Origins of Modern Physics

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notes at:
http://www.tcd.ie/physics/foams/Lecture_Notes/PY1P20_origins_of_modern_physics

1. The existence of atoms
2. Fingerprints of Matter: Spectra
3. The nature of light
4. The discovery of X-rays and electrons
5. Models of the atom
6. Divisibility of atoms: radioactivity
7. Motivation for Einstein’s theories of relativity
References

• **main text:** Young H.D. and Freedman R.H., University Physics, 12th edition, Addison-Wesley, 2008

• chapter 1: Abraham Pais, “‘Subtle is the Lord…’ The Science and the Life of Albert Einstein”, Oxford University Press, 1982
1. The existence of atoms

1.1 Speculations and Indications

1st edition Encyclopaedia Britannica, 1771:
“Atom. In philosophy, a particle of matter, so minute as to admit no division. Atoms are the minima naturae [smallest bodies] and are conceived as the first principles or component parts of all physical magnitude.”

Similar to speculations of Greek philosophers Demokrit (460-370 BC) and Epikur (342-271 BC), over 2000 years earlier!
• 1808, 1810: John Dalton, New System of Chemical Philosophy: finite number of atomic species (18 were known at the time)

• Throughout 19th century discussions concerning the definitions of atoms and molecules

**QUESTION:** Are atoms *real* or just a useful *concept* to explain chemical reactions?
Dalton’s law of multiple proportions, 1808

if two elements combine, they do so in a ratio of small integer numbers

Gay-Lussac, 1809

ratio of volumes of gases that combine are simple numbers

(production of NO₂ and N₂O₃, ie. Ratios 1/2 or 2/3)

in line with Dalton’s law
**Avogadro’s hypothesis, 1811**: in gases at constant pressure and temperature the number of particles per volume is constant

**Prout, 1815**: speculation that masses of atoms are multiples of hydrogen
Kinetic theory

Daniel Bernoulli, 18th century: gas *pressure* due to collision of particles (atoms, molecules) with walls of container;

leads to derivation of law of Boyle-Mariotte: $pV = \text{const.}$, (1662,1676)

Consider box of volume $V$ containing $N$ particles, each of mass $m$

Simplifications: all particles have same magnitude of velocity $v$, only movement in three directions normal to box wall are possible

In time $\Delta t$, a number of particles contained in the (imaginary) cylinder will hit the wall and undergo a change in velocity of $2v$. 

[Diagram of gas particles colliding with a wall]
number of particles in cylinder: fraction \( \frac{Av \Delta t}{V} N \);

of these only 1/6 have will hit (left) area A of the cylinder

force \( F = ma = m \frac{\Delta v}{\Delta t} \); acceleration \( a \), pressure \( p = \frac{F}{A} \);

total force: \( \frac{1}{6} \frac{Av \Delta t}{V} Nm \frac{2v}{\Delta t} \), where set \( \Delta v = 2v \)

pressure: \( p = \frac{Nm v^2}{3V} \)

thus \( pV = \frac{Nm v^2}{3} = \) constant, as in law of Boyle - Mariotte
Further theoretical progress of kinetic theory: **Clausius, Maxwell, Boltzmann (19th century)**, including statistical interpretation of the 2nd law of thermodynamics (increase in entropy).

However, debate about atoms continued until the beginning of the 20th century. It was eventually concluded by increasing amount of **direct experimental evidence** (determination of Avogadro’s number, size of atoms, detection of their motion).
1.2 Determination of atomic size and Avogadro's number

Rough estimate of size of atoms using macroscopic quantities

thought-experiment (*Gedankenexperiment*): cube of material, side length 1 cm
perform $S$ cuts in x-direction, **down to one layer of atoms**, then cut in y-direction, then z
$3S$ cuts $\rightarrow$ collection of $S^3$ individual atoms

required energy $E_V$ is equivalent to evaporation energy per cm$^3$
• Each cut: 2 new surfaces of 1 cm², corresponding to surface energy per cm² of 2 $E_s$ ($E_s$ is the surface energy per cm²).

