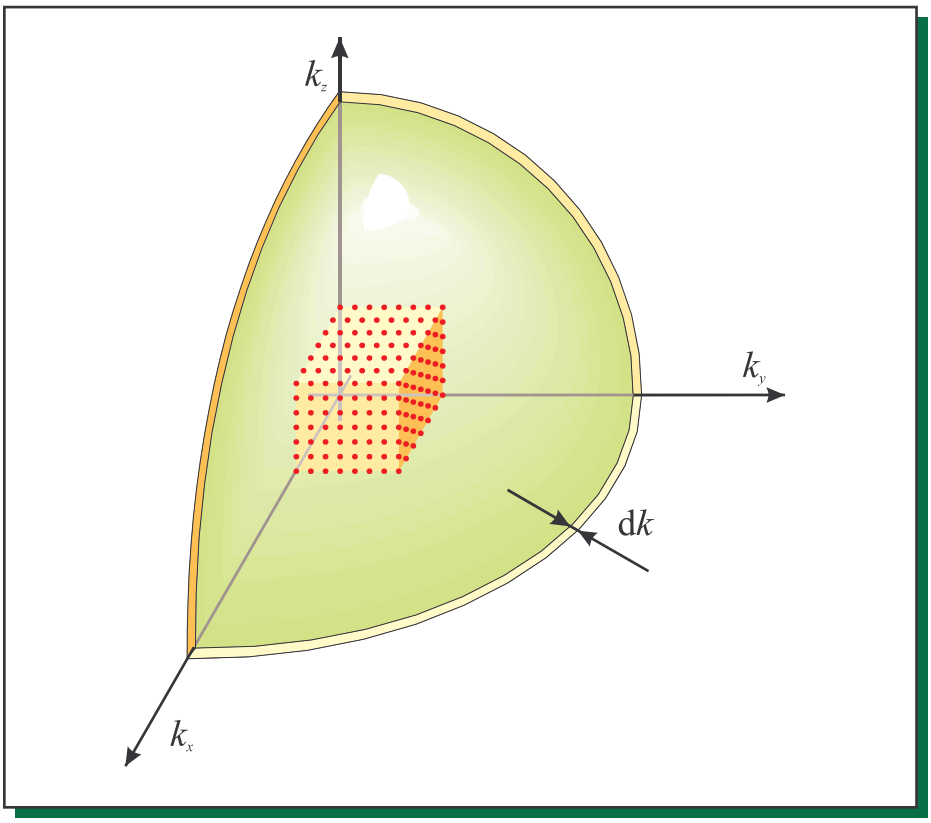
Lecture 4: Ideal monatomic gas

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.

$$\Psi(r,t) = A\sin(l\pi\, x/a)\sin(m\pi\, y/a)\sin(n\pi\, z/a)$$

With $l,\ m,\ n = 1,2,3,4\ldots\ldots$

  - 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.

