

# Role of Partition Function in Statistical Mechanics

K. M. Udayanandan, R. K. Sathish<sup>1</sup> and Augustine. A<sup>2</sup>

<sup>1</sup>Department of Physics  
Nehru Arts and Science College,  
Kerala-671 314, INDIA  
udayanandan@gmail.com

<sup>2</sup>Department of Physics  
University of Kannur,  
Kerala 673 635, INDIA.

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## Abstract

In this article we give a simple method of introducing statistical mechanics and also highlight the importance of Partition Function[PF] in Statistical Mechanics[SM].

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## 1 Introduction

In every branch of physics there will be some key equation or equations around which the whole subject is developed. In classical mechanics for undergraduates, the subject is developed around the equation

$$\vec{F} = m \vec{a}$$

where  $\vec{F}$  is the force  $m$  is the mass and  $\vec{a}$  is the acceleration of an object. In post grad-

uate classical mechanics course we have Lagrange's equations

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_j} \right) = \frac{\partial L}{\partial q_j}$$

or Hamilton's equations of motion

$$\frac{dp}{dt} = - \frac{\partial \mathcal{H}}{\partial q}$$

$$\frac{dq}{dt} = + \frac{\partial \mathcal{H}}{\partial p}$$

In quantum mechanics we have Schroedinger equation

$$H\psi = E\psi$$

where H the Hamiltonian,  $\psi$  is the wave function which can be found and E is the energy eigen value. In electrodynamics we have Maxwell's equations,

$$\begin{aligned} \nabla \cdot \mathbf{E} &= \frac{\rho}{\epsilon_0} \\ \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\ \nabla \times \mathbf{B} &= \mu_0 \left[ \vec{J} + \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right] \end{aligned}$$

where  $\vec{E}$  is the electric field,  $\vec{B}$  is the magnetic field,  $\rho$  is the charge density,  $\vec{J}$  is the current density,  $\mu_0$  is the permeability of free space and  $\epsilon_0$  is the permittivity of free space. Thus any branch of physics is developed around some central equation or equations. Here we are discussing about SM. There fore in statistical mechanics which is the central equation?. In the preface to his book [1] Daniel Mattis comments that once when he started studying statistical mechanics and asked about it to his friend he simply wrote  $e^{-\beta H}$ . Feynman starts his statistical mechanics book [2] by saying ' The key principle of statistical mechanics is as follows- If a system in equilibrium can be in one of N states, then the probability of the system having energy  $E_n$  is  $\frac{1}{Q} e^{-\frac{E_n}{kT}}$  where  $Q = \sum_{n=1} e^{-\frac{E_n}{kT}}$ . Q is called partition function.' The above two comments highlight the importance of partition function. From

where these equations come from? They are obtained from Gibbs[3] ensemble theory. Gibbs in his ensemble theory defines three ensembles Micro Canonical Ensemble (MCE), Canonical Ensemble (CE) and Grand Canonical Ensemble (GCE). These ensembles give three equations for probability. They are

$$p_i = \frac{1}{\Omega}$$

for constant energy

$$p_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

if energy is varying and

$$p_{r,s} = \frac{e^{-\beta(E_s - \mu N_r)}}{\sum_{r,s} e^{-\beta(E_s - \mu N_r)}}$$

if both energy and number of particles are varying respectively for MCE, CE and GCE where  $E_i$  or  $E_s$  represents instantaneous energy of a system,  $N_r$  represents instantaneous number of particles and  $\beta = \frac{1}{kT}$ . Using these equations we can obtain the three bridging equations that link a microscopic quantity with a macroscopic thermodynamic quantity. They are

$$S = k \ln \Omega(E, V, N) \tag{1}$$

$$A = -kT \ln Q(T, V, N) \tag{2}$$

$$\phi = -kT \ln \mathcal{Z}(T, V, \mu) \tag{3}$$

for respective ensembles, where S is the entropy, A is the Helmholtz free energy and  $\phi$  is the Landau free energy which are macroscopic parameters and the microscopic parameters  $\Omega$  is the number of micro states

available for particles,  $Q$  is the canonical partition function and  $\mathcal{Z}$  is the grand partition function.

## The importance of the partition function

Statistical mechanics is a branch of physics whose basic objective was to find the physical properties of matter which are temperature dependent. Now a days statistical mechanics goes beyond this objective but, in principle this was primarily the aim while formulating this subject. Based on this principle physicists applied statistical mechanics to obtain properties of blackbody (Planck's distribution law, Stefan-Boltzmann law), solids(specific heat), metals(photo electric effect, thermionic emission)etc. All the explanations regarding magnetism, Pauli para magnetism, Landau diamagnetism and Ising Ferro magnetism are applications of statistical mechanics. Thus we can see hundreds of applications of statistical mechanics in text books. Recently, statistical mechanics is even used in politics[4], economics[5], biology[6] and almost all walks of life. It is interesting to see that it can be even used to explain the swinging movement of a ponytail[7]. Going back we see that Eq[1,2,3] show that all thermodynamics of a system can be obtained if we know  $\Omega$  or  $Q$  or  $\mathcal{Z}$ . Finding  $Q$  or  $\mathcal{Z}$  is much easier than finding  $\Omega$ . Thus in SM we will heavily depend on partition functions in CE and GCE. Thus PF has a central role in statistical thermodynamics because once it is known as a function of the

variables on which it depends, all thermodynamic quantities may be calculated from it directly. Now let us briefly go through ensemble theory[8],[9] and find out how these equations are obtained.

