Physics 415 - Lecture 25: Maxwell Distribution and Kinetic Theory

March 19, 2025

Summary

- Maxwell velocity distribution: $f(\vec{v}) = \left(\frac{m}{2\pi T}\right)^{3/2} e^{-m|\vec{v}|^2/(2T)}$
- $f(\vec{v})d^3v$ = probability that a gas particle has velocity in the range $(\vec{v}, \vec{v} + d^3v)$.
- (Derived in Lecture 18 by applying canonical distribution to a single gas molecule in equilibrium at temp T).

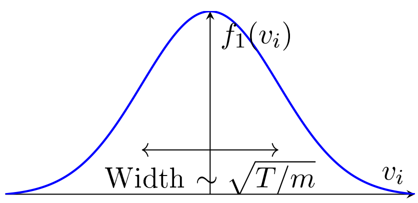
Summarize properties of $f(\vec{v})$ and use to deduce some simple properties of weakly interacting gases ("Kinetic Theory").

Properties of $f(\vec{v})$

- Factorization: $f(\vec{v})$ can be factorized:

  $$f(\vec{v})d^3v = [f_1(v_x)dv_x][f_1(v_y)dv_y][f_1(v_z)dv_z]$$

  where $f_1(v_i) = \sqrt{\frac{m}{2\pi T}} e^{-mv_i^2/(2T)}$ for $i = x, y, z$. This means individual velocity components are statistically independent.



- Averages involving v_i:
  - $\overline{v_i} = \int_{-\infty}^{\infty} dv_i\, v_i f_1(v_i) = 0$ (integral of odd function).
  - $\overline{v_i^2} = \int_{-\infty}^{\infty} dv_i\, v_i^2 f_1(v_i) = \sqrt{\frac{m}{2\pi T}} \int_{-\infty}^{\infty} v_i^2 e^{-mv_i^2/(2T)} dv_i$. Using $\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$ with $a = m/(2T)$: $\overline{v_i^2} = \sqrt{\frac{m}{2\pi T}} \left[\frac{1}{2(m/2T)}\sqrt{\frac{\pi}{m/(2T)}}\right] = \sqrt{\frac{m}{2\pi T}} \left[\frac{T}{m}\sqrt{\frac{2\pi T}{m}}\right] = \frac{T}{m}$. So, $\overline{v_i^2} = T/m$ for $i = x, y, z$.

  This matches the equipartition theorem result: $\frac{1}{2}m\overline{v_i^2} = \frac{1}{2}T$. ✓

- Distribution for speed $v = |\vec{v}|$: Let $F(v)dv$ = probability that a gas particle has speed in the range $(v, v+dv)$. To find $F(v)$, integrate $f(\vec{v})$ over angles in spherical velocity coordinates ($d^3v = v^2 dv \sin\theta d\theta d\phi$).

$$F(v)dv = \left(\int_{\text{angles}} f(\vec{v}) v^2 \sin\theta d\theta d\phi \right) dv$$

  Since $f(\vec{v})$ only depends on v^2, it is isotropic. $\int \sin\theta d\theta d\phi = 4\pi$.

$$F(v)dv = f(v) \times 4\pi v^2 dv = 4\pi \left(\frac{m}{2\pi T}\right)^{3/2} v^2 e^{-mv^2/(2T)} dv$$

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

- Characteristic Speeds:
  - Average speed $\overline{v}$: $\overline{v} = \int_0^\infty vF(v)dv$. $\overline{v} = 4\pi(\frac{m}{2\pi T})^{3/2} \int_0^\infty v^3 e^{-mv^2/(2T)} dv$. Let $u^2 = mv^2/(2T)$, $v = \sqrt{2T/m}u$, $dv = \sqrt{2T/m}du$. Integral becomes $\int_0^\infty (\sqrt{2T/m}u)^3 e^{-u^2} (\sqrt{2T/m}du) = (\frac{2T}{m})^2 \int_0^\infty u^3 e^{-u^2} du$. Use $\int_0^\infty x^3 e^{-x^2} dx = 1/2$. Integral value is $(2T/m)^2 \times (1/2) = 2T^2/m^2$. $\overline{v} = 4\pi(\frac{m}{2\pi T})^{3/2}(\frac{2T^2}{m^2}) = 4\pi \frac{m^{3/2}}{(2\pi T)^{3/2}} \frac{2T^2}{m^2} = \frac{8\pi T^2 m^{3/2}}{(2\pi T)^{3/2} m^2} = \sqrt{\frac{64\pi^2 T^4 m^3}{8\pi^3 T^3 m^4}} = \sqrt{\frac{8T}{\pi m}}$.

