General Physics I

Lect.19 Applications of Kinematics

Based on Feynman Lectures Ch.42

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Applications of Kinetic Theory

Previously, we saw that the probability of finding a particle in different places, per unit volume, varies as $e^{-\text{potential energy}/kT}$ based on kinetic theory.

We can use such basic observation to explain phenomena such as:

- a **liquid evaporating**, or
- **electrons in a metal** coming out of the **surface**, or
- a **chemical reaction** with a large number of atoms involved.

It is **no longer possible** to make from the **kinetic theory**, to describe above processes with 100% accuracy, because the situation is too complicated. But we can understand ***more or less*** how things ought to behave.

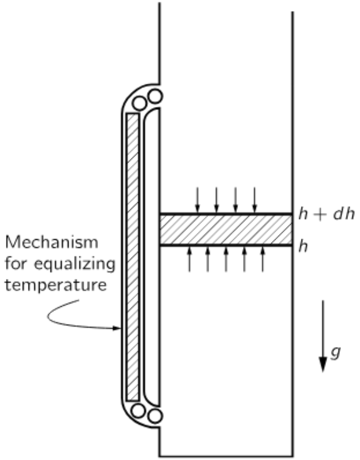
In the cases we will discuss, **potential energy >> kT** for it to be the dominant effect.

Evaporation – view one

Suppose we have a box with a large volume, partially filled with **liquid** in equilibrium and with the **vapor** at a certain temperature. The ratio of the molecules in the vapor phase, compared to the ones in the liquid at temperature T can be written as:

$$nV_a = e^{-W/kT}$$ <<1 when W>>kT

where n is the number of molecules per unit volume **in the vapor**, and $1/V_a$ is the number of atoms per unit volume **in the liquid**, given the **volume occupied to be V_a**. The **energy difference** in the two phases is **W**=E_{vapor}-$E_{liquid.}$ To understand this, simply recall the Maxwell-Boltzmann distribution we discussed in L17.



$$n = n_0 e^{-mgh/kT}$$ (specific)

$$n = (\text{constant})e^{-\text{P.E.}/kT}$$ (generalize)

$$n_2/n_1 = e^{-(E_2-E_1)/kT}$$

Evaporation – view two

Alternatively, vapor molecules continually bombard the surface of the liquid, at a given moment a **certain number of atoms condense onto the surface of the liquid**, given by $\mathbf{N_c=nv}$ (v is the mean velocity related to kT)

Molecules in liquid can also be kicked out with excess energy due to strong attraction forces, e.g., Van der Waals. The probability of picking up more than W work is $\mathbf{e^{-W/kT}}$. Consider a surface of the liquid occupies a certain **cross-sectional area A**, and the molecule with **average speed v** have to move one molecular diameter D (the thickness of the first layer). Number evaporating $\mathbf{N_e}$ in a chunk of D*A liquid is $(1/A)(v/D)e^{-W/kT}$

In equilibrium, $\mathbf{N_c= N_e}$, $nv = (v/V_a)e^{-W/kT}$

To be more precise, not all molecule hit the liquid are absorbed. One can assume an unknown reflection coefficient R, as we add a correction term (1-R) in the above equilibrium relation:

$$N_e = nv(1-R) = (v(1-R)/V_a)e^{-W/kT}$$

Thermionic emission – "evaporation with pumping"

A heated tungsten filament with a positively charged plate to attract the electrons, any electron that escapes from the surface of the tungsten is immediately swept away to the plate. How many **electrons per second** can we get out of a piece of tungsten? Equivalently, what is the balancing e- density around the metal?
The only difference is the $\mathbf{W=q_e\phi}$, where ϕ is the so-called work function. The current per unit area **I** is equal to the charge times the number that arrive per second per unit area, which is the number per unit volume times the velocity:

$$I = q_e n v = (q_e v / V_a) e^{-q_e \phi / kT}$$

Now one electron volt (**eV**) corresponds to **kT** at a temperature of 11,600 K, so at the operating at a temperature of 1000 K, this exponential factor is about $\mathbf{e^{-10}}$.

