Gibbs-Boltzmann-Verteilung

$$p_j = \frac{1}{Z}\exp\left(-\beta E_j\right) = \frac{1}{Z}\exp\left(-\frac{E_j}{k_B T}\right)$$

Zustandssumme

$$Z = \sum_j \exp\left(-\frac{E_j}{k_B T}\right)$$

Maxwell-Verteilung

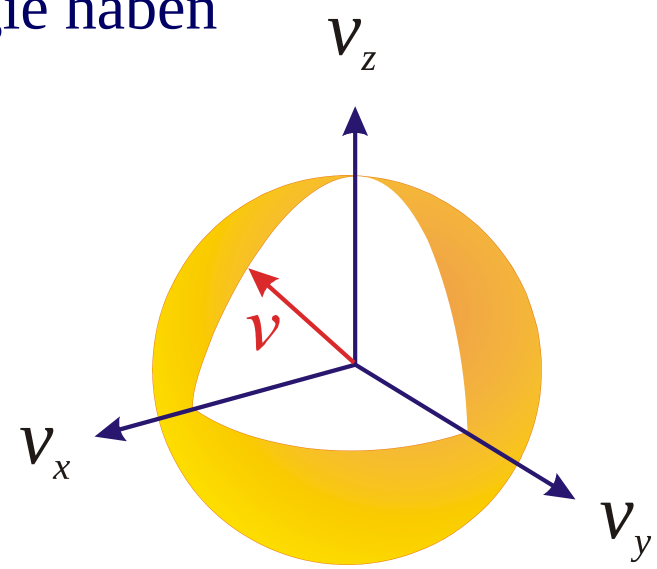
Verteilung der Molekülgeschwindigkeiten in einem idealen Gas

Energien der Moleküle kontinuierlich: $\frac{mv^2}{2}$

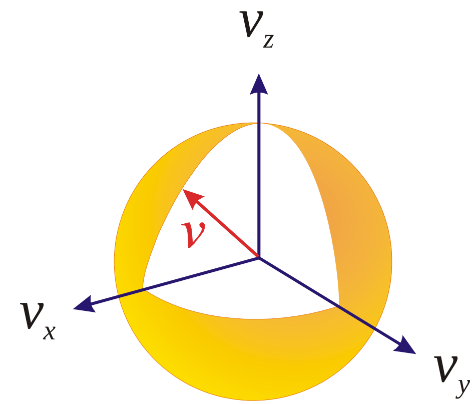
Energien entartet: verschiedene Bewegungsrichtungen können gleiche Energie haben

Phasenraum: $\{x,y,z,v_x,v_y,v_z\}$

Zahl der Zustände gleicher Energie ist proportional zu v^2



Maxwell-Verteilung



$$p(v) = \frac{v^2}{Z}\exp\left(-\frac{\beta m v^2}{2}\right)$$

Normierung: $$\int_0^\infty dv\, p(v) = \int_0^\infty dv \frac{v^2}{Z}\exp\left(-\frac{\beta m v^2}{2}\right) = 1$$

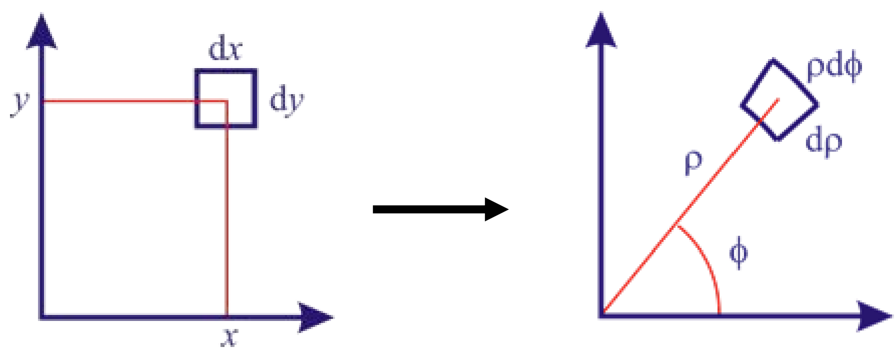
Wir benötigen:

$$\int_0^\infty dx\, x^2 \exp\left(-\lambda x^2\right) = -\frac{d}{d\lambda}\int_0^\infty dx \exp\left(-\lambda x^2\right)$$

