



Some discussions on Equipartition Theorem

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Abstract: During the development of physics, we can see that the Equipartition theorem (EPT) has been redefined many times. In this paper, we start with the description of the historical development of the theorem along with the various definitions given by different scientists. Then we found the expressions for classical, quantum and discrete energy systems and redefined EPT.

Keywords: equipartition theorem; classical systems; energy systems

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Introduction

In his paper *On the physics of media that are composed of free and elastic molecules in a state of motion*, submitted to the Royal Society in 1845, but not published until 1892, Waterston states that "In mixed media, the mean square velocity is inversely proportional to the specific weight of the molecules" (Waterston, 1892). In this paper Waterston put forward three postulates, (a) Heat is some kind of motion of the smallest parts of bodies (b) The molecules move so rapidly and in so many directions, with frequent "fortuitous encounters", that one can compute the properties of the system at any time by simply averaging over all the possible molecular states and (c) In a mixture of elastic particles of different masses in thermal equilibrium, each kind of particle will have the same average kinetic energy.

In 1857, Rudolf Clausius independently stated the same idea put forth by Waterston in a more convincing, comprehensive and authoritative manner receiving greater attention (Clausius, 1859). The next step in the development of EPT came in 1859 by James Clark Maxwell who in his paper titled "Illustrations of the Dynamical Theory of Gases" argued that the kinetic heat energy of a gas is equally divided between linear and rotational energy (Maxwell, 1860). In the paper he summarizes that, "A discussion of collisions between perfectly elastic bodies of any form leads to the conclusion that final equilibrium state of any number of systems of moving particles of any form is that in which the average kinetic energy of translation along each of the three axes is the same in all the systems and equal to the average kinetic energy of rotation about each of the three principle axes of each particle". In 1876, Ludwig Boltzmann expanded Maxwell's principle by showing that the average energy was divided equally among all the independent components of motion in a system (Cercignani & Penrose, 2006). Boltzmann applied the equipartition theorem to provide a theoretical explanation of the Dulong-Petit

law for the specific heat capacities of solids. Boltzmann argued that the specific heat of a system can be rationalized on the basis of $\frac{1}{2}kT$ of energy per degree of freedom of molecular motion, where k is a suitable constant and T is the temperature.

Though studies by Dulong and Petit (Fox, 1968) showed that the specific heat capacities of solid elements at room temperature were inversely proportional to the atomic weight of the element, further investigations by James Dewar and Heinrich Friedrich Weber in 1872 showed that this Dulong-Petit law holds only at high temperatures. Lord Kelvin, in his Baltimore lectures (Thomson, Baron Kelvin, 2010) suggested that the derivation of the equipartition theorem must be incorrect considering its failure to account for the experimental results. The important idea regarding EPT was provided by Einstein (Einstein, 1907) by showing that the anomalies in the specific heat were due to the quantum effects. Einstein's theory was supported by W H Nernst's measurements of specific heats at low temperatures in 1910, and resulted in the acceptance of quantum theory (Barkan, 1991).

In his book (Reif, 2009) F. Reif define EPT as "If a system described by classical statistical mechanics is in equilibrium at the absolute temperature T , every independent quadratic term in its energy has a mean value equal to $\frac{1}{2}kT$ ". In "Thermodynamics and Statistical Mechanics" by Greiner, Neise and Stocker, the definition of the same is given as "For each degree of freedom of the system at a temperature T has the mean thermal kinetic energy $\frac{1}{2}kT$ ". The above two definitions represent the equipartition theorem (equal distribution theorem), which says that the thermal energy is uniformly distributed over all degrees of freedom of the system (Greiner, Neise, & Stöcker, 2001).

The remarkable proof furnished by L. E. Turner for the non-quadratic terms found its validity only for one homogeneous degree of freedom or for a single canonical variable (Turner Jr, 1976). R.C. Tolman developed a general expression for the EPT which is applicable to non-quadratic Hamiltonian as well (Tolman, 1979). The definitions provided in textbooks does not clearly say for which type of systems this theorem is valid and the definitions give the impression that it is valid for all systems (Beale & Pathria, 2011; Huang, 2009). So we provide alternate statements based on the study of some statistical systems, which is given in the coming sections.

