Maxwellian Distribution: Equilibrium f

- What f_o satisfies our equilibrium requirement $f_o(c_i')\, f_o(z_i') = f_o(c_i)\, f_o(z_i)$
  - since mean speed fixed, also $f_o(C_i')\, f_o(Z_i') = f_o(C_i)\, f_o(Z_i)$
- Consider this requirement in terms of $\ln(f_o)$

$$\ln f_o(C_i') + \ln f_o(Z_i') = \ln f_o(C_i) + \ln f_o(Z_i)$$

  - so $\Sigma \ln f_o$ is a "conserved" quantity (before vs. after collision) at equilibrium
- As already shown, the kinetic energy and momentum are also conserved in the collision
  - "guess": $\ln f_o$ is some linear combination of other conserved quantities

$$\ln f_o(C_i) = \alpha_0 + \overbrace{\alpha_1 mC_1 + \alpha_2 mC_2 + \alpha_3 mC_3}^{momentum} - \overbrace{\beta\ \tfrac{1}{2} mC^2}^{energy}$$

Equilibrium Distribution Constraints

- Rewriting assumed distribution requirement

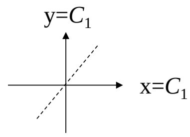
$$\ln f_o(C_i) = \alpha_0 + \alpha_1 mC_1 + \alpha_2 mC_2 + \alpha_3 mC_3 - \beta\ \tfrac{1}{2} mC^2$$

$$f_o(C_i) = A\, e^{\alpha_1 mC_1}\, e^{\alpha_2 mC_2}\, e^{\alpha_3 mC_3}\, e^{-\beta mC^2/2} \qquad C^2 = C_1^2 + C_2^2 + C_3^2$$

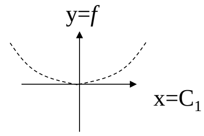
- Other constraints?
  1) random velocity $\overline{C_1} = \overline{C_2} = \overline{C_3} = 0$
  2) PDF normalized $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f_o(C_i)\, dV_C = 1$
  3) TPG result $p = nkT = \frac{1}{3} nm\overline{C^2}$

Constraints

- Apply constraint 1
  - e.g., $\overline{C_1} \equiv \int_{-\infty}^{\infty} C_1 f_o(C_i) dV_C = 0$



  - C_1 is odd function



  - integral zero only if f even/symmetric in C_1
    - odd×even = odd

$$f_o(C_i) = Ae^{\alpha_1 m C_1} \underbrace{e^{-\beta \frac{m C_1^2}{2}}}_{\text{even}} e^{\alpha_2 m C_2} e^{\alpha_3 m C_3} e^{-\beta \frac{m\left(C_2^2+C_3^2\right)}{2}}$$

only even if α_1=0 $\Rightarrow e^{\alpha_1 m C_1} = 1$

  - similar analysis: $\alpha_1=\alpha_2=\alpha_3=0$

Constraints

- So now $f_o(C_i) = Ae^{-\beta \frac{m C_1^2}{2}} e^{-\beta \frac{m C_2^2}{2}} e^{-\beta \frac{m C_3^2}{2}}$
- Apply constraint 2 $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f_o(C_i) dV_c = 1$

$$A\int_{-\infty}^{\infty} e^{-\beta \frac{m C_1^2}{2}} dC_1 \int_{-\infty}^{\infty} e^{-\beta \frac{m C_2^2}{2}} dC_2 \int_{-\infty}^{\infty} e^{-\beta \frac{m C_3^2}{2}} dC_3 = 1$$