Gauß-Integral

$$I = \int_0^{\infty} dx \exp\left(-\lambda x^2\right)$$

$$I^2 = \left[\int_0^{\infty} dx \exp\left(-\lambda x^2\right)\right]\left[\int_0^{\infty} dy \exp\left(-\lambda y^2\right)\right] = \int_0^{\infty}\int_0^{\infty} dx dy \exp\left(-\lambda x^2 - \lambda y^2\right)$$



$$I^2 = \int_0^{\infty} d\rho \int_0^{\pi/2} d\phi \rho \exp\left(-\lambda \rho^2\right)$$

Gauß-Integral

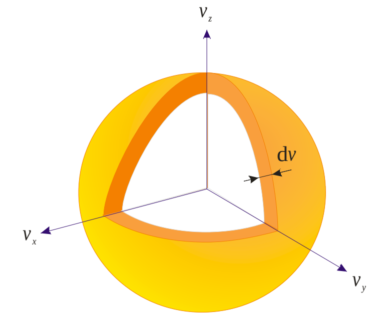
$$I^2 = \int_0^\infty d\rho \int_0^{\pi/2} d\phi \rho \exp\left(-\lambda\rho^2\right) \qquad I^2 = \frac{\pi}{2}\int_0^\infty d\rho\rho \exp\left(-\lambda\rho^2\right)$$

$$I^2 = \frac{\pi}{4}\int_0^\infty d\left(\rho^2\right)\exp\left(-\lambda\rho^2\right)$$

$$I^2 = -\frac{\pi}{4\lambda}\left[\exp\left(-\lambda\rho^2\right)\right]_{\rho^2=0}^{\rho^2=\infty} = \frac{\pi}{4\lambda}$$

$$I = \int_0^\infty dx \exp\left(-\lambda x^2\right) = \frac{1}{2}\sqrt{\frac{\pi}{\lambda}}$$

Maxwell-Verteilung



$$p(v) = \frac{v^2}{Z} \exp\left(-\frac{\beta m v^2}{2}\right)$$

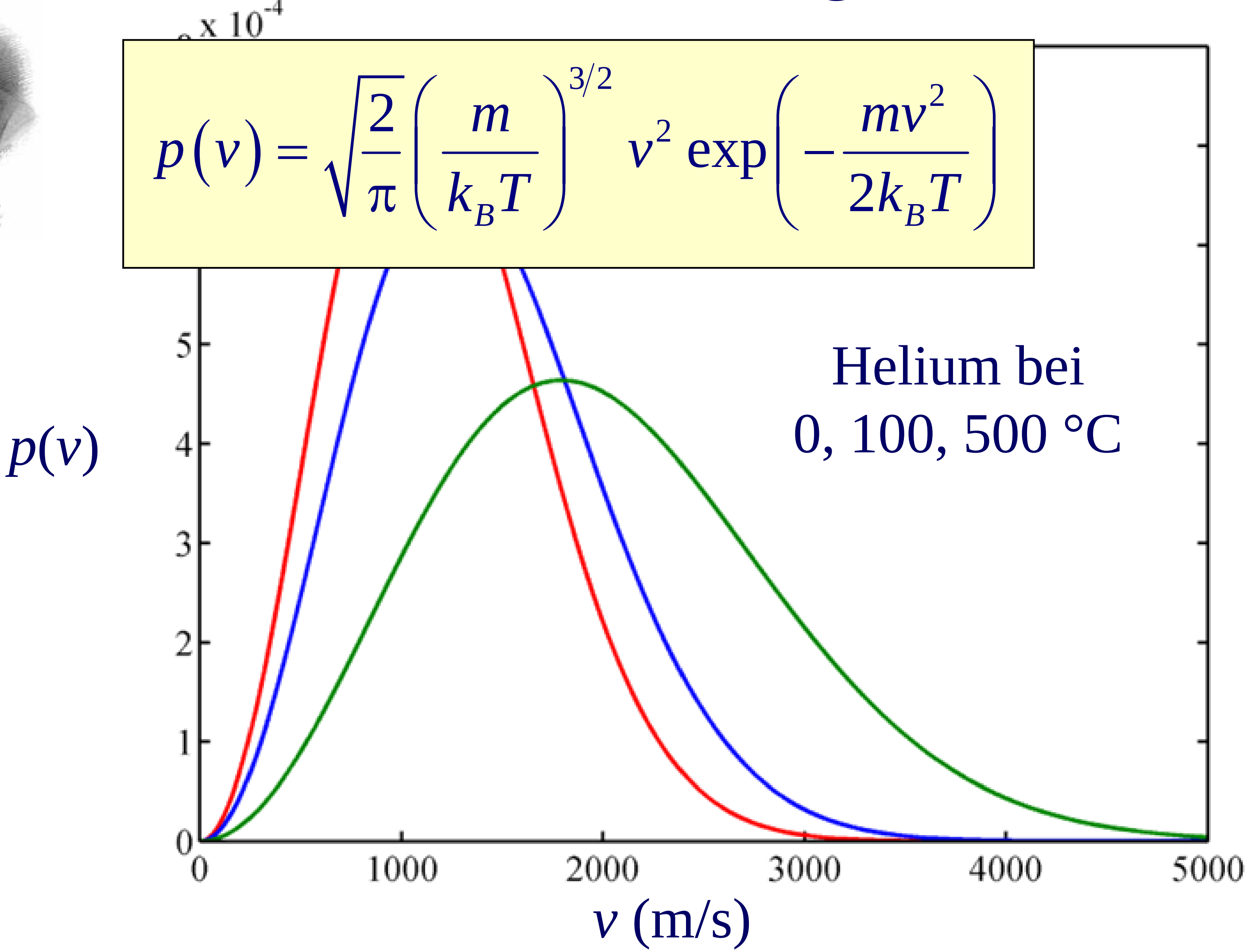
Normierung: $$\int_0^\infty dx v^2 \exp\left(-\frac{\beta m v^2}{2}\right) = -\frac{d}{d(\beta m/2)} \int_0^\infty dx \exp\left(-\frac{\beta m v^2}{2}\right)$$