Energy balance per volume: $3S \times 2E_s = E_V$

• $S$ is number of cuts per centimeter,
$S^3$ is number of atoms per cm³

• $d$: size of atom (~radius)

• $d = 1/S$; \[ S = \frac{1}{d} = \frac{1}{6 \frac{E_v}{E_s}} \]

• Experimental data for water:
$E_s = 7.3 \times 10^{-6}$ J/cm²; $E_v = 2.26 \times 10^3$ J/cm³

$\rightarrow S = 5.15 \times 10^7$ cm⁻¹ and $d = 1.9 \times 10^{-8}$ cm = $1.9 \times 10^{-10}$ m

right order of magnitude!
**Historical values**

**Size of atoms:**

- Thomas Young, 1816 (based on surface tension):
  \[ d = 0.5 - 2.5 \times 10^{-10} \text{ m} \]
- Loschmid 1866: \( d \approx 10^{-9} \text{ m} \) (gas) (method: see below)
- Kelvin 1870: \( d \) larger than \( 2 \cdot 10^{-11} \text{ m} \) (gas)
- Maxwell, van der Waals 1873:
  \[ d \approx 6 \cdot 10^{-10} \text{ m} \] (Hydrogen molecule)
- End of 19th century, Hydrogen molecule,
  \[ d = 2.4 \cdot 10^{-10} \text{ m} \]
**1 mole (SI unit):** amount of a substance of a system that contains as many elementary entities as there are atoms in 12 gram Carbon-12. The number of entities in a mole of a substance is given by **Avogadro’s number** $N_A$.

**Molecular mass** $M$:

$$M = N_A m \quad (m: \text{mass of one molecule/atom})$$

- Loschmid 1866: $N_A \approx 0.5 \cdot 10^{23} \text{ mol}^{-1}$
- Maxwell $N_A \approx 4 \cdot 10^{23} \text{ mol}^{-1}$ (+ further similar 19th century estimates)

Important for belief in the actual existence of atoms: **values converge!**

- 2005: $N_A = 6.02214199 \cdot 10^{23} \text{ mol}^{-1}$
Loschmidt’s determination of atomic diameter $d$ and $N_A$

- 2 unknowns $\rightarrow$ need 2 equations
- kinetic theory of gases, atoms are spherical particles
  $N$ particles per volume $V_g$ of gas: define $n = N / V_g$ (number density)

- mean free path length $\lambda$ that atom can travel without collision with other particle: $\lambda = 1 / (\sqrt{2} \ n \ \sigma)$, (eqn. I)
- scattering cross-section $\sigma = d^2 \pi$

- Liquid (of volume $V_l$): dense packing of atoms (volume $V_a$) of volume packing density $\phi$; $\phi = N \ V_a / V_l$
  Loschmidt: $\phi \approx 0.85$ (1960s, random packing of spheres, $\phi \approx 0.64$)
Now consider ratio of density of gas and liquid
\[ \frac{\rho_g}{\rho_l} = \frac{V_l}{V_g} = N \frac{V_a}{(V_g \varphi)} = n \frac{V_a}{\varphi} \]

Inserting \( V_a = d^3 \pi / 6 \) one obtains
\[ n \pi \frac{d^3}{6} = \varphi \frac{\rho_g}{\rho_l} \] (eqn. II)

Mean free path and \( \rho_g / \rho_l = V_l / V_g \) were known for air, so \( n \) (and thus \( N_A \)) and \( d \) could be determined by combining eqns. I and II (and using the ideal gas equation)
Return to kinetic gas theory: Boltzmann constant

\[ pV = \frac{Nmv^2}{3} \]  \hspace{1cm} (*) \hspace{1cm} \text{pressure } p, \text{ volume } V, \text{ number of particles } N, \text{ mass } m, \text{ velocity } v

ideal gas equation: \[ pV = nRT \]  \hspace{1cm} (**)

\( n \): number of mols, \( R = 8.314 \ \text{J/(mol K)} \): universal gas constant, \( T \): temperature

using \( n = N/N_A \) we obtain from (*) and (**): \[ N_A \frac{mv^2}{3} = RT \]

thus \[ \frac{1}{2}mv^2 = \frac{3}{2} \frac{R}{N_A} T \]

define Boltzmann constant \( k_B = \frac{R}{N_A} = 1.3810^{-23} \ \text{J/K} \)

\[ \frac{1}{2}mv^2 = \frac{3}{2} k_B T \]

where \( \frac{1}{2}mv^2 \) is the average translational kinetic energy of one particle
1.3 Brownian motion and Einstein’s interpretation