The constant factors in front is quite wrong, as a limit for the classical theory. And if W is a linear function of T, like $W=W_0+\alpha kT$, then it will appear as a correction factor.

$$e^{-W/kT} = e^{-(W_0+\alpha kT)/kT} = e^{-\alpha} e^{-W_0/kT}$$

Thermal ionization $\text{Atom} \rightleftharpoons \text{Ion} + e^-$

Suppose that in a gas total of N atoms are in the neutral state, but the gas is hot and the atoms can become ionized. The number of atoms and positive ions follows the **number conservation** $n_a+n_i=N$, and **charge conservation** $n_e=n_i$ for electrons.

The energy to lift an electron out of the atom, the **ionization energy**, **W**.

Now the "Boltzmann factor" (i.e., $e^{-W/kT}$) represents the ratio of the number of **free electrons** per unit volume in the "vapor" over the number of **bound electrons** per unit volume in the atoms.

The total number of places for electrons is n_i (two electron cannot occupy the same atom state) and they are bound within a certain volume V_a. The total amount of volume which is available to **bounded electrons** is n_iV_a. Equating this to the number of **free electrons** per unit volume, n_e, we have

$$n_e = \frac{n_a}{n_i V_a} e^{-W/kT}$$

recombination ⟶

ionization ⟶

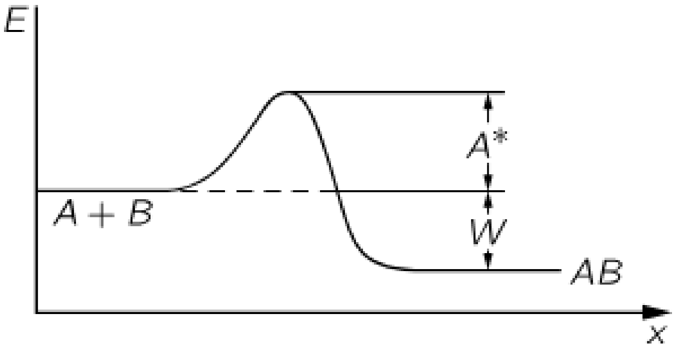
$$\frac{n_e n_i}{n_a} = \frac{1}{V_a} e^{-W/kT}$$

Saha ionization equation

or $$\frac{f^2}{1-f}\frac{N}{V} = \frac{e^{-W/kT}}{V_a}$$, with $n_e = f N/V = n_i$ and $n_a = (1-f)N/V$

If V goes up, fraction **f** of electrons/ions also goes up -> interstellar ions

Chemical kinetics



Now consider chemical reaction where A and B combine into a compound AB, with a work W released. And the same relation holds in terms of the respective density $n_{A/B/AB}$, up to an unknown constant c. W governs the proportions of A/B/AB.

$$\frac{n_A n_B}{n_{AB}} = c e^{-W/kT}$$ equilibrium

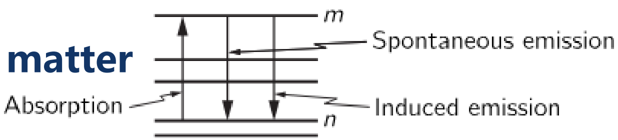
In reality, A and B need to hit each other with sufficient energy **above activation energy**, **A*.** So, the reaction of A+B->AB is $e^{-A^*/kT}$ suppressed,

$$R_f = n_A n_B v \sigma_{AB} e^{-A^*/kT} \qquad R_r = c' n_{AB} e^{-(W+A^*)/kT}$$ Non-equilibrium

A* also controls the rate of the reaction. Using intermediate state, or a special surface of the reaction can effectively **decrease the energy barrier** to increase the rates. These are called **catalysts** 催化剂.

