Lecture Notes Thermal Physics

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October 5, 2019

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1 Introduction: a short overview of important notions

The mole

A **mole** of a certain atom is equivalent to an **Avogadro number** N_a of atoms. Where $N_A = 6.022 \cdot 10^{23}$.

The ideal gas law

Suppose we have N particles in a gas, then we can relate the pressure, volume, temperature, and amount of particles as follows:

$$pV = Nk_BT \tag{1}$$

where k_B is Boltzmann's constant. In order to apply this formula one assumes that (i) there are no intermolecular forces and (ii) that the particles are point-like and have zero size.

Combinatorics

Suppose we have n atoms, and r of those atoms are for instance in an excited state. If we want to calculate the number of possible configurations Ω we apply the following formula,

$$\Omega = \frac{n!}{(n-r)!r!} \equiv {}^nC_r \tag{2}$$

Since factorials grow incredibly quick, we shall often use $\ln \Omega$ instead of Ω.

$$\ln \Omega = \ln(n!) - \ln([n-r]!) - \ln(r!) \tag{3}$$

We also have **Sterling's formula**:

$$\ln(n!) \approx n \ln n - n \tag{4}$$

2 Heat

Heat (Q, measured in Joules) is thermal energy in transit. Note that in contrast to for instance fuel in a car, one cannot say that something has a certain quantity of heat. One can only add heat to something, like adding fuel to a car.

2.1 Heat capacity

We can ask the question, how much heat needs to be supplied to an object to raise its temperature by a small amount dT. The answer is $dQ = CdT$, such that we define the **heat capacity** C of an object using

$$C = \frac{dQ}{dT} \tag{5}$$

There is also c, the **specific heat capacity** in $\mathrm{J\,K^{-1}\,kg^{-1}}$. And the **molar heat capacity**, the heat capacity of one mole of a substance.

If we were to add heat to a system, we'd have to constrain, either the volume of the gas or the pressure of the gas to be fixed. We should therefore change the definition of heat capacity, we need new quantities: C_V, the heat capacity at constant volume, and C_p, the heat capacity at constant pressure.

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \tag{6}$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p \tag{7}$$

In practice $C_p > C_V$, due to more heat being added whilst heating at constant pressure. While heating at constant volume will expend additional energy on doing work on the atmosphere as the gas expands.

3 Probability

3.1 Discrete probability distributions

Let x be a discrete random variable which takes values x_i with probability P_i. The sum of P_i's must always be $\sum P_i = 1$. And we define the **mean** of x to be

$$\langle x \rangle = \sum_i x_i P_i \tag{8}$$

and in general

$$\langle f(x) \rangle = \sum_i f(x_i) P_i \tag{9}$$

3.2 Continuous probability distributions

Let x be a continuous random variable which has a probability $P(x)\,dx$ of having a value between x and $x + dx$. We require that

$$\int P(x)\,dx = 1 \tag{10}$$

With the mean defined as

$$\langle x \rangle = \int x P(x)\,dx \tag{11}$$

and in general

$$\langle f(x) \rangle = \int f(x)P(x)\,dx \tag{12}$$

3.3 Linear transformation

If one want to relate say a random variable x to the random variable y by e.g. $y = ax + b$ then

$$\langle y \rangle = \langle ax + b \rangle = a\langle x \rangle + b \tag{13}$$

where a and b are just constants.

3.4 Variance

One measurement of spread in a distribution is the variance (the square root of it is the standard deviation), defined as

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 \tag{14}$$

3.5 Independent variables

If u and v are independent random variables the probability that they are in there respective range is given by

$$P_u(u)\,du\,P_v(v)\,dv \tag{15}$$

and by taking the double integral of that product we obtain

$$\langle uv \rangle = \langle u \rangle \langle v \rangle \tag{16}$$

3.6 Binomial distribution

It is a probability distribution based on **Bernoulli trials**, which are experiments with two outcomes, success and failure. Where the success happens with a probability p, and failure with probability $1 - p$. The **binomial distribution** is the discrete probability distribution of getting k successes from n independent Bernoulli trials. It is defined as

$$P(n, k) = p^k(1 - p)^{n-k}\left({}^nC_k\right) \quad \text{where} \quad {}^nC_k = \frac{n!}{(n - k)!k!} \tag{17}$$

and the mean of the distribution is $\langle k \rangle = np$ and the variance is $\sigma_k^2 = np(1-p)$.

