

Structure of Matter

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29 March 2024

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1 Introduction

This article is produced with truth, beauty, and hatred.

2 Preliminaries

There are **extensive** and **intensive** properties of matter. The volume V , mass m , amount n , and number of particles N are all extensive ones.

Any ratio of the extensive quantities becomes intensive, like the density ρ and the number density n_d .

The equation of state relates many quantities together:

$$pV = Nk_B T = nRT, \quad (1)$$

where $k_B \approx 1.381 \times 10^{-23} \text{ JK}^{-1}$ is the **Boltzmann's constant** and $R \approx 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ is the **gas constant**. They are related to the **Avogadro's number**:

$$\frac{R}{k_B} = \frac{N}{n} = N_A \approx 6.022 \times 10^{23} \text{ mol}^{-1}. \quad (2)$$

3 Atomic Structure & Bonding

Electrons and nuclei are bound by the Coulomb forces. The Coulomb potential, with spherical symmetry, is exactly a central potential, so the states of the electrons are described by the complete set of corresponding compatible observables:

$$\{\hat{\mathcal{H}}, \hat{L}^2, \hat{L}_3, \hat{S}_3\} \Rightarrow \{n, l, m_l, m_s\}. \quad (3)$$

We will apply the ansatz that these 4 quantum numbers (principal, angular momentum, magnetic, and spin) still apply to the states of any many-electron atom, which they don't in atomic physics.

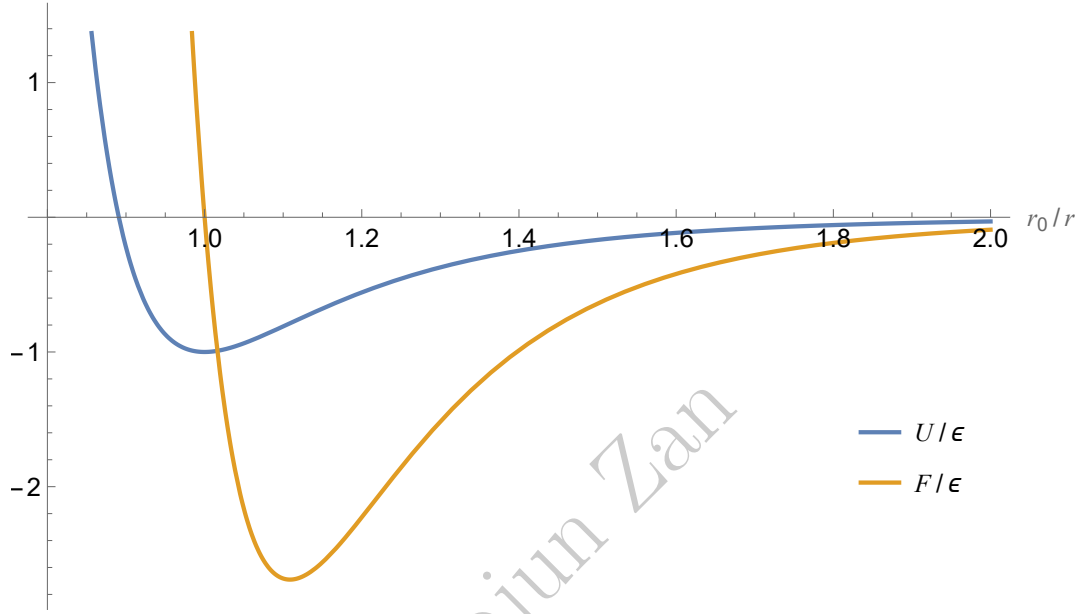
There are strong chemical bonds like ionic, covalent, and metallic ones. When it comes to IMF's, the Van der Waals force (IMF's in theoretical model) plays the chief role. The **Lennard-Jones potential** is one of the best empirical fits. The attractive force is given by the **London interaction**, and the repulsive force is given by **Pauli repulsion**. The combined potential is

$$U_{LJ} = \epsilon \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right], \quad (4)$$

where ϵ is the binding energy between the atoms and r_0 is the equilibrium separation. The corresponding force is given by

$$F = -\frac{dU}{dr} = 12\frac{\epsilon}{r} \left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6 \right]. \quad (5)$$

The following plot shows a graph of scaled U and F against scaled distance.



4 Solids

We shall investigate the properties of solids under changes of thermal and mechanical variables T and F .