1916

Einstein's laws of radiation – interaction w/ matter



Consider the mth level and the nth level of an atom, Einstein assumed that there are three kinds of processes: **absorption** proportional to the intensity of light B_{nm}, **emission** proportional to the intensity of light B_{mn}, called **stimulated emission**, and **spontaneous emission** independent of light A_{mn}. The gap between levels is $E_m - E_n = \hbar\omega$.

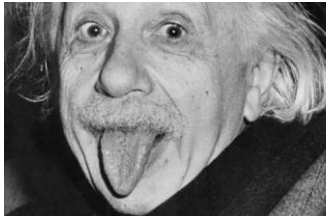
Now we have, in equilibrium at temperature T, a certain number of atoms N_n in the state n and another number N_m in the state m, then each second

$$R_{n\to m} = N_n B_{nm} I(\omega) \qquad R_{m\to n} = N_m[A_{mn} + B_{mn} I(\omega)].$$

At equilibrium, equating the two rates gives

$$B_{nm} I(\omega) e^{\hbar\omega/kT} = A_{mn} + B_{mn} I(\omega).$$

Substitute using $N_m = N_n e^{-\hbar\omega/kT}$, the intensity $I(\omega) = \dfrac{A_{mn}}{B_{nm} e^{\hbar\omega/kT} - B_{mn}}$



Albert Einstein
(1879-1955)
"light->photons"

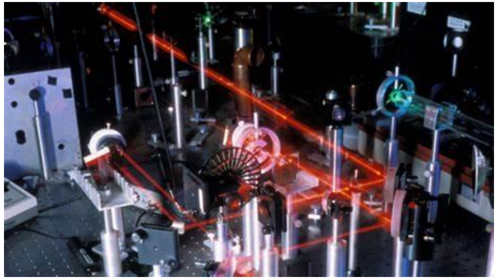
Compare with Planck's result, $I(\omega)\,d\omega = \dfrac{\hbar\omega^3\,d\omega}{\pi^2 c^2 \left(e^{\hbar\omega/kT} - 1\right)}$ we have $A_{mn}/B_{mn} = \hbar\omega^3/\pi^2 c^2$

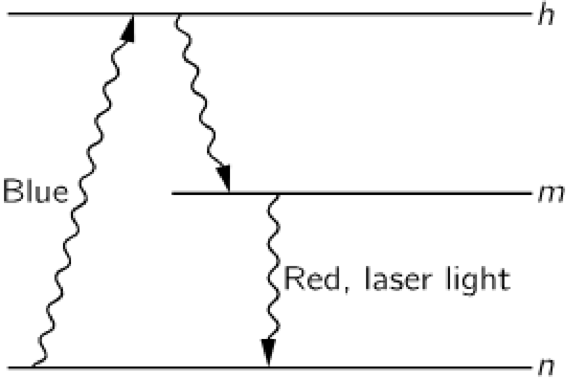
induced emission = absorption probability $B_{mn} = B_{nm}$

LASER

Laser is an acronym for “light amplification by the stimulated emission of radiation.” Imagine we can prepare the m **metastable state** far above equilibrium than $e^{-(Em-En)/kT}$. Then they are all dumped down together by induced emissions. Nearly perfect mirrors can be placed on each side of a “box”, allowing light to be emitted multiple times, **increased stimulation**. Also, it strongly **selects** which frequencies for only cavity-supported modes. Mirrors are almost 100% reflecting, but a slight transmission allows some light being **emitted**.

In the end, from the conservation of energy, all the light goes out in a nice **uniform straight direction** which makes the strong light beams that we call laser -- **low divergence and high directionality**.