Method

For systems, energy can be of the different forms, discrete like ϵ , $2\epsilon, \dots$, quantum like $(n_1 + \frac{1}{2})\hbar\omega$, $\frac{n^2\hbar^2}{8mL^2}$ or continuous like $\frac{p^2}{2m}$, pc , $\frac{p^2}{2m} + \frac{1}{2}Kq^2$ where ω is the angular frequency, n is the quantum number, \hbar is the reduced Planck constant, m is the mass of a constituent particle, L is the size of the container, p is the momentum, c is the velocity of light, q is the displacement and K is the spring constant. The properties of the systems with different types of energies will be different. By obtaining the average energy of different types of systems we arrive at a generalized equation for equipartition in different regime of physics such as in classical and quantum world.

Results and Discussion

Average energy for classical systems

Let us find average energy for a continuous energy system or a classical ideal gas system where we have energy $\epsilon = \frac{p^2}{2m}$. For an ideal gas we know partition function is $Q = \frac{V}{\lambda^3}$ (Beale & Pathria, 2011) where $\lambda = \frac{h}{(2\pi mkT)^{\frac{1}{2}}}$ is the de Broglie thermal wavelength and V is the volume. So Q_N is $\left(\frac{V}{\lambda}\right)^N$, $\left(\frac{A}{\lambda^2}\right)^N$ and $\left(\frac{L}{\lambda^3}\right)^N$ for one, two and three dimensions respectively. On solving we get $\langle E \rangle = \frac{3}{2}NkT$ in 3 dimensions, NkT for two dimensions and $\frac{1}{2}NkT$ for one dimension. This is an interesting result. Here the average is only a function of temperature. Repeating for continuous systems like mass less relativistic gas ($E = pc$) and harmonic oscillator $\frac{p^2}{2m} + \frac{1}{2}Kq^2$ we get the average energy as $3NkT$ in both cases. Here also total

energy is equally shared among each dimension. For the mechanical energy you can never guarantee it. In 3D, the systems with continuous energy, $\frac{p^2}{2m}$ will have their average energy as (Beale & Pathria, 2011)

$$\langle E \rangle = \frac{3}{2} NkT = \frac{1}{2} NkT + \frac{1}{2} NkT + \frac{1}{2} NkT \quad (1)$$

Now let us apply the results to any type of mechanical energy.

Expressing EPT as an equation for classical energy systems

Tolman gave an expression for the EPT for N particle system (Tolman, 1979). Consider a particle with only kinetic energy $\frac{p^2}{2m}$. Then (Beale & Pathria, 2011)

$$Q = \int_{-\infty}^{\infty} \frac{dp_1 L}{h} e^{-\beta E(p_1)} \quad (2)$$

$$d[p_1 e^{-\beta E}] = [dp_1 e^{-\beta E}] + [p_1 e^{-\beta E} \times -\beta \frac{\partial E}{\partial p_1} dp_1]$$

$$dp_1 e^{-\beta E} = d[p_1 e^{-\beta E}] + \beta p_1 \frac{\partial E}{\partial p_1} e^{-\beta E} dp_1$$

Substituting in the equation for Q and solving we get

$$Q = \int_{-\infty}^{\infty} \frac{C}{kT} [p_1 \frac{\partial E}{\partial p_1}] e^{-\beta E} dp_1 \quad (3)$$

where $\frac{L}{h} = C$. Rearranging

$$kT = \frac{\int_{-\infty}^{\infty} C [p_1 \frac{\partial E}{\partial p_1}] e^{-\beta E} dp_1}{Q}$$

$$kT = \left\langle p_1 \frac{\partial E}{\partial p_1} \right\rangle \quad (4)$$

For 2 particles with momenta p_1 and p_2 we get

$$(kT)^2 = \left\langle \left(p_1 \frac{\partial E}{\partial p_1} \right) \left(p_2 \frac{\partial E}{\partial p_2} \right) \right\rangle \quad (5)$$

and for a harmonic oscillator with energy $E = \frac{p^2}{2m} + \frac{1}{2} K q_1^2$ we get

$$(kT)^2 = \left\langle \left(p_1 \frac{\partial E}{\partial p_1} \right) \left(q_1 \frac{\partial E}{\partial q_1} \right) \right\rangle \quad (6)$$

In general the Tolman equation for EPT is $\left\langle q \frac{\partial E}{\partial q} \right\rangle = kT$ or $\left\langle p \frac{\partial E}{\partial p} \right\rangle = kT$.

