical coupling to the internal energy U

$$H = U + PV$$

This has the effect of changing the independent variables from $\{S, V, N\}$ to $\{S, P, N\}$. From (3)

$$dH \leq TdS + VdP + \mu dN$$

For a reversible process at constant $\{S, P, N\}$, work can be stored as enthalpy and can be recovered completely. For processes involving no work being done on the system $\Delta H \leq 0$ e.f.r.i.f.i/s. An equilibrium state at fixed $\{S, P, N\}$ is a state of minimum enthalpy H .

4. Gibbs free energy G

Useful for systems which are closed but mechanically and thermally coupled to the outside world. It is obtained by adding additional terms due to thermal and mechanical coupling to the internal energy U

$$G = U - ST + PV$$

This has the effect of changing the independent variables from $\{S, V, N\}$ to $\{T, P, N\}$. From (3)

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

For a reversible process at constant $\{T, P, N\}$, work can be stored as Gibbs free energy and can be recovered completely. For processes involving no work being done on the system $\Delta G \leq 0$ e.f.r.i.f.i/s. An equilibrium state at fixed $\{T, P, N\}$ is a state of minimum Gibbs free energy G .

5. Grand potential Ω

Useful for systems which are open (the number of particles can change), mechanically isolated and thermally coupled to the outside world. It is obtained by adding an additional energies due to thermal coupling and particle exchange to the internal energy U

$$\Omega = U - ST - \mu N$$

This has the effect of changing the independent variables from $\{S, V, N\}$ to $\{T, V, \mu\}$. From (3)

$$d\Omega \leq -SdT - PdV - Nd\mu$$

For a reversible process at constant $\{T, V, \mu\}$, work can be stored as grand potential energy and can be recovered completely. For processes involving no work being done

on the system $\Delta\Omega \leq 0$ e.f.r.i.f.i/s. An equilibrium state at fixed $\{T, V, \mu\}$ is a state of minimum grand potential Ω .

Macro- and micro-states

The macrostate for a gas is complete specified by P, V, T and N (or any 3 thereof if we have an equation of state such as $PV = NRT$). Macrostates are states specified at the level of thermodynamics.

The microstate of a system is described by the precise state of each particle. In principle its position, momentum and quantum state. Such exact specification requires $O(N_A \approx 6 \times 10^{23})$ bits of information per mole. Huge (unfeasible) task. Luckily we never need to specify them exactly but rather we take averages over them. The *ensemble average* of any measurement is the average over many thermodynamically identical systems. Sometimes states are *degenerate* when more than one different state has the same energy E (say). This degeneracy is quantified by the density of states $D(E)$, defined so that the number of states between E and $E + dE$ is $D(E)dE$. When we average we need to take account of *all* accessible states, by which we mean those that are compatible with both the macroscopic conditions and any quantum restrictions, e.g. the Pauli exclusion principle for fermions.

A system is *ergodic* if there is an equivalence between time average and ensemble average measurements taken on it. Equivalently ergodicity requires that a system explores all states compatible with macroscopic restrictions (i.e. all of “phase space”). Since we usually measure time averages but calculate ensemble averages we often assume that they coincide. They do for systems which are ergodic. This is usually the case for real many body problems but there are examples where its isn't.

The principle of equal a priori probability states that, “All accessible microstates are equally probable a priori”

Entropy; Boltzmann's definition

Boltzmann proposed the definition of Entropy according to $S = k \log \Omega$. This equation relates the entropy to the number of accessible microstates. Here we will use the symbol W , not Ω to denote the number of accessible microstates to avoid confusion with the grand potential Ω . Boltzmann's constant is often given a subscript B and is found to be $k_B = 1.38 \times 10^{-23} JK^{-1}$.

The entropy can also be related to the probability distribution that the system is in the i^{th} state, written P_i . Consider a large system consisting of N_v subsystems. These subsystems might be particles, if we are interested in excitations in a crystal, or subvolumes if we are interested dilute gas particles in a box. Each of the subsystems can be in any one of several states, e.g. quantum states (particles) or occupied/unoccupied (subvolumes). The total number of ways of arranging N_v indistinguishable particles in one of *two* states is a result from the Binomial distribution

$$W = \frac{N_v!}{(N_v - n_1)!n_1!}$$

where $N_v - n_1$ is the number in the zeroth state and n_1 is the number in the first state. For three states this generalises to

$$W \rightarrow \frac{N_v!}{(N_v - n_1)!n_1!} \frac{(N_v - n_1)!}{(N_v - n_1 - n_2)!n_2!} = \frac{N_v!}{(N_v - n_1 - n_2)!n_1!n_2!}$$

which is the product of the number of ways of arranging n_1 particles to be in the 1st state. Followed by the number of ways of arranging n_2 in the second from the remaining number. For an arbitrary number of states this becomes

$$W = \frac{N_v!}{n_0!n_1!n_2!\dots}$$

Assuming that N_v is so large that all the $n_i \gg 1$ the entropy follows from Stirling's approximation $\log n_i! = n_i \log n_i - n_i$, where the term $\sim n_i \log n_i$ dominates.