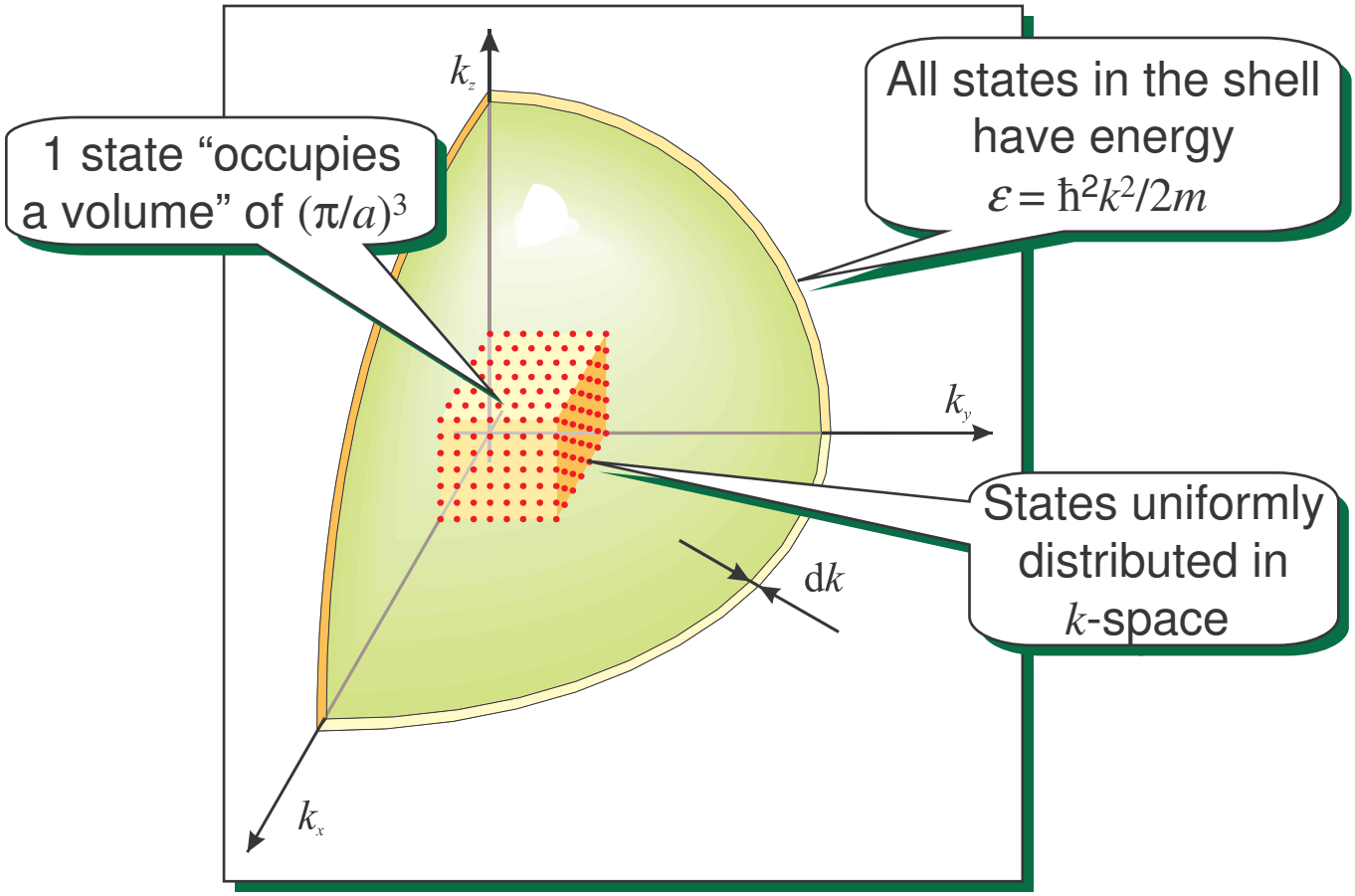
$$Z = \sum_i p_i = \sum_{l,m,n} \exp\left(-\beta\varepsilon_{l,m,n}\right)$$

$$\langle\varepsilon\rangle = -\frac{1}{Z}\frac{\mathrm{d}Z}{\mathrm{d}\beta}$$

  - 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 $\mathrm{d}\varepsilon$ at energy ε, $g(\varepsilon)\mathrm{d}\varepsilon$.
  - It is the number of states in 1/8th of a spherical shell, width $\mathrm{d}k$. (Remember $l, m, n > 0$)



- $$g(\varepsilon)\mathrm{d}\varepsilon = g(k)\mathrm{d}k = \left(\frac{4\pi k^2\,\mathrm{d}k}{8}\right) \Big/ \left(\frac{\pi}{a}\right)^3.$$

Volume of shell

Vol. of one state

Mean energy of a gas

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

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

- Partition function

$$Z = \int_0^\infty g(\varepsilon)\exp(-\beta\varepsilon)\,\mathrm{d}\,\varepsilon$$

$$= \int_0^\infty A\varepsilon^{1/2}\exp(-\beta\varepsilon)\,\mathrm{d}\,\varepsilon \qquad x^2 = \beta\varepsilon$$

$$= \frac{1}{\beta^{3/2}}\int_0^\infty A\exp\left(-x^2\right)x^2\,\mathrm{d}\,x$$

Integral is simply a constant

- $$\langle\varepsilon\rangle = -\frac{1}{Z}\frac{\mathrm{d}\,Z}{\mathrm{d}\,\beta} = \frac{3}{2\beta}$$

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

$$\boxed{\beta = 1/kT}$$

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,

      $$\langle \varepsilon \rangle V^{2/3} = const$$

      or

      $$T V^{2/3} = const$$
  - Quantum theory and Statistical mechanics confirm the results of classical thermodynamics.