Substituting the energies we will get a general expression for EPT as

$$\langle E \rangle = \frac{dNkT}{n} \quad (7)$$

where n is the power of energy function and d is the dimension. In the next section we give an alternate proof using statistical mechanics.

Derivation of the general expression of EPT for classical systems

Volume of a 'd' dimensional hyper sphere is given by (Beale & Pathria, 2011)

$$V_d = \frac{\pi^{\frac{d}{2}} R^d}{\frac{d!}{2}} \quad (8)$$

Differentiating

$$dV_d = \frac{\pi^{\frac{d}{2}} dR^{d-1} dR}{\frac{d!}{2}} \quad (9)$$

For a momentum space,

$$R = p \quad (10)$$

Then

$$dV_d = \frac{\pi^{\frac{d}{2}} dp^{d-1} dp}{\frac{d!}{2}} \quad (11)$$

Let the general expression for energy be $E = ap^n$, where a is a constant and n is the exponent of momentum (The same procedure can be used for the position variable as well). Now the single particle canonical partition function Q_1 is given by (Beale & Pathria, 2011; Huang, 2009)

$$Q_1 = \int_0^\infty g(p) dp e^{-\beta E} \tag{12}$$

Substituting, the number of states between p and p + dp

$$Q_1 = \int_0^\infty \frac{\pi^{\frac{d}{2}} dp^{d-1} V dp}{\frac{d!}{2} h^d} e^{-\beta ap^n} \tag{13}$$

where V is the d-dimensional spatial volume

$$Q_1 = \frac{\pi^{\frac{d}{2}} dV}{\frac{d!}{2} h^d} \int_0^\infty p^{d-1} e^{-\beta ap^n} dp \tag{14}$$

Let $p^n = x$, then on substitution,

$$Q_1 = \frac{\pi^{\frac{d}{2}} dV}{n^{\frac{d}{2}} h^d} \int_0^\infty x^{\frac{d-n}{n}} e^{-\beta ax} dx \tag{15}$$

Integrating,

$$Q_1 = \frac{\pi^{\frac{d}{2}} dV}{n^{\frac{d}{2}} h^d} \left(\frac{d}{n} - 1\right)! (a\beta)^{-\frac{d}{n}} \tag{16}$$

and N particle partition function is $Q_N = \frac{1}{N!} Q_1^N$

$$\langle E \rangle = - \left(\frac{\partial \ln Q_N}{\partial \beta} \right)_{V,N} = kT^2 \left(\frac{\partial \ln Q_N}{\partial T} \right)_{V,N} \tag{17}$$

On substitution, we get

$$\langle E \rangle = \frac{dNkT}{n} \tag{18}$$

In the next two sections we will find average energy for discrete and quantum energy systems which will show that equal division or partition principle is applicable for all these energies also.

Average energy for discrete and quantum systems

Consider a system which has two levels with energies $E_1 = 0$ and $E_2 = \epsilon$. Then single particle partition function (PF) is

$$Q_1 = [1 + e^{-\beta \epsilon}]$$

N particle PF in one dimension is

$$Q_N = [Q_1]^N = [1 + e^{-\beta \epsilon}]^N$$

Using the expression for average energy

$$\langle E \rangle = - \left(\frac{\partial \ln Q}{\partial \beta} \right)_{T,V}$$

Substituting we get

$$\langle E \rangle = \frac{N\epsilon}{(e^{\beta \epsilon} + 1)}$$

For 2 and 3 dimensions average energy will be $\frac{2N\epsilon}{(e^{\beta \epsilon} + 1)}$ and $\frac{3N\epsilon}{(e^{\beta \epsilon} + 1)}$ respectively. We can see that energy is equally partitioned in 3 dimensions. Here average energy is a function of the basic unit of energy and temperature T. Next let us find the average energy for a quantized system.

