Average Particle Energy in an Ideal Gas

- the total energy of the system is found by summing up (integrating) over all particles \( n(\varepsilon) \) at different energies \( \varepsilon \)

\[
E = \int_0^\infty \varepsilon \, n(\varepsilon) \, d\varepsilon = \frac{2\pi N}{(kT)^{3/2}} \int_0^{3/2} \varepsilon^{1/2} \, e^{-\varepsilon/kT} \, d\varepsilon
\]

- with the integral

\[
\int_0^{3/2} x^{1/2} \, e^{-\beta x} \, dx = \frac{3}{4} \beta^{1/2} \sqrt{\frac{\pi}{\beta}}
\]

- we find

\[
E = \frac{2\pi N}{(kT)^{3/2}} \left( \frac{3}{4} \right) \left( \frac{kT}{2\pi} \right)^{1/2} \frac{1}{\sqrt{\pi}} = \frac{3}{2} kT
\]

- note:
  - the total energy is proportional to temperature \( T \) and the number of particles \( N \)
  - the energy is independent of the specifics of the particle, e.g. its mass

- average energy per particle

\[
\overline{\varepsilon} = \frac{E}{N} = \frac{3}{2} kT
\]

- characteristic energy per particle at room temperature \( T = 300 \, K \)

\[
\overline{\varepsilon} = \frac{3}{2} kT \approx \frac{1}{25} \, eV
\]

The Equipartition Theorem

in thermal equilibrium at temperature \( T \) the average energy \( \overline{\varepsilon} \) stored in a particle with \( f \) degrees of freedom is

\[
\overline{\varepsilon} = \frac{1}{2} \, f \, kT
\]

- there are \( f = 3 \) independent degrees of freedom for linear motion along the \( x, y, z \) coordinates

\[
\overline{\varepsilon}_{lin} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}
\]

- in a diatomic molecule there are additionally \( f = 2 \) rotational degrees of freedom along the two axis perpendicular to the bond axis

\[
\overline{\varepsilon}_{rot} = \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2
\]

- any harmonic oscillator has \( f = 2 \) vibrational degrees of freedom

\[
\overline{\varepsilon}_{vib} = \frac{p_x^2}{2m} + \frac{\omega_x^2}{2}
\]

any independent degree of freedom per particle (e.g. position or momentum) that appears quadratically in the total energy (Hamiltonian) of a system contributes \( 1/2 \, k \, T \) to its average energy.
Maxwell-Boltzmann Velocity Distribution

- the velocity distribution of particles in an ideal gas can be found from the energy distribution

\[ \mathcal{E} = \frac{1}{2} m v^2 \quad \text{with} \quad d\mathcal{E} = m v \, dv \]

- thus the number of particles with velocity in an interval $dv$ around $v$ is

\[ n(v) \, dv = 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 \, e^{-m v^2 / 2 kT} \, dv \]

- plot of Maxwell's velocity distribution

- rms (root-mean-squared) velocity of a molecule with average energy of $3/2 \, kT$ (from equipartition theorem)

\[ \left< \frac{1}{2} m v^2 \right> = \frac{3}{2} kT \]

\[ \Rightarrow \quad \sqrt{\left< v^2 \right>} = \sqrt{\frac{3kT}{m}} \]

Differences between most probable, average and rms particle velocity

- rms velocity

\[ \sqrt{\left< v^2 \right>} = \sqrt{\frac{3kT}{m}} \]

- most probable velocity

\[ v_p = \sqrt{\frac{2kT}{m}} \]

\[ \text{from} \quad \frac{dn(v)}{dv} = 0 \]

- average velocity

\[ \bar{v} = \frac{1}{N} \int v \, n(v) \, dv = \sqrt{\frac{8kT}{\pi m}} \]

note: - both the average velocity and the rms velocity are larger than the most probable velocity
Variation of Velocity Distribution

- velocity distribution of oxygen (O2) at two different temperatures
- velocity distribution of hydrogen (H) at 273 K
- increase of velocity with decrease in mass \( \sim m^{-1/2} \) and increase of temperature \( \sim T^{1/2} \)

- average velocity:
  \[
  \bar{v} = \frac{1}{V} \int v m(v) \, dv = \sqrt{\frac{8 k T}{\pi m}}
  \]

- example He:
  mass: \( 4 \frac{g}{mol} = 6.6 \times 10^{-27} \text{ kg per atom} \)
  \[
  \bar{v} = 1285 \sqrt{\frac{m}{M}} \text{ at } T = 300 \text{ K}
  \]
  de Broglie wave length
  \[
  \lambda = \frac{h}{m \bar{v}} = 7.7 \times 10^{-12} \alpha \frac{1}{\sqrt{T}}
  \]