Heat and Work

- System of non-interacting particles.
  - Energy levels ε_i, and occupation numbers n_i.
  - Internal energy U.

$$U = \sum_i n_i \varepsilon_i$$

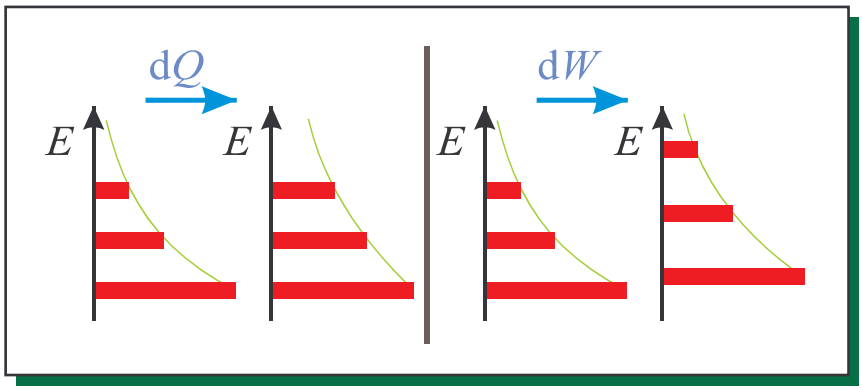
$$\mathrm{d}U = \sum_i \left(\varepsilon_i \, \mathrm{d}n_i + n_i \, \mathrm{d}\varepsilon_i\right)$$

Change in populations, with energy levels fixed

Change in energy levels, populations fixed

$$= \underbrace{T\,\mathrm{d}S}_{\mathrm{d}Q} - \underbrace{p\,\mathrm{d}V}_{\mathrm{d}W}$$

  - 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).



A (minor) problem with entropy

- Entropy
  - We avoided calculating the entropy, which is

$$S = k \ln(g)$$

Number of configurations

A pure number

  - 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 $\mathrm{d}U$, the number of configurations is $g(U)\mathrm{d}U$. BUT, what value of $\mathrm{d}U$ do we use?
  - Answer: it doesn't matter (much), as the following rough calculation shows:
    - Typical entropy of a macroscopic body is $1\ \mathrm{JK}^{-1}$.
    - Compare $\ln(g(U)\ \mathrm{d}U)$ with
      - $\mathrm{d}U$ =1 Joule and
      - $\mathrm{d}U$ =10^{-100} J ($\approx 10^{-81}$eV).
      - Difference in S is

$$k \ln(10^{-100}) = -230\ \mathrm{k} = 3.2\mathrm{x}10^{-21}\ \mathrm{J\ K}^{-1}.$$

  - Difference is irrelevant!

Maxwell distribution

- The Boltzmann distribution gives the mean energy and the distribution of speeds:

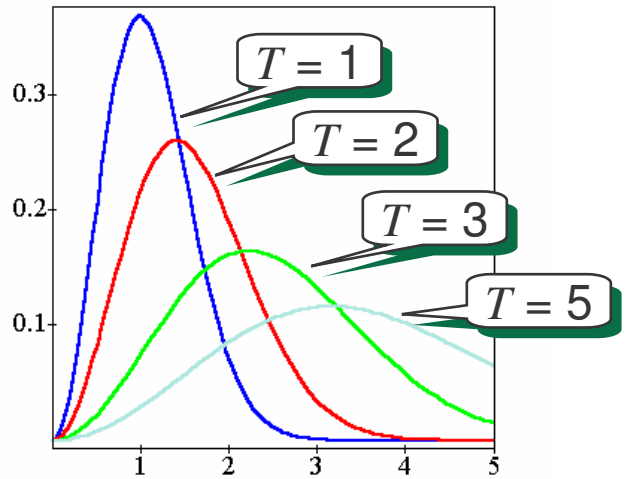
$$\exp(-\varepsilon/kT) = \exp\left(-\frac{1}{2}m\left(u^2+v^2+w^2\right)/kT\right)$$

- The velocity distribution, a 3-D Gaussian.
- To get the distribution of speeds we add all probabilities lying inside a spherical-shell of thickness $\mathrm{d}c$.

$$p(c)\,\mathrm{d}c \propto 4\pi c^2\,\mathrm{d}c\,\exp\left(-mc^2/2kT\right)$$

$$p(c)\,\mathrm{d}c = \frac{4\pi c^2\,\mathrm{d}c\,\exp\left(-mc^2/2kT\right)}{\int_0^\infty 4\pi c^2\,\mathrm{d}c\,\exp\left(-mc^2/2kT\right)}$$

Standard integral



$$p(c)\,\mathrm{d}c = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi c^2\,\mathrm{d}c\,\exp\left(-mc^2/2kT\right)$$