

Equipartition Theorem, Classical & Quantum Limits



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Dr. Ajai Kumar Gupta

Professor
Department of Physics
Mahatma Gandhi Central
University
Motihari-845401, Bihar
E-mail: akgupta@mgcub.ac.in

Equipartition Theorem

Each quadratic energy dependence of the system is called a mode of the system. It is also called a degree of freedom of the system. If such a system described by classical statistical concepts is in equilibrium at temperature T then every independent quadratic term in the energy contribute a mean value $\frac{1}{2}kT$ to the energy of the system. It is called as equipartition theorem. It tells that energy of the system is equally partitioned among all the separate modes of the system and each mode have a mean energy equal to $\frac{1}{2}kT$.

Let us consider a system which is described classically in terms of f coordinates q_1, q_2, \dots, q_f and f corresponding momenta p_1, p_2, \dots, p_f .

The energy E of the system is then function of $q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_f$ variables.

$$E = E(q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_f) \quad \text{--- ①}$$

The energy E of the system could be written as

$$E = E_i(p_i) + E'(q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_{i-1}, p_{i+1}, \dots, p_f) \quad \text{--- ②}$$

where E_i is function of particular momentum p_i only whereas E' depends on all coordinates except p_i . Such assumption could arise because kinetic energy of a particle depends only on momentum coordinate whereas its potential energy depends only on its position.

The system is in thermal equilibrium at temperature T . The probability of finding system with its coordinates and momenta

in the range $(q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_f)$ is obtained by canonical distribution.

The mean value of energy E_i if energy of the system is given by eqnⁿ (2) can be obtained as

$$\begin{aligned}
 \bar{E}_i &= \frac{\int e^{-\beta E(q_1, q_2, \dots, p_f)} \cdot E_i \, dq_1, dq_2, \dots, dp_f}{\int e^{-\beta E(q_1, q_2, \dots, p_f)} \, dq_1, dq_2, \dots, dp_f} \\
 &= \frac{\int e^{-\beta(E_i + E')} \cdot E_i \, dq_1, \dots, dp_f}{\int e^{-\beta(E_i + E')} \, dq_1, \dots, dp_f} \\
 &= \frac{\int e^{-\beta E_i} \cdot E_i \, dp_i \int e^{-\beta E'} \, dq_1, dq_2, \dots, dp_1, dp_2, \dots, dp_{i-1}, dp_{i+1}, \dots, dp_f}{\int e^{-\beta E_i} \, dp_i \int e^{-\beta E'} \, dq_1, \dots, dq_f \, dp_1, \dots, dp_{i-1}, dp_{i+1}, \dots, dp_f} \\
 \bar{E}_i &= \frac{\int e^{-\beta E_i} \cdot E_i \, dp_i}{\int e^{-\beta E_i} \, dp_i}
 \end{aligned}$$

$$\bar{E}_i = \frac{-\frac{\partial}{\partial \beta} \left\{ \int e^{-\beta E_i} dp_i \right\}}{\int e^{-\beta E_i} dp_i}$$

$$= -\frac{\partial}{\partial \beta} \ln \left[\int e^{-\beta E_i} dp_i \right]$$

If the energy contribution E_i is a quadratic function of p_i as it would be if it represents a kinetic energy then E_i can be written as

$$E_i = b p_i^2, \quad b \text{ is a constant} \quad \text{--- (3)}$$

Then the mean value of E_i will be

$$\bar{E}_i = -\frac{\partial}{\partial \beta} \left[\ln \left\{ \int_{-\infty}^{\infty} e^{-\beta b p_i^2} dp_i \right\} \right]$$

integral extends over all possible values of p_i i.e. $-\infty$ to ∞

Now $\int_{-\infty}^{\infty} e^{-\beta b p_i^2} dp_i$

put $y = \sqrt{\beta b} p_i$

then $\int_{-\infty}^{\infty} e^{-\beta b p_i^2} dp_i = \frac{1}{\sqrt{\beta}} \int_{-\infty}^{\infty} e^{-by^2} dy$

