Introduction To Statistical Mechanics

5. Behaviour of the Density of States

A macroscopic system is one which has very many degrees of freedom (e.g., a copper block, a bottle of wine, etc.). Denote the energy of the system by E. Subdivide the energy scale into equal small ranges of magnitude δE, the magnitude of δE determining the precision within which one chooses to measure the energy of the system. For a macroscopic system, even a physically very small interval δE contains many possible states of the system. We shall denote by $\Omega(E)$ the number of states whose energy lies between E and $E + \delta E$.

Then $\Omega(E)$ must be proportional to δE, i.e., one can write

$$\Omega(E) = \rho(E)\delta E$$

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Where, $\rho(E)$ is independent of the size of δE. Thus $\rho(E)$ is a characteristic property of the system which measures the number of states per unit energy range, i.e., the "density of states". Since all statistical calculations involve the counting of states, it worth examining how sensitively $\Omega(E)$ (or equivalently $\rho(E)$) depends on the energy E of a macroscopic system.

Consider a system of f quantum numbers are required to specify each of this possible states. Let E be the energy of the system measured from its lowest possible energy (i.e., measured from the energy of its quantum-mechanical ground state) and let $\Phi(E)$ denote the total number of possible quantum states of the system which are characterized by energies less than E. Clearly $\Phi(E)$ increases.

Consider first one typical degree of freedom of the system. Denote by $\Phi_1(\varepsilon)$ the total number of possible values which can be assumed by the quantum number associated with this particular degree of freedom when it contributes to the system an amount of energy ε or less.

$$\varepsilon \approx \frac{E}{f}$$

and, corresponding to this amount of energy or less, there are roughly $\Phi_1(\varepsilon)$ possible values which can be assumed by the quantum number describing this degree of freedom.

The total number of $\Phi(E)$ of possible sets of values of the f quantum numbers is approximately given by

$$\Phi(E) \approx \left[\Phi_1(e)\right]^f , \text{ where } e = \frac{E}{f}$$

This gives the total number of states of the system when it has energy E or less. The number of states $\Omega(E)$ in the range between E and $E + \delta E$ is then

$$\Omega(E) = \Phi(E + \delta E) - \Phi(E) = \frac{\partial \Phi}{\partial E} \delta E$$

This gives,

$$\boxed{\Omega \approx \Phi_1^f \propto E^f}$$

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Example: Discuss Ideal gas in the classical limit.

Solution: $E = K + U + E_{\text{int}}$

$$K = K\left(p_1, p_2, ..., p_N\right) = \frac{1}{2m}\sum_{i=1}^{N} p_x^2$$

The quantity $U = K\left(r_1, r_2, ..., r_N\right)$ represents the potential energy of mutual interaction between the molecules. If the molecules are not monatomic P and Q are the coordinates of intra-molecular motion.

$$\Omega(E) \propto \int_E^{E+\delta E} \cdots \int d^3 r_1 \cdots d^3 r_N d^3 p_1 \cdots d^3 p_N dQ_1 \cdots dQ_M dP_1 \cdots dP_M$$

$$d^3 r_i \equiv dx_i dy_i dz_i, \ d^3 p_i = dp_{ix} dp_{iy} dp_{iz}$$

$$\Omega(E) \propto V^N \chi(E)$$

where $\chi(E) \propto \int_E^{E+\delta E} \cdots \int d^3 p_1 \cdots d^3 p_N dQ_1 \cdots dQ_M dQP_1 \cdots dP_M$

$$2mE = \sum_{i=1}^{N}\sum_{\alpha=1}^{3} p_{i\alpha}^2$$
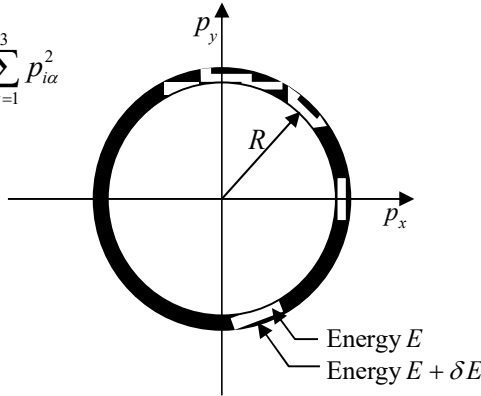

Figure: Illustration in two dimensions of the "sphere" in momentum space for a single particle (of mass m) moving in two dimensions. Here $(2m)^{-1}\left(p_x^2 + p_y^2\right) = E$, the energy of the particle.

The radius of the shell is $R = \left(2mE\right)^{1/2}$.

$$\Phi(E) \propto R^f = \left(2mE\right)^{f/2}$$

$$\Omega(E) \propto E^{(f/2)-1} \propto E^{(3N/2)-1}$$

One obtains for the classical monatomic ideal gas (N is very large so 1 neglected)

$$\boxed{\Omega(E) = BV^N E^{3N/2}}$$

$\Omega(E)$ is highly increasing function of E.

