Second series — Talk #1

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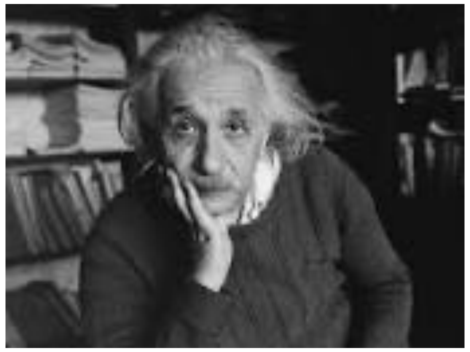
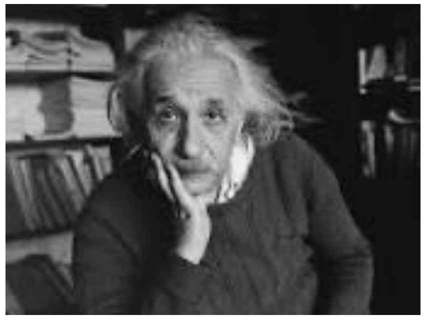
The transition from a continuous to a quantized world



Atoms and molecules
Are they really real?



Brownian motion:

Everyone knows atoms exist, right?
Prove it!!

460 - 370bce the Greeks - indivisible atoms exist
322bce Aristotle, “No!, matter is continuous!”
14th century, the church, “Atoms are heresy!”
17th century atoms are mostly back in favor

18th and 19th century - ideas or theories

Some physicists also did not trust mathematical abstractions
Namely - Ernst Mach

Idea #1 - Chemistry proportions:
Two “amounts” of hydrogen plus one “amount” of oxygen gives one “amount” of water: The hydrogen amount is 1, the oxygen amount is 16 and the water “amount” is 18, etc. etc.

Feels like things - things like tinker toys, no?

OK. You have to do a lot of reactions to show that the ratios are resonably small whole numbers - like 2:16 for water and 4:12 for methane etc. etc. etc.

Idea #2 - Oil spread on water can only be so thin

Idea #3 - Evaporation:
Liquids became extremely thin - that is vapors. Didn’t the liquids somehow “fall completely apart”?

You can imagine two continuous liquids or two continuous gases mixing. But doesn’t the liquid “dissolve” into the gas “a piece” at a time?
A “finite” piece?

Idea #4 - Statistical Mechanics
The statistical math seemed to work. But Mach had a point, was this just math or was there a reality to it?

Idea #4 The first estimate of a atom’s size.
In 1865 Joseph Loschmidt made possible the first estimate of the size of atoms. He used #4 statistical mechanics.

Idea #4 Statistical Mechanics
a) Assume gases consist of a huge number of particles with a fixed amount of energy.
b) The particles interact only by colliding.
c) Determine the distribution of properties among the particles as the most random.

The way Maxwell and Boltzmann described what was going on used statistical ideas - Statistical Mechanics.

Some amazing results:

1)The calculations fit and explained properties of gases.

2) The method had something to say about the size of the particles and Loschmidt said it.

2) While many physicists liked the idea, some did not. Mach thought you should study the properties of real fluids, not make up imaginary ones analyzed with complex math. ☹ ☹ ☹

The debate with Mach was acrimonious!!

Many others contributed to the development of statistical mechanics

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For Mach, only seeing was believing

But first — what Loschmidt did

Before we begin: PV=NRT
If this is correct then for a box with the same P, V and T you have the same number of atoms and/or molecules

Loschmidt looked at two things (I think)
First: Look at the "geometry" of the condensed and gas phases.
Second: Look at the gas phase transport properties

