

The Boltzmann Factor & Kinetic Theory

The physical model of **heat**, *thermodynamics*, is in essence a theory of the statistical average motion of a large number of *microscopic* particles which constitute the *macroscopic* entity (e.g. a litre of liquid water) being studied.

The basic idea is that **temperature** is proportional to the **mean kinetic energy of molecules**, and **heat** is the **total amount of energy transferred** (e.g. to your hand when you insert it into a warm bath). Temperature is therefore a microscopic concept (e.g. an average quantity of molecules) whereas heat is a macroscopic quantity. This explains why passing your hand (briefly!) through a hot flame will typically incur less damage than placing it in a pan of boiling water. Although the average kinetic energy of molecules is much less in the latter example, the number of molecules colliding with your hand is significantly higher. Therefore the overall amount of energy transferred in the boiling pan example is higher, which means more heat transferred and hence a greater chance of injury.



Ludwig Boltzmann
1844-1906

The Boltzmann Factor and the Boltzmann distribution

Consider a large number of particles which can exchange energy. They have an average energy which is proportional to their (absolute) temperature T (measured in Kelvin). The probability that a particle will have energy between ε and $\varepsilon + d\varepsilon$ is:

$$p(\varepsilon)d\varepsilon \propto e^{-\frac{\varepsilon}{k_B T}} d\varepsilon$$

$e^{-\frac{\varepsilon}{k_B T}}$ is called the *Boltzmann Factor*.
 T is the absolute temperature /Kelvin
and Boltzmann's constant is
 $k_B = 1.381 \times 10^{-23} \text{ m}^2 \text{ kgs}^{-2} \text{ K}^{-1}$

This is for a continuous distribution of energies, like a *Classical* gas. In a Quantum Mechanical scenario only *discrete* energy levels may be allowed. In this case, the probability of energy state ε_i is given by:

$$p(\varepsilon_i) = \frac{e^{-\frac{\varepsilon_i}{k_B T}}}{\sum_j e^{-\frac{\varepsilon_j}{k_B T}}}$$

This is the *Boltzmann discrete probability distribution* which is derived over the next few pages.

Consider a large number, N , of particles, which have discrete possibilities for their energy. The total amount of energy is U . Out of the particles, n_i have (fixed) energy ε_i .

$$U = \sum_i n_i \varepsilon_i \quad \therefore dU = \sum_i \varepsilon_i dn_i = 0$$

$$N = \sum_i n_i \quad \therefore dN = \sum_i dn_i = 0$$

There are $N!$ ways of arranging the particles, but since n_i in level i all have the *same* energy, the number of possible energy configurations is:

$$W = \frac{N!}{n_1! n_2! \dots} = \frac{N!}{\prod_i n_i!}$$

Let us assert that the distribution of energy is such that *maximizes* the number of possible energy arrangements.

We can make more analytical progress by considering maximizing the natural logarithm of W , rather than W , since by using the logarithm we can turn products into summations, and division into subtraction.

$$\ln W = \ln N! - \sum_i \ln n_i!$$

If the number of particles in each energy level is large*, and since N is large, we can use *Stirling's approximation*. In its crudest form:

$$\ln N! = \sum_{n=1}^N \ln n \approx \int_1^N \ln n dn \quad \leftarrow \text{i.e. the sum of rectangles of height } \ln n \text{ and width } n \text{ has area equal to this sum, which is the same as the integral if we have many strips.}$$

$$\int_1^N \ln n dn = [n \ln n - n]_1^N = N \ln N - N + 1$$

$$\therefore \ln N! \approx N \ln N - N$$

Hence:

$$\ln W \approx N \ln N - N - \sum_i n_i \ln n_i + \sum_i n_i$$

$$\ln W \approx N \ln N - \sum_i n_i \ln n_i$$

$$\therefore d(\ln W) = -\sum_i (n_i d(\ln n_i) + \ln n_i dn_i)$$

$$d(\ln W) = -\sum_i \left(n_i \frac{1}{n_i} dn_i + \ln n_i dn_i \right)$$

$$d(\ln W) = -\sum_i (1 + \ln n_i) dn_i$$

$$d(\ln W) \approx -\sum_i \ln n_i dn_i$$

Now we want to maximize $\ln W$ such that the total amount of energy and number of particles is fixed. We can do this via the *Method of Lagrange Multipliers* i.e. combining the (zero) differentials, and solving for the constants