**Observations**

*Irregular motion of small particles suspended in fluid noticed soon after invention of microscope*

**Video:** 1μm polystyrene spheres suspended in water
*Result from tracking 107 spheres: \( N_A \approx 5.9 \times 10^{23} \)  
(Nakroshis et al., Am. J. Phys, 2003)

- Anton van Leeuwenhoek (1632-1723): life?
- Jan Ingenhousz (1730-1799): also inorganic material
- Robert Brown (1773-1858): summer 1827, motion of pollen grains suspended in water, also inorganic grains
- Adolphe Brogniart, 1827
• **Initial attempts of explanation:** *external factors* (vibrations, microscopic currents, thermal variations, capillarity, electrical effects, polarity, surface tension)

• Leon Gouy, 1880s: comprehensive experiments: 

  *motion is fundamental physical property of fluid matter*

  **Results:** decrease of vigour of motion with increasing particle size and fluid viscosity

• **The problem of measurements:** measured *velocities* (distance divided by observation time) **increase** as observation **time** is **decreased**.
1905: Einstein’s interpretation: existence of atoms

dynamical equilibrium as superposition of two processes

1. Systematic viscous drag force acting on each suspended particle.

2. Fluctuating statistical force, due to thermal molecular motion of water molecules which collide with suspended macroscopic particles.

Result is a random motion of the particles, described by a diffusion equation.

Diffusion coefficient linked to universal and material constants.

animation: http://www.phy.davidson.edu/brownian.html
Dr. Wolfgang Christian, Davidson College, USA
Computer simulations of random walks in 1, 2 and 3 dimensions

Simulation by Iwo and Iwona Bialynicki-Birula (Modeling Reality, OUP 2004) [smoluchowski]

Also called “The drunken sailor problem”.

normal walk : distance proportional time

random walk : distance proportional $\sqrt{\text{time}}$
Theory: Einstein 1905, Langevin 1908

Force on a particle has average, dissipative part (drag constant $\gamma_0$) and stochastic part (with certain properties)

$$F(t) = m \frac{dv}{dt} = \gamma_0 v + F_{stoch}(t);$$

Solution for mean square displacement in time:

$$(x(t)$$ is position at time $t)$$

$$\left\langle \left[ x(t) - \langle x(t) \rangle \right]^2 \right\rangle = 2Dt$$

Diffusion constant $D$:

$$D = \frac{RT}{N_A} \frac{1}{6\pi\eta r}$$

$N_A$: Avogadro’s number, $T$: absolute temperature; $R$ universal gas constant, $r$: radius of particle (sphere), $\eta$: viscosity of liquid, $\gamma_0 = 6\pi\eta r$
Comparison with experiment:

- \( N_A = 6 \times 10^{23} \); viscosity of water \( \eta = 1 \text{mPa} \cdot \text{s} \); \( r = 0.001 \text{mm} \), \( R = 8.31 \text{J/(mol K)} \) gas constant, \( T \) (room) temperature; thus mean square displacement of 6 micron per minute; observable!
- Alternatively, measure displacement and determine \( N_A = 6.6 \times 10^{23} \) (1911)
- 1908, 1909, 1911 Jean Perrin *et al.* sedimentation measurements, confirmation of Einstein’s results; Nobel Prize for Perrin (1926)
- Yet another determination of \( N_A \) consistent with previous measurements, in addition to this the motion of atoms is made visible.
Comment: Louis Bachelier (1870-1946)

- Result: price changes can be modelled as random walk or diffusion process
- No influence on contemporaries, despite having eminent mathematician/physicist Henri Poincaré as examiner.
- Thesis rediscovered in the 1960s, this area of research is now called econophysics
The large amount of experimental and theoretical results regarding atoms resulted in the acceptance of atoms as a physical reality from the beginning of the 20th century onwards.

Now, scanning tunneling microscope: direct images of atoms.
Alternatively: Atomic Force Microscopy

“Make a pointer with a single atom at the end – very carefully poke at the atoms on a surface and measure the force.”

AFM image of NaCl - lattice constant of face-centred cubic lattice = 0.564 nm

Atomic Force Microscopy and Scanning Tunnelling Microscopy were invented by Binnig and Rohrer - Nobel 1986