#1 For the condensed phase: $V_l = (4/3)(\pi r^3)(N)$

ie the liquid is a bunch of spheres

#2 For the gas phase: $V_g = \pi r^2 \lambda(N) * (3/4)$

ie the gas phase is a bunch of empty mean free path tubes

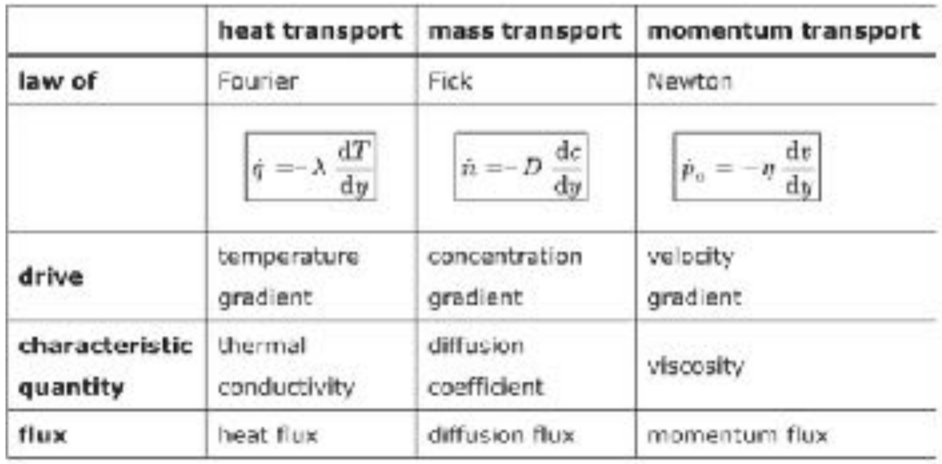
Notes:
a. V_g is a standard volume. V_l is that volume condensed.
b. N is the number of atoms. λ is the mean free path.
c. The V_l formula assumes spheres fill the space and ignores BCC, FCC, HCP nearest neighbors etc.
d. The Vg formula is from Maxwell and assumes that mean free paths fill 3/4 of empty space.

Loschmidt used the two equations to get:

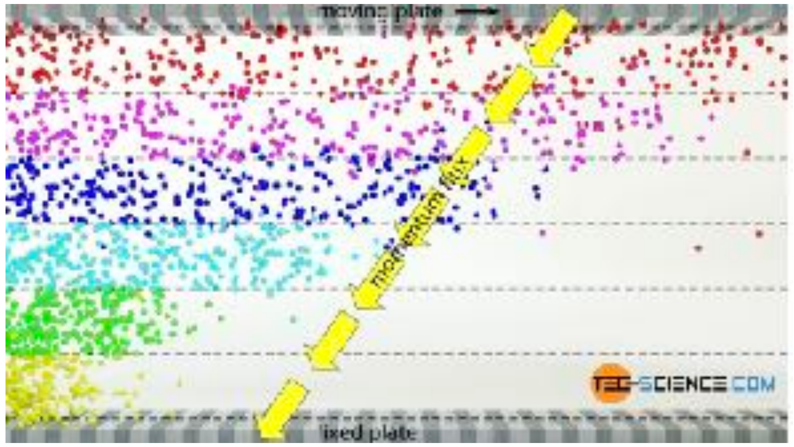
$$d = 8\frac{V_l}{V_g}\ell$$

There were differences in how Maxwell, Loschmidt and others got numerical factors for the mean free path from geometry.

The next step is to get the mean free path from statistical mechanics and dynamics.



	heat transport	mass transport	momentum transport
law of	Fourier	Fick	Newton
	$\boxed{\dot{q} = -\lambda \frac{dT}{dy}}$	$\boxed{\dot{n} = -D \frac{dc}{dy}}$	$\boxed{\dot{p}_v = -\eta \frac{dv}{dy}}$
drive	temperature gradient	concentration gradient	velocity gradient
characteristic quantity	thermal conductivity	diffusion coefficient	viscosity
flux	heat flux	diffusion flux	momentum flux



Newton's derivation of the relation of viscosity to mean free path

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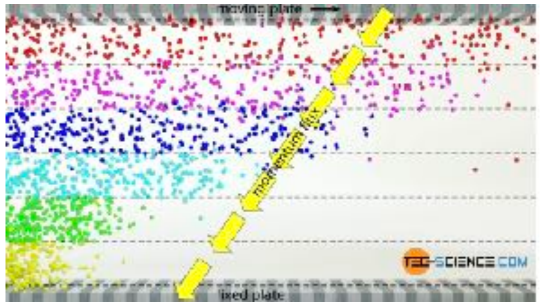


For heat transport, the extra random motion diffuses between layers.
For momentum transport extra momentum diffuses between layers.