4.1 Temperature Changes

Typically, solids expand due to temperature increases:

$$\frac{dL}{dT} = \alpha L, \quad (6)$$

where α is the **coefficient of thermal expansion** (units in K^{-1}). For small changes in length,

$$L = L_0(1 + \alpha\Delta T). \quad (7)$$

4.2 Elastic Deformation

The response of an object to a force is characterized by the material's **elastic modulus**. There are a total of three main elastic moduli. They all are ratios of stress to strain and are all intensive variables with units in Pa:

$$\begin{cases} \text{Stress:} & \text{applied force per unit area;} \\ \text{Strain:} & \text{relative amount of deformation.} \end{cases} \quad (8)$$

4.2.1 Young's Modulus

The Young's modulus is defined with an external force parallel to the surface normal. We define the **tensile stress** as the force per cross sectional area and the **tensile strain** as the ratio of change in length to original length. From these two we define the **Young's modulus**:

$$\sigma_t = \frac{F}{A}, \quad \epsilon_t = \frac{\Delta L}{L} \Rightarrow Y = \frac{\sigma_t}{\epsilon_t} = \frac{LF}{A\Delta L}. \quad (9)$$

4.2.2 Shear Modulus

The shear modulus is defined with the external force perpendicular to the surface normal. The **shear stress** is the force per area over which the force is applied, and the **shear strain** is the ratio of horizontal displacement (ΔL) to object thickness (t). From these two we define the **shear modulus**:

$$\sigma_s = \frac{F}{A}, \quad \epsilon_s = \frac{\Delta L}{t} \Rightarrow S = \frac{\sigma_s}{\epsilon_s} = \frac{tF}{A\Delta L}. \quad (10)$$

4.2.3 Bulk Modulus

If the material experiences uniform external pressure (like hydrostatic pressure), we define the **volumetric strain** as the ratio of change in volume ($\Delta V < 0$ for compression) to the original volume:

$$\text{Volumetric strain} = \frac{\Delta V}{V}. \quad (11)$$

Hence, the **bulk modulus** is

$$B = -\frac{p}{\Delta V/V}. \quad (12)$$

Elastic deformation only occurs in solids over a certain range of forces. Once a force reaches a certain threshold value, then the solid would either break or start to undergo plastic deformation.

5 Fluids

We define the dynamical viscosity of the fluid with the equation

$$\tau = \mu \frac{du}{dy}, \quad (13)$$

where τ is the force per unit area applied to the surface of the fluid, and du/dy is the velocity gradient. μ is the **dynamical viscosity**, in units of Pa s.

The **kinematic viscosity** (units in m^2s^{-1}) is defined as the ratio of dynamic viscosity to density:

$$\nu = \frac{\mu}{\rho}. \quad (14)$$

The hydrostatic equation for the variation in pressure with respect to height or depth in fluid is given by

$$\frac{dp}{dz} = -\rho g. \quad (15)$$

For incompressible fluids (typically, liquids) the formula is

$$p = p_0 + \rho gh. \quad (16)$$

In the case of gases (compressible fluids), the number density is found to be related by the equation

$$n_d = n_0 \exp\left(-\frac{mgz}{k_B T}\right), \quad (17)$$

where $\lambda = k_B T/mg$ is called the scale length. To derive this equation, we can return to the hydrostatic equation and the ideal gas equation:

$$\frac{dp}{dz} = -g\rho = -g \frac{mN}{V} = -g \frac{mp}{k_B T}.$$

When we measure pressure on a gauge, we are measuring **gauge pressure**, which is the pressure relative to the atmospheric pressure. Therefore,

$$\text{Absolute pressure} = \text{Atmospheric pressure} + \text{Gauge pressure}. \quad (18)$$

6 Velocity Distribution in Ideal Gas Particles

By Boltzmann's formula, for a system in thermal equilibrium,

$$\mathbb{P}[E \in (E_0, E_0 + dE)] \propto \exp\left(-\frac{E_0}{k_B T}\right) \quad (19)$$

up to a normalization constant. For 1D velocity component, we can identify

$$A \int_0^\infty dv_x \exp\left(-\frac{mv_x^2}{2k_B T}\right) = 1,$$

and this gives

$$f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{mv_x^2}{2k_B T}\right). \quad (20)$$