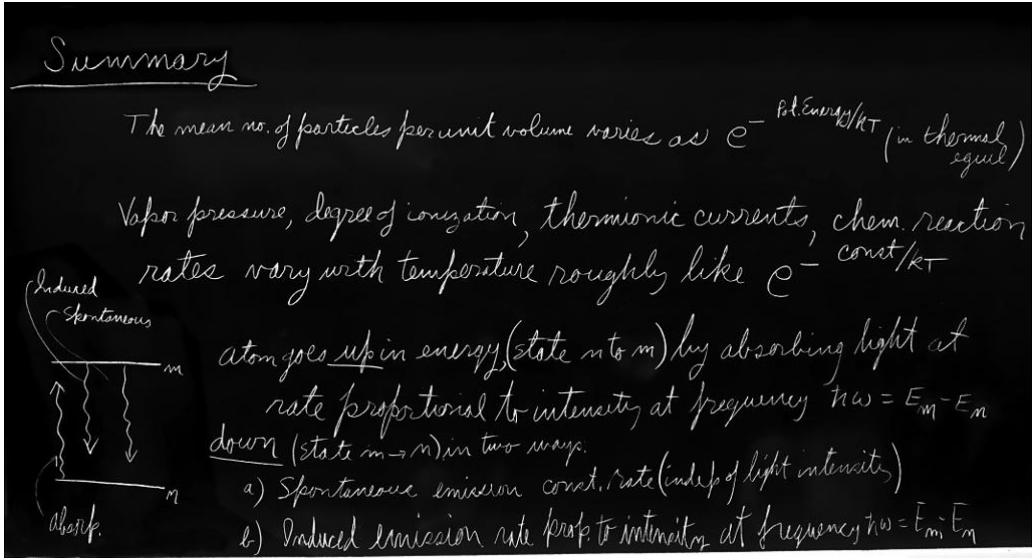




By exciting, say by blue light, a higher state h, which may emit a photon leaving atoms in state m, the number in this state m becomes sufficiently large to start laser action.

Summary

- **Liquid evaporation**
- **Thermionic emission of electrons** in a metal surface
- **Ionization** and Saha equation
- **Chemical reaction** and catalysts
- **Einstein's laws of radiation**
- **Laser**



Summary

The mean no. of particles per unit volume varies as $e^{-\text{Pot. Energy}/kT}$ (in thermal equil)

Vapor pressure, degree of ionization, thermionic currents, chem. reaction rates vary with temperature roughly like $e^{-\text{const}/kT}$

atom goes up in energy (state n to m) by absorbing light at rate proportional to intensity at frequency $\hbar\omega = E_m - E_n$

down (state $m \to n$) in two ways.

a) Spontaneous emission const. rate (indep of light intensity)

b) Induced emission rate prop. to intensity at frequency $\hbar\omega = E_m - E_n$

Time constant and mean free path

Now let’s discuss what happens when things are near, but not exactly in, equilibrium, e.g., the diffusion of ions in a gas. In a gas with a small ion concentration, an electric field causing the ion to accelerate only until it collides with another molecule, losing its momentum. We can define a time constant, $\boldsymbol{\tau}$, which is the average time between collisions, and a total number N_0. The number/probability of each collision follows

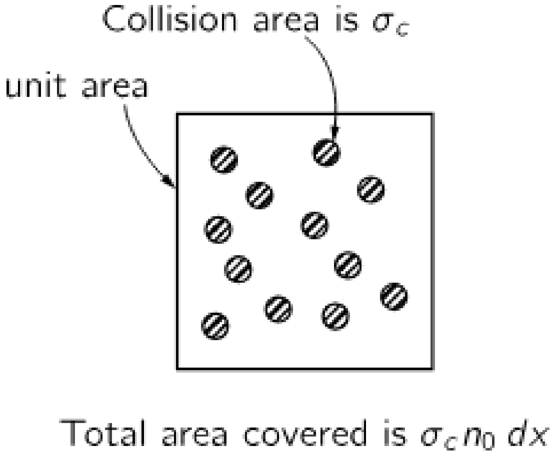
$$N(t+dt) = N(t) - N(t)\,\frac{dt}{\tau} \longrightarrow \frac{dN(t)}{dt} = -\frac{N(t)}{\tau} \longrightarrow N(t) = N_0 \boxed{e^{-t/\tau}}$$

probability of no collision

Rather than the time between collisions, we now about how far the particle moves between collisions, the mean free path

$$\boldsymbol{l = \tau v}$$

Consider a moving particle which travels a distance dx through a gas which has n_0 scatterers per unit volume, then we shall have $\sigma_c n_0 l = 1$, which is saying there should be one collision, on the average, when the particle travel a distance $\boldsymbol{l}$, where $\sigma_c = \pi(r_1 + r_2)^2$ is the classical cross section.