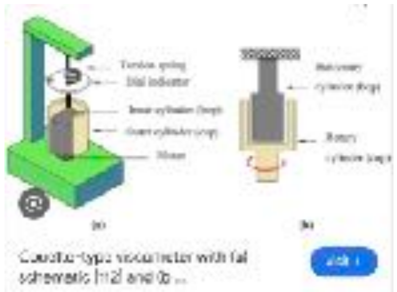
We will see that the relation between viscosity and diffusivity.

Measuring things like viscosity, diffusivity and thermal conductivity at different temperatures gave the mean free path.

With the mean free path, you could compute the atom's size, (Really the volume density of atoms in the condensed phase.)

These experiments were tough. Even for density, it was twelve years after Loschmidt for a good sample of liquid nitrogen.

How do you measure the viscosity of a gas?



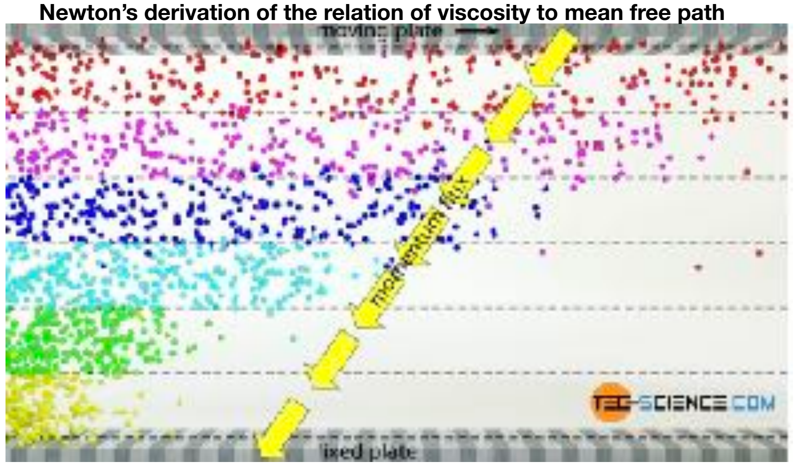
Gas viscosity dependence: $\mu = a_1[(RT/N)^{1/2}]\rho\lambda$ **or** $(\rho v\lambda)$

It is interesting to note that μ is independent of the density for a given temperature.

When Maxwell first derived this fact, he was so surprised that he put it to experimental test by observing the damping of a pendulum in gasses of different densities.

As you compress a gas density goes up but mean free path goes down.

Newton's derivation of the relation of viscosity to mean free path



The number of collisions between top and bottom is N. So the momentum transfer at the bottom is mv/N. So low density big impact per molecule hit. But the number of molecules in the chain is proportional to N. So viscosity is independent of density.

By 1900 statistical mechanics was widely, but not completely, accepted. BUT Ernst Mach still held

SEEING IS BELIEVING

X-rays were discovered in 1895, but atoms were not measured until 1912. Even then it was, "The chicken or the egg?"

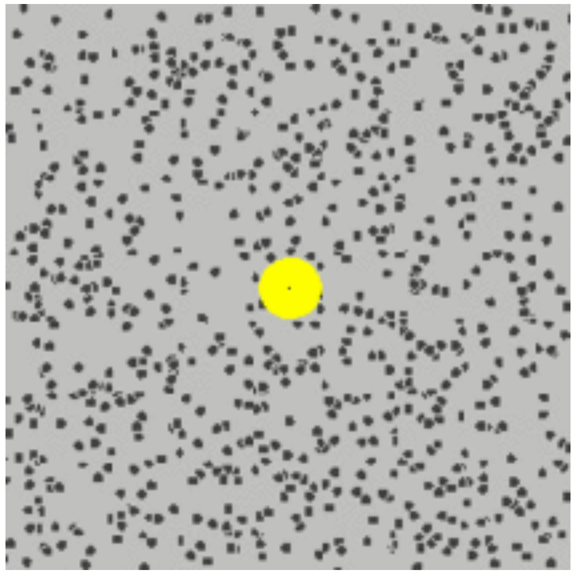
“SHOW ME THE MONEY”