$$d(\ln W) = 0 \quad \text{Maximize } \ln W$$

$$dU = 0, dN = 0 \quad \text{Constraints}$$

$$\therefore 0 = d(\ln W) + \alpha dN + \beta dU$$

$$0 = -\sum_i \ln n_i dn_i + \alpha \sum_i dn_i + \beta \sum_i \varepsilon_i dn_i$$

$$0 = \sum_i (\beta \varepsilon_i + \alpha - \ln n_i) dn_i$$

For this to be true for all i

$$\beta \varepsilon_i + \alpha - \ln n_i = 0$$

$$n_i = e^{\alpha + \beta \varepsilon_i}$$

continued on the next page

Derivation of the Boltzmann distribution (cont...)

$$n_i = e^{\alpha + \beta \epsilon_i} \quad N = \sum_j n_j \quad N = e^\alpha \sum_j e^{\beta \epsilon_j}$$

$$\therefore e^\alpha = \frac{N}{\sum_j e^{\beta \epsilon_j}} \quad \therefore n_i = \frac{N e^{\beta \epsilon_i}}{\sum_j e^{\beta \epsilon_j}}$$

$$\therefore p(\epsilon_i) = \frac{n_i}{N} = \frac{e^{\beta \epsilon_i}}{\sum_j e^{\beta \epsilon_j}} \quad \text{The Lagrange Multiplier } \beta \text{ is: } -\frac{1}{k_B T}$$

The choice for the Lagrange multiplier requires an application of the Boltzmann distribution to determine the average speed of molecules in a Classical gas, and hence the average kinetic energy.

Maxwell-Boltzmann speed distribution

For a molecule of mass m moving *freely* in three x, y, z dimensions, inter-molecular forces are ignored and hence the molecular energy is pure kinetic energy

$$\epsilon = \frac{1}{2} m v^2$$

If the molecule speed is v : $v^2 = v_x^2 + v_y^2 + v_z^2$

$$\text{Hence: } \epsilon^2 = \epsilon_x^2 + \epsilon_y^2 + \epsilon_z^2$$

Using the Boltzmann factor, we can therefore write an expression for the probability function of the kinetic energy distribution, and also the speed distribution. Note since we assume x, y, z motion is *uncorrelated*, we can *multiply* the probabilities.

$$p(\epsilon) d\epsilon = p(v_x) dv_x \times p(v_y) dv_y \times p(v_z) dv_z$$

$$p(v_{x,y,z}) \propto e^{\beta \times \frac{1}{2} m v_{x,y,z}^2}$$

$$\therefore p(\epsilon) d\epsilon = A e^{\frac{1}{2} m \beta v^2} dv_x dv_y dv_z$$

If one imagines a Cartesian grid of possible velocities, we can convert the 'velocity volume element' into a spherical shell

$$dv_x dv_y dv_z = 4\pi v^2 dv$$

We can now start to find the constants from the fact that the probability of finding any speed *must* be unity.

$$p(\epsilon) d\epsilon = p(v) dv = 4\pi v^2 A e^{\frac{1}{2} m \beta v^2} dv$$

$$\int_0^\infty p(v) dv = 1$$

$$\therefore \int_0^\infty 4\pi v^2 A e^{\frac{1}{2} m \beta v^2} dv = 1$$

It is clear for this to be true then β must be *negative*. So redefine

$$\beta \rightarrow -\beta$$

To evaluate this integral consider the following standard integration results:

