PHYS 3014: Statistical Mechanics

Lecture Notes
Part 8

Canonical Ensemble: Classical and Quantum Oscillators

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System of N distinguishable classical Oscillators

Consider a system of N distinguishable and independent classical oscillators oscillating with same angular frequency ω. (one dimensional)

The hamiltonian of the system is

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

where m is the mass of oscillators.

The single oscillator partition function is

$$Z(T, V, 1) = Z_1 = \frac{1}{h} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left(-\beta \left\{ \frac{1}{2} m\omega^2 q^2 + \frac{p^2}{2m} \right\}\right) dq\, dp$$

$$= \frac{1}{h} \left(\frac{2\pi}{\beta m \omega^2} \right)^{1/2} \cdot \left(\frac{2\pi m}{\beta} \right)^{1/2}$$

$$= \frac{1}{\beta \hbar \omega}$$

$\therefore$ partition function of the system of N oscillators

$$Z(T,V,N) = \frac{1}{h^N}\int \exp\{-\beta H(q,p)\}\, dq^N dp^N$$

$$= \frac{1}{h^N}\prod_{i=1}^{N}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\{-\beta \tfrac{1}{2} m\omega^2 q_i^2\}\, dq_i^N \cdot \exp\{-\beta \tfrac{p_i^2}{2m}\} dp_i^N$$

$$= \frac{1}{h^N}\left(\frac{2\pi}{\beta m\omega^2}\right)^{N/2}\cdot\left(\frac{2m\pi}{\beta}\right)^{N/2}$$

$$= \left(\frac{1}{\beta\hbar\omega}\right)^N = \left[Z(T,V,1)\right]^N$$

$$= \left(\frac{KT}{\hbar\omega}\right)^N$$

Helmholtz free energy of the systems

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

$$= -NKT\ln\left(\frac{KT}{\hbar\omega}\right)$$

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

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = NK \ln\left(\frac{KT}{\hbar w}\right) + NKT \frac{\hbar w}{KT} \cdot \frac{K}{\hbar w}$$

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

$$U = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial}{\partial \beta}\{N \ln(\beta \hbar w)\}$$

$$= N \hbar w \frac{1}{\beta \hbar w}$$

$$= NKT$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = NK$$

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

$$\therefore \quad S(U,V,N) = NK\left[1 + \ln\left\{\frac{U}{N\hbar w}\right\}\right]$$

$$\therefore \quad T = \left[\left(\frac{\partial S}{\partial U}\right)_N\right]^{-1} = \frac{U}{NK}$$

System of N distinguishable quantum oscillators (one dimensional)

Consider a system of N distinguishable one dimensional quantum oscillators. The energy eigen values of an one dimensional oscillator are given as

$$\epsilon_n = \left(n + \tfrac{1}{2}\right)\hbar\omega \qquad n = 0, 1, 2, \cdots$$

$\therefore$ Single oscillator partition function is

$$Z(T, V, 1) = \sum_{n=0}^{\infty} \exp[-\beta \epsilon_n]$$

$$= \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})}$$

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

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

$\therefore$ partition function of the system is

$$Z(T, V, N) = [Z(T, V, 1)]^N$$

$$Z(T,V,N) = \left[2 \sinh \frac{\beta \hbar \omega}{2}\right]^{-N}$$

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

Helmholtz free energy of the system

$$F(T,V,N) = -KT \ln\{Z(T,V,N)\}$$

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

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

Entropy $S(T,V,N) = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -NK\ln\{1-e^{-\beta\hbar\omega}\} + (-1)NKT \frac{1}{1-e^{-\beta\hbar\omega}}\left(-e^{-\beta\hbar\omega}\right)\cdot\frac{\hbar\omega}{KT^2}$

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

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

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

$$= NK\left[\frac{\beta\hbar\omega}{2}\cdot\coth\left(\frac{\beta\hbar\omega}{2}\right) - \ln\left\{2\sinh\left(\tfrac{1}{2}\beta\hbar\omega\right)\right\}\right]$$

Pressure

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

internal energy

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

$$= \tfrac{1}{2}N\hbar\omega\coth\left(\tfrac{1}{2}\beta\hbar\omega\right)$$

$$= F + ST$$

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

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \frac{1}{2}\hbar\omega + KT\ln\left\{1 - e^{-\beta\hbar\omega}\right\}$$

$$= \frac{F}{N}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = NK\left(\frac{1}{2}\beta\hbar\omega\right)^2 \cdot \operatorname{Cosech}^2\left(\frac{1}{2}\beta\hbar\omega\right)$$

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

Now

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

$$= N\langle E_n\rangle$$

So U can be considered as equal to N-times the mean energy of one oscillator.