4 Temperature and the Boltzmann factor

4.1 Thermal equilibrium

Suppose two bodies are in thermal contact with one another, heat will flow from the hotter to the colder body. At a certain moment no net flow of heat will happen, the energy and temperature will no longer change with time. This is called the **Thermal equilibrium**, the process of reaching it is called **thermalization**.

4.2 The zeroth law of thermodynamics

It says that two systems, each, separately in thermal equilibrium with a third, are in equilibrium with each other.

4.3 On thermometers

A working thermometer should have a heat capacity that is less than that of the measured object. Some common methods of measuring temperature include (i) the fact that liquids expand, (ii) that the resistance of certain materials depend on temperature, or (iii) letting liquid coexist with the vapour and measuring the pressure of the vapour.

4.4 Microstates and macrostates

Let's consider the example of a hundred coin flips. Here the **microstates** would be either heads or tails (note microstates are all equally likely). Macrostates would be the total outcome, so how many heads or tails (these are not equally likely).

4.5 The statistical definition of temperature

Let's imagine two systems in thermal contact, otherwise they are isolated. The total energy is $E = E_1 + E_2 = $ constant. The first system can be in any one of $\Omega_1(E_1)$ microstates and the second system can be in any one of $\Omega_2(E_2)$. The total system can then be in any of $\Omega_1(E_1)\Omega_2(E_2)$ microstates.

If we assume that the system is in thermal equilibrium, the energies E_1 and E_2 are fixed. To continue we'll try to maximize $\Omega_1(E_1)\Omega_2(E_2)$.

$$\frac{d}{dE_1}\left\{\Omega_1(E_1)\Omega_2(E_2)\right\} = \Omega_2(E_2)\frac{d\Omega_1(E_1)}{dE_1} + \Omega_1(E_1)\frac{d\Omega_2(E_2)}{dE_2}\frac{dE_2}{dE_1} = 0 \quad (18)$$

Note that $dE_1 = -dE_2$ therefore $dE_1/dE_2 = -1$, since $E = E_1 + E_2$. We can use that to rewrite the previous expression to

$$\frac{1}{\Omega_1}\frac{d\Omega_1}{dE_1} = \frac{1}{\Omega_2}\frac{d\Omega_2}{dE_2} \quad \Rightarrow \quad \frac{d\ln\Omega_1}{dE_1} = \frac{d\ln\Omega_2}{dE_2} \quad (19)$$

Let $d\ln\Omega/dE$ be identified with a temperature T such that $T_1 = T_2$. We can then define temperature by

$$\frac{1}{k_B T} = \frac{d\ln\Omega}{dE} \quad \Rightarrow \quad \frac{1}{T} = \frac{dS}{dE} \tag{20}$$

Where S is called entropy. Often we will use

$$\beta \equiv \frac{1}{k_B T} \tag{21}$$

since it is a frequently used quantity.

4.6 Ensembles

Ensembles are idealizations consisting of a large number of virtual copies of a system, considered all at once, each which represent a possible state of the real system. The main ensembles are

1. Micro canonical ensemble: an ensemble of systems that each have the same fixed energy.

2. Canonical ensemble: an ensemble of systems, each that exchange its energy with a large reservoir of heat. This fixes the temperature.

3. Grand canonical ensemble: aside from the canonical ensemble also particles can be exchanged with the reservoir. This fixes the temperature and the chemical potential.