$$-\frac{d}{d(\beta m/2)} \int_0^\infty dx \exp\left(-\frac{\beta m v^2}{2}\right) = -\frac{d}{d(\beta m/2)} \frac{1}{2}\sqrt{\frac{2\pi}{\beta m}} = \frac{\sqrt{\pi}}{4}\left(\frac{2}{\beta m}\right)^{3/2}$$

$$Z = \sqrt{\frac{\pi}{2}}\left(\frac{1}{\beta m}\right)^{3/2} = \sqrt{\frac{\pi}{2}}\left(\frac{k_B T}{m}\right)^{3/2}$$

Maxwell-Verteilung

$$p(v) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T} \right)^{3/2} v^2 \exp\left(-\frac{m v^2}{2 k_B T} \right)$$



Mittlere Energie der Moleküle: 1d-Maxwell

Berechne $\overline{\frac{m}{2}v_x^2} = \int_{-\infty}^{\infty} dv_x\, p(v_x) \frac{m}{2} v_x^2$

Gibbs-Boltzmann: $p(v_x) = \frac{1}{Z} \exp\left(-\frac{m v_x^2}{2 k_B T}\right)$

Normierung: $\int_{-\infty}^{\infty} dv_x\, p(v_x) = 1 = \int_{-\infty}^{\infty} dv_x \frac{1}{Z} \exp\left(-\frac{m v_x^2}{2 k_B T}\right) = \frac{1}{Z}\sqrt{\frac{2\pi k_B T}{m}}$

$$p(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{m v_x^2}{2 k_B T}\right)$$

Mittlere Energie der Moleküle: 1d-Maxwell

$$\overline{\frac{m}{2}v_x^2} = \int_{-\infty}^{\infty} dv_x \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{mv_x^2}{2k_B T}\right)\frac{m}{2}v_x^2$$

$$\beta = \frac{1}{k_B T} \qquad \overline{\frac{m}{2}v_x^2} = \sqrt{\frac{\beta m}{2\pi}}\left(-\frac{d}{d\beta}\right)\int_{-\infty}^{\infty} dv_x \exp\left(-\frac{\beta m v_x^2}{2}\right)$$

$$\overline{\frac{m}{2}v_x^2} = \sqrt{\frac{\beta m}{2\pi}}\left(-\frac{d}{d\beta}\right)\sqrt{\frac{2\pi}{\beta m}}$$

$$\overline{\frac{m}{2}v_x^2} = \frac{1}{2\beta} = \frac{k_B T}{2}$$

Gleichverteilungs-Satz

$$\overline{\frac{m}{2} v_x^2} = \frac{1}{2\beta} = \frac{k_B T}{2}$$

Jeder Freiheitsgrad, der in die Gesamtenergie quadratisch eingeht, hat im thermischen Gleichgewicht die mittlere Energie $k_B T/2$

Beispiel: potentielle Energie einer Sprungfeder ~ $kx^2/2$

$$\overline{\frac{k}{2} x^2} = \frac{k_B T}{2}$$