PHYS 3014: Statistical Mechanics

Lecture Notes
Part 6

Canonical Ensemble: Physical signifacance of statistical quantities

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Physical significance of various statistical quantities

When a system is in equilibrium in thermal contact of heat reservoir and has a specified mean energy U, then the canonical distribution is given by

$$P_r = \frac{n_r}{\mathcal{N}} = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} \quad \text{--- (1)}$$

Its mean energy U is given by

$$U = \langle E_r \rangle = \frac{\sum_r E_r n_r}{\sum_r n_r}$$

$$= \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} = -\frac{\partial}{\partial \beta} \ln\left\{\sum_r \exp(-\beta E_r)\right\} \quad \text{--- (2)}$$

If we define $Z = \sum_r \exp(-\beta E_r)$ then

$$U = -\frac{\partial}{\partial \beta} \ln Z$$

The quantity $Z = \sum_r \exp(-\beta E_r)$ is called as canonical partition function. It is "sum over states". It is representing the way in which Z measures how energy is distributed or partitioned among states of the system.

We know that Helmholtz free energy of the system

$$F(T,V,N) = U - TS \quad \text{--- } (3)$$

$$dF = dU - Tds - sdT = Tds - Pdv + \mu dN - Tds - sdT$$

$$= -sdT - Pdv + \mu dN$$

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

and $U = F + TS$

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

$$= -T^2\left[\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right]_{N,V} = \left[\frac{\partial\left(\frac{F}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right]_{N,V} \quad \text{--- (4)}$$

Comparing (2) and (4),

$$\beta = \frac{1}{KT} \quad \text{and} \quad -\frac{F}{KT} = \ln\left[\sum_r \left\{\exp(-\beta E_r)\right\}\right]$$

K is Boltzmann Constant.

$$\therefore \quad F(N,V,T) = -KT \ln Z(N,V,T)$$

specific heat capacity at constant volume

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{N,V} = \frac{\partial}{\partial T}\left[F - T\left(\frac{\partial F}{\partial T}\right)_{N,V}\right]$$

Gibb's free energy $G = F + PV$

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

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

$$= -KT \ln Z + KTV\left(\frac{\partial \ln Z}{\partial V}\right)_{N,T}$$

Entropy S

we have $P_r = \dfrac{\exp(-\beta E_r)}{Z}$

$\therefore \ln P_r = -\ln Z - \beta E_r$

$\therefore \langle \ln P_r \rangle = -\ln Z - \beta \langle E_r \rangle$

$$= \beta F - \beta U$$

$$= \beta (F - U)$$

$$= \beta(-TS) = -\frac{S}{K}$$

$$\therefore \quad S = -K \langle \ln P_r \rangle$$

$$= -K \sum_r P_r \ln P_r$$

therefore entropy of a physical system is completly determined by probability values P_r.

$$S = -K \langle \ln P_r \rangle$$

$$= -K \left[-\ln Z - \beta \langle E_r \rangle \right]$$

$$= K \ln Z + K\beta \langle E_r \rangle$$

$$= K \ln Z + K\beta U = K \ln Z + \frac{U}{T}$$

Value of β

$$S = K \ln Z + K\beta U$$

$$\frac{\partial S}{\partial U} = \frac{1}{T} \Rightarrow \frac{\partial}{\partial U}(K \ln Z) + K\beta + KU\frac{\partial \beta}{\partial U} = \frac{1}{T}$$

Now $\frac{\partial}{\partial U}(K \ln Z) = \frac{\partial}{\partial \beta}(K \ln Z) \cdot \frac{\partial \beta}{\partial U}$

$$= \frac{\partial \beta}{\partial U} \cdot \frac{K}{Z} \frac{\partial Z}{\partial \beta}$$

$$= \frac{\partial \beta}{\partial U} \cdot \frac{K}{Z} \left[-\sum_r E_r \exp(-\beta E_r) \right]$$

$$= -\frac{\partial \beta}{\partial U} \cdot K \langle E_r \rangle$$

$$= -\frac{\partial \beta}{\partial U} K U$$

$\therefore \quad -KU \frac{\partial \beta}{\partial U} + K\beta + KU \frac{\partial \beta}{\partial U} = \frac{1}{T}$

$$\Rightarrow \quad \beta = \frac{1}{KT}$$

Internal Energy

$$U = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial \left(\frac{F}{KT}\right)}{\partial \beta}$$

$$= KT^2 \frac{\partial \ln Z}{\partial T} \Rightarrow C_v = 2KT \left(\frac{\partial \ln Z}{\partial T}\right)_v + KT^2 \left(\frac{\partial^2 \ln Z}{\partial T^2}\right)_v$$

Pressure

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$= KT\left(\frac{\partial(\ln z)}{\partial V}\right)_T$$

Enthalpy

$$H = U + PV$$

$$= KT^2\left(\frac{\partial \ln z}{\partial T}\right)_V + V\,KT\left(\frac{\partial \ln z}{\partial V}\right)_T$$

$$= KT\left[T\left(\frac{\partial \ln z}{\partial T}\right)_V + V\left(\frac{\partial \ln z}{\partial V}\right)_T\right]$$

$$= \frac{\partial}{\partial \beta}\left(\frac{F}{KT}\right) + V\left\{-\left(\frac{\partial F}{\partial V}\right)_T\right\}$$

$$= \frac{\partial}{\partial \beta}(\beta F) - V\left(\frac{\partial F}{\partial V}\right)_T$$

Systems consisting of degenerate energy levels

If the energy levels accessible to a system are degenerate i.e a group of g_r states belong to the same energy level E_r, then partition function of the system is

$$Z = \sum_r g_r \exp(-\beta E_r)$$

The probability P_r that the system be in a state with energy E_r is

$$P_r = \frac{g_r \exp(-\beta E_r)}{\sum_r g_r \exp(-\beta E_r)}$$

$$= \frac{g_r \exp(-\beta E_r)}{Z}$$

All the g_r states with common energy E_r are equally likely to occur. The probability that the system be in the state with energy E_r is proportional to multiplicity g_r of the energy level. So g_r acts as weight factor for the energy level E_r. The actual probability is determined by weight factor g_r as well as Boltzmann factor $\exp(-\beta E_r)$.

Ensemble average of a Physical Quantity

The ensemble average $\langle f \rangle$ of a physical quantity $f(q, p)$ is

$$\langle f \rangle = \frac{\int f(q,p)\, \rho(q,p)\, dq^{3N} dp^{3N}}{\int \rho(q,p)\, dq^{3N} dp^{3N}}$$

where $\rho(q,p)$ is the density of representative points in phase space or phase space density in Canonical ensemble.

It is a measure of the probability of finding a representative point in the vicinity of phase point (q, p).

In canonical ensemble

$$\rho(q,p) \propto \exp\{-\beta H(q,p)\}$$

$$\therefore \langle f \rangle = \frac{\int f(q,p) \exp\{-\beta H(q,p)\} \, d^{3N}q \, d^{3N}p}{\int \exp\{-\beta H(q,p)\} \, d^{3N}q \, d^{3N}p}$$

where $d^{3N}q \, d^{3N}p = d\omega$ is the volume element in the phase space.

References:

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- Elementary Statistical Physics by C. Kittel
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Thank You

For any questions/doubts/suggestions and submission of assignments

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