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Example: Suppose that we were asked to pick a card at random from a well-shuffled pack. It is accepted that we have an equal probability **of picking any card** in the pack. There is nothing which would favor one particular card over all of the others. So, since there are fifty-two cards in a normal pack, we would expect the probability of picking the Ace of Spades, say, to be $\dfrac{1}{52}$.

Solution: We could now place some constraints on the system. For instance, we could **only count red cards**, in which case the probability of picking the Ace of Hearts, say, would be $\dfrac{1}{52} + \dfrac{1}{52} = 2 \times \dfrac{1}{52} = \dfrac{1}{26}$, by the same reasoning. In both cases, we have used the principle of equal **a priori probabilities**. People really believe that this principle applies to games of chance such as cards, dice.

In statistical mechanics, we treat a many particle system a bit like an extremely large game of cards. Each accessible state corresponds to one of the cards in the pack. The interactions between particles cause the system to continually change state. This is equivalent to constantly shuffling the pack. Finally, an observation of the state of the system is like picking a card at random from the pack. The principle of equal **a priori probabilities** then boils down to saying that we have an equal chance of choosing any particular card.

Example: If there are four identical molecule in one dimensional container and it is given that molecule can be found only either right or left end of container .

(a) What are possible configuration and no of ways to arrange these configuration? What are corresponding probability of each configuration?

(b) What is most probable configuration?

(c) If some one is doing the experiment in which he observed molecule position to right of container what is mean value of particle being in right?

(d) How postulates of a priori probability apply on the experiment?

Solution: The number of different ways of arranging N molecules with n on one side and (N-n) on the other side is given by $\dfrac{N!}{N!(N-n)!}$, where ! represents the factorial function. The total number of possible ways of arranging the molecules is $2^N = 2^4 = 16$

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(a)

Configuration	No. of ways to arrange given configuration	Probability
1. (L,L,L,L)	1	$1 \times \dfrac{1}{16} = \dfrac{1}{16}$
2. (L,L,L) and (R)	4	$4 \times \dfrac{1}{16} = \dfrac{4}{16}$
3. (L,L) and (R,R)	6	$6 \times \dfrac{1}{16} = \dfrac{6}{16}$
4. (L) and (R,R,R)	4	$4 \times \dfrac{1}{16} = \dfrac{4}{16}$
5. only (R,R,R,R)	1	$1 \times \dfrac{1}{16} = \dfrac{1}{16}$

(b) Most probable configuration is the one in which half the molecules are on one side and half on the other, i.e. the molecules are uniformly distributed over the space.

Most probable configuration is configuration (L,L) and(R,R) which has maximum probability .

(c) $\langle R \rangle = \sum_r p_r R_r = 0R \times \dfrac{1}{16} + 1R \times \dfrac{4}{16} + 2R \times \dfrac{6}{16} + 3R \times \dfrac{4}{16} + 4R \times \dfrac{1}{16} = 2R$

(d) We will now apply a fundamental postulate of statistical mechanics which states that an isolated system which can be in any one of a number of accessible states (=16 in this example) is equally likely to be in any one of these states at equilibrium. Therefore, the probability that the molecules are distributed in any one of these 16 possible ways is simply 1/16. But there are 4 ways in which the molecules can be arranged so that 3 are on the left side and 1 on the right side, and therefore, the probability of finding that configuration is 4/16. Similarly other configuration can be weighted.

Example: Suppose we know 3 particle being spin 1/2 kept into homogeneous magnetic B field at temperature T.

(a) Show all possible microstate and corresponding probability.

(b) Find average value of z component of spin.

(c) If μ_0 is magnetic moment Which configuration has maximum energy what is corresponding probability.

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Solution: (a) There is total 8 microstate is possible they are

configuration	Microstate	Probability
All are in up state	↑ ↑ ↑	$\dfrac{1}{8}$
Two are up and one is down	↑ ↑ ↓ ↑ ↓ ↑ ↓ ↑ ↑	$\dfrac{3}{8}$
One up and two down	↓ ↓ ↑ ↑ ↓ ↓ ↓ ↑ ↓	$\dfrac{3}{8}$
All three are down	↓ ↓ ↓	$\dfrac{1}{8}$

(b) Average value of $\langle s_z \rangle = \dfrac{3\hbar}{2} \times \dfrac{1}{8} + \dfrac{\hbar}{2} \times \dfrac{3}{8} + \dfrac{-\hbar}{2} \times \dfrac{3}{8} + \dfrac{-3\hbar}{2} \times \dfrac{1}{8} = 0$

(c) The energy is given by $E = -\mu_0 B$ the magnetic moment of configuration in which all three are down ↓↓↓ have magnetic moment -3 μ_0 so this configuration has maximum energy which is equal to $3\mu_0 B$ the corresponding probability is given by $\dfrac{1}{8}$

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