

Physics 112

Maxwell distributions for the speed and velocity of molecules in a gas (Kittel and Kroemer, p. 392–3)

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The probability that a single orbital k is occupied in the classical ideal gas is given by the classical distribution

$$f_{cl}(\epsilon_k) = \exp(\beta(\mu - \epsilon_k)). \quad (1)$$

We recall that this number is very small compared with unity.

We are more interested in the number of particles in a given *range* of energy, $d\epsilon$ rather than the mean number in a single level. This is equal to

$$f_{cl}(\epsilon)\rho(\epsilon) d\epsilon, \quad (2)$$

where $\rho(\epsilon) \propto \epsilon^{1/2}$ is the density of states. Hence, if we observe a particle, the probability that its energy lies between ϵ and $\epsilon + d\epsilon$, is

$$P(\epsilon) d\epsilon = A f_{cl}(\epsilon)\rho(\epsilon) d\epsilon, \quad (3)$$

where

$$A = \left[\int_0^\infty f_{cl}(\epsilon)\rho(\epsilon) d\epsilon \right]^{-1} \quad (4)$$

is a normalization constant. Since $\rho(\epsilon) \propto \epsilon^{1/2}$ we have

$$P(\epsilon) d\epsilon = B \epsilon^{1/2} \exp(-\beta\epsilon) d\epsilon, \quad (5)$$

where B is another normalization constant, into which we have absorbed the factor $\exp(\beta\mu)$.

It is particularly convenient to convert this last expression to a distribution of speeds, which we will denote by $P_M(v)$. Since $\epsilon = \frac{1}{2}mv^2$, where m is the mass, we have

$$P_M(v) dv = P(\epsilon) d\epsilon \quad (6)$$

so

$$\begin{aligned} P_M(v) &= B \left(\frac{1}{2}mv^2\right)^{1/2} \exp\left(-\frac{mv^2}{2k_B T}\right) \frac{d\epsilon}{dv} \\ &= \text{const. } v^2 \exp\left(-\frac{mv^2}{2k_B T}\right). \end{aligned} \quad (7)$$

The normalization constant is determined from the requirement that

$$\int_0^\infty P_M(v) dv = 1, \quad (8)$$

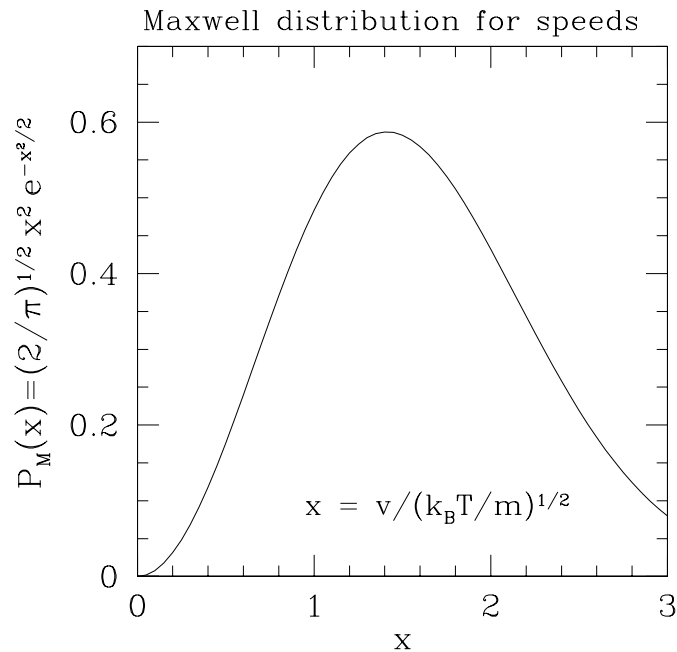
and using the following the Gaussian integral,

$$\int_0^\infty x^2 e^{-a^2 x^2/2} dx = \sqrt{\frac{\pi}{2}} \frac{1}{a^3}, \quad (9)$$

with $a^2 = m/k_B T$. This gives the final result,

$$\boxed{P_M(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)} \quad (10)$$

for the Maxwell distribution for the speeds. It is shown in the figure below. Note that the exponent is just (minus) the kinetic energy divided by $k_B T$, as expected from Boltzmann statistics, see Eq. (1).



The probability tends to zero both for $v \rightarrow 0$ and for $v \rightarrow \infty$. A characteristic speed is $\sqrt{k_B T/m}$ which is about 300 m/s for air. A problem in which you evaluate Gaussian integrals to determine several specific measures of the distribution is set in the homework.

It is also useful to determine the distribution not only of the speed $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$ but also of each component of the velocity. To do this note that $P_M(v) dv$ is the probability to find $\vec{v} = (v_x, v_y, v_z)$ in a spherical shell of radius v and width dv . The volume of this shell is $4\pi v^2 dv$. Hence, if $P(v_x, v_y, v_z) dv_x dv_y dv_z$ is the probability of finding a particle with velocity in a small box in \vec{v} -space of volume $dv_x dv_y dv_z$ we have

$$P(v_x, v_y, v_z) 4\pi v^2 dv = P_M(v) dv, \quad (11)$$

and so

$$P(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv_x^2/2k_B T} e^{-mv_y^2/2k_B T} e^{-mv_z^2/2k_B T}. \quad (12)$$

As expected this factorizes,

$$P(v_x, v_y, v_z) = \tilde{P}(v_x) \tilde{P}(v_y) \tilde{P}(v_z) \quad (13)$$

in which

$$\tilde{P}(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mv_x^2/2k_B T}, \quad (14)$$

is the distribution of single velocity component v_x . Note that this is Gaussian. We should point out that while the speed v is positive, the individual velocity components can have either sign. Note too that the exponent is just (minus) the kinetic energy of the motion along x divided by $k_B T$.