$$I_n = \int_0^\infty x^n e^{-ax^2} dx$$

$$I_0 = \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

$$I_1 = \frac{1}{2a}$$

$$I_n = \frac{n-1}{2a} I_{n-2}$$

In our case: $x = v$

$$n = 2$$

$$a = \frac{1}{2} m \beta$$

$$\int_0^\infty 4\pi v^2 A e^{-\frac{1}{2} m \beta v^2} dv = 1$$

$$\Rightarrow \int_0^\infty v^2 e^{-\frac{1}{2} m \beta v^2} dv = \frac{1}{4\pi A}$$

$$\frac{2-1}{2(\frac{1}{2} m \beta)} \frac{1}{2} \sqrt{\frac{\pi}{\frac{1}{2} m \beta}} = \frac{1}{4\pi A}$$

$$\frac{1}{m\beta} \sqrt{\frac{2\pi}{m\beta}} = \frac{1}{2\pi A} \quad \therefore A = \left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}}$$

$$\therefore p(v) dv = 4\pi \left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2} m \beta v^2} dv$$

Which is the particle speed distribution.

$$p(\epsilon) d\epsilon = p(v) dv$$

$$\epsilon = \frac{1}{2} m v^2 \therefore v = \sqrt{\frac{2\epsilon}{m}} \quad d\epsilon = m v dv \therefore v dv = \frac{d\epsilon}{m}$$

$$p(\epsilon) d\epsilon = 4\pi \left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2} m \beta v^2} dv$$

$$p(\epsilon) d\epsilon = 4\pi \left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} \sqrt{\frac{2\epsilon}{m}} \frac{1}{m} e^{-\beta \epsilon} d\epsilon$$

$$p(\epsilon) d\epsilon = 2^{2-\frac{3}{2}+\frac{1}{2}} \pi^{1-\frac{3}{2}} \beta^{\frac{3}{2}} \sqrt{\epsilon} e^{-\beta \epsilon} d\epsilon$$

$$p(\epsilon) d\epsilon = \frac{2}{\sqrt{\pi}} \beta^{\frac{3}{2}} \sqrt{\epsilon} e^{-\beta \epsilon} d\epsilon$$

Which is the energy distribution.

The expected energy is proportional to the *square* of speed:

$$E[v^2] = \int_0^\infty v^2 p(v) dv$$

$$E[v^2] = \int_0^\infty 4\pi \left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} v^4 e^{-\frac{1}{2} m \beta v^2} dv$$

$$E[v^2] = 4\pi \left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} \int_0^\infty v^4 e^{-\frac{1}{2} m \beta v^2} dv$$

$$E[v^2] = 4\pi \left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} \frac{4-1}{2 \times \frac{1}{2} m \beta} \frac{\sqrt{\pi}}{4 \left(\frac{1}{2} m \beta\right)^{\frac{3}{2}}}$$

$$E[v^2] = \frac{3}{m\beta}$$

$$\therefore E\left[\frac{1}{2} m v^2\right] = \frac{3}{2} \frac{1}{\beta}$$

If temperature is proportional to the mean kinetic energy then it makes sense to define

$$\beta = \frac{1}{k_B T}$$

$$\text{Hence: } E\left[\frac{1}{2} m v^2\right] = \frac{3}{2} k_B T \quad k_B = 1.381 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$$

$$I_n = \int_0^\infty x^n e^{-ax^2} dx$$

$$I_n = \frac{n-1}{2a} I_{n-2}$$

$$I_0 = \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

$$I_1 = \frac{1}{2a}$$

$$I_2 = \frac{\sqrt{\pi}}{4a^{\frac{3}{2}}}$$

$$x = v$$

$$n = 4$$

$$a = \frac{1}{2} m \beta$$

Temperature and equipartition

$$E\left[\frac{1}{2}mv^2\right] = \frac{3}{2}k_B T \quad k_B = 1.381 \times 10^{-23} \text{ m}^2 \text{ kgs}^{-2} \text{ K}^{-1}$$

The assignment of β above means the mean particle kinetic energy is proportional to temperature. The constant of 3/2 is consistent with the idea of classical thermodynamics idea of *equipartition*, i.e. each independent mode of movement contributes *equally* to the mean energy. i.e. each 3D x,y,z component contributes $\frac{1}{2}k_B T$