$$\begin{aligned} \therefore \ln \int_{-\infty}^{\infty} e^{-\beta b p_i^2} dp_i &= \ln \left[\frac{1}{\sqrt{\beta}} \int_{-\infty}^{\infty} e^{-by^2} dy \right] \\ &= \ln \left(\frac{1}{\sqrt{\beta}} \right) + \ln \int_{-\infty}^{\infty} e^{-by^2} dy. \end{aligned}$$

$$\begin{aligned} \therefore \bar{\epsilon}_i &= - \frac{\partial}{\partial \beta} \left[\ln \left(\frac{1}{\sqrt{\beta}} \right) + \ln \int_{-\infty}^{\infty} e^{-by^2} dy \right] \\ &= - \frac{-\frac{1}{2}(\beta)^{-3/2}}{\beta^{-3/2}} + 0 \quad \text{Second integral is independent of } \beta. \\ &= \frac{1}{2\beta} = \frac{KT}{2} \end{aligned}$$

or, $\boxed{\bar{\epsilon}_i = \frac{1}{2} KT}$

If a system which is in equilibrium at temperature T and is described by classical statistical mechanics then mean value of each independent quadratic

term in its energy is equal to $\frac{1}{2}kT$. This statement is known as equipartition theorem.

If in the assumption in equation ① and ②, the variable is not a momentum p_i but a coordinate q_i then again we will get the same equipartition theorem. Only restriction is that the contribution to the energy must have a quadratic form.

Applications

① Specific heat of monoatomic gas

The energy of a molecule of gas is only its kinetic energy

$$E = \frac{p^2}{2m} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

There are three quadratic terms. According to Equipartition theorem, mean value of each of them will be $\frac{1}{2}kT$.

So mean energy of a molecule of the gas is

$$\bar{E} = \frac{3}{2} kT$$

Mean energy of one mole of gas is

$$\begin{aligned} E &= N_a \bar{E} & N_a &= \text{Avogadro no.} \\ &= \frac{3}{2} N_a kT \\ &= \frac{3}{2} RT \end{aligned}$$

\therefore molar specific heat at constant volume

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v = \frac{3}{2} R$$

(2) Harmonic Oscillator

Consider a particle is oscillating simple harmonic oscillations in one dimension. Its energy will be

$$E = \frac{p_x^2}{2m} + \frac{1}{2} kx^2 = K.E + P.E$$

Energy contains two quadratic terms. So at equilibrium at temperature T , the mean energy of the oscillator

$$\begin{aligned}\bar{E} &= \frac{1}{2}kT + \frac{1}{2}kT \\ &= kT\end{aligned}$$

(3) Specific heat of solid

In solids atoms are bound by linear elastic forces. They are located at regular positions in a crystal lattice. Each atom is free to move by small distance about its equilibrium position. The force acting on the atom due to neighbouring atoms tend to restore the atom to its equilibrium position. This force called as restoring force is zero when the atom is at its equilibrium position. When displacement is small, the restoring force is proportional to the atomic displacement.

The energy associated with the atom when it is oscillating in one-dimension is

$$E_x = \frac{p_x^2}{2m} + \frac{1}{2} \kappa x^2$$

These are two quadratic terms. So according to equipartition theorem, the mean energy associated with this movement of atom

$$E_x = \frac{1}{2} kT + \frac{1}{2} kT$$

$$= kT$$

at equilibrium temperature T .

If the atom is moving along three dimensions, then its mean energy

$$\bar{E} = 3kT$$

Mean energy of one mole of solid

$$E = 3N_A kT = 3RT$$

specific heat at constant volume

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v = 3R \quad \text{Dulong-Petit law.}$$

This law states that at sufficiently high temperatures all solids have the same temperature independent molar specific heat C_v equal to $3R$.

Classical and Quantum limit

Classically we can specify both q_i and p_i of a particle simultaneously but quantum mechanically we can not. i.e. specification of q_i and p_i must obey the restrictions imposed by Heisenberg uncertainty principle.

Consider the motion of a particle in a gas. If p_{av} denotes its mean momentum and r_{av} is its mean separation from other identical particles then classical description is valid when the exchange effect between the particles becomes negligible.

