Statistical Mechanics
Lecture 6

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Equipartition Theorem:

Let x_i be either p_i or q_i $(i = 1,2,3, \ldots \ldots 3N)$. Let us now calculate the ensemble average of $x_i(\frac{\partial H}{\partial x_j})$ where H is Hamiltonian. Using $dpdq = d^{3N}p\, d^{3N}q$,we can write

$$< x_i \frac{\partial H}{\partial x_j} > = \frac{1}{\Gamma(E)} \int_{E<H<E+\Delta} dp\, dq\, x_i \frac{\partial H}{\partial x_j} \rightarrow (i)$$

$$< x_i \frac{\partial H}{\partial x_j} > = \frac{\Delta}{\Gamma(E)} \frac{\partial}{\partial E} \int_{H<E} dpdq x_i \frac{\partial H}{\partial x_j}$$

Noting that $\frac{\partial E}{\partial x_j} = 0$, we may calculate the integral as

$$\int_{H<E} dp\, dq\, x_i \frac{\partial H}{\partial x_j} = \int_{H<E} dp\, dq\, x_i \frac{\partial}{\partial x_j}(H - E) \rightarrow (ii)$$

$$= \int_{H<E} dp\, dq \frac{\partial}{\partial x_j} x_i(H - E) - \delta_{ij} \int_{H<E} dp\, dq(H - E) \rightarrow (iii)$$

First integral vanishes as on boundary $H - E = 0$ putting $\Gamma(E) = \omega(E)$ then we can obtain

$$< x_i \frac{\partial H}{\partial x_j} > = \frac{\delta_{ij}}{\omega(E)} \frac{\partial}{\partial E} \int_{H<E} dpdq(E - H) \rightarrow (iv)$$

$$= \frac{\delta_{ij}}{\omega(E)} \int_{H<E} dpdq$$

$$= \frac{\delta_{ij}}{\omega(E)} \sum(E)$$

$$= \delta_{ij} \frac{\sum(E)}{\frac{\sum(E)}{\partial E}}$$

$$= \delta_{ij} \left[\frac{\partial}{\partial E} \log \sum(E)\right]^{-1}$$

$$= \delta_{ij} \frac{K}{\frac{\partial S}{\partial E}}$$

Therefore

$$< x_i \frac{\partial H}{\partial x_j} > = \delta_{ij} KT \rightarrow (v)$$

This is the generalised Equipartition Theorem. For special case $i = j$, $x_i = p_i$ then we have

$$< p_i \frac{\partial H}{\partial p_i} > = KT \rightarrow (vi)$$

For $i = j$, $x_i = q_i$, we get

$$< q_i \frac{\partial H}{\partial q_i} > = KT \rightarrow (vii)$$

According to canonical equation of motion we can write

$$\frac{\partial H}{\partial q_i} = -\dot{p_i} \rightarrow (viii)$$

Therefore

$$< \sum_{i=1}^{3N} q_i \, p_i > = -3NKT \rightarrow (ix)$$

This is known as Virial Theorem.

Again many system have Hamiltonian through canonical transformation, then

$$H = \sum_{I} A_i P_i^{\,2} + \sum_{i} B_i Q_i^{\,2} \;\rightarrow (x)$$

Where P_i and Q_i are canonically conjugate variables and A_i and B_i are constants. For such system we have

$$\sum_{i} \left(P_i \frac{\partial H}{\partial p_i} + Qi \frac{\partial H}{\partial Q_i} \right) = 2H \rightarrow (xi)$$

Suppose f of constant A_i and B_i are nonvanishing then

$$< H > = \frac{1}{2} f K T \rightarrow (xii)$$

That is each harmonic term in Hamiltonian contributes $\frac{1}{2} KT$ to the average energy of the system. This is known as Equipartition Theorem of Energy.

Again

$$\frac{C_V}{K} = \frac{f}{2} \rightarrow (xiii)$$

Where C_V is the heat capacity. Thus heat capacity is directly related to

the number of degrees of freedom of the system.

A paradox arises from the theorem of Equipartition of Energy. In classical physics every system must have an infinite number of degrees of freedom, for after we have resolved matter into atoms we must continue to resolve an atom into its constituent atoms and the constituents are infinities. Therefore the heat capacity of any system is infinite.

This is a real paradox in classical physics and is resolved by quantum mechanics. Quantum mechanics possesses the feature that the degrees of freedom of a system are manifest only when there is sufficient energy to excite them and that those degrees of freedom that are not excited can be forgotten. Therefore the equation $(xiii)$ is valid only when the temperature is sufficiently high.