4.7 The canonical ensemble

To examine the canonical ensemble we shall imagine a reservoir with energy $E - \epsilon$, where ϵ is the energy of the system and E the total energy. (We shall assume that for each allowed energy there is one microstate.) The probability $P(\epsilon)$ that the system has energy ϵ is proportional to $\Omega(E-\epsilon)$ times the number microstates, which is one.

$$P(\epsilon) \propto \Omega(E - \epsilon) = \Omega(E)e^{-\epsilon/k_B T} \tag{22}$$

$$P(\epsilon) \propto e^{-\epsilon/k_B T} \tag{23}$$

Which is called the **Boltzmann distribution** and $e^{-\epsilon/k_B T}$ is called the **Boltzmann factor**. If a system is in contact with a reservoir and has a microstate r, with energy E_r, then

$$P(\text{microstate } r) = \frac{e^{-E_r/k_B T}}{\sum_i e^{-E_i/k_B T}} = \frac{e^{-E_r/k_B T}}{Z} \tag{24}$$

where Z is called the **partition function**.

5 The Maxwell-Boltzmann distribution

5.1 Multilevel systems and the Boltzmann distribution

Suppose you have a system with multiple energy levels, then the higher the state the smaller the occupancy and the higher the temperature, the more probable it is that higher states are occupied. This statement is summarized by

$$\frac{N_i}{N_j} = e^{-\frac{E_i - E_j}{k_B T}} \tag{25}$$

5.2 The velocity distribution

The velocity distribution is defined as the fraction of molecules with velocities between $\boldsymbol{v}$ and $\boldsymbol{v} + d\boldsymbol{v}$. Assuming we are only looking in one direction, say x, then the velocity distribution is given as

$$g(v_x) \propto e^{-mv_x^2/2k_B T} \quad \Rightarrow \quad g(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \, e^{-mv_x^2/2k_B T} \tag{26}$$

The rightmost expression is found by normalization. For this distribution we have that

$$\langle v_x \rangle = 0 \tag{27}$$

$$\langle |v_x| \rangle = \sqrt{\frac{2k_B T}{\pi m}} \tag{28}$$

$$\langle v_x^2 \rangle = \frac{k_B T}{m} \tag{29}$$

$$\tag{30}$$

Now to generalize, and go back to the original statement, between $\boldsymbol{v}$ and $\boldsymbol{v} + d\boldsymbol{v}$

$$g(v_x) \, dv_x \, g(v_y) \, dv_y \, g(v_z) \, dv_z \propto e^{-mv^2/2k_B T} \, dv_x \, dv_y \, dv_z \tag{31}$$

5.3 The speed distribution

Now we are looking at the molecules between v and $v + dv$. Which in velocity space is a spherical shell of radius v, with thickness dv. The volume of that part of the shell is given as $4\pi v^2 \, dv$. Such that the speed distribution is given as

$$f(v) \, dv \propto v^2 \, dv \, e^{-mv^2/2k_B T} \tag{32}$$

Note that the 4π is absorbed into the proportionality. Now to normalize it, integrate from 0 to ∞ (since $v > 0$):

$$\int_0^\infty f(v) \, dv = 1 \quad \Rightarrow \quad f(v) \, dv = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} v^2 \, e^{-mv^2/2k_B T} \, dv \tag{33}$$

This expression is called the Maxwell-Boltzmann distribution. For which

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} \tag{34}$$

$$\langle v^2 \rangle = \frac{3k_B T}{m} \tag{35}$$

$$v_{rms} = \sqrt{\langle v^2 \rangle} \propto m^{-1/2} \tag{36}$$

From this we can derive an expression for the mean kinetic energy of a gas molecule:

$$\langle T \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T \tag{37}$$

We can also derive the value of v such that $f(v)$ is at a maximum, this is simply

$$\frac{df}{dv} = 0 \quad \Rightarrow \quad v_{max} = \sqrt{\frac{2k_B T}{m}} \tag{38}$$

Such that $v_{max} < \langle v \rangle < v_{rms}$.