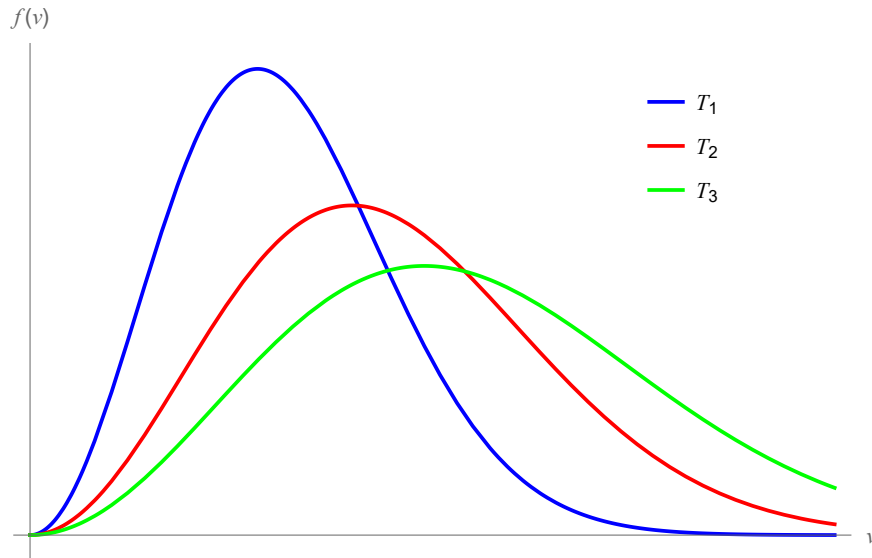
To derive the 3D speed distribution, we can multiply the three individual components together:

$$d\mathbb{P} = d^3\mathbf{v} A^3 \exp\left(-\frac{mv^2}{2k_B T}\right).$$

The speed distribution implies the use of spherical coordinates. Therefore,

$$\begin{aligned} f(v) &= \frac{d\mathbb{P}}{dv} = \int \sin\theta d\theta \int d\phi v^2 A^3 \exp\left(-\frac{mv^2}{2k_B T}\right) \\ &= \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right). \end{aligned} \quad (21)$$

The following graph shows the Maxwell-Boltzmann distribution at temperatures $T_1 < T_2 < T_3$:



From the above we define the average speed, the most probable speed, and the root-mean-squared speed:

$$\langle v \rangle = \int dv v f(v) = 2\sqrt{2} \sqrt{\frac{k_B T}{m}}, \quad (22)$$

$$\frac{df}{dv} = 0 \Rightarrow v_p = \sqrt{2} \sqrt{\frac{k_B T}{m}}, \quad (23)$$

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{3} \sqrt{\frac{k_B T}{m}}. \quad (24)$$

Also, the mean translational energy follows the rms speed:

$$\langle K \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T. \quad (25)$$

7 Ideal Gases

The internal energy U is the expectation value of the total energy. If the total energy is just the kinetic energy, we see

$$U = \frac{3}{2} N k_B T = \frac{3}{2} pV. \quad (26)$$

This further indicates that

$$p = \frac{1}{3} N m \langle v^2 \rangle = \frac{1}{3} \rho \langle v^2 \rangle. \quad (27)$$

The mean free path is the average distance between collisions:

$$\lambda = \frac{1}{\sqrt{2} n_d \pi d^2}, \quad (28)$$

where d is the diameter of the particle.

Ironically, as the lecture notes said, the derivation can be found in many sources.

8 Heat Capacity & Transfer

The heat capacity is the amount of heat needed to raise the temperature by an unit:

$$C = \frac{\delta Q}{dT}. \quad (29)$$

This is an extensive property, so we want to divide it by an extensive quantity to get an intensive one. From this we find specific heat capacity and molar heat capacity.

The **heat conduction** mainly occurs in solids and near-solids. Fourier's law of heat conduction in 1D is

$$\frac{dQ}{dt} = -\lambda A \frac{dT}{dx}, \quad (30)$$

where λ is the thermal conductivity. In 3D we see

$$\mathbf{q} = -\lambda \nabla T, \quad (31)$$

where \mathbf{q} is the heat flux density.

If we identify the thermal diffusivity, which measures how quickly a material dissipates its thermal energy,

$$\kappa = \frac{\lambda}{\rho c}, \quad (32)$$

with density ρ and specific heat capacity c , we can get the heat equation:

$$\frac{\partial T}{\partial t} = \kappa \nabla^2 T. \quad (33)$$

Convection is a means of both heat and material transfer in fluids and is usually the dominant method of heat transfer in fluids.

The distribution of heat is partly by conduction in the fluid and partly by bulk movement of the material (advection).