This means if a molecule were large enough and hot enough to rotate or vibrate, we might activate more modes. In general, equipartition states

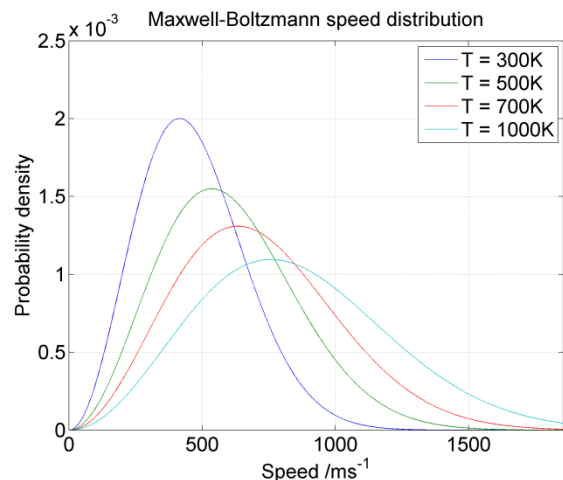
$$E[\varepsilon] = \text{degrees of freedom} \times \frac{1}{2}k_B T$$

Summary of molecular speed* and kinetic energy distributions using the Boltzmann factor

$$p(v)dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2}mv^2/k_B T} dv$$

$$\overline{v^2} = E[v^2] = \frac{3k_B T}{m} \quad \therefore v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}}$$

$$p(\varepsilon)d\varepsilon = \frac{2}{\sqrt{\pi}} (k_B T)^{-\frac{3}{2}} \sqrt{\varepsilon} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon$$



Particle flux in a 'Boltzmann gas' is the number of collisions expected per unit area upon a surface in contact with the gas.

Assume a gas has n particles per unit volume.

Consider a surface centred at the origin of the x,y plane, whole normal is the z axis. The number of particles that impact the surface (of unit area) in one second (i.e. the particle flux) is:

$$\Phi = \int_{\theta=0}^{\frac{1}{2}\pi} \int_{\phi=0}^{2\pi} \int_{v=0}^{\infty} \underbrace{n}_{\text{I}} \times \underbrace{\frac{\sin \theta d\theta d\phi}{4\pi}}_{\text{II}} \times \underbrace{v \cos \theta}_{\text{III}} \times p(v) dv$$

I Fraction of particles that are arriving from polar angle θ from the z axis and ϕ anticlockwise from the x axis. This is the ratio of an area element of a unit sphere divided by the area of the unit sphere. This is essentially a 'solid angle'

II Projection of (incoming) velocity in the z direction. Note we don't include outgoing particles, hence the range of θ is 0 to $\pi/2$ radians, not π .

III Number of particles with velocity between v and $v + dv$

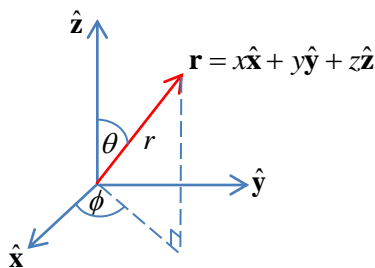
$$\Phi = \frac{1}{4\pi} n \int_{\theta=0}^{\frac{1}{2}\pi} \sin \theta \cos \theta d\theta \int_{\phi=0}^{2\pi} d\phi \int_{v=0}^{\infty} v p(v) dv$$

$$\Phi = \frac{1}{4\pi} n \int_{\theta=0}^{\frac{1}{2}\pi} \frac{1}{2} \sin 2\theta d\theta \times 2\pi \int_{v=0}^{\infty} v p(v) dv$$

$$\Phi = \frac{1}{4} n \left[-\frac{1}{2} \cos 2\theta \right]_0^{\frac{1}{2}\pi} \times \int_{v=0}^{\infty} v p(v) dv$$

$$\Phi = \frac{1}{4} n \left\{ \left(-\frac{1}{2}(-1)\right) - \left(-\frac{1}{2}(1)\right) \right\} \times \bar{v}$$

$$\therefore \Phi = \frac{1}{4} n \bar{v}$$



Conversion between Cartesian and polar coordinates

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

Pressure from kinetic theory – a simplified derivation that gives the correct more general result!