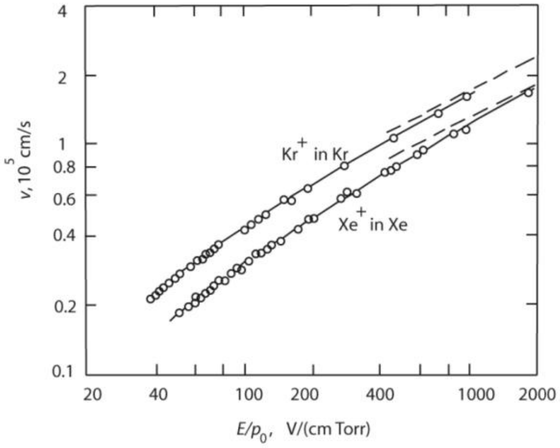


Drift speed

Consider special molecule is acted on by some force F (e.g., electric currents in batteries, sedimentation, centrifugal separation), plus the collisions with the background molecules. First let’s assume each collision gets a completely “fresh” start. **Drift speed** is the net progress in the direction of the acceleration F/m, proportional to τ, mind that we do not have ½ factor here:

mobility

$$v_{\text{drift}} = \frac{F\tau}{m} = \mu F$$



In the case of electrical field, F=Eq. The drift velocity of atomic ions in krypton and xenon at normal conditions, where we find v_{drift}~E.

Suppose our special molecule is a heavy object in a background of lighter molecules, i.e., it will not lose its “forward” momentum in each collision. It would take several collisions before its motion was “randomized” again. We can define a new time constant τ, which corresponds to the average time it loses a certain fraction of its momentum. Such a longer τ means the system has a longer average “forgetting time”.

Diffusion: spreading by molecular motions

Diffusion involves a “background" gas in thermal equilibrium, and a “special” gas spreads slowly. The diffusion is controlled mainly by the molecules of the special gas getting knocked about by the molecules of the background gas (in x).
Consider the *net flow* of molecules of the “special” gas due to nonuniform distribution. The number of molecules pass from left to right of a unit area is given by $n_- v\Delta T$. So the molecular current J is:

$$J = \frac{n_- v\,\Delta T - n_+ v\,\Delta T}{\Delta T} \longrightarrow J = (n_- - n_+)v$$

We say n_- (n_+) is the number per unit volume to the left (right), evaluated one mean free path ***l*** away from the imaginary surface. So we relate their difference by a gradient

$$(n_+ - n_-) = \frac{dn_a}{dx}\Delta x = \frac{dn_a}{dx}\cdot 2l \xrightarrow[\text{average v/3}]{\text{substitute}} J_x = -\boxed{\frac{lv}{3}}\frac{dn_a}{dx}$$

Diffusion coefficient, ***D***

Now substitute $l = v\tau$ and $\tau = \mu m$, so $J_x = -\frac{1}{3}mv^2\mu\frac{dn_a}{dx}$

Use $mv^2/2 = 3kT/2$

$$J_x = -\mu kT\frac{dn_a}{dx}$$

D, the *diffusion* coefficient, is just kT times μ, the *mobility* coefficient

Derivation from stat mech

Imagine we have a diffusion current proportional to the density gradient. We now apply a force field F in the x-direction. According to the definition of the mobility μ there will be a drift velocity given by $v_{\mathrm{drift}} = \mu F$, and thus the drift current is $J_{\mathrm{drift}} = n_a \mu F$.
Making $J_x + J_{\mathrm{drift}} = 0$, so the drift current from F balance the diffusion, we have