  - three identical integrals
  - from V&K Appendix A.1 $I_0(a) \equiv \int_0^{\infty} e^{-aC^2} dC = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$

$$\int_{-\infty}^{\infty} e^{-aC^2} dC = 2\int_0^{\infty} e^{-aC^2} dC$$

  - so $A = \left(\frac{\beta m}{2\pi}\right)^{3/2}$

Constraints

- Apply constraint 3 $\overline{C^2} = \frac{3kT}{m}$ $\overline{C_j^2} = \frac{1}{3}\overline{C^2} = \frac{kT}{m}$

$$\overline{C_j^2} \equiv \int_{-\infty}^{\infty} C_j^2 f_o(C_i)\,dV_C$$

  - e.g., for direction 1

$$\frac{kT}{m} = \left(\frac{\beta m}{2\pi}\right)^{3/2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} C_1^2 e^{-\beta\frac{mC_1^2}{2}} e^{-\beta\frac{mC_2^2}{2}} e^{-\beta\frac{mC_3^2}{2}} dC_1 dC_2 dC_3$$

$$\frac{kT}{m} = \left(\frac{\beta m}{2\pi}\right)^{3/2} \underbrace{\int_{-\infty}^{\infty} C_1^2 e^{-\beta\frac{mC_1^2}{2}} dC_1}_{\substack{2I_2(a) = 2\int_0^\infty x^2 e^{-ax^2}dx = \frac{1}{2}\left(\frac{\pi}{a^3}\right)^{1/2} \\ = (2\pi)^{1/2}(\beta m)^{-3/2}}} \underbrace{\int_{-\infty}^{\infty} e^{-\beta\frac{mC_2^2}{2}} dC_2}_{\substack{2I_0(a) \\ = (2\pi/\beta m)^{1/2}}} \underbrace{\int_{-\infty}^{\infty} e^{-\beta\frac{mC_3^2}{2}} dC_3}_{\substack{2I_0(a) \\ = (2\pi/\beta m)^{1/2}}}$$

V&K A.1

$$\Rightarrow \beta = \frac{1}{kT}$$

same thing we found in Stat. Mech. for Boltzmann Distribution

Mawellian Velocity Distribution

- Result

$$\boxed{f_o(C_i) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mC^2}{2kT}}}$$

Maxwellian Velocity Distribution

  - Gaussian distribution
  - related to translational kinetic energy distribution
- In equilibrium, probability of finding molecule in class $C_1 \rightarrow C_1 + dC_1$ independent of other directions

$$f_o(C_i) = \Phi(C_1)\Phi(C_2)\Phi(C_3)$$

$$\boxed{\Phi(C_1) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{m}{2kT}C_1^2}}$$

also Gaussian

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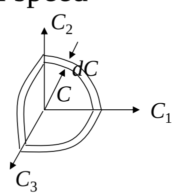
Maxwellian Speed Distribution

- Sometimes don't care about direction, just magnitude $C \equiv |C_i| = \sqrt{C_1^2 + C_2^2 + C_3^2}$
- Define speed PDF, χ
  - $n\chi(C)dC$=number density of molec. with speed $C \rightarrow C+dC$
  - this is volume of spherical shell in velocity space



$$\cancel{n}\chi(C)\cancel{dC} = \cancel{n}4\pi C^2 f(C_i)\cancel{dC}$$

$$\boxed{\chi_o(C) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi C^2 e^{\frac{-m}{2kT}C^2}}$$

$$1 = \int_0^\infty \chi(C)dC$$

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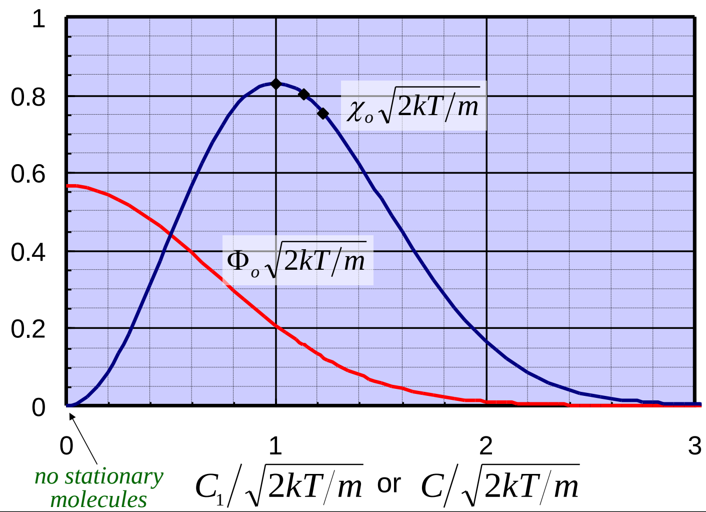
Maxwellian Distributions