Thus the entropy of the N_v subsystems is

$$S = k_B \left(N_v \log N_v - \sum_i n_i \log n_i \right) = -k_B \sum_i n_i (\log n_i - \log N_v) = -k_B N_v \sum_i \frac{n_i}{N_v} \log \frac{n_i}{N_v}$$

and the entropy of each is $S' = S/N_v$

$$S' = -k_B \sum_i P_i \log P_i \quad (4)$$

where $P_i = n_i/N_v$ corresponds to the probability that a given subsystem is in state i at equilibrium.

This analysis carries over to the entropy of a **lattice gas**.

Consider a gas of N particles, each of volume v , in rigid box of constant volume V held at constant temperature T . Particles are allowed to enter or leave the box, controlled by a constant chemical potential μ . [Aside: For μ to remain constant there must be a very large external reservoir of particles, as well as of heat to separately maintain T .] Thus the system is in the constant $\{T, V, \mu\}$ ensemble in which Ω reaches a minimum at equilibrium. We will adopt a "lattice gas" approach in which we divide the vessel into N_v so-called "lattice volumes", each of volume v . There are thus $N_v = V/v$ such volumes. There are two possible states for each lattice volume (neglecting quantum excitation of the gas). These states are merely specified by whether they are occupied by a gas particle (with probability P_1) or unoccupied (with probability P_2). A fraction $\phi = N/N_v$ of sites contains particles and $\phi_h = (N_v - N)/N_v$ are empty or contain "holes". All sites are one or the other so $\phi + \phi_h = 1$. At equilibrium the probabilities are simply $P_1 = \phi$ and $P_2 = \phi_h = 1 - \phi$. The entropy inside the entire box is therefore obtained from Eq. (4)

$$S = N_v S' = -k_B N_v (\phi \log \phi + (1 - \phi) \log(1 - \phi)) \quad (5)$$

This expression simplifies for $\phi \ll 1$ to

$$S = -k_B N_v \phi (\log \phi - 1)$$

For non-interacting particles $U = 0$. Substituting this, together with Eq. (5), into the definition $\Omega = U - ST - \mu N$ we obtain

$$\Omega = k_B T N_v \phi (N) (\log \phi(N) - 1 - \mu/k_B T)$$

which reaches a minimum at equilibrium in this ensemble. The value of ϕ that minimises this is given by

$$\frac{d\Omega}{d\phi} = N_v (k_B T \log \phi - \mu) = 0$$

Thus we derive the well known relation between the chemical potential and volume fraction of such a gas

$$\mu = k_B T \log \phi \quad \Leftrightarrow \quad \phi = e^{\beta\mu} \quad \text{for } \phi \ll 1$$

If instead the box becomes rather full of particles then, in the opposite limit, $\phi_h \ll 1$ and we instead have a picture in which the box is occupied by a gas of dilute holes surrounded by particles. This analogy can be shown to be rather complete, with $\phi_h = e^{\beta\mu_h}$ with $\mu_h = -\mu$ when $\phi_h \ll 1$. In this limit $\mu_h = -\mu$ since in order to move a hole *into* the system we have to move a gas particle out with the system losing, rather than gaining, energy μ per hole.

Thus, two vessels containing a dilute gas of identical particles will exchange particles with one another, if they are suitably permeable, until the chemical potential in the two vessels is matched. This occurs when $\mu_1 = \mu_2$, which, for vessels with the same temperature $T_1 = T_2$ occurs at $\phi_1 = \phi_2$.

The Boltzmann distribution

We can use Boltzmann's definition of S to derive the Boltzmann distribution for a system at fixed $\{T, V, N\}$ by the requirement that F be a minimum at equilibrium. This is an ensemble in which Boltzmann's result holds.

