Description of the Module "**probabilities**"

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The normalized Maxwell-Boltzmann distribution is [e.g. see http://mathworld.wolfram.com/MaxwellDistribution.html]:

$$F(v)dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv. \qquad (1)$$

Using the auxiliary variable:

$$a = \sqrt{\frac{k_B T}{m}}. \qquad (2)$$

one can simplify this result to:

$$F(v)dv = \sqrt{\frac{2}{\pi}} a^{-3} v^2 \exp\left(-\frac{v^2}{2a^2}\right) dv. \qquad (3)$$

The cumulative probability function is given by:

$$D(v) = \operatorname{erf}\left(\frac{v}{a\sqrt{2}}\right) - \sqrt{\frac{2}{\pi}} \frac{v}{a} \exp\left(-\frac{v^2}{2a^2}\right). \qquad (4)$$

$$m = \frac{k_B T}{a^2}. \qquad (5)$$

$$E = \frac{mv^2}{2} = \frac{k_B T}{a^2}\frac{v^2}{2} = \frac{k_B T}{2}\left(\frac{v}{a}\right)^2 \rightarrow \frac{v}{a} = \left(\frac{2E}{k_B T}\right)^{1/2}. \qquad (6)$$

So:

$$D(E) = \operatorname{erf}\left(\left(\frac{E}{k_B T}\right)^{1/2}\right) - \sqrt{\frac{4}{\pi}} \left(\frac{E}{k_B T}\right)^{1/2} \exp\left(-\frac{E}{k_B T}\right). \qquad (7)$$

Lets compute the energy probability distribution function:

$$P(E) = \frac{dD}{dE} = \frac{2}{\sqrt{\pi}} \frac{1}{k_B T} \left(\frac{E}{k_B T}\right)^{-1/2} \exp\left(-\frac{E}{k_B T}\right) - \sqrt{\frac{4}{\pi}} \frac{1}{k_B T} \left(\frac{E}{k_B T}\right)^{-\frac{1}{2}} \exp\left(-\frac{E}{k_B T}\right) + \frac{1}{k_B T} \sqrt{\frac{4}{\pi}} \left(\frac{E}{k_B T}\right)^{\frac{1}{2}} \exp\left(-\frac{E}{k_B T}\right) = \frac{1}{k_B T} \sqrt{\frac{4}{\pi}} \left(\frac{E}{k_B T}\right)^{\frac{1}{2}} \exp\left(-\frac{E}{k_B T}\right)$$

which agrees with the result here:
https://en.wikipedia.org/wiki/Maxwell%E2%80%93Boltzmann_distribution

Consider a harmonic oscillator with a frequency of mode i, ω_i. The HO can be in any vibrational state.

The fraction of the first N states [0,…N-1] in the total sum:

$$Z_N = \sum_{n=0}^{N} \exp\left(-\frac{\hbar\omega_i\left(n+\frac{1}{2}\right)}{k_B T}\right) = \exp\left(-\frac{\hbar\omega_i}{2k_B T}\right)\sum_{n=0}^{N} r^n = \exp\left(-\frac{\hbar\omega_i}{2k_B T}\right)\frac{1-r^{N+1}}{1-r} = \exp\left(-\frac{\hbar\omega_i}{2k_B T}\right)\frac{1-\exp\left(-\frac{\hbar\omega_i}{k_B T}N\right)}{1-\exp\left(-\frac{\hbar\omega_i}{k_B T}\right)}. \tag{8}$$

Total number of states:

$$Z_\infty = \exp\left(-\frac{\hbar\omega_i}{2k_B T}\right)\frac{1}{1-\exp\left(-\frac{\hbar\omega_i}{k_B T}\right)}. \tag{9}$$

The probability to be in the vibrational state n is given by:

$$P_n = \frac{\exp\left(-\frac{\hbar\omega_i}{k_B T}\left(n+\frac{1}{2}\right)\right)}{Z_\infty} = \frac{\exp\left(-\frac{\hbar\omega_i}{k_B T}\left(n+\frac{1}{2}\right)\right)}{\exp\left(-\frac{\hbar\omega_i}{2k_B T}\right)}\left(1-\exp\left(-\frac{\hbar\omega_i}{k_B T}\right)\right) = \exp\left(-\frac{\hbar\omega_i}{k_B T}n\right)\left(1-\exp\left(-\frac{\hbar\omega_i}{k_B T}\right)\right). \tag{10}$$

The probability to be in any of states below state N:

$$P_{<N} = \frac{Z_N}{Z_\infty} = \frac{\exp\left(-\frac{\hbar\omega_i}{2k_B T}\right)\frac{1-\exp\left(-\frac{\hbar\omega_i}{k_B T}N\right)}{1-\exp\left(-\frac{\hbar\omega_i}{k_B T}\right)}}{\exp\left(-\frac{\hbar\omega_i}{2k_B T}\right)\frac{1}{1-\exp\left(-\frac{\hbar\omega_i}{k_B T}\right)}} = 1-\exp\left(-\frac{\hbar\omega_i}{k_B T}N\right). \tag{11}$$

The probability that any of the states above N (including it) are occupied is given by:

$$P_{\geq N} = 1 - P_{<N} = \exp\left(-\frac{\hbar\omega_i}{k_B T}N\right). \tag{12}$$