Statistics of Quantum Particles

- bosons are indistinguishable particles with symmetric wave functions
  \[
  \Psi_{B}^{(1,2)} = \frac{1}{\sqrt{2}} \left( \Psi_{a}^{(1)} \Psi_{b}^{(2)} + \Psi_{a}^{(2)} \Psi_{b}^{(1)} \right)
  \]
- bosons can be in the same quantum state
  \[
  \Psi_{B}^{(1,2)} = \frac{1}{\sqrt{2}} \left( \Psi_{a}^{(1)} \Psi_{a}^{(2)} + \Psi_{a}^{(2)} \Psi_{a}^{(1)} \right) = \frac{2}{\sqrt{2}} \Psi_{a}^{(1)} \Psi_{a}^{(2)}
  \]
- for bosons the presence of a particle in a certain quantum state increases the probability of other particles to be found in that state
- their statistics is described by the Bose-Einstein distribution function
  \[
  f_{BE}(E) = \frac{1}{e^{\frac{E}{kT}} - 1}
  \]
- for photons \( \alpha = 0 \), generally \( \alpha \) depends on the system parameters and is determined from the normalization condition
  \[
  N = \oint g(c) f_{BE}(E) \, dE = \oint \varepsilon m(c) \, d\varepsilon
  \]
- the distribution function is named after the Indian physicist Bose and after Einstein who extended Bose's original calculation for photons to massive particles
- Fermions are indistinguishable particles with anti-symmetric wave functions

\[ \psi_F(1,2) = \frac{1}{\sqrt{2}} \left( \psi_a(1) \psi_b(2) - \psi_a(2) \psi_b(1) \right) \]

- Particles with anti-symmetric wave function cannot be in the same state

\[ \psi_F(1,2) \cdot \frac{1}{\sqrt{2}} \left( \psi_a(1) \psi_a(2) - \psi_a(2) \psi_a(1) \right) = 0 \]

- For fermions, the presence of a particle in a certain state prevents any other particles from being in that state.

- Their statistics is described by the Fermi-Dirac distribution function

\[ f_{FD} = \frac{1}{e^\frac{\varepsilon}{kT} + 1} \]

- The Fermi energy is defined by

\[ f_{FD}(\varepsilon_F) = \frac{1}{2} \Rightarrow \varepsilon_F = -\alpha kT \]

- The distribution function is named after Enrico Fermi and Paul Dirac who realized that the exclusion principle would lead to statistics different from that for bosons or classical particles.

**Comparison of the different distribution functions**

- \( f_{BE} > f_{MB} > f_{FD} \) at any temperature.

- In the large \( kT \) limit, all distribution functions approach the Maxwell-Boltzmann distribution.

**Fermi-Dirac distribution function in terms of the Fermi energy \( \varepsilon_F \)**

\[ f_{FD}(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} \]

- Consider the Fermi-Dirac distribution function in the zero temperature limit.

- This allows one to draw some important conclusions about the relevance of \( \varepsilon_F \) for electrons in metals.

- Later we will calculate the energy of free electrons in a metal and also their specific heat.
FD - Distribution function at $T = 0$

$$ f(T = 0, \varepsilon < \varepsilon_F) = \frac{1}{e^{\varepsilon/\varepsilon_F} + 1} = \frac{1}{e^0 + 1} = 1 $$

$$ f(T = 0, \varepsilon > \varepsilon_F) = \frac{1}{e^{\varepsilon/\varepsilon_F} + 1} = \frac{1}{e^0 + 1} = 0 $$

- all states at $\varepsilon < \varepsilon_F$ are occupied $f = 1$
- all states at $\varepsilon > \varepsilon_F$ are empty $f = 0$

- for a systems with $N$ electrons the Fermi energy is determined by filling up all states string from $\varepsilon = 0$ obeying the exclusion principle until all states are filled at $\varepsilon = \varepsilon_F$

- as $T$ is increased from zero electrons below the Fermi energy will fill up states above the Fermi energy
- for temperatures on the order of the Fermi energy the occupation even at low energies will be reduced and states at higher energies will be filled

Blackbody Radiation

- consider a thermal emitter of radiation, called a blackbody, as a cavity at temperature $T$ filled with photons
- considering the cavity as a box with perfectly reflecting walls, then the radiation inside the box must be standing electromagnetic waves
- the standing waves must have wavelengths $\lambda$ the half integer multiples of which correspond to the cavity length $L = j \lambda/2$
- for a cubic cavity of dimension $L^3$ the number $j$ of half integer wavelengths along each dimension $x, y, z$ is

$$ j_x = \frac{2L}{\lambda} = 1, 2, 3, ... $$
$$ j_y = \frac{2L}{\lambda} = 1, 2, 3, ... $$
$$ j_z = \frac{2L}{\lambda} = 1, 2, 3, ... $$

- for a standing wave in an arbitrary direction

$$ j_x^2 + j_y^2 + j_z^2 = \left(\frac{2L}{\lambda}\right)^2 $$

$$ j_x, j_y, j_z \in \{0, 1, 2, ...\} $$

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Counting the Number of Photon Modes in a Cavity