If a fluid is heated, the relative amounts of conduction and convection are defined by the Rayleigh number:

$$R = \frac{g\beta\Delta TL^3}{\nu\kappa}, \quad (34)$$

where g is the gravitational field strength, β the thermal expansivity, ν the fluid kinematic viscosity, and some other atrocious symbols.

Finally, **radiation** is only significant when the objects are much hotter than those that transfer heat mainly by conduction and convection. The Stefan-Boltzmann equation describes the rate of emission of energy:

$$\frac{\delta Q}{dT} = A\epsilon\sigma T^4, \quad (35)$$

where A is the surface area of the objects, ϵ is the emissivity (unity for a black body), and σ is the Stefan-Boltzmann constant:

$$\sigma \approx 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}. \quad (36)$$

9 “Bonus”: Derivation of Ideal Gas Law & Mean Free Path

9.1 Ideal Gas Law

Assuming azimuthal symmetry, we can find the fraction of molecules in polar angles $\theta \sim \theta + d\theta$ ($\theta = 0$ points to the direction of the walls):

$$\text{fraction} = \frac{d\Omega}{4\pi} = \frac{1}{4\pi} \frac{dS}{r^2} = \frac{1}{4\pi} \int d\phi \sin \theta d\theta = \frac{1}{2} \sin \theta d\theta. \quad (37)$$

Therefore, we found the number of molecules with particular speed and direction per unit volume:

$$\tilde{n}(v, \theta) = n \cdot f(v) dv \cdot \frac{1}{2} \sin \theta d\theta. \quad (38)$$

The number of molecules hitting a wall in time dt is:

$$dV = Av \cos \theta dt \Rightarrow dN = \tilde{n} dV. \quad (39)$$

As we also know the momentum change $\Delta p = 2mv \cos \theta$, we can work out the pressure:

$$\begin{aligned} p &= \frac{dp/dt}{A} = \iint 2mv \cos \theta \cdot v \cos \theta \cdot n f(v) dv \frac{1}{2} \sin \theta d\theta \\ &= nm \int_0^\infty dv v^2 f(v) \int_0^{\pi/2} d\theta \cos^2 \theta \sin \theta \\ &= \frac{1}{3} nm \langle v^2 \rangle. \end{aligned} \quad (40)$$

The ideal gas law follows $\langle v^2 \rangle = 3k_B T/m$.

9.2 Mean Free Path

Firstly, we assume all particles are stationary except our particle in research. To compensate this, we use the relative velocity v_r . The particles collide when one runs to another with collision cross-section σ .

In time dt , the probability of collision is equal to the number of particles swept in the volume:

$$dP = dN = n dV = n \sigma v_r dt. \quad (41)$$

By Taylor's expansion,

$$\begin{aligned} P(t + dt) &= P(t)P(dt) = P(t) + \frac{dP}{dt} dt \\ P(t)(1 - n \sigma v_r dt) &= P(t) + \frac{dP}{dt} dt. \end{aligned}$$

This leaves us with a simple differential equation. Normalization helps us determine the arbitrary constant:

$$dP = e^{-xt} x dt, \quad (42)$$

where $x = n\sigma v_r$. Therefore, we get the mean collision time:

$$\begin{aligned} \tau = \langle t \rangle &= \int_0^\infty t e^{-xt} x dt \\ &= -x \frac{d}{dx} \int_0^\infty e^{-xt} dt \\ &= \frac{1}{x} = \frac{1}{n\sigma v_r}. \end{aligned} \quad (43)$$

The mean free path is the mean speed times the mean collision time:

$$\lambda = \langle v \rangle \tau = \frac{\langle v \rangle}{n\sigma \langle v_r \rangle}.$$

The relative speed relates to the speed by:

$$\begin{aligned} \langle v_r \rangle &= \sqrt{\langle (\mathbf{v}_2 - \mathbf{v}_1)^2 \rangle} \\ &= \sqrt{\langle \mathbf{v}_2^2 \rangle + \langle \mathbf{v}_1^2 \rangle - 2 \langle \mathbf{v}_2 \cdot \mathbf{v}_1 \rangle} \\ &= \sqrt{2} \langle v \rangle, \end{aligned} \quad (44)$$

where $\langle \mathbf{v}_2 \cdot \mathbf{v}_1 \rangle = 0$ because $\langle \cos \theta \rangle = 0$.

Finally, we get the mean free path:

$$\lambda = \frac{1}{\sqrt{2} n \sigma}, \quad (45)$$

where $\sigma = \pi d^2$ and d is the diameter of a particle. In better theories, this d is a variable that decreases with temperature.