VIVEKANANDA COLLEGE
THAKURPUKUR
KOLKATA-700063

NAAC ACCREDITED 'A' GRADE

Topic: System of Harmonic Oscillators (https://www.youtube.com/watch?v=1m7K_bmU61Y)

Course Title: Statistical Mechanics

Paper: PHY 423

Unit: 2

Semester: 2

Name of the Teacher: Arvind Pan

Name of the Department: Physics PG

Application of canonical ensemble to two most important problems in physics:

1. Collection of Harmonic oscillators:
2. Statistics of Paramagnetism.

A system of Harmonic oscillators

N-independent, identical linear harmonic oscillators

Hamiltonian $H = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} + \frac{1}{2} m\omega^2 q_i^2 \right)$

a) Classical Approach

$$Q_1 = \frac{1}{h} \int e^{-\beta H} d^3q_i \, d^3p_i$$

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

$$= \frac{1}{h} \int_{-\infty}^{+\infty} e^{-\beta p_i^2/2m} d^3p_i \int_{-\infty}^{+\infty} e^{-\frac{\beta m\omega^2}{2} q_i^2} d^3q_i$$

$$= \frac{1}{h} \sqrt{\frac{\pi}{(\beta/2m)}} \times \sqrt{\frac{\pi}{(\beta m\omega^2/2)}} = \frac{1}{\beta\hbar\omega} = \frac{KT}{\hbar\omega}$$

Hence for the collection of N independent distinguishable linear harmonic oscillators

$$Q = (Q_1)^N = (\beta\hbar\omega)^{-N}$$

No division by N! as these oscillators are representation of the energy levels, <u>not</u> particles or quasiparticles (photons & phonons) which are actually indistinguishable. Now the corresponding thermodynamic properties are

\# Helmholtz Free Energy $A = -KT \ln Q = NKT \ln(\hbar\omega/KT)$

\# Entropy $S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = -\left[NK \ln(\hbar\omega/KT) + \frac{NKT}{\hbar\omega/KT}\left(\frac{-\hbar\omega}{KT^2}\right)\right]$

$$= NK \ln\left(\frac{KT}{\hbar\omega}\right) + NK$$

$$= NK \left[\ln\left(\frac{KT}{\hbar\omega}\right) + 1\right]$$

\# Internal Energy $U = A + TS = NKT \cancel{\ln}\left(\frac{\hbar\omega}{KT}\right) + NKT\left[\ln\left(\frac{KT}{\hbar\omega}\right) + 1\right]$

$$= NKT$$

~~Specific heats~~ ~~C_p~~

\# Pressure $P = -\left(\frac{\partial U}{\partial V}\right)_{N,T} = 0$

\# Chemical Potential $\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T} = KT \ln\left(\frac{\hbar\omega}{KT}\right)$

\# ~~Internal~~ Specific heats $C_p = C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = NK$

The ~~last~~ expression for internal energy / mean energy is in complete agreement with principle of equipartition of energy namely $2 \times \frac{1}{2} KT$ as we have two ~~quadratic~~ quadratic term in the Hamiltonian.

Let us do the above problem for quantum harmonic oscillator.

(b) Quantum mechanical approach: The energy for a quantum harmonic oscillator is:

$$\epsilon_n = \left(n+\frac{1}{2}\right)\hbar\omega \quad , \quad n = 0, 1, 2, 3 \ldots$$

Now single particle partition function is

$$Q_1 = \sum_{n=0}^{\infty} e^{-\beta\epsilon_n} = e^{-\beta\frac{\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}$$

$$= \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} = \frac{1}{e^{\beta\hbar\omega/2}-e^{-\beta\hbar\omega/2}}$$

$$= \frac{1}{2\sinh(\hbar\omega\beta/2)} = \left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]^{-1}$$

For N oscillator system

$$Q = (Q_1)^N = \left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]^{-N}$$