- number of modes $g(\lambda) \, d\lambda$ in the cavity with wavelengths $\lambda$ in the interval $d\lambda$

- consider a vector $\mathbf{j}$ with length

$$j = \sqrt{j_x^2 + j_y^2 + j_z^2}$$

- in the interval $dj$ around $j$ there is a number of combinations of $j_x, j_y, j_z$ that result in the same absolute value of $j$ and thus the same wavelength

- the total number of $\mathbf{j}$ states with positive $j_1$ is

$$\frac{1}{8} 4\pi j^2 \, dj = \frac{\pi j^2}{2} \, dj$$

- as there are two different polarizations for the standing waves

$$g(\mathbf{j}) \, dj = \pi j^2 \, dj$$

with $\mathbf{j} = \frac{2L}{\lambda} = \frac{2Lv}{c}$

- number of standing waves

$$g(\nu) \, d\nu = \pi \left( \frac{2Lv}{c} \right)^2 \frac{2L}{\lambda} \, d\nu = \frac{8\pi v^2}{c^3} L^3 \, d\nu$$

Density of Standing Waves per Volume

- the number of modes per unit volume is found by dividing by the cavity volume $L^3$

$$G_1(\nu) \, d\nu = \frac{1}{L^3} \, g(\nu) \, d\nu = \frac{8\pi v^2}{c^3} \, d\nu$$

- the number of possible modes increases quadratically with frequency and is independent of the shape of the cavity

- from the classical equipartition theorem we expect every mode in thermal equilibrium at temperature $T$ to contribute an energy of $kT$ (there are two degrees of freedom per mode that can be described as a harmonic oscillator) to the total energy

- thus the energy density of the radiation in the cavity is

$$u(\nu) \, d\nu = \frac{E}{G_1(\nu) \, d\nu} = \frac{kT}{c^3} G_1(\nu) \, d\nu$$

$$= \frac{8\pi v^2}{c^3} kT \, d\nu$$

- this is the Rayleigh-Jeans formula that is accurate only for $\nu$ small in comparison to $kT$

- this energy density diverges (ultraviolet catastrophe) for large $\nu$ and thus must be wrong, this problem could not be resolved with just classical physics
Planck Radiation Law:
- as photons are bosons the Bose-Einstein distribution function should hold for describing their statistical properties
\[
\Delta_{BE}(v) = \frac{1}{e^{\frac{h}{kT}} - 1}
\]
- the energy per mode is
\[
\frac{h}{v} \Delta_{BE}(v) = \frac{h}{e^{\frac{h}{kT}} - 1}
\]
- the total energy density of the cavity is then
\[
\frac{h}{v^3} \Delta_{BE}(v) = \frac{8 \pi^3}{c^5} \frac{h^3}{e^{\frac{h}{kT}} - 1} d\nu
\]
- this formula is known as the Planck law of blackbody radiation (we will also discuss Einstein's derivation of this equation)
- it describes the radiation spectrum emitted by any body at a thermal equilibrium temperature $T$ (e.g. the sun, light bulbs)

Black Body Spectrum
- fusion ($H_2 \rightarrow He$)
- power $\sim 100. 10^9$ GW
- temperature $T \sim 6000$ Kelvin
- continuous spectrum
- power on earth $1 \text{ kW/m}^2$
- largest intensity in visible part of the spectrum
Wien's Displacement Law:

- find the wavelength at which the spectral density of the emitted radiation is maximum

- express the Planck law in terms of wave lengths $\lambda$

- calculate the derivative

$$\frac{dU(\lambda)}{d\lambda} = 0 \quad \Rightarrow \quad \lambda = \lambda_{\text{max}}$$

- the result is Wien's displacement law

$$\lambda_{\text{max}} T = \frac{h c}{4.965 \, \text{k}} = 2.9 \times 10^{-3} \, \text{m} \cdot \text{k}$$

- shows that the wavelength of maximum radiation emission shifts to lower values as $T$ increases, e.g. bodies at a few thousand degrees emit visible radiation whereas bodies at room temperature emit infrared radiation

- example: the sun

$$T = 6000 \, \text{k}$$

$$\lambda_{\text{max}} = 480 \, \text{nm}$$
Stefan-Boltzmann Law

- find the total energy density of a black body at temperature $T$

$$u = \int_0^\infty u(v) \, dv = \frac{8\pi^5 k^4}{15\epsilon^3 c^3} \, T^4 = a T^4$$

- with a universal constant $a$
- note that the total energy depends on the fourth power of temperature

- the energy $R$ radiated by an object per unit time and unit area is also proportional to $T^4$
  as stated in the Stefan-Boltzmann law

$$R = \varepsilon a T^4$$

- with the Stefan constant

$$\sigma = \frac{a c}{4} = 5.67 \times 10^{-8} \frac{W}{m^2 \cdot K^4}$$

- and the emissivity $\varepsilon$ of the blackbody which can range form 0.07 for polished steel to 0.97 for matte black paint