That is what Einstein did, ie Brownian motion

On the movements of small particles suspended in stationary liquids required by the molecular-kinetic theory of heat

By A. Einstein (*Annalen der Physik 17)*

This paper is dependent on two previous:
Ann. d. Phys. 9 (1902) Kinetic Theory of Equilibrium and Second Law
Ann. d. Phys 11 (1903) General Molecular Theory of Heat



Note: Einstein refers to two theoretical approaches:
1) “classical thermodynamics”
2) “the molecular-kinetic theory of heat”

Of course, today the term “thermodynamics” includes the “molecular-kinetic” theory.

Apparently IT DIDN’T THEN

On the movements of small particles suspended in stationary liquids required by the molecular-kinetic theory of heat

By A. Einstein

“It will be shown in this paper that, according to the molecular-kinetic theory of heat, bodies of microscopically visible size suspended in liquids must, as a result of thermal molecular motions, perform motions of such magnitude that the motions can easily be detected by a microscope. It is possible that the motions to be discussed here are identical with the so-called “Brownian molecular motions”; however, the data available to me on the matter are so imprecise that I could not form a definite opinion on this matter.

If it is really possible to observe the motion to be discussed here, along with the laws it is expected to obey, then classical thermodynamics can no longer be viewed as strictly valid even for microscopically distinguishable spaces, and an exact determination of the real size of atoms becomes possible. Conversely, if the prediction of this motion were to be proved wrong, this fact would provide a weighty argument against the molecular-kinetic conception of heat.”

Einstein refers to two different theories:
Classical thermodynamics and
The molecular-kinetic theory of heat

Today we think of thermo as including the molecular theory.

At the time many did too. But Ernst Mach DID NOT.

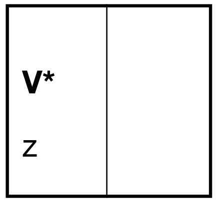
On the movements of small particles suspended in stationary liquids required by the molecular-kinetic theory of heat

By A. Einstein (Ann, d. Phys. 17 (1905)

Part 1) Osmotic pressure formula
Part 2) Equivalence of dissolved and suspended particles
Part 3) Diffusivity related to osmotic pressure and viscosity
Part 4) Obserable random motion of suspended particles
Part 5) A predictive “proof of atoms”

The paper relies on two of Einstein’s earlier papers;
Ann. d. Phys. 9 (1902) and Ann. d. Phys. 11 (1903)

#1



Part 1 of the paper briefly reviews osmotic pressure:

Two membrane separated liquid volumes:
Then $pV^* = RTz$
where p is osmotic pressure and
z moles of a substances is dissolved in V^*

#1

It then argues that suspended particles will have exactly the same effect.

The problem is that the suspended amounts (ie number density) are small, difficult measure and produce extremely little osmotic pressure.

#1

"But from the standpoint of the molecular-kinetic theory of heat we are led to a different conception. According to this theory, a dissolved molecule differs from a suspended body is size alone, and it is difficult to see why suspended bodies should not produce the same osmotic pressure as a equal number of dissolved molecules. We will have to assume that the suspended bodies perform an irregular, even though very slow, motion in the liquid due to the liquid's molecular motion; if prevented by the wall from leaving the volume V^*, they will exert forces on the wall exactly as dissolved molecules do."

#1

If n suspended bodies are present in V^*, ie $\gamma = n/V^*$, and
if the separation between bodies is large,
there will correspond to them an osmotic pressure

$$p = (RT/V^*)(n/N) = (RT/N)\gamma$$

where N denotes the number of true molecules per gram mole, ie. Avagodro's number.

Einstein was not the first to develop the expression for osmotic pressure.