If we compare the mean energy of one oscillator with energy eigen value $E_n = (n+\frac{1}{2})\hbar\omega$ of the oscillator then we can obtain

$$\langle n \rangle = \frac{1}{e^{\beta\hbar\omega}-1} \qquad \text{as} \qquad \langle E_n \rangle = \left[\tfrac{1}{2} + \langle n \rangle\right]\hbar\omega$$

$\langle n \rangle$ can be interpreted as mean quantum number i.e mean level of excitation of an oscillator at temperature T.

Unlike to classical oscillator, quantum oscillators do not obey equipartition theorem. For classical oscillator

$$U = NKT$$

but $U \neq NKT$ for quantum oscillators.

For quantum mechanical oscillator

$$U = N\langle E_n \rangle$$

$$\langle E_n \rangle = \frac{1}{Z}\sum_n E_n e^{-\beta E_n} = \frac{1}{Z}\sum_{n=0}^{\infty} \hbar\omega\left(n+\tfrac{1}{2}\right) e^{-\beta E_n}$$

$$= \frac{\hbar\omega}{Z}\left[\sum_{n=0}^{\infty} n\, e^{-\beta \epsilon_n} + \frac{1}{2}\sum_{n=0}^{\infty} e^{-\beta\epsilon_n}\right]$$

$$= \frac{\hbar\omega}{Z}\left[\frac{1}{2}Z + \sum_{n=0}^{\infty} n\, e^{-\beta(n+\frac{1}{2})\hbar\omega}\right]$$

$$= \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{Z}\cdot e^{-\frac{1}{2}\beta\hbar\omega}\sum_{n=0}^{\infty} n\, e^{-\beta n\hbar\omega}$$

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

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

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

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

In the limiting case when $T \to \infty$, then $\beta \hbar \omega \to 0$

$$\therefore \quad U = \frac{N}{2}\hbar\omega + N\hbar\omega \frac{1}{1 + \beta\hbar\omega + \frac{1}{2}(\beta\hbar\omega)^2 + \cdots - 1}$$

$$\simeq \frac{N\hbar\omega}{2} + \frac{N}{\beta\left(1 + \frac{1}{2}\beta\hbar\omega + \cdots\right)}$$

$$\simeq \frac{N\hbar\omega}{2} + \frac{N}{\beta}\left(1 - \frac{1}{2}\beta\hbar\omega\right)$$

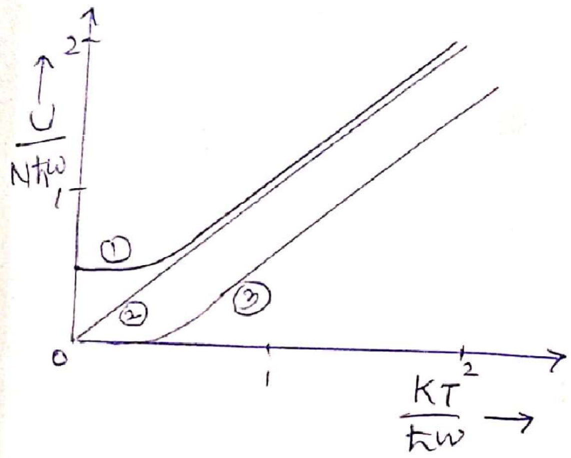
$$\simeq NKT$$

So at high temperature, quantum mechanical oscillator converts to classical oscillator.

when $T \to 0$ then $\beta\hbar\omega \to \infty$

$$\therefore \quad U \simeq \frac{N}{2}\hbar\omega$$

Therefore, for $T = 0$, there is zero point energy whereas for $T \to \infty$, we obtain the classical result.



In the figure, mean energy per oscillator is plotted as a function of temperature. Curve ① represent the correct quantum mechanical result i.e Schrodinger oscillator.

Curve ③ represents the case of a Planck oscillator where zero point energy is absent. The mean energy is always reduced by $\frac{1}{2}\hbar\omega$. Its limiting value is $KT - \frac{1}{2}\hbar\omega$ not KT. Curve ② represents the case of a classical oscillator.

We say that at high temperatures only, mean energy per oscillator for quantum oscillator tend to the equipartition value.

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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