The free energy of the whole system is simply the number of subsystems (particles) multiplied by the free energy per subsystem

$$F = U - TS = \sum_i (P_i E_i + k_B T P_i \log P_i)$$

where E_i is the i^{th} energy *eigenstate*. Requiring $\frac{\partial F}{\partial P_i} = 0$ for all excitation states (i) we have

$$\frac{\partial F}{\partial P_i} = E_i + k_B T (1 + \log P_i) = 0 \Rightarrow P_i \propto \exp[-(E_i + 1)/k_B T] \propto e^{-\beta E_i}$$

Hence, for a closed system at thermal equilibrium in contact with a heat bath the probability that a particle (subsystem) is in its i^{th} energy *eigenstate*, with energy E_i , is given by the Boltzmann distribution

$$P_i = \frac{1}{Z} e^{-\beta E_i} \quad (6)$$

[Aside: We have performed a little "sleight of hand" here, actually we should insert a constant Lagrange multiplier λ so that $F = \sum_i (P_i E_i + k_B T P_i \log P_i - \lambda P_i)$. This just takes $F \rightarrow F + \text{const}$. This trick won't effect the position of its minimum: $F + \text{const}$. has a minimum in the same place as F . Furthermore the absolute value of F isn't important since we can only ever measure free energy differences anyway. What this trick *does* do is allow us to choose λ so that $\sum_i P_i = 1$. With $P_i = \exp[-(E_i + 1 + \lambda)/k_B T]$ we would simply choose λ so that $\exp[-(1 + \lambda)/k_B T] = 1/Z$, i.e. $\lambda = k_B T \log Z - 1$.]

The partition function

$$Z = \sum_i e^{-\beta E_i}$$

where the sum is over all states can be thought of as a normalisation constant. The summation is often labelled \sum_i but we must remember to count all states, including each

one of any states which have degenerate energies. We can sum over each distinct energy eigenvalue (labelled E_j) if we explicitly include the degeneracy $Z = \sum_j D(E_j)e^{-\beta E_j}$.

The partition function can be factorised arbitrarily over collections of particles or particular degrees of freedom (momentum, spin etc) to $Z_{tot} = \prod_i Z_i$. We will often employ this technique if we are interested in measurements which depend on only some of the degrees of freedom (the x-momentum say for the pressure exerted by a gas on a piston).

Hence the free energy can be related to the partition function according to

$$F = U - TS = -k_B T \log Z \quad (7)$$

This equation and (6) are two of the most important equations in Statistical Mechanics.

The grand canonical distribution

If instead the system can exchange particles with a reservoir at constant chemical potential equilibrium is instead reached when the Grand potential $\Omega = U - TS - \mu N$ reaches a minimum (see its definition). The resulting “grand canonical” distribution may be derived in an analogous way to the Boltzmann distribution and yields the probability of a particle (subsystem) being in the state with energy E_i

$$P_{N,i} = \frac{1}{\Xi} e^{\beta(\mu N - E_i(N))} \quad (8)$$

The grand partition function Ξ is the natural extension to the regular partition function Z and can be thought of as a normalisation constant

$$\Xi = \sum_N \sum_i e^{\beta(\mu N - E_i(N))} \quad (9)$$

with the same health warning concerning the sum over i mentioned for Z above.

Examples 1

1 What thermodynamic potential reaches a minimum for a system held at constant volume, with no flux of matter in or out and in thermal contact with a thermal reservoir? Derive an expression relating changes in this thermodynamic potential to changes in the state variables. Explain in words why it reaches a minimum at equilibrium?

2 Consider a box held at constant $\{P, T, N\}$. Write down and minimise an appropriate free energy in order to calculate the equilibrium volume V of the box assuming that this corresponds to a very low volume fraction $\phi \ll 1$. If a piston then acts to increase the pressure to a new value P' , which is then held constant until the system (particles) equilibrate, what is the new volume V' of the box? What is the minimum amount of work that needs to be done to make this change of volume? [Hint: calculate the change in free energy.]

3 Consider a system of particles in the constant $\{V, T, N\}$ ensemble. These particles reside in a harmonic potential of form $U = \frac{1}{2}kx^2$? (i) What is the resulting probability distribution $P(x)$ and why? (ii) What is the partition function for the particle? [see hint below] (iii) What is the mean-squared x -displacement of the particle, defined by $\int_{-\infty}^{\infty} x^2 P(x) dx$ [Hint: you may use the results that, with $I_n = \int_{-\infty}^{\infty} x^n \exp[-\alpha x^2] dx$, $I_0 = \sqrt{\pi/\alpha}$ and $I_2 = \pi^{1/2} \alpha^{-3/2} / 2$.] (iv) Calculate the mean potential energy corresponding to this mean-squared position. (v) Derive an expression for the Helmholtz free energy F in terms of the partition function Z and hence calculate F per particle. (vi) What is the significance of this value of F .