Quantum energy system

All Consider a quantum harmonic oscillator without zero-point energy with energy

$$E_n = n\hbar\omega \text{ where } n = 0, 1, 2, \dots$$

Let $\epsilon = \hbar\omega$, then $E_n = 0, \epsilon, 2\epsilon, \dots, \infty$

$$Q_1 = \sum_0^\infty e^{-\beta n\hbar\omega} = \frac{1}{1 - e^{-\beta \hbar\omega}} \tag{19}$$

For N particles in one dimension

$$Q_N = \left(\frac{1}{1 - e^{-\beta\hbar\omega}} \right)^N$$

Substituting PF in the expression for average energy we get

$$\langle E \rangle = \frac{N\hbar\omega}{(e^{\beta\hbar\omega} - 1)} \quad (20)$$

Extending to the two and three dimensions

$$\langle E \rangle = \frac{2N\hbar\omega}{(e^{\beta\hbar\omega} - 1)} \quad (21)$$

$$\langle E \rangle = \frac{3N\hbar\omega}{(e^{\beta\hbar\omega} - 1)} \quad (22)$$

For 2 and 3 dimensions respectively. Here also energies are equally divided among the 3 dimensions and are functions of basic unit of energy and absolute temperature.

So defining EPT as equally distributed $\frac{kT}{2}$ for quadratic energies is insufficient and hence we propose to redefine EPT as *Equal partitioning of average energy is applicable for all types of energies, but for systems with classical energies, the average energy, which will be only temperature dependent, is equally distributed in each dimension such that each component is given by $\frac{kT}{n}$ where n is the exponent of the position or momentum term in the classical energy.*

Conclusion

Equipartition theorem had been restated many times in the history of physics because a complete understanding of this fundamental concept was lacking in earlier years. We obtained the average energy for classical, quantum and discrete energy systems and showed that energy is equally partitioned in 3 dimensions for all these systems. But for quantum and discrete systems energy is not only temperature dependent. Now that statistical mechanics has developed much more, a revised definition is required, which we have done in this paper.

References

- Barkan, D. (1991). *Walther Nernst and Quantum Theory*. 151–162. https://doi.org/10.1007/978-94-011-3164-3_14
- Beale, P. D., & Pathria, R. K. (2011). *Statistical Mechanics*. Elsevier Science.
- Cercignani, C., & Penrose, R. (2006). Ludwig Boltzmann: The Man Who Trusted Atoms. *Ludwig Boltzmann: The Man Who Trusted Atoms*, 1–352. <https://doi.org/10.1093/ACPROF/OSO/9780198570646.001.0001>
- Clausius, R. (1859). X. On the mean length of the paths described by the separate molecules of gaseous bodies on the occurrence of molecular motion: together with some other remarks upon the mechanical theory of heat. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 17(112), 81–91. <https://doi.org/10.1080/14786445908642626>
- Einstein, A. (1907). Die Plancksche Theorie der Strahlung und die Theorie der spezifischen Wärme. *Annalen Der Physik*, 327(1), 180–190. <https://doi.org/10.1002/ANDP.19063270110>
- Fox, R. (1968). The background to the discovery of Dulong and Petit's law. *The British Journal for the History of Science*, 4(1), 1–22.
- Greiner, W., Neise, L., & Stöcker, H. (2001). *Thermodynamics and Statistical Mechanics (Classical Theoretical Physics)*.
- Huang, K. (2009). Introduction to Statistical Physics. *Introduction to Statistical Physics*. <https://doi.org/10.1201/9781439878132/INTRODUCTION-STATISTICAL-PHYSICS-KERSON-HUANG>

- Maxwell, J. C. (1860). V. Illustrations of the dynamical theory of gases. —Part I. On the motions and collisions of perfectly elastic spheres . *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 19(124), 19–32. <https://doi.org/10.1080/14786446008642818>
- Reif, F. (2009). *Fundamentals of statistical and thermal physics*. Waveland Press.
- Thomson, Baron Kelvin, W. (2010). Baltimore Lectures on Molecular Dynamics and the Wave Theory of Light. In *Baltimore Lectures on Molecular Dynamics and the Wave Theory of Light*. Cambridge University Press. <https://doi.org/10.1017/cbo9780511694523>
- Tolman, R. (1979). *The principles of statistical mechanics*. Dover Publications.
- Turner Jr, L. E. (1976). Generalized Classical Equipartition Theorem. *American Journal of Physics*, 44, 104–105.
- Waterston, J. (1892). I. On the physics of media that are composed of free and perfectly elastic molecules in a state of motion. *Philosophical Transactions of the Royal Society of London. (A.)*, 183. <https://doi.org/10.1098/rsta.1892.0001>