$$\overline{v} = \sqrt{\frac{8T}{\pi m}} \approx 1.596\sqrt{T/m}$$

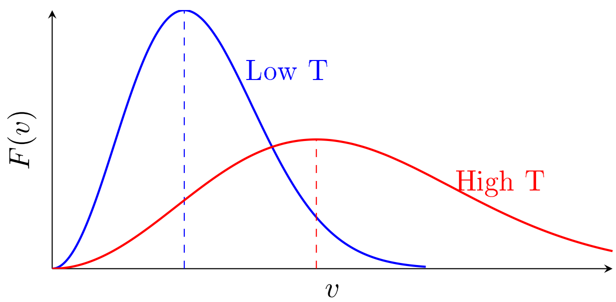
  - RMS speed v_{RMS}: $v_{\text{RMS}} = \sqrt{\overline{v^2}}$. $\overline{v^2} = \overline{v_x^2 + v_y^2 + v_z^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = T/m + T/m + T/m = 3T/m$.

$$v_{\text{RMS}} = \sqrt{\frac{3T}{m}} \approx 1.732\sqrt{T/m}$$

    (Matches equipartition $\frac{1}{2}m\overline{v^2} = \frac{3}{2}T$).
  - Most probable speed $\tilde{v}$: Find v where $F(v)$ is maximum. $\partial F/\partial v = 0$. Need $\partial/\partial v(v^2 e^{-mv^2/(2T)}) = 0$. $(2v)e^{-mv^2/(2T)} + v^2 e^{-mv^2/(2T)}(-mv/T) = 0$. $2v - mv^3/T = 0$. $2 = mv^2/T$. $v^2 = 2T/m$.

$$\tilde{v} = \sqrt{\frac{2T}{m}} \approx 1.414\sqrt{T/m}$$

  Ordering: $\tilde{v} < \overline{v} < v_{\text{RMS}}$.



Simple Examples in Kinetic Theory

"Kinetic Theory" = study of macroscopic properties of large numbers of particles starting from microscopic equations of motion (or distributions like $f(\vec{v})$). It can be used to study equilibrium and how systems reach equilibrium (transport phenomena). Here, only simplest equilibrium situations.

Number of Particles Striking a Surface (Flux)

Calculate the number of particles striking a unit area of a wall per unit time.

Consider particles with velocity $\vec{v}$. In time dt, particles within a slanted cylinder based on area dA on the wall, with height $v_z dt = (v\cos\theta)dt$ (where θ is angle to normal $\hat{z}$), will strike dA. Volume of cylinder $= (v_z dt)dA$. Number density of particles $n = N/V$. Number of particles in this volume $= n(v_z dt dA)$. Number of particles with velocity in $(\vec{v}, \vec{v} + d^3v)$ in this volume $= [f(\vec{v})d^3v] \times [nv_z dt dA]$. (This is valid only for particles moving towards the wall, i.e., $v_z > 0$).

Let $\Phi(\vec{v})d^3v$ be the number of particles with velocity $(\vec{v}, \vec{v} + d^3v)$ striking the wall per unit area per unit time. Divide the above expression by $dAdt$:

$$\Phi(\vec{v})d^3v = nf(\vec{v})v_z d^3v = nf(\vec{v})(v\cos\theta)d^3v \quad \text{(for } v_z > 0\text{)}$$

This is the differential particle flux.

The total particle flux Φ_0 (particles per area per time) striking the wall is obtained by integrating $\Phi(\vec{v})$ over all velocities directed towards the wall ($v_z > 0$, or $\theta \in [0, \pi/2]$).

$$\Phi_0 = \int_{v_z>0} \Phi(\vec{v})d^3v = \int_{v_z>0} nf(\vec{v})v_z d^3v$$

Use spherical coordinates $d^3v = v^2 dv \sin\theta d\theta d\phi$, $v_z = v\cos\theta$. $f(\vec{v})$ depends only on v.

$$\Phi_0 = n\int_0^\infty dv\, v^2 f(v) \int_0^{\pi/2} d\theta\, \sin\theta \int_0^{2\pi} d\phi(v\cos\theta)$$

Angle integrals: $\int_0^{2\pi} d\phi = 2\pi$. $\int_0^{\pi/2} \sin\theta\cos\theta d\theta = [\frac{1}{2}\sin^2\theta]_0^{\pi/2} = 1/2$.