## Ensemble theory

We want to obtain equations for thermodynamics quantities of a system. The system may be a collection of atoms, electrons, quarks, photons etc. An ensemble is an idealization (mental construction) consisting of a large number of virtual copies of a system, **considered all at once**, each of which represents a possible state that the real system might be in. Thus the system at different time is considered together. We usually construct three different types of ensembles with  $E, V, N = \text{constant}$ ,  $T, V, N = \text{constant}$  and  $T, V, \mu = \text{constant}$  in physics to solve our problems in Statistical mechanics and they are called MCE, CE and GCE respectively.

## Micro Canonical Ensemble

Consider two systems with number of micro states  $\Omega_1$  and  $\Omega_2$  with entropies  $S_1$  and  $S_2$ . If they are made to contact then their resultant entropy  $S = S_1 + S_2$  because of the extensive property of entropy. We can show that

$$\Omega = \Omega_1 \Omega_2$$

Boltzmann proposed that

$$S \propto f(\Omega)$$

For the first system

$$S_1 \propto f(\Omega_1)$$

For the second system

$$S_2 \propto f(\Omega_2)$$

Then to satisfy the Boltzmann proposal

$$S \propto \ln \Omega$$

Shortly Max Planck introduced the constant of proportionality  $k$  and hence the Boltzmann equation takes the form

$$S = k \ln \Omega$$

where,  $k$  is the Boltzmann constant.

### Thermodynamics

We got  $S = k \ln \Omega(E, V, N)$ . Now  $S$  is a constant and will be a function of  $E$ ,  $V$  and  $N$ . The statistical mechanics ends here and we will use thermodynamics to derive other physical quantities by varying the quantities mathematically or mentally. The I law of thermodynamics is given by

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

Taking partial derivatives

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

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}$$

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

Thus from I equation we get  $E$  and from others we get  $P$  and  $\mu$  and we can derive  $C_P$ ,  $C_V$  and other thermodynamics from these quantities. If we need other thermodynamic quantities we can modify 1st law of thermodynamics suitably and obtain them.

## Canonical Ensemble

We will consider an ensemble with  $T$ ,  $V$  and  $N$  constants. To make  $T$  constant the system has to be immersed in a heat reservoir. Then we have  $E_{tot} = E_{res} + E_i$  where  $E_i$  is the system energy at any instant  $i$  or state  $i$ .  $E_i$  is continuously changing. Hence another property of the system is known to us which is the average energy  $U$  can be defined as  $U = \sum_i p_i E_i$ . Taking  $U$  we can write

$$E_{res} = E_t - U - (E_i - U)$$

Similarly

$$E_{tot} = E_{tot} - U + U$$

The probability that system will have energy  $E_i$  is

$$p_i = \frac{\Omega_{res}(E_{tot} - E_i)}{\Omega_{tot}(E_{tot})}$$

$$p_i = \frac{\Omega_{res}(E_t - U - (E_i - U))}{\Omega_{tot}(E_{tot} - U + U)}$$

The numerator is function of the form  $f(x + h)$  which demands an expansion using Taylor series and denominator is like  $f(a)$  which cannot be expanded.

$$f(x + h) = f(x)|_{x_0} + \frac{\partial f}{\partial x} h$$

We modify the Boltzmann equation as

$$\Omega = e^{\frac{S}{k}}$$

and we get

$$p_i = \frac{e^{\frac{S_{res}}{k}}}{e^{\frac{S_{tot}}{k}}}$$

$$p_i = \frac{e^{\frac{S_{res}}{k}(E_t - U - (E_i - U))}}{e^{\frac{S_{tot}}{k}(E_t - U + U)}}$$

Since entropy shows additive nature and now using Taylor expansion for numerator

$$p_i = \frac{e^{\frac{S_{res}}{k}(E_t - U) - \frac{1}{kT}(E_i - U)}}{e^{\frac{S}{k}(E_t - U) + \frac{S}{k}(U)}}$$

