Speed distributions and statistical ensembles

GRE undergraduate preparation · local supported objectives

Speed distributions and statistical ensembles

- Normalise and read probability densities.
- Use the **Maxwell distribution** 麦克斯韦分布 and its three typical speeds.
- Apply **equipartition** 能量均分.
- Find canonical probabilities with **degeneracy** 简并度.

Velocity is not speed

- Opposite velocities cancel in an average; speeds, which are always positive, do not.
- In still air the molecules' average velocity is zero, because every direction is equally likely.

Densities, not probabilities

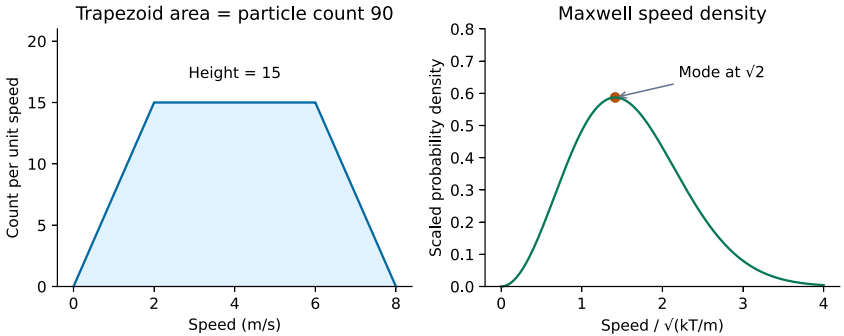
- f has units of $1/\text{speed}$, and $\int_0^\infty f(v)\,dv = 1$. A count density integrates to N instead.
- For a continuous distribution, the probability of one exact value is zero; only intervals carry probability.

The Maxwell distribution

- Most probable speed $\sqrt{2kT/m}$ < mean speed $\sqrt{8kT/\pi m}$ < **root-mean-square speed 方均根速率** $\sqrt{3kT/m}$.
- $f(0) = 0$ because of the v^2 factor, which counts the shell of velocity vectors with speed v.
- All speeds scale as $\sqrt{T/m}$: four times the temperature doubles them.

$$f(v) \propto v^2 \, e^{-mv^2/2kT}$$

Figure: The Maxwell distribution



- The area under a distribution counts the particles; the Maxwell mode is $\sqrt{(2kT/m)}$
- Read the axes and units first.

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Equipartition

- A molecule's translational kinetic energy has three terms, so its average is $\frac{3}{2}kT$.
- A diatomic molecule adds two rotational terms: $\frac{5}{2}kT$ in total, so $C_V = \frac{5}{2}R$ per mole.
- Quantum effects freeze out terms whose energy steps are large compared with kT (vibrations at room temperature).

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Canonical probabilities with degeneracy

- Each state counts equally, not each level.
- Ground level $g = 1$ and excited level $g = 2$ at a gap of $kT \ln 2$: weights 1 and $2 \times \frac{1}{2} = 1$. Each level has probability $\frac{1}{2}$, and each excited state $\frac{1}{4}$.

$$P(\text{level } i) = \frac{g_i \, e^{-E_i/kT}}{Z}$$

Worked example: normalising a trapezoid

- Area: $\frac{1}{2} a v_0 + 2 a v_0 + \frac{1}{2} a v_0 = 3 a v_0$.
- $3a(2.0) = 90$, so $a = 15$ particles per (m/s).
- Particles on the flat part: $15 \times 4.0 = 60$.

Worked example: nitrogen at 300 K

- rms speed: $\sqrt{3(1.38\times10^{-23})(300)/(4.65\times10^{-26})}=517$ m/s.
- Mean speed: $\sqrt{8/3\pi}\times517=476$ m/s. Most probable: $\sqrt{2/3}\times517=422$ m/s.
- At 1200 K, all three double.

Common errors

- Reading a density value as a probability.
- Giving a non-zero probability to one exact speed.
- Putting the peak of the Maxwell speed distribution at $v = 0$.

Common errors (2)

- Mixing up the order of the mode, mean and rms speeds.
- Forgetting the **degeneracy** g_i before dividing by Z.

Key terms

- **probability density**: A function whose area over an interval gives the probability of that interval.
- **Maxwell distribution**: The **probability density** of molecular speeds in an ideal gas in equilibrium.
- **root-mean-square speed**: The square root of the average of v^2.
- **equipartition**: Each quadratic energy term has an average of $\frac{1}{2}kT$ in classical equilibrium.

Check yourself

- The temperature of a gas is quadrupled. What happens to its rms speed?
- What is the probability that a molecule has a speed of exactly 400 m/s?
- A ground level ($g = 1$) and an excited level ($g = 3$) are $kT \ln 3$ apart. What is the probability of each level?