4 Consider a hypothetical particle in the constant $\{V, T, N\}$ ensemble that has a continuum of non-degenerate energy levels at $\alpha, 2\alpha, 3\alpha \dots, n\alpha, \dots$. (i) What is the corresponding (“non-degenerate”) partition function $Z_{\text{nd}} = \sum_n e^{-\beta E_n}$? [Hint: The sum of an infinite geometric progression $\sum_{i=1}^{\infty} r^i = r/(1-r)$] (ii) What is the probability of finding the particle in an n^{th} excited state? (iii) Consider now a particle that has a degeneracy $D(E_n) = n$. What is the corresponding partition function Z_1 [Hint: consider $\frac{\partial Z_{\text{nd}}}{\partial \alpha \beta}$]. (iv) What is the corresponding probability of finding a particle in an n^{th} excited state? (v) Finally consider a particle that has a degeneracy $D(E_n) = n^2$. What is the corresponding partition function Z_2 [Hint: consider $\frac{\partial^2 Z_{\text{nd}}}{\partial \alpha \beta^2}$]. (vi) What is the corresponding probability of finding a particle in an n^{th} excited state?

Solutions 1

1 The Helmholtz free energy F is a minimum at thermodynamic equilibrium in the constant $\{T, V, N\}$ ensemble appropriate here. It is obtained by adding an additional term to the internal energy (a Legendre transform) and is defined as $F = U - ST$. This has the effect of changing the independent variables from $\{S, V, N\}$ to $\{T, V, N\}$. From (3) given in the notes $dF \leq -SdT - pdV + \mu dN$. At constant $\{T, V, N\}$ we have $\Delta F \leq 0$ thus equilibrium must be a state of minimum F as it is only when F is a minimum that it cannot change further, given that only changes $\Delta F \leq 0$ are allowed. The system reaches a minimum because for irreversible, spontaneous changes $dF < 0$ and hence F decreases until it reaches this minimum.

2 The Gibbs free energy $G = U - TS + PV$ reaches a minimum at equilibrium in this ensemble. Substituting for S from Eq. (5) we have, within a lattice gas approximation,

$$G = k_B TN(\log Nv/V - 1) + PV$$

The value of V that minimises this is given by

$$\frac{dG}{dV} = -Nk_B T/V + P = 0$$

Thus we derive the well known ideal gas law, valid for small volume fractions $\phi \ll 1$

$$PV = Nk_B T \quad \Leftrightarrow \quad V = Nk_B T/P$$

At the new pressure this equation still applies once the system reaches equilibrium and so $V' = Nk_B T/P'$. The minimum amount of work that needs to be done to make this change of volume is

$$\Delta G = G' - G = Nk_B T \log(V/V') + P'V' - PV = Nk_B T \log(V/V')$$

3 (i) Assuming thermodynamic equilibrium the Boltzmann distribution applies and yields $P(x) = \exp[-\frac{1}{2}\beta kx^2]/Z$ (ii) The partition function is the sum over all states (here *positions*) $Z = \int_{-\infty}^{\infty} \exp[-\frac{1}{2}\beta kx^2] = \sqrt{2\pi/(\beta k)}$ using the hint. (iii) The mean-squared position $(\beta k)^{-1}$ also follows from the hint. (iv) The mean potential energy $\bar{U} = \frac{1}{2}k\bar{x}^2 = (2\beta)^{-1} = k_B T/2$. We remark here that this is a consequence of equipartition of energy. (v) $\bar{F} = -k_B T \log Z = \frac{1}{2}k_B T(\log(\beta k) - \log(2\pi))$ (vi) This value of \bar{F} is the minimum value, given that we have assumed that the system is in thermodynamic equilibrium.

4 (i) The corresponding partition function $Z_{\text{nd}} = \sum_{n=1}^{\infty} e^{-\beta\alpha n}$ is a geometric progression and as such is $Z_{\text{nd}} = e^{-\beta\alpha}/(1 - e^{-\beta\alpha}) = 1/(e^{\beta\alpha} - 1)$. (ii) $P_n = e^{-\beta\alpha n}/(e^{\beta\alpha} - 1)$ (iii) $Z_1 = \sum_{n=1}^{\infty} n e^{-\beta\alpha n} = -\frac{\partial Z_{\text{nd}}}{\partial \beta} = e^{\beta\alpha}/(e^{\beta\alpha} - 1)^2$ (iv) The corresponding probability of finding a particle in *any one* of the n^{th} excited states is $P_n = n e^{-\beta\alpha n}/(e^{\beta\alpha} - 1)^2$ (v) For degeneracy $D(E_n) = n^2$ the corresponding partition function is $Z_2 = \sum_{n=1}^{\infty} n^2 e^{-\beta\alpha n} = \frac{\partial^2 Z_{\text{nd}}}{\partial \alpha \partial \beta^2} = e^{\beta\alpha}(1 + e^{\beta\alpha})/(e^{\beta\alpha} - 1)^3$. (vi) The corresponding probability of finding a particle in *any one* of the n^{th} excited states is merely $P_n = n^2 e^{-\beta\alpha n}/(e^{\beta\alpha} - 1)^3/(e^{\beta\alpha}(1 + e^{\beta\alpha}))$