

DEGENERACY AND ALL THAT

The Nature of Thermodynamics, Statistical Mechanics and Classical Mechanics

Thermodynamics

The study of the equilibrium bulk properties of matter within the context of four laws or 'facts of experience' that relate measurable properties, like temperature, pressure, and volume etc. It is important to understand that from the viewpoint of thermodynamics the microscopic nature of matter is irrelevant, that is, thermodynamics would apply equally well if matter formed a continuum. In addition, thermodynamics is a measurement or laboratory based science and is not a branch of metaphysics.

Statistical Mechanics

Statistical Mechanics is a statistical approach to solving the classical n body problem in order to study the same bulk properties of matter as thermodynamics but doing so at the microscopic level. In this way Statistical Mechanics allows an understanding of the equilibrium properties of matter at a molecular level. Statistical Mechanics makes heavy use of Thermodynamics, Classical Mechanics and Quantum Mechanics for its development and hence the prerequisites for this course.

Classical Mechanics

The Classical Mechanical approach to studying the n body problem involves solving six simultaneous differential equations for each particle in the system. This assumes one knows the initial position $q(t)$ and momentum $p(t)$ of each particle at time t_0 . Since the bulk properties of the system of interest are themselves functions of the q and p , i.e., $G=G[p(t),q(t)]$ we can then do a time average of the form

$$\bar{G} = G_{obs} = \frac{1}{\tau} \int_{t_0}^{\tau+t_0} G[p(t),q(t)] dt$$

where τ is long enough to ensure G is independent of τ , i.e., fluctuations are negligible.

Until the early 1950's, such computations were largely beyond reach but since then with the advent of computers, the subject of 'molecular simulation' or 'molecular dynamics' has progressed to the point where the classical mechanical computations of the bulk equilibrium properties of all states of matter are often considered more accurate than the actual experimental measurements of the same properties.

Quantum Mechanics:

The n body problem in quantum mechanics is similar to the problem in classical mechanics although the formalism is quite different. Here one attempts to solve the n body Hamiltonian,

$$\hat{H}_s \Psi_s = E_s \Psi_s$$

for a system s , of n particles which, provided the particles are distinguishable and non-interacting, we can write,

$$\Psi_s = \prod_{i=1}^n \Psi_i(q, t)$$
$$\hat{H}_s = \sum_{i=1}^n \hat{H}_i(p, q, t)$$

$$E_s = \sum_{i=1}^n E_i$$

The more general situation is where the system consists of n indistinguishable and non-interacting particles, in which case the system wave function is not a simple product over the single particle wave functions as in the case of distinguishable particles, but is instead given by the determinant:

$$\Psi_{\pm} = \sqrt{n!} \begin{vmatrix} \Psi_1(1) & \cdots & \Psi_1(n) \\ \vdots & \ddots & \vdots \\ \Psi_n(1) & \cdots & \Psi_n(n) \end{vmatrix}_{\pm}$$

where the \pm symbol on the determinant denotes the distinction between Fermion and Boson systems. This distinction arises naturally because it seems all known particles are one or the other.

Thus:

$\Psi_{+} \equiv \Psi_{sym}$ - Bosons (photons, mesons and atoms with an even number of fermions)

$\Psi_{-} \equiv \Psi_{anti-sym}$ - Fermions (electrons, protons, neutrons and atoms with an odd number of fermions)

For fermions the occupation number of any quantum state is 0 or 1 (Pauli Exclusion Principle) while bosons have no such restriction. Incidentally, if a collection of fermions are sufficiently far apart so there is no wave function overlap, then these particles can be treated as distinguishable and the Pauli principle does not hold.

Finally, quantum mechanical averages for system properties is given by the usual expression

$$G_{obs} = \bar{G} = \int \Psi_s^* \hat{G}_s \Psi_s d\tau$$

Quantum Mechanical Degeneracy

Degeneracy plays a fundamental role in the development of Statistical Mechanics and so we will remind of you of what you probably already know since the prerequisite for the course includes a course in Quantum Mechanics.