Assume particles collide elastically with the walls of a container. Since in an elastic collision the speed of wall approach = speed of recession the impulse exerted on the walls in each x,y,z direction per collision is:

$$\Delta p_{x,y,z} = 2mv_{x,y,z}$$

If we assume particles are contained within a cube of side a , the time between collisions with a given wall is:

$$\Delta t_{x,y,z} = \frac{2a}{v_{x,y,z}}$$

The factor of two is there because in any or the x,y,z directions, a particle must collide with the opposite wall before rebounding to make a second collision with a given wall.

The total average force exerted on a given wall of area a^2 is the average rate of change of momentum times the number of particles N in the cube

$$f_{x,y,z} = \frac{\Delta p_{x,y,z}}{\Delta t_{x,y,z}} = \frac{2mv_{x,y,z}}{2a/v_{x,y,z}} = \frac{mv_{x,y,z}^2}{a} \quad \text{force due to one collision}$$

$$\therefore \overline{F_{x,y,z}} = \frac{Nmv_{x,y,z}^2}{a} \quad \text{Total average force on one wall}$$

$$\text{Define the particle density } \rho = \frac{Nm}{a^3} \quad \therefore \frac{Nm}{a} = \rho a^2 \quad \therefore \overline{F_{x,y,z}} = \rho a^2 \overline{v_{x,y,z}^2}$$

Now particle speed is given by $v^2 = v_x^2 + v_y^2 + v_z^2$

Hence since all velocities are deemed to be random, the mean squared speed is

$$\overline{v^2} = 3\overline{v_{x,y,z}^2}$$

Therefore average pressure on each wall is: $P = \frac{\overline{F_{x,y,z}}}{a^2}$

$$\text{Hence: } P = \frac{1}{3} \rho \overline{v^2}$$

*The speed distribution is called the Maxwell-Boltzmann speed distribution, in order to also recognise the contributions of James Clerk Maxwell 1831-1879

Entropy

In Classical Thermodynamics, Rudolf Clausius proposed the Second Law, which is most simply stated as "for any physical process, the total entropy of the Universe must increase." The change in entropy S is defined as the ratio of the reversible heat change to the absolute temperature.

$$dS = \frac{dQ}{T}$$

Boltzmann and Gibbs proposed a *statistical* basis for entropy. The most general form is the Gibbs definition:

$$S = -k_B \sum_i p_i \ln p_i$$

$$k_B = 1.381 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$$

which corresponds to a sum over all possible microstates of a system, with each state having probability p_i .

The simplest case is where each state is equally probable. Consider N particles (or indeed energy quanta) and assume these can be arranged in W distinct ways (see definition on page 1)

$$p_i = \frac{1}{W}$$

$$W = \frac{N!}{\prod_i n_i!} \quad n_i \text{ in level } i \text{ all have the same energy}$$

$$\sum_i p_i = 1$$

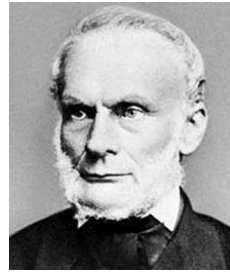
$$S = -k_B \sum_i p_i \ln p_i$$

$$S = -k_B \sum_i p_i (-\ln W)$$

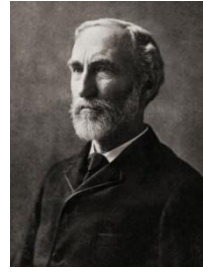
$$S = k_B \ln W \sum_i p_i$$

$$S = k_B \ln W$$

This yields Boltzmann's definition of entropy, which is proportional to the natural logarithm of the number of ways of arranging microstates of a thermodynamic system.