$$p_i = e^{-\frac{(E_i - U)}{kT}} e^{-\frac{(ST)}{kT}}$$

$$p_i = e^{-\frac{E_i}{kT}} e^{\frac{U - TS}{kT}}$$

$$p_i = e^{-\beta E_i} e^{\frac{A}{kT}}$$

$$\sum_i p_i = 1 \text{ and defining } \sum_i e^{-\beta E_i} = Q$$

$$e^{-\beta A} = Q$$

or

$$A = -kT \ln Q$$

### Thermodynamics

$$A = U - TS$$

Differentiating and using I law of TD we get

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

$$\mu = \left( \frac{\partial A}{\partial N} \right)_{V,T}$$

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

Substituting the value of S in the equation for A we get

$$U = kT^2 \left( \frac{\partial}{\partial T} \ln Q \right)_{V,N}$$

Thus all thermodynamics can be obtained. For N free particles

$$Q_N = \left( \frac{V}{\lambda^3} \right)^N$$

where V is the volume and  $\lambda$  is the thermal wavelength. For N harmonic oscillators

$$Q_N = \left[ \left( \frac{kT}{\hbar\omega} \right)^3 \right]^N$$

## Grand Canonical Ensemble

Consider a reservoir which can supply both energy and particles so that our system has two variables, energy and number of particles. We have then

$$E_t = E_{res} + E_s$$

$$N_t = N_{res} + N_r$$

As done in canonical ensemble we can write

$$E_{res} = (E_{tot} - U) - (E_s - U)$$

$$N_{res} = N_{tot} - N - (N_r - N)$$

where N is the average number of particles.

$$\Omega_{tot} = \Omega_{tot}(E_s, N_r)$$

$$\Omega_{res} = \Omega_{res}(E_{res}, N_{res})$$

$$p_{r,s} = \frac{\Omega_{res}}{\Omega_{tot}} = \frac{e^{\frac{S_{res}}{k}}}{e^{\frac{S_{tot}}{k}}}$$

Substituting and canceling terms as in canonical ensemble and using the equation

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

$$p_{r,s} = e^{-\beta(E_s - \mu N_r)} e^{+\beta(U - TS - \mu N)}$$

Taking  $\phi = U - TS - \mu N$  which is called Landau free energy and taking the sum over all the states,

$$e^{\beta\Phi} \mathcal{Z} = 1$$

$$e^{-\beta\Phi} = \mathcal{Z}$$

$$\Phi = -kT \ln \mathcal{Z}$$

where

$$\mathcal{Z} = \sum_{r,s} e^{-\beta(E_s - \mu N_r)}$$

Let us define fugacity

$$z = e^{\beta\mu} = e^{\frac{\mu}{kT}}$$

Then

$$\mathcal{Z} = \sum_{r,s} z^{N_r} Q_{N_r}$$

## Thermodynamics

$$\Phi = U - TS - \mu N$$

Differentiating and substituting I law

$$d\Phi = -PdV - SdT - Nd\mu$$

$$S = -\left(\frac{\partial\Phi}{\partial T}\right)_{V,\mu}$$

$$P = -\left(\frac{\partial\Phi}{\partial V}\right)_z$$

$$N = -\left(\frac{\partial\Phi}{\partial\mu}\right)_{V,T}$$

$$\ln z = \beta\mu$$

$$N = z \left(\frac{\partial \ln \mathcal{Z}}{\partial z}\right)_{V,T}$$

$$\Phi = U - TS - \mu N$$

Multiplying with  $\beta$  and taking a partial derivative with  $\beta$

$$U = \left(-\frac{\partial}{\partial\beta} \ln \mathcal{Z}\right)_z = kT^2 \left(\frac{\partial}{\partial T} \ln \mathcal{Z}\right)_z$$

If single particle PF is known we can find the GPF as

$$\mathcal{Z} = \sum_{r,s} (zQ_1)^{N_r}$$

which will become

$$\mathcal{Z} = \frac{1}{1 - zQ_1}$$

for distinguishable particles and

$$\mathcal{Z} = \sum_{r,s} \frac{(zQ_1)^{N_r}}{N_r!}$$

which is equal to

$$\mathcal{Z} = e^{zQ_1}$$

for indistinguishable particles. All the thermodynamics are obtained as partial derivatives of logarithm of PF. Thus we can see that the aim of statistical mechanics to determine TD will be satisfied only if we know PF. Thus PF plays a **key role in SM**

## Conclusions

**The partition function is a measure of the degree to which the particles are spread out over, or partitioned among, the energy levels.** In canonical ensemble we have  $\sum_i e^{-\beta E_i} = Q$ . Energy and  $\beta$  have

the same units and exponent becomes a number and hence  $Q$  is a number and is dimensionless. This appears as mysterious to many students that, how a dimensionless quantity is so much important. We had large number of similar situations in physics. We know that refractive index( $n$ ) which is dimensionless plays a great role in optics. In dispersion  $n$  plays decisive role. Another example is Reynolds number which has a value 2500. Actually it is the ratio of inertial forces to viscous forces in a liquid flowing in a pipe. The lowest possible value for the partition function is 1, the value it could have when the temperature of the system is 0 K, the temperature at which all particles in the system are in the ground state and the fractions in the excited states are zero. The highest value for the partition function can be very large, but not infinite. In the history of statistical mechanics there are many cases like Ising model where the whole concept of Ferro magnetism was changed when the proper partition function is obtained for the system.

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