#2

Osmotic pressure from the standpoint of the molecular-kinetic theory of heat

This section relies on two of Einstein's earlier papers;
Ann. d. Phys. 9 (1902) and Ann. d. Phys. 11 (1903)

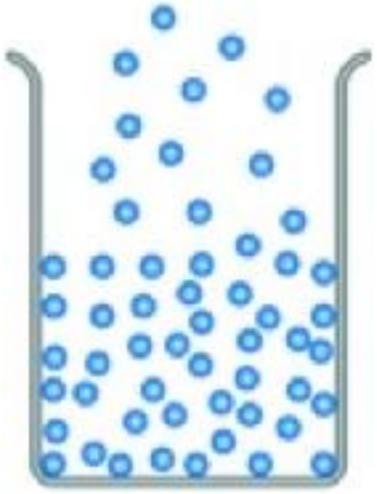
#2

Part 2 "derives" the equivalence of the osmotic pressure between suspended particles and dissolved molecules.

It uses the formalism of Einstein's earlier papers.
Einstein's arguments, like others, involve integrals over phase for the entropy and free energy.
As long as the particles are sufficiently dilute the expressions for the entropy and free energy are similar.

#3

Theory of diffusion of small suspended spheres



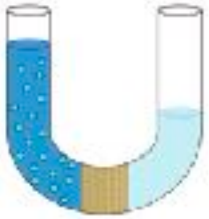
This is a bad picture it is supposed to show the concentration increasing as you go down.

#3

$P_{os}=-kTn(x+Dx)$

$P_{os}=-kTn(x)$

X

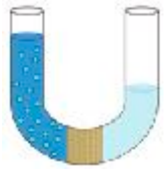


First, osmotic pressure is the defined by concentration at a point
$P_{os} = n(x)kT$ where n(x) is the number density

If n(x) is not constant, then the net force (per unit volume) acting on a particle is $F = -kT[dn(x)/d(x)]$

Einstein's earlier methods treat osmotic pressure, but he is not the first. J.F. van t'Hoff's work in the 1880's lead to the Nobel in 1901.

#3



An aside
gravity and fine particle dispersions

osmotic pressure is the defined by concentration at a point
$P = =n(x)kT$ where $n(x)$ is the number density

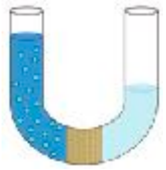
If $n(x)$ is not constant, then the net force per unit volume
acting on a particle is $F = -kT[dn(x)/d(x)]$

$$F_{grav} = -mgn(x) \quad F_{osmos} = -kT[dn(x)/d(x)] \text{ and } mgn(x)=kT[dn(x)/d(x)]$$

$$\text{Ergo } n(x)=n(0)e^{-mgx/kT}$$

Einstein predicted this exponential decay and it has been measured.

#3



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Einstein predicted this exponential decay and it has been measured.

This is strange stuff!!! The particles do not interact directly. But they do change the velocity of the water molecules that hit them. That change is “diffused” throughout the fluid. And other particles “feel” the effect!!!

#3

Let’s look at the fine particle dispersion again.

This time gravity would give the particles a net downward velocity determined by the viscosity. Also the diffusivity would give them a net upward velocity:

$V_u = D[dn(x)/dx]$ and By Stokes law $V_d = n(x)mg/(6\pi r\eta)$ where
r is the radius of the particle and η is the viscosity

But we have previously $dn(x)/d(x) = mgn(x)/(kT)$
substituting and solving for D we get

$$D = kT/(6\pi r\eta)$$

Diffusivity is the relation between a flux, J, and the gradient dp/dx $J=-Ddp/dx$

#3

Difffusion upward velocity	$D[dn(x)/d(x)]$
Osmotic force	$kTdn(x)/d(x)$
Gravity force	$mgn(x)$
Stokes velocity	$n(x)mg/(6\pi\eta r)$

$$D = kT/(6\pi r\eta)$$

The diffusivity, D, depends only on measurable quanties the radius of the particle (r) and viscosity of the fluid (η)

#4

On the random motion of particles suspended in a liquid and their relation to diffusion

Until now everything has been steady state. The velocities have produced constant fluxes and the plus and minus fluxes have been equal.

In part 4, Einstein examines the time component of the diffusion equation. I am not sure if he was unique. But that was his the genius!

