Lecture 4: Ideal monatomic gas

Statistical mechanics of the perfect gas

- **Aims:**
  - Key new concepts and methods:
    - Counting states
    - Waves in a box.
  - Demonstration that $\beta = 1/kT$
  - Heat, work and Entropy in statistical mechanics
    - Proof of Boltzmann’s conjecture
  - Maxwell distribution of velocities.
Ideal monatomic gas

Counting states:

- We need to quantise the atoms in the gas
- Waves in a box, a cube of side $a$.  
- Wavefunction vanishes at the edges.  
\[ \Psi(r,t) = A \sin\left(l\pi x/a\right)\sin\left(m\pi y/a\right)\sin\left(n\pi z/a\right) \]
With $l, m, n = 1, 2, 3, 4 \ldots$
- Plane standing waves with
\[ k = \frac{\pi}{a}\left(l^2 + m^2 + n^2\right)^{1/2} \]
\[ \varepsilon_{l,m,n} = \frac{\hbar^2 k^2}{2m} = \frac{\pi^2 \hbar^2}{2ma^2}\left(l^2 + m^2 + n^2\right) \]
- States form a (closely spaced) lattice of points.
- Calculate the mean energy of the gas using partition function.
\[ Z = \sum_i p_i = \sum_{l,m,n} \exp\left(-\beta \varepsilon_{l,m,n}\right) \]
\[ \langle \varepsilon \rangle = -\frac{1}{Z} \frac{dZ}{d\beta} \]
- To calculate $Z$ we need the “density of states”.
Density of states

- Exchange sum in $Z$ for an integral
  
  Need the density of states. i.e. no. of states in $d\varepsilon$ at energy $\varepsilon$, $g(\varepsilon) d\varepsilon$.

  It is the number of states in 1/8th of a spherical shell, width $dk$. (Remember $l, m, n > 0$)

\[ g(\varepsilon) d\varepsilon = g(k) dk = \frac{4\pi k^2 \, dk}{8} \cdot \left(\frac{\pi}{a}\right)^3. \]

Volume of shell

Vol. of one state

1 state “occupies a volume” of $(\pi/a)^3$
Mean energy of a gas

- Replace $k$ with $\sqrt{(2m\epsilon)/\hbar}$

$$g(\epsilon)\, d\epsilon = \left(\frac{a^3}{4\pi^2}\right)\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2} \, d\epsilon = A \epsilon^{1/2} \, d\epsilon$$

- Partition function

$$Z = \int_{0}^{\infty} g(\epsilon)\exp(-\beta\epsilon) \, d\epsilon$$

$$= \int_{0}^{\infty} A \epsilon^{1/2} \exp(-\beta\epsilon) \, d\epsilon \quad x^2 = \beta\epsilon$$

$$= \frac{1}{\beta^{3/2}} \int_{0}^{\infty} A \exp(-x^2)x^2 \, dx$$

- Integral is simply a constant

$$\langle \epsilon \rangle = -\frac{1}{Z} \frac{dZ}{d\beta} = \frac{3}{2\beta}$$

- Kinetic theory shows $\langle \epsilon \rangle = 3kT/2$. Thus,

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

in agreement with our earlier guess.
Adiabatic changes

♦ Note:

- We can derive the law of adiabatic compression from the density of states.

\[ \varepsilon_{l,m,n} \propto \frac{1}{a^2} \propto V^{-2/3} \]

- Now compress box.
  - Energy levels all raise. BUT
  - Particles remain in the same states. \( p(\varepsilon_i) \) does not change. So,
    \[ \langle \varepsilon \rangle V^{2/3} = \text{const} \]
    or
    \[ TV^{2/3} = \text{const} \]
  - Quantum theory and Statistical mechanics confirm the results of classical thermodynamics.
Heat and Work

- **System of non-interacting particles.**
  - Energy levels $\varepsilon_i$, and occupation numbers $n_i$.
  - Internal energy $U$.
  
  \[
  U = \sum_i n_i \varepsilon_i 
  \]
  
  \[
  dU = \sum_i (\varepsilon_i \, dn_i + n_i \, d\varepsilon_i) 
  \]

We, thus, have a consistent view of heat and work in statistical mechanics.

- **Heat**: changes the occupation of energy levels (no change in the levels).
- **Work**: changes the energy levels themselves (no change in the occupations).
We avoided calculating the entropy, which is

\[ S = k \ln(g) \]

If \( U \) is defined exactly then \( g \) is a small number, e.g. 0, 1, 2… An unreasonable value!

If \( U \) is slightly ill-defined, say by \( dU \), the number of configurations is \( g(U)dU \). BUT, what value of \( dU \) do we use?

Answer: it doesn’t matter (much), as the following rough calculation shows:

- Typical entropy of a macroscopic body is \( 1 \text{ JK}^{-1} \).
- Compare \( \ln(g(U) \, dU) \) with
  - \( dU = 1 \) Joule and
  - \( dU = 10^{-100} \) J (=10^{-81}eV).
- Difference in \( S \) is
  \[ k \ln(10^{-100}) = -230 \, k = 3.2 \times 10^{-21} \text{ JK}^{-1} \]
- Difference is irrelevant!
Maxwell distribution

- The Boltzmann distribution gives the mean energy and the distribution of speeds:
  \[ \exp(-\varepsilon/kT) = \exp\left(-\frac{1}{2}m\left(u^2 + v^2 + w^2\right)/kT\right) \]

- The velocity distribution, a 3-D Gaussian.

- To get the distribution of speeds we add all probabilities lying inside a spherical-shell of thickness \(dc\).

\[
p(c) \, dc \propto 4\pi c^2 \, dc \exp\left(-mc^2/2kT\right)
\]

\[
p(c) \, dc = \frac{4\pi c^2 \, dc \exp\left(-mc^2/2kT\right)}{\int_0^\infty 4\pi c^2 \, dc \exp\left(-mc^2/2kT\right)}
\]

\[
p(c) \, dc = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi c^2 \, dc \exp\left(-mc^2/2kT\right)
\]