Consider a single free particle constrained to move in three dimensions in a cubic box of length L on a side. The potential in the box is zero everywhere and the potential outside the box is infinite (what is the purpose of this constraint?). The wave equation for this so called 'particle in a three dimensional box problem' is given by:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \Psi = E \Psi$$

For problems in which the potential energy can be separated in terms of Cartesian coordinates we can write

$$V(x, y, z) = V_1(x_1) + V_2(x_2) + V_3(x_3)$$

and

$$E = E_x + E_y + E_z$$

Then, the assumption of a solution of the form:

$$\Psi(x, y, z) = X(x)Y(y)Z(z)$$

leads to the separation of the three dimensional second order partial differential equation into three identical ordinary second order differential equations, one for each coordinate, x, y, and z, and of the form:

$$\frac{d^2 X}{dx^2} - \frac{2m}{\hbar^2} [E_x - V(x)] X(x) = 0$$

Solution leads to three identical expressions for the energy of the form:

$$E_x = \frac{\pi^2 \hbar^2 n_x^2}{2mL^2} = \frac{n_x^2 \hbar^2}{8mL^2} \quad \text{where } n_x \text{ is a non-zero integer}$$

with the wave function

$$\Psi(x) = \sqrt{2/L_x} \sin \frac{n_x \pi x}{L_x}$$

Here n_x is the particle quantum number and L_x is the x dimension of the box.

The three dimensional solution follows immediately since the energies add and the wave functions multiply giving

$$E = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

and where again the n's are non-zero integers.

The corresponding wave function is the product given by,

$$\Psi(x, y, z) = \Psi(x)\Psi(y)\Psi(z) = \sqrt{8/V} \left(\sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z} \right)$$

This brings us the point of this discussion, namely the concept of degeneracy.

Definition of Degeneracy:

If a subset of wave functions $\Psi_j, \Psi_{j+1}, \dots, \Psi_k$, give, when substituted back into $\hat{H}\Psi = E\Psi$ the same value for E_n , we say E_n is k-j+1 degenerate. Understanding the concept of degeneracy is critical to understanding statistical mechanics.

Example:

For the ground state of our particle in a 3 dimensional box we have $n_x = n_y = n_z = 1$ and is clearly non-degenerate. However, if $n_x = 2$ and $n_y = n_z = 1$ we have $E = \frac{6h^2}{8mL^2}$ corresponding to the following three wave functions:

$$\Psi_1 = \sqrt{8/V} \left(\sin \frac{2\pi x}{L_x} \sin \frac{\pi y}{L_y} \sin \frac{\pi z}{L_z} \right) \quad (2,1,1)$$

$$\Psi_2 = \sqrt{8/V} \left(\sin \frac{\pi x}{L_x} \sin \frac{2\pi y}{L_y} \sin \frac{\pi z}{L_z} \right) \quad (1,2,1)$$

$$\Psi_3 = \sqrt{8/V} \left(\sin \frac{\pi x}{L_x} \sin \frac{\pi y}{L_y} \sin \frac{2\pi z}{L_z} \right) \quad (1,1,2)$$

All three give the same value of $E = \frac{6h^2}{8mL^2}$ on substitution back into the wave equation. We say then that the energy level $6h^2/8mL^2$ is 3 fold degenerate. You might wish to show that the energy level in which $E=14$ is 6 fold degenerate.

States vs Levels

In the previous case of $E = \frac{6h^2}{8mL^2}$ we saw that the energy **level** 6 had a degeneracy of 3 corresponding to three different wave functions. In other words there exists a one to one correspondence between an energy state and its wave function, i.e.,

$$\Psi_j \rightarrow E_j = 6 \text{ for } j = 1, 2, 3$$

The important point here is that in this course we will typically refer to a systems energy 'state', not its energy level. In other words, if we say that a particular energy level is 10 fold degenerate we mean that there are 10 wave functions or alternatively 10 energy states, E_1, E_2, \dots, E_{10} corresponding to that particular energy level. There will also be times when we have to use 'levels' as in the evaluation of the electronic partition function, but in those cases we will usually include the degeneracy, g_i in our formulism.