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Statistical Characteristics

- What are most probable velocity and speed?

$$C_{j\,mp} \Rightarrow \frac{df_o}{dC_j} = 0 \Rightarrow C_{j\,mp} = 0 \qquad C_{mp} \Rightarrow \frac{d\chi_o}{dC} = 0 \Rightarrow \boxed{C_{mp} = \sqrt{2kT/m}}$$

- Can find other statistical properties from moments
  - 1st moment of speed distribution

$$\overline{C} = \int_0^\infty C\chi_o(C)dC = \int_0^\infty C\left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi C^2 e^{\frac{-m}{2kT}C^2} dC$$

$$= \frac{4}{\pi^{1/2}}\sqrt{\frac{2kT}{m}}\int_0^\infty \left[\sqrt{\frac{m}{2kT}}C\right]^3 e^{-\left[\sqrt{\frac{m}{2kT}}C\right]^2}\left[\sqrt{\frac{m}{2kT}}dC\right]$$

$x \equiv \sqrt{m/2kT}\,C$

$dx = \sqrt{m/2kT}\,dC$

$$= \sqrt{\frac{8kT}{\pi m}}\int_0^\infty x^3 e^{-x^2} dx \Rightarrow \boxed{\overline{C} = \sqrt{\frac{8kT}{\pi m}}}$$

$I_3(1) = 1/2$

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Statistical Characteristics

- 2nd Moment

$$\overline{C^2} = \int_0^\infty C^2\chi_o(C)dC = \int_0^\infty C^2\left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi C^2 e^{\frac{-m}{2kT}C^2} dC$$

⋮

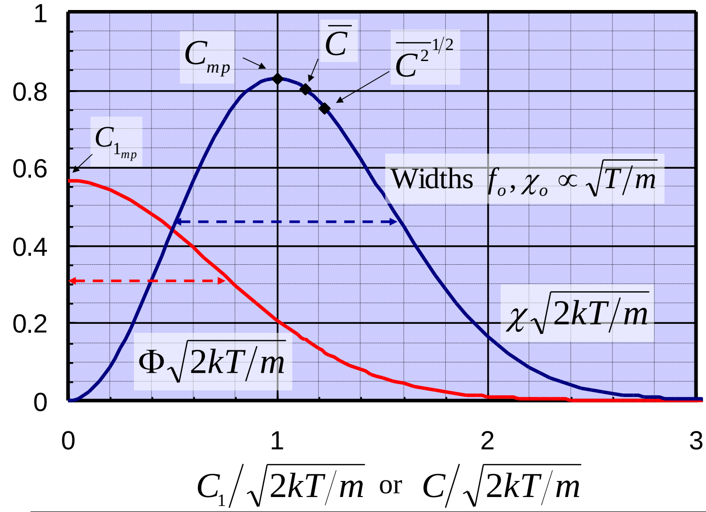
  - but already know $\frac{1}{2}m\overline{C^2} = \frac{3}{2}kT \Rightarrow \overline{C^2} = \frac{3kT}{m}$

$$\boxed{\sqrt{\overline{C^2}} = \sqrt{\frac{3kT}{m}}}$$

- Comparing $\sqrt{2kT/m} < \sqrt{(8/\pi)kT/m} < \sqrt{3kT/m}$

$$C_{mp} < \overline{C} < \sqrt{\overline{C^2}}$$

Maxwellian Distributions



characteristic speeds are similar

$\overline{C}/C_{mp} \cong 1.128$

$\overline{C^2}^{1/2}/C_{mp} \cong 1.225$