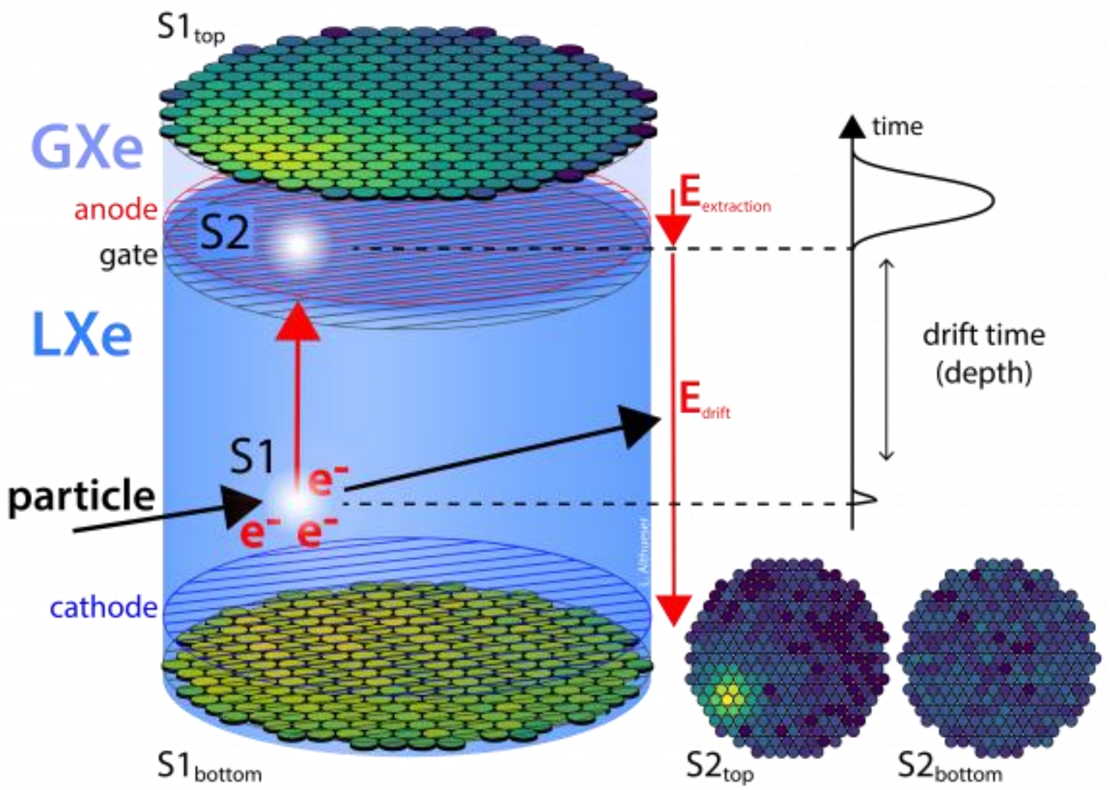
$$D \frac{dn_a}{dx} = n_a \mu F \longrightarrow \frac{dn_a}{dx} = \frac{n_a \mu F}{D}$$

Since we are describing an equilibrium condition, the number density n_a follows the Boltzmann distribution w.r.t. potential energy U: $n_a = n_0 e^{-U/kT}$

$$\frac{dn_a}{dx} = -n_0 e^{-U/kT} \cdot \frac{1}{kT} \frac{dU}{dx} \xrightarrow{dU/dx=-F} \frac{dn_a}{dx} = \frac{n_a F}{kT}$$

Comparing the above two equations, we have again reached $D=\mu kT$. Thus this relation is in general true.
Similarly, we can derive the relation of <u>thermal conductivity</u>, as an exercise for homework.

Dark Matter Detector: a drift chamber



- **Drift time** is the time for electrons to travel up the detector under the electrical field, which tells about the z position of the event.
- Ring of electron signal undergoes **diffusion** as it drift: bigger radius with longer drift time
- **Phase transition** is a core piece of xenon distillation, purification and slow control