Rudolf Clausius
1822-1888



Josiah Willard Gibbs
1839-1903

We showed previously that maximizing W yields the Boltzmann distribution

$$p(\epsilon_i) = \frac{e^{-\frac{\epsilon_i}{k_B T}}}{Z} \quad Z = \sum_j e^{-\frac{\epsilon_j}{k_B T}}$$

$$dS = -k_B \sum_i d(p_i \ln p_i) \quad \text{Gibbs entropy}$$

$$dS = -k_B \sum_i \left(dp_i \ln p_i + p_i \frac{1}{p_i} dp_i \right)$$

$$dS = -k_B \sum_i (\ln p_i + 1) dp_i$$

$$\sum_i dp_i = 0 \quad \therefore dS = -k_B \sum_i (\ln p_i) dp_i$$

$$p_i = \frac{e^{-\frac{\epsilon_i}{k_B T}}}{Z} \quad \therefore \ln p_i = -\frac{1}{k_B T} \epsilon_i - \ln Z$$

$$Z = \sum_j e^{-\frac{\epsilon_j}{k_B T}}$$

$$dS = -k_B \sum_i \left(-\frac{1}{k_B T} \epsilon_i - \ln Z \right) dp_i$$

$$dS = \sum_i \frac{\epsilon_i}{T} dp_i + k_B \ln Z \sum_i dp_i$$

$$dS = \sum_i \frac{\epsilon_i}{T} dp_i$$

By definition these differential quantities tend to zero!

Using Boltzmann distribution

$$dU = \sum_i d(\epsilon_i p_i) \quad \text{Total energy } U \text{ of a system}$$

$$dU = \sum_i \epsilon_i dp_i + \sum_i p_i d\epsilon_i$$

$$dU = dQ + dW \quad \text{Conservation of energy}$$

heat work

$$\therefore dS = \frac{dQ}{T}$$

$$\therefore dQ = \sum_i \epsilon_i dp_i$$

i.e. assign the meaning of heat (rather than work done) to this term

i.e. Gibbs entropy + Boltzmann distribution is consistent with the Classical definition of entropy.

Pressure from kinetic theory – using Boltzmann statistics

$$P = \int_{\theta=0}^{\frac{1}{2}\pi} \int_{\phi=0}^{2\pi} \int_{v=0}^{\infty} n \times \underbrace{\frac{\sin \theta d\theta d\phi}{4\pi}}_I \times \underbrace{v \cos \theta}_{II} \times \underbrace{mv \cos \theta}_{III} \times \underbrace{p(v) dv}_{IV}$$

I Fraction of particles that are arriving from polar angle θ from the z axis and ϕ anticlockwise from the x axis. This is the ratio of an area element of a unit sphere divided by the area of the unit sphere. This is essentially a 'solid angle'

II Projection of (incoming) velocity in the z direction. Note we don't include outgoing particles, hence the range of θ is 0 to $\pi/2$ radians, not π .

III Projection of impulse applied to the x, y plane unit surface in the z direction. Purely elastic collisions are assumed.

IV Number of particles with velocity between v and $v + dv$

$$P = \frac{1}{2\pi} nm \int_{\theta=0}^{\frac{1}{2}\pi} \sin \theta \cos^2 \theta d\theta \int_{\phi=0}^{2\pi} d\phi \int_{v=0}^{\infty} v^2 p(v) dv$$

$$P = \rho \bar{v}^2 \int_{\theta=0}^{\frac{1}{2}\pi} \sin \theta \cos^2 \theta d\theta$$

$$\frac{d}{d\theta} \cos^3 \theta = -3 \cos^2 \theta \sin \theta$$

$$\therefore \int_{\theta=0}^{\frac{1}{2}\pi} \sin \theta \cos^2 \theta d\theta = \left[-\frac{1}{3} \cos^3 \theta \right]_0^{\frac{1}{2}\pi} = (0) - \left(-\frac{1}{3} \right) = \frac{1}{3}$$

$$\therefore P = \frac{1}{3} \rho \bar{v}^2$$