6 Pressure

Pressure is on of the most fundamental variables in the study of gasses and is defined as the force over the area on which it is acting. The pressure p in a volume V depends on the temperature T via an equation of state $p = f(T, V, N)$, one such example is the ideal gas law.

6.1 Molecular distributions

If we consider a sphere in which molecular are moving in different directions, we define the **solid angle** Ω (measured in **steradians**; analogous to the angle θ in 2D), as

$$\Omega = \frac{A}{r^2} \tag{39}$$

A full sphere subtends a solid angle of $\Omega = 4\pi$. Such that the fraction of molecules whose trajectories lie in an elemental solid angle $d\Omega$ is

$$\frac{d\Omega}{4\pi} \tag{40}$$

If we pick a specific direction then $d\Omega$ corresponds to molecules traveling at angles between θ and $\theta + d\theta$. In the end the number of molecules per unit volume given by

$$n f(v) dv \frac{1}{2} \sin \theta \, d\theta \tag{41}$$

have speeds between v and $v + dv$ and are traveling at angles between θ and $\theta + d\theta$. If we consider a molecules hitting a wall with an angle θ to the normal then the number of molecules hitting it per unit area and unit time is

$$v \cos \theta \, n f(v) dv \frac{1}{2} \sin \theta \, d\theta \tag{42}$$

6.2 The ideal gas law

We can now calculate the pressure of a gas on its container. First note that each molecule hitting the walls of it have a momentum change of $2mv\cos\theta$. Such that if we multiply it with the result from equation (42) and integrate over all v and over the angles $0 \to \pi/2$ we get the pressure p:

$$p = \frac{1}{3}nm\langle v^2 \rangle \;,\;\; n = \frac{N}{V} \tag{43}$$

Which can be rewritten as

$$pV = Nk_BT \quad \Rightarrow \quad p = nk_BT \tag{44}$$

The familiar ideal gas law.

6.3 Dalton's law

If you have a mixture of gases in thermal equilibrium then the total pressure is the sum of partial pressures $p_i = n_i k_B T$

$$p = \left(\sum_i n_i \right) k_B T = \sum_i p_i \tag{45}$$

7 Effusion

Effusion is the process by which gas escapes from a small hole, the rate of a gas doing so is given to be proportional to $1/\sqrt{m}$ (also called **Graham's law of effusion**).

7.1 Flux

Let's determine the molecular flux Φ, the number of molecules striking a unit area per second. It is given as

$$\Phi = \frac{1}{4}n\langle v \rangle = \frac{p}{\sqrt{2\pi m k_B T}} \tag{46}$$

This expression shows us that indeed, the effusion rate is as given by Graham's law.

7.2 Effusion rate

The effusion rate (given a hole of area A) is given as ΦA. Effusion preferentially selects faster molecules, therefore the speed distribution isn't Maxwellian. This is due to faster molecules having a greater probability of reaching the hole. Now

$$f(v) \propto v^3 e^{-mv^2/2k_B T} \tag{47}$$

Therefore the molecules in an effusing gas have a higher energy. Note for effusion the diameter of the hole has to be much less than the mean free path λ.

8 The mean free path & collisions

8.1 The mean collision time

in a time dt, our molecule will sweep out $\sigma v dt$. If we have n molecules per unit volume then the probability of a collision in that time is given by $n\sigma v\, dt$. We then obtain the probability of a molecule surviving without colliding up until time t, which is

$$P(t) = e^{-n\sigma vt} \tag{48}$$

The probability of doing so and then colliding in the next interval dt is given by

$$e^{-n\sigma vt}n\sigma v\, dt \tag{49}$$

Which in the end yields the **mean scatter time** τ, the time between collisions:

$$\tau = \frac{1}{n\sigma v} \tag{50}$$

8.2 The collision cross-section

What is σ? for two colliding particles the collision cross-section depends on the hard-sphere radii of both particles, so $\sigma_{12} = \pi(a_1 + a_2)^2$. For two identically sized particles that is πd^2, where d is their diameter.

