

Equipartition of Energy

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Equipartition of energy, law of statistical mechanics stating that, in a system in thermal equilibrium, on the average, an equal amount of energy will be associated with each independent energy state. Based on the work of physicists James Clerk Maxwell of Scotland and Ludwig Boltzmann of Germany, this law states specifically that a system of particles in equilibrium at absolute temperature T will have an average energy of $\frac{1}{2}kT$ associated with each degree of freedom in which k is the Boltzmann constant. In addition, any degree of freedom contributing potential energy will have another $\frac{1}{2}kT$ associated with it. For a system of s degrees of freedom, of which t have associated potential energies, the total average energy of the system is $\frac{1}{2}(s + t)kT$.

For example, an atom of a gas has three degrees of freedom (the three spatial, or position, coordinates of the atom) and will, therefore, have an average total energy of $\frac{3}{2}kT$. For an atom in a solid, vibratory motion involves potential energy as well as kinetic energy, and both modes will contribute a term $\frac{1}{2}kT$, resulting in an average total energy of $3kT$.

The theorem of equipartition of energy states that molecules in thermal equilibrium have the same average energy associated with each independent degree of freedom of their motion and that the energy is

$$\frac{1}{2}kT \text{ per molecule}$$

$$\frac{1}{2}RT \text{ per mole}$$

k = Boltzmann's constant

R = gas constant

$$\frac{3}{2}kT$$

$$\frac{3}{2}RT$$

For three translational degrees of freedom, such as in an ideal monoatomic gas.

The equipartition result

$$KE_{avg} = \frac{3}{2}kT$$

serves well in the definition of kinetic temperature since that involves just the translational degrees of freedom, but it fails to predict the specific heats of polyatomic gases because the increase in internal energy associated with heating such gases adds energy to rotational and perhaps vibrational degrees of freedom. Each vibrational mode will get $kT/2$ for kinetic energy and $kT/2$ for potential energy - equality of kinetic and potential energy is addressed in the virial theorem. Equipartition of energy also has implication for electromagnetic radiation when it is in equilibrium with matter, each mode of radiation having kT of energy in the Rayleigh-Jeans law.

For the translational degrees of freedom only, equipartition can be shown to follow from the Boltzmann distribution.

$$KE_{avg} = \left[\overline{\frac{1}{2}mv^2} \right] = \frac{3}{2}kT$$

Law of Equipartition of Energy

A single atom is free to move in space along the X, Y and Z axis. However, each of these movements requires energy. This is derived from the energy held by the atom. The Law of Equipartition of Energy defines the allocation of energy to each motion of the atom (translational, rotational and vibrational). Before we understand this law, let's understand a concept called 'Degrees of Freedom'.

The law states that: "In thermal equilibrium, the total energy of the molecule is divided equally among all Degrees of Freedom of motion". Before delving into the calculations, let's understand the law better. If a molecule has 1000 units of energy and 5 degrees of freedom (which includes translational, rotational and vibrational movements), then the molecule allocates 200 units of energy to each motion.

Now, let us look at some equations!

Kinetic Energy of a single molecule: $KE = 1/2 mv^2$. A gas in thermal equilibrium at temperature T, the average Energy is:

$$E_{avg} = 1/2 mv_x^2 + 1/2 mv_y^2 + 1/2 mv_z^2 = 1/2KT + 1/2 KT + 1/2 KT = 3/2 KT$$

where K = Boltzmann's constant. In case of a monoatomic molecule, since there is only translational motion, the energy allotted to each motion is $1/2KT$. This is calculated by dividing total energy by the degrees of freedom:

$$3/2 KT \div 3 = 1/2 KT$$

In case of a diatomic molecule, translational, rotational and vibrational movements are involved. Hence the Energy component of translational motion = $1/2 mv_x^2 + 1/2 mv_y^2 + 1/2 mv_z^2$. Energy component of rotational motion = $1/2 I_1 w_1^2 + 1/2 I_2 w_2^2$ { I_1 & I_2 moments of inertia. w_1 & w_2 are angular speeds}

And, the energy component of vibrational motion = $\frac{1}{2} m (dy/dt)^2 + \frac{1}{2} ky^2$. Where k is the force constant of the oscillator and y is the vibrational coordinate. It is important to note here that this has both kinetic and potential modes.

According to the Law of Equipartition of Energy, in thermal equilibrium, the total energy is distributed equally among all energy modes. While the translational and rotational motion contributes $\frac{1}{2} KT$ to the total energy, vibrational motion contributes $2 \times \frac{1}{2}KT = KT$ since it has both kinetic and potential energy modes.

Proof: Let's consider a dynamical system of ' f ' degrees of freedom having ' f ' position co-ordinates ($q_1, q_2, q_3, \dots q_f$) and ' f ' momentum co-ordinates ($p_1, p_2, p_3, \dots p_f$). Then the total energy of the system can be represented as -

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

Let p_i be any particular momentum, then the total energy can be represented as -

$$E = \epsilon_i (p_i) + E' (q_1, q_2, q_3, \dots q_f, p_1, p_2, p_3, \dots p_f) \quad \text{----- (2)}$$

where $\epsilon_i (p_i)$ is the function of p_i alone and the 2nd term is the function of all other position and momentum co-ordinates excluding the momentum p_i .

Classically, the mean energy is given by -

$$\bar{\epsilon}_i = \frac{E}{N} = \frac{\int \epsilon_i e^{-E/kT} dq_1 \dots dp_f}{\int e^{-E/kT} dq_1 \dots dp_f}$$

Since $E = \epsilon_i + E'$, therefore -

$$\bar{\epsilon}_i = \frac{\int \epsilon_i e^{-(\epsilon_i + E')/kT} dq_1 \dots dp_f}{\int e^{-(\epsilon_i + E')/kT} dq_1 \dots dp_f} = \frac{\int_{-\infty}^{+\infty} \epsilon_i e^{-\epsilon_i/kT} dp_i \int_{-\infty}^{+\infty} e^{-E'/kT} dq_1 \dots dp_f}{\int_{-\infty}^{+\infty} e^{-\epsilon_i/kT} dp_i \int_{-\infty}^{+\infty} e^{-E'/kT} dq_1 \dots dp_f} = \frac{\int_{-\infty}^{+\infty} \epsilon_i e^{-\epsilon_i/kT} dp_i}{\int_{-\infty}^{+\infty} e^{-\epsilon_i/kT} dp_i}$$

Putting $\epsilon_i = \frac{p^2}{2m}$, we have -

$$\bar{\epsilon}_i = \frac{\int_{-\infty}^{+\infty} \frac{p^2}{2m} e^{-p_i^2/2mkT} dp_i}{\int_{-\infty}^{+\infty} e^{-p_i^2/2mkT} dp_i}$$

Using standard integrals - $\int_{-\infty}^{+\infty} x^2 e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a^3}}$ and $\int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$, we have-

$$\bar{\epsilon}_i = \frac{1}{2m} \left[\frac{\frac{1}{2} \sqrt{\pi 8 m^3 k^3 T^3}}{\sqrt{\pi 2 m k T}} \right] = \frac{1}{4m} \sqrt{\frac{8 m^3 k^3 T^3}{2 m k T}}$$

$$\boxed{\bar{\epsilon}_i = \frac{1}{2} k T}$$

(3)

which completes the proof.

Limitations: The limitations of the equipartition theorem are -

1. The theorem is valid for the particles in which the energy distribution is continuous.

2. The theorem is applicable to independent, identical but distinguishable particles i.e. particles obeying Maxwell - Boltzmann (M - B) statistics.

