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 help explain chemistry reactions?

1.1 (ctd) - concept of atoms in chemistry
- Dalton's law of multiple proportions, 1808: if there is more than one possible combination of two elements then the ratios of the masses of the element that combines with the same amount of the other element are small integer numbers.
- Gay-Lussac, 1809: ratio of volumes of gases that combine are simple numbers
- 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
- Daniel Bernoulli, 18th century: gas pressure due to collision of particles with walls of container;
  \[ F = ma = \frac{dv}{dt}, \quad p = \frac{F}{A} = \frac{m\Delta v}{A} \]  
  (explains Boyle-Mariotte pV = const.)
- Further theoretical progress: Clausius, Maxwell, Boltzmann (19th century), including statistical interpretation of the 2nd law of thermodynamics (increase in entropy).
- Debate about atoms continued until the beginning of the 20th century, ended 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

Can we use macroscopic quantities to give us a rough estimate of the size of atoms and the number per unit volume?

Perform thought experiment - Gedanken experiment
- Take cube of material 1 cm on side
- Perform 5 cuts in x-direction, down to one layer of atoms, then cut in y-direction and then in z direction
- After 3.5 cuts - the material is divided into single atoms

Energy required equivalent to...
1.2 (ctd) – atomic size

- Each cut produces 2 new surfaces each of area 1 cm² - if $E_s$ is the
  surface area per cm² - the energy required for one cut is $2E_s$
- Total energy is thus $3 \times S \times 2 \times E_s = E_s$
- Since $S$ is the number of cuts per cm required to separate atoms, then
  $S^3$ is the number of atoms per cm³.
- $d$: size of the atom (~diameter)
  $d$ is inverse of $S$

$E_s = 2.26 \times 10^3$ J cm⁻¹; $E_s = 7.3 \times 10^3$ J cm⁻²
$S = 5.15 \times 10^4$ cm⁻¹; $d = 1.9 \times 10^{-10}$ m

The right order of magnitude

1.2 (ctd) – historical values

Size of atoms:
- Thomas Young, 1816 – based on surface tension – $d \approx 0.5 - 2.5 \times 10^{-10}$ m
- Loschmidt, 1866 – $d \approx 10^{-10}$ m – gas
- Kelvin, 1870 – $d \approx 2 \times 10^{-10}$ m – gas
- Maxwell, van der Waals, 1873 – $d \approx 6 \times 10^{-10}$ m
- End of 19th century – hydrogen molecule – $d \approx 2.4 \times 10^{-10}$ m

1 mole (SI unit): amount of substance of a system that contain as many
“elementary entities” as there are atoms in a 12 grams of Carbon-12.
The number of entities in a Mole of a substance is given by Avogadro’s
Number $N_A$

Molecular mass $M$: $M = N_A \cdot m$

2006 value: $N_A = 6.022 141 79(31) \times 10^{23}$ mol⁻¹.
It is important for belief in the actual existence of atoms that values
obtained from different methods converge with each other.

1.2 (ctd) – Loschmidt’s determination of $d$ and $N_A$

2 unknowns $\Rightarrow$ need 2 equations to solve
- kinetic theory of gases - atoms are spherical particles, $n$ particles per
  volume of gas
- mean free path is the length $\lambda$ that atom can travel without collision
  with other particles $\lambda = c / (n \cdot \sigma)$ (I)
  scattering cross section: $\sigma = \pi d^2$ constant $c = \sqrt{2}$
- liquid - dense packing of atoms: $\frac{n \pi d^3}{6} = \frac{\rho_f}{\rho_g}$ (II)
  $\rho_f, \rho_g$ - densities of fluid and gas
  $\phi$: packing density of atoms in a liquid, Loschmidt: $\phi = 0.85$
- Mean free path and were known for air and from (I) and (II) above, so
  $n$ (and thus $N_A$) and $d$ could be determined.

So the existence of atoms was a firm theoretical model, supported by all
the experimental data. There still awaited experimental proof.

1.3 Brownian motion and Einsteins perception

Observations:
- Irregular motion of small particles suspended in fluid noticed soon
  after the invention of the 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 Boggiart, 1827

Exercise: - what about other solids and liquids? - investigate
Take data for Nitrogen: $L_s = 0.201 \times 10^3$ cm⁻¹; $\tau_s = 8.91$ dyn cm⁻¹; $8.91$ mN cm⁻¹
And data for Lead: $L_s = 0.871 \times 10^3$ cm⁻¹; $\tau_s = 467$ dyn cm⁻¹; $467$ mN cm⁻¹
Find values of $E_s$ in table 17.6 p 587 of UP, values of surface tension, $E_s$ or $\gamma_s$, from other sources.
1.3 (ctd) Brownian motion

- 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 measuring 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.
   - short sharp transfers of momentum

Result is a random motion of the particles, described by a diffusion equation.
Diffusion coefficient linked to universal and material constants.

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)

The drunken sailor problem.
normal walk: distance proportional to time
random walk: distance proportional to $\sqrt{\text{time}}$

Diffusion equation

- root mean square displacement in x-direction:
  $\lambda_x = \sqrt{\langle x^2 \rangle} = \sqrt{\frac{RT}{N_A 3 \pi \eta r}}^{1/2}$
- $N_A = 6 \times 10^{23}$; viscosity of water $\eta = 1 \text{ mPa} \cdot \text{s}$; $r=0.001 \text{ mm}$, R gas constant,
  $T$ (room) temperature, take time $t = 1$ minute; obtain a mean square displacement of $\lambda_x = 6 \text{ micron in one minute}$: 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.

All of this resulted in the acceptance of atoms as a physical reality from the beginning of the 20th century onwards.
Can you see single atoms?

Not with optical light (~400-700nm) - need much smaller wavelengths than visible light to "see" an atom - x-rays for instance, but cannot make lenses for x-ray easily.

BUT we can use other atoms to feel the force from a single atom. Make a pointer with a single atom at the end - very carefully poke at the atoms on a surface and measure the force - get Atomic Force Microscopy.

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

AFM image of NaCl - lattice constant of cubic lattice = 0.564 nm.


Visualising single atoms

Can you see single atoms?

Electronic microscopy can now also be used to obtain atomic resolution.

A further question: Can you see the light from a single atom?

Yes - you can trap and catch a single ion.

You can then perform experiments on it for days or weeks on end.

If you excite it continuously with a laser, you can watch it fluoresce.

Has been done with Ba ions since 1983.

See: http://www.flickr.com/photos/fatllama/13222415/

Single atom ion trap

Mounted in ultra high vacuum ~ 10^-9 mbar.

Made from tantalum and tungsten and crocodile clips.

Barium shavings in pocket oven.

Current through oven evaporates Ba atoms.

Hot filaments produce electrons, ionising some Ba atoms.

Occasionally Ba+ ion trapped in ring in center (1mm diameter) in oscillating electric and magnetic field.

Laser (not shown) excites and scatters light off Ba ion.

See: http://www.flickr.com/photos/fatllama/13222415/