8.3 The mean free path

The mean free path, given that $\langle v_r \rangle = \sqrt{2}\langle v \rangle$, is defined as

$$\lambda = \frac{1}{n\sigma\sqrt{2}} \quad \Rightarrow \quad \lambda = \frac{k_B T}{p\sigma\sqrt{2}} \tag{51}$$

Note that both τ and λ decrease by increasing pressure at fixed temperature. Thus the frequency of collision increases with an increase in pressure.

9 Transport properties in gases

9.1 Viscosity

Viscosity is the transfer of momentum. And it is the measure of the resistance of a fluid to the deformation produced by a shear stress. For instance for a shear stress

$$\tau_{xz} = \frac{F}{A} = \eta\frac{d\langle u_x \rangle}{dz} \tag{52}$$

where η is the viscosity. The velocity gradient also drives a momentum flux

$$\Pi_z = -\eta\frac{\partial\langle u_x \rangle}{\partial z} \tag{53}$$

where

$$\eta = \frac{1}{3} nm\lambda\langle v\rangle \tag{54}$$

Note that viscosity is not a function of pressure if it is not too high, or too low. $\eta \propto \sqrt{T}$ (this is a gas specific property). $\eta \propto \sqrt{m}/d^2$. These statements are all true assuming that $L >> \lambda >> d$, where L is the container size, and d the molecular diameter.

9.2 Thermal conductivity

This concerns the transport of heat. The heat flux $\boldsymbol{J}$ is given by

$$\boldsymbol{J} = \kappa\nabla T \tag{55}$$

where κ is the thermal conductivity. Note that the heat capacity of a gas molecule is $C_{molecule} = \frac{3}{2}k_B$ (is can be higher), and $\kappa = \frac{1}{3}C_V\lambda\langle v\rangle$ for $C_V = nC_{molecule}$. Similar to viscosity, the thermal conductivity is not a function of pressure and is proportional to the square root of the temperature, $\kappa \propto 1/\sqrt{m}d^2$. A relation between the viscosity and thermal conductivity is given by

$$\frac{\kappa}{\eta} = \frac{C_{molecule}}{m} \tag{56}$$

9.3 Diffusion

Diffusion is the transport of particles. Let there be $N^*(z)$ labeled molecules per unit volume. Such that the flux of molecules, e.g. parallel to the z-direction, is given by

$$\Phi_z = -D\left(\frac{\partial n^*}{\partial z}\right) \tag{57}$$

where D is the coefficient of self-diffusion. From this follows the diffusion equation:

$$\frac{\partial n^*}{\partial t} = D\nabla^2 n^* \ , \quad D = \frac{1}{3}\lambda\langle v\rangle \tag{58}$$

Note that $D \propto p^{-1}$, $D \propto T^{3/2}$, $D\rho = \eta$, and lastly $D \propto 1/\sqrt{m}d^2$

10 Thermal diffusion

So here we're talking about how heat appears to diffuse from one place to another. First note that hte total heat flow out of a closed surface S is given by

$$\int_S \boldsymbol{J} \cdot d\boldsymbol{S} = -\frac{\partial}{\partial t}\int_V CT\, dV \ , \quad C = \rho c \tag{59}$$

This is the rate of losing energy. By the divergence theorem we obtain

$$\nabla \cdot \boldsymbol{J} = -C\frac{\partial T}{\partial t} \quad \Rightarrow \quad \frac{\partial T}{\partial t} = D\nabla^2 T \tag{60}$$

where $D = \kappa/C$, the thermal diffusivity. The rightmost equation is called the **thermal diffusion equation**.