Density of States for Large n for the Particle in a Box

All material particles, atoms, electrons etc. are either Fermions or Bosons and strictly speaking, the form of statistics we use to describe these systems should reflect that fact. However, provided that the average quantum state available to a particle is unoccupied, that is, $\bar{c}_j \ll 1$ where \bar{c}_j is the average occupation number of particle state j, then we can alternatively use the Maxwell Boltzmann equation that allows us to factor the system partition function into the product of single particle partition functions for relatively easy computation. The validity of this approximation usually depends on the fact that translational motion alone ensures that this condition holds. Furthermore, since the

model for translational motion is the three dimensional particle in a box it behooves us to look at the question of the density of quantum states for a typical particle.

If one calculates the degeneracy of each energy level for a particle in a cubic box for, say a dozen or so values of n , they will see that the degeneracy does not vary uniformly in any predictable way with increasing E except to say that while the trend is erratic, it does increase with E and becomes more uniform and dense for large E . In particular, we see that three dimensional energy expression is actually an equation of a sphere of radius R and whose values of $R(n_x, n_y, n_z)$, when plotted, are confined to 1/8 quadrant of the sphere because all of the n 's must be positive and non-zero. Why?

$$n_x^2 + n_y^2 + n_z^2 = \frac{8mL^2 \varepsilon}{h^2} \equiv R^2$$

Note that we have written $\varepsilon \equiv E$ for consistently with the text.

For large values of the energy the density of points essentially fills the volume of the quadrant. We can now treat R or ε as a continuous variable so we can calculate the number of lattice points consistent with an energy $\leq \varepsilon$ which is essentially the volume of the eighth quadrant of the sphere. We can now write for the number of energy states, $\Phi(\varepsilon)$

$$\Phi(\varepsilon) = \frac{1}{8} V_{\text{sphere}} = \frac{1}{8} * \frac{4}{3} \pi R^3 = \frac{\pi}{6} (R^2)^{3/2} = \frac{\pi}{6} \left(\frac{8mL^2 \varepsilon}{h^2} \right)^{3/2}$$

and calculate the number of states in a thin shell of thickness $\Delta\varepsilon$. Thus,

$$\omega(\varepsilon, \Delta\varepsilon) \equiv (\partial\Phi / \partial\varepsilon) \Delta\varepsilon = \frac{\pi}{4} \left(\frac{8mL^2}{h^2} \right)^{3/2} \varepsilon^{1/2} \Delta\varepsilon$$

Taking $T=300K$, $m=10^{-25}$ kg, $L=10$ m and $\Delta\varepsilon=0.01\varepsilon$ we find that the degeneracy of a single particle (atom, molecule, etc.) moving in 3 dimensions at room temperature in a typical room 10 m on a side is approximately 10^{30} which is a huge degeneracy. This means that the average energy level corresponding to $3/2kT$ has associated with it roughly 10^{30} energy states all with equal probability from the point of view of our particle. We now look at how the degeneracy changes when the system contains N non-interacting particles.

The system energy then follows from the single particle expression by obvious extension,

$$E = \frac{h^2}{8mL^2} \sum_{j=1}^N (n_{x,j}^2 + n_{y,j}^2 + n_{z,j}^2) = \frac{h^2}{8mL^2} \sum_{j=1}^{3N} s_j^2$$

Again, by analogy with single particle case, we have an equation for an N dimensional hypersphere of radius R whose volume is given by

$$V_N = \frac{\pi^{N/2} R^N}{\Gamma(N/2 + 1)}$$

and the corresponding degeneracy for the entire system of N particles takes the form,

$$\Omega(E, \Delta E) = \frac{1}{\Gamma(N+1)\Gamma(3N/2)} \left(\frac{2\pi mL^2}{h^2} \right)^{3N/2} E^{(3N/2-1)} \Delta E$$

Here $\Gamma(N)$ is the usual gamma function defined as

$$\Gamma(n) = \int_0^{\infty} x^{n-1} e^{-x} dx$$

with the property that

$$\Gamma(n+1) = n\Gamma(n) = n!$$

However, as large as the single particle degeneracy was found to be it is completely insignificant compared to a system of N particles in the same volume. Using the same conditions as for the one dimensional case we find our N particle degeneracy to be on the order of $O(10^N)$ or typically, $O(10^{10^{20}})$. Now there's a number to be reckoned with!

The value of this discussion will become evident when we get to chapter 4 at which time we will revisit this issue.