Since λ_{av} measures the spread of a particle in space i.e. de-Broglie wavelength associated with the particle then classical description holds when particle wavefunctions do not overlap and particles are distinguished by their position. That is when

$$r_{av} \gg \lambda_{av} \quad (\text{classical limit})$$

classical description is valid.

$$\text{or, } r_{av} \gg \frac{h}{p_{av}}$$

$$\text{or, } r_{av} p_{av} \gg h \quad \text{classical limit}$$

Therefore for classical description effect of h is negligible. When exchange effects are dominating, then particle wavefunctions are overlapping each other and particles cannot be localized and distinguished by their positions. They become indistinguishable and.

quantum effects become significant. That is when

$$r_{av} \ll \lambda_{av} \quad (\text{quantum limit})$$

Suppose each particle occupies a tiny cube of side r_{av} and these cubes fill the volume V , then

$$r_{av}^3 N = V$$
$$\Rightarrow r_{av} = \left(\frac{V}{N}\right)^{1/3}$$

at temperature T , the average energy \bar{E} is

$$\frac{p_{av}^2}{2m} = \frac{3}{2} kT$$

$$\therefore p_{av} = \sqrt{3mkT}$$

de-Broglie wavelength

$$\lambda_{av} = \frac{h}{\sqrt{3mkT}}$$

$$\therefore \frac{N}{V} \left(\frac{h^2}{3mKT} \right)^{3/2} \ll 1 \quad \text{classical limit}$$

It means that the classical description is valid when

1. N is small (dilute gas) low density
2. T is large and
3. m is not too small.

The exchange effect becomes negligible when gas is dilute to the extent that the average distance r_{av} between the particles is much larger than the de-Broglie wavelength λ_{av} associated with them. Therefore, quantum effects are negligible.

If the gas is sufficiently rarefied, so that number of particles in it is very much smaller than the available particle states then the states will be thinly populated.

Let n_r be the number of particles in the r th particle state. The numbers n_r are called as occupation numbers of various quantum states.

The mean number \bar{n}_r of these occupation numbers will then be given by

$$\bar{n}_r \ll 1$$

It means that no quantum state is occupied by more than one particle at any instant. Under such condition the quantum interactions become insignificant and only classical limit is valid.

The average number of particles of a classical gas having energy between ϵ and $\epsilon + d\epsilon$ is

$$N(\epsilon)d\epsilon = 2\pi N \left(\frac{1}{\pi kT} \right)^{3/2} e^{-\frac{\epsilon}{kT}} \epsilon^{1/2} d\epsilon$$

For a particle in a box, the number of particle states lying between energy ϵ and $\epsilon + d\epsilon$ is

given by $g(\epsilon) d\epsilon = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon$

For classical approximation, the number of particles should be extremely small as compared to number of particle states available to them.

$$\frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon \gg 2\pi N \left(\frac{1}{\pi kT}\right)^{3/2} e^{-\frac{\epsilon}{kT}} \epsilon^{1/2} d\epsilon$$

or, $\frac{V}{h^3} (2m)^{3/2} \gg N \left(\frac{1}{\pi kT}\right)^{3/2} e^{-\frac{\epsilon}{kT}}$

For this inequality to hold good for all values of energy ϵ up to zero, we must have

$$\frac{V}{h^3} (2m)^{3/2} \gg N \left(\frac{1}{\pi kT}\right)^{3/2}$$

or, $\frac{N}{V} \left(\frac{h^2}{2\pi m kT}\right)^{3/2} \ll 1$

or, $\frac{N}{V} \lambda_{th}^3 \ll 1$

where $\lambda_{th} = \frac{h}{\sqrt{2\pi m kT}}$
 mean thermal wavelengths of particles

References:

- Statistical Mechanics by R. K. Pathria
- Statistical Mechanics by B. K. Agarwal and M. Eisner
- An Introductory Course of Statistical Mechanics by P. B. Pal
- Elementary Statistical Physics by C. Kittel
- Fundamentals of Statistical and Thermal Physics by F. Reif
- Statistical and Thermal Physics by R. S. Gambhir and S. Lokanathan

Thank You

For any questions/doubts/suggestions and submission of assignments

Write at E-mail: akgupta@mgcub.ac.in