10.1 Solving for the 1D case

In one dimension we for instance have

$$\frac{\partial T}{\partial t} = D\frac{\partial^2 T}{\partial x^2} \tag{61}$$

Note that it resembles the wave equation. We can therefore try a solution of the form

$$T(x,t) \propto e^{i(kx-\omega t)} \ , \quad k = \frac{2\pi}{\lambda} \quad \text{and} \quad \omega = 2\pi f \tag{62}$$

Such that $k^2 = i\omega/D$ which can be rewritten as $k = \pm(1+i)\sqrt{\omega/2D}$. Let's limit ourselves to $x \geq 0$, such that we assume the solution

$$T(x,t) = \sum_{\omega} A(\omega)e^{(i-1)\sqrt{\omega/2D}\,x}e^{-i\omega t} \tag{63}$$

We have the boundary condition

$$T(0,t) = T_0 + \frac{\Delta T}{2}\left(e^{i\Omega t} + e^{-i\Omega t}\right) \tag{64}$$

$$T(0,t) = \sum_{\omega} A(\omega)e^{-i\omega t} \tag{65}$$

Such that $A(0) = T_0$ and $A(\Omega) = A(-\Omega) = \Delta T/2$. Therefore

$$T(x,t) = T_0 + \Delta T e^{-x/\delta}\cos\left(\Omega t - \frac{x}{\delta}\right) \ , \quad \delta = \sqrt{\frac{2D}{\Omega}} \tag{66}$$

where δ is called the **skin depth**.

10.2 The 1D steady state solution

In general if

$$\frac{\partial T}{\partial t} = 0 \quad \Rightarrow \quad \nabla^2 T = 0 \tag{67}$$

Such that in 1D for $0 \leq x \leq L$, and $T_2 < T_1$ we can obtain an expression for $T(x,t)$ and J_x (the heat flux):

$$T = \frac{(T_2 - T_1)x}{L} + T_1 \quad \text{and} \quad J_x = \frac{\kappa}{L}(T_1 - T_2) \tag{68}$$

where κ/L is called the **thermal conductance** (or U-value) and $L/kappa$ is called the **thermal resistance** (or R-value).

10.3   Thermal diffusion for a sphere

If the temperature is independent of the angles ϕ and θ then

$$\frac{\partial T}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) \tag{69}$$

Such that the steady state solution is given by

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) = 0 \tag{70}$$

Note that the partial derivative w.r.t r should be constant. Therefore $T \propto 1/r$, such that

$$T = \frac{B}{r} + A \tag{71}$$

10.4   Newton's law of cooling

The heat loss of a surface to the surrounding gas is proportional to the area of contact times the temperature difference, such that it can be described by

$$\boldsymbol{J} = \boldsymbol{h}\Delta T \tag{72}$$

where $\boldsymbol{h}$ is the vector normal to the surface of the body.

10.5   Definition of convection

Convection is heat transfer by motion within the fluid. Warmer fluids expand and rise whereas colder fluids contract and sink.

10.6   The Prandtl number

Convection dominates if momentum diffusion dominates, whereas conduction dominates if heat diffusion dominates.

The Prandtl number tells us which dominates:

$$\sigma_p = \frac{\nu}{D} = \frac{\eta c_p}{\kappa} \tag{73}$$

where $\nu = \eta/\rho$ is called the kinematic viscosity. Note that for an ideal gas $\sigma_p = 2/3$. Now if $\sigma_p \gg 1$ then the diffusion of momentum (viscosity) dominates and thus convection dominates.

10.7   Extra heat sources

if heat is generated at a rate H per unit volume, then

$$\frac{\partial T}{\partial t} = D\nabla^2 T + \frac{H}{C} \tag{74}$$

10.8 Particle diffusion

Here we've discussed the diffusion of heat, but essentially the same laws also apply to the diffusion of particles:

$$\frac{\partial n}{\partial t} = D\nabla^2 n \qquad (75)$$

where D is the diffusion constant.