$$\Phi_0 = n\int_0^\infty dv\, v^2 f(v)(v)(2\pi)(1/2) = \pi n \int_0^\infty v^3 f(v)dv$$

Recall the speed distribution $F(v) = 4\pi v^2 f(v)$ and average speed $\overline{v} = \int_0^\infty vF(v)dv = 4\pi\int_0^\infty v^3 f(v)dv$. So, $\int_0^\infty v^3 f(v)dv = \overline{v}/(4\pi)$.

$$\Phi_0 = \pi n(\overline{v}/(4\pi)) = \frac{1}{4}n\overline{v}$$

Using $\overline{v} = \sqrt{8T/(\pi m)}$:

$$\Phi_0 = \frac{1}{4}n\sqrt{\frac{8T}{\pi m}}$$

Using ideal gas law $p = nT$ (with T in energy units): $n = p/T$.

$$\Phi_0 = \frac{p}{4T}\sqrt{\frac{8T}{\pi m}} = p\sqrt{\frac{8T}{16\pi m T^2}} = p\sqrt{\frac{1}{2\pi m T}}$$

$$\Phi_0 = \frac{p}{\sqrt{2\pi m T}}$$

Application: Effusion Effusion is the process where molecules emerge from a small hole/slit in a container. "Small" means the hole does not significantly disturb the equilibrium of the gas inside. If the hole has area A, the number of particles emerging per unit time (rate I) is:

$$I = \Phi_0 \times A = \frac{pA}{\sqrt{2\pi m T}}$$

Since $I \propto 1/\sqrt{m}$, lighter molecules escape at a faster rate. This is used for isotopic separation (e.g., separating ^{235}U from ^{238}U for nuclear applications).

Pressure of Ideal Gas from Kinetic Theory

Pressure arises from the momentum transfer of particles colliding with the walls. Assume elastic collisions with a wall normal to $\hat{z}$. A particle with momentum $\vec{p} = m\vec{v}$ collides. p_x, p_y are unchanged. $p_z \to -p_z$. Change in particle momentum $\Delta\vec{p} = (0, 0, -2p_z)$. Momentum imparted to the wall $= -\Delta\vec{p} = (0, 0, +2p_z)$. The momentum transferred is $2p_z = 2mv_z$ (in z-direction).

Consider particles with velocity $(\vec{v}, \vec{v} + d^3v)$ hitting area dA in time dt. Number hitting $= nf(\vec{v})v_z d^3v\, dt\, dA$ (from flux calculation, for $v_z > 0$). Momentum transferred to wall by these particles in dt:

$$dp_{\vec{v},wall} = (\text{momentum per collision}) \times (\#\text{ collisions})$$

$$dp_{\vec{v},wall} = (2mv_z) \times (nf(\vec{v})v_z d^3v\, dt\, dA) = 2mnv_z^2 f(\vec{v})d^3v\, dt\, dA$$

Force on area dA due to these particles: $dF_{\vec{v}} = dp_{\vec{v},wall}/dt = 2mnv_z^2 f(\vec{v})d^3v\, dA$. Total force F on area dA: Integrate over all velocities hitting the wall ($v_z > 0$).

$$F = \int_{v_z>0} dF_{\vec{v}} = \left(\int_{v_z>0} 2mnv_z^2 f(\vec{v})d^3v \right) dA$$

Pressure $p = F/dA$:

$$p = 2mn \int_{v_z>0} v_z^2 f(\vec{v})d^3v$$

The integral $\int_{v_z>0} v_z^2 f(\vec{v})d^3v$ is the average of v_z^2 for particles moving towards the wall ($v_z > 0$). Since $f(\vec{v})$ depends only on v^2 (isotropic), the average for $v_z > 0$ is the same as for $v_z < 0$, and is half the average over all velocities:

$$\int_{v_z>0} v_z^2 f(\vec{v})d^3v = \frac{1}{2} \int v_z^2 f(\vec{v})d^3v = \frac{1}{2}\overline{v_z^2}$$

$$p = 2mn \left(\frac{1}{2}\overline{v_z^2} \right) = mn\overline{v_z^2}$$

Finally, using the equipartition result $\overline{v_z^2} = T/m$:

$$p = mn(T/m) = nT$$

This recovers the ideal gas law $p = nT$ (or $pV = NT$) from kinetic theory. ✓