#4

On the random motion of particles suspended in a liquid and their relation to diffusion

In part 4, *f*(x,t) is the number density of the microscopic particles suspended in a fluid. Part 4 uses the methods of statistical mechanics to examine how f(x,t) would vary in time. The result is a diffusion equation. The coefficient is that of part 3, ie D.

$$\delta f/\delta t = D\ \delta^2 f/\delta x^2$$

Look at each of the n particles for a short period of time τ. Each will increase its position by Δ. Δ will have a frequency distribution $\phi(\Delta)$. The number of particles experiencing a displacement between Δ and $\Delta+d\Delta$ is $dn=n\phi(\Delta)d\Delta$. And therefore:

$$f(x, t+\tau)dx = dx \int f(x+\Delta)\phi(\Delta)d\Delta$$

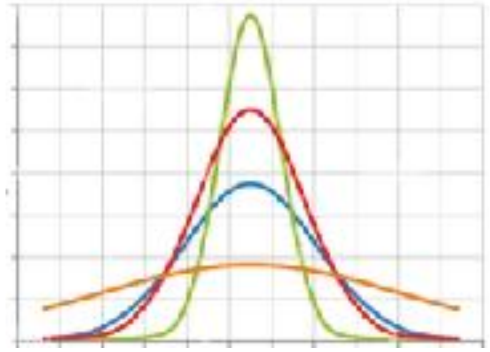
When you expand both sides you get $df/dt = d^2f/dx^2 * D$

Where D is the diffusion coefficient $1/(2\tau) \int \Delta^2\phi(\Delta)d\Delta$

#4

The solution is the frequency distribution:

$$f(x,t) = [n/4\pi Dt)^{1/2}] * \exp(x^2/4Dt)$$



#4

$$\delta f/\delta t = D\,\delta^2 f/\delta x^2$$

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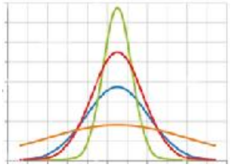


The test for the reality of molecules is:

Follow a large number of particles.
Record how far they go at various time intervals.
Check that the width of the distribution widens as $t^{1/2}$
Check that the $t^{1/2}$ slope has the value $(2D)^{1/2}$

#5

The Formula for the root square mean displacement of suspended particles shows a slope of $t^{1/2}$ and a $T^{1/2}$ as well as a $r^{-1/2}$ dependence. Einstein says test it.
If it is true, ATOMS ARE REAL

$$f(x,t) = [n/4\pi Dt)^{1/2}] * \exp(x^2/4Dt)$$

The mean directional displacement of a particle is λ
And $\lambda = (2Dt)^{1/2}$
This allows the prediction $\lambda^2 = t(kT/(3\pi r\eta))$

The one second λ^* is 0.8 microns for a 0.001mm particles in water

Take that Ernst

Note: The discussion of osmotic pressure has assumed the value of the Boltzman constant, k, or alternatively Avagadro's number, N, is known. The first good measurement of k was by Ernst Plank. The second talk addresses black body radiation.

Appendix 1 - Time Dependence

At time 0, the points have the positions shown. At time τ, each has moved an individual amount Δ. Δ is different for each particle. But there are constraints on ϕ(Δ), the frequency distribution of delta Δ's.

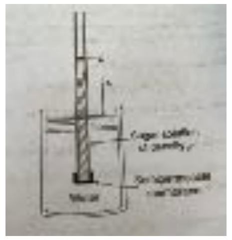
1) The integral of ϕ(Δ) is 1,

2) ϕ(Δ) is symmetric

The second moment of ϕ(Δ) is D. $\sum \Delta^2\,\Phi(\Delta) = D$

Einstein defines f(x,t) the number density particles. First, he looks at the change of f(x,t) for short times, τ, and in a thin slice of space of width Δ. He expands f(x+Δ,t+τ) in taylor series and obtains the diffusion equation. Then he interprets the expanding width of the distribution in terms of the mean motion of particles.

Appendix 2 - Osmotic Pressure



Osmotic pressure is real. If the membrane was a soft flexible balloon, it would expand and the levels would match.