Thermodynamic Properties are

Helmholtz free Energy $A = -KT\ln Q = NKT\ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]$

$$= NKT\ln\left[e^{\beta\hbar\omega/2}-e^{-\beta\hbar\omega/2}\right] = NKT\ln\left[e^{\beta\hbar\omega/2}(1-e^{-\beta\hbar\omega})\right]$$

$$= N\left[KT\ln e^{\beta\hbar\omega/2} + KT\ln(1-e^{-\beta\hbar\omega})\right]$$

$$= N\left[\cancel{KT}\,\cancel{\beta}\hbar\omega/2 + KT\ln(1-e^{-\beta\hbar\omega})\right]$$

$$= N\left[\frac{\hbar\omega}{2} + KT\ln(1-e^{-\beta\hbar\omega})\right]$$

Entropy $S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = -NK\ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right] - \frac{NK\cancel{T}}{\cancel{2}\sinh\left(\frac{\beta\hbar\omega}{2}\right)}\cancel{2}\cosh\left(\frac{\beta\hbar\omega}{2}\right)\times\left(\frac{-\hbar\omega}{2KT^{2}}\right)$

$$= NK\beta\frac{\hbar\omega}{2}\coth\left(\beta\frac{\hbar\omega}{2}\right) - NK\ln\left[2\sinh\left(\beta\frac{\hbar\omega}{2}\right)\right]$$

$$= NK\left[\frac{\beta\hbar\omega}{2}\,\frac{e^{\beta\hbar\omega/2}+e^{-\beta\hbar\omega/2}}{e^{\beta\hbar\omega/2}-e^{-\beta\hbar\omega/2}} - \ln\left[e^{\beta\hbar\omega/2}(1-e^{-\beta\hbar\omega})\right]\right]$$

$$= NK\left[\frac{\beta\hbar\omega}{2}\left(\frac{1+e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right) - \frac{\beta\hbar\omega}{2} - \ln(1-e^{-\beta\hbar\omega})\right]$$

$$= NK\left[\frac{\beta\hbar\omega}{2}\left(\frac{\cancel{1}+e^{-\beta\hbar\omega}-\cancel{1}+e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right) - \ln(1-e^{-\beta\hbar\omega})\right]$$

$$= NK\left[\frac{\beta\hbar\omega\,\cancel{2}e^{-\beta\hbar\omega}}{\cancel{2}(1-e^{-\beta\hbar\omega})} - \ln(1-e^{-\beta\hbar\omega})\right]$$

$$= NK\left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1} - \ln(1-e^{-\beta\hbar\omega})\right]$$

Internal Energy $U = A + TS = NKT\beta\frac{\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right)$

$$= N\frac{\hbar\omega}{2}\left[\frac{e^{\beta\hbar\omega/2}+e^{-\beta\hbar\omega/2}}{e^{\beta\hbar\omega/2}-e^{-\beta\hbar\omega/2}}\right]$$

$$= \frac{N\hbar\omega}{2}\left[\left\{\frac{1+e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right\}+1-1\right]$$

$$= \frac{N\hbar\omega}{2}\left[1+\frac{1+e^{-\beta\hbar\omega}-1+e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right]$$

$$= \frac{N\hbar\omega}{2}\left[1+\frac{2e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right]$$

$$U = N\frac{\hbar\omega}{2}\left[1 + \frac{2}{e^{\beta\hbar\omega}-1}\right] = N\left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right]$$

Not in accordance with law of equipartition of energy, presence of zero point energy $\hbar\omega/2$.

\# Pressure $P = -\left(\frac{\partial U}{\partial V}\right)_{N,T} = 0$

\# Chemical Potential $\mu = \frac{A}{N} = \left[\frac{\hbar\omega}{2} + KT\ln\left(1-e^{-\beta\hbar\omega}\right)\right]$

\# Specific heat $(C_p = C_v) = \left(\frac{\partial U}{\partial T}\right)_{N,V} = N\left(\frac{\hbar\omega}{2}\right)\left(-\mathrm{Cosec}^2\left(\frac{\beta\hbar\omega}{2}\right)\right)\times\left(\frac{-\hbar\omega}{2KT^2}\right)$

$$= NK\left(\frac{\hbar\omega}{2}\beta\right)^2 \mathrm{Cosec}^2\left(\frac{\hbar\omega}{2}\beta\right)$$

$$= NK\,(\beta\hbar\omega)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

All these result would approach classical limits for $KT \gg \hbar\omega$