Q. So how does the the semi-permeable membrane do what it does?
A. Entropy is real! (And maximized) In the water, the energy can be distributed among all the molecules. In the solution, the number of ways of distributing the energy is less because some has to go to the water and some to the sugar molecules.

$$A = U - TS$$

The free energy is the difference between the work and the entropy-temperature product

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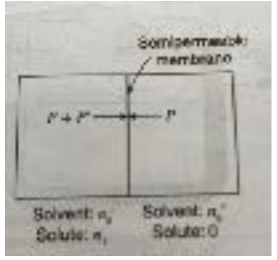
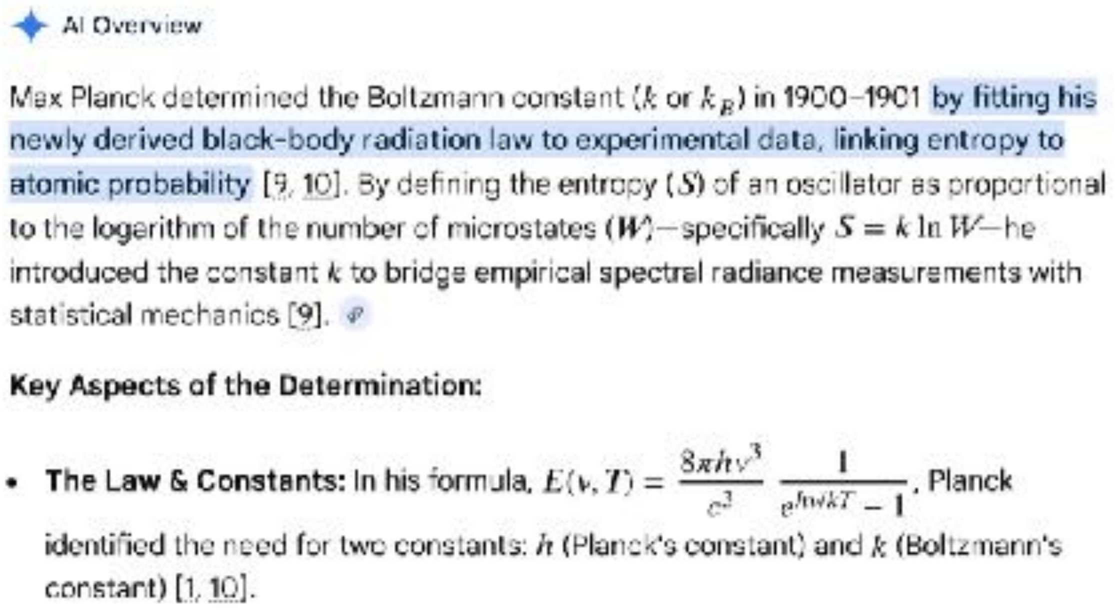
Appendix 2 - Osmotic Pressure



Two chambers are separated by a semi-permeable membrane. Initially the volumes are v_0 and v_1. Move the membrane a small distance. The water flows. The sugar molecules don't. n_0' decreases by dn_0 and n_0 increases by the same amount.

The work done is $dW = P'v_0\,dn_0$
The entropy of mixing is proportional to $RT\log(n_1/n_0)$.
Therefore the change to the entropy of mixing is $RT(n_1/n_0)$. Finally

$$P' = n_1RT/(n_0v_0) \quad \text{or} \quad P' = n_1RT/V$$



AI Overview

Max Planck determined the Boltzmann constant (k or k_B) in 1900–1901 by fitting his newly derived black-body radiation law to experimental data, linking entropy to atomic probability [9, 10]. By defining the entropy (S) of an oscillator as proportional to the logarithm of the number of microstates (W)—specifically $S = k\ln W$—he introduced the constant k to bridge empirical spectral radiance measurements with statistical mechanics [9].

Key Aspects of the Determination:

- **The Law & Constants:** In his formula, $E(\nu, T) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}$, Planck identified the need for two constants: h (Planck's constant) and k (Boltzmann's constant) [1, 10].