CLUSTERS: CHEMISTRY AND PHYSICS IN A FINITE WORLD

TONY STACE
University of Nottingham

Clusters:

Small collections (~ 1000) of atoms and/or molecules that are typically studied in the gas phase. These could behave as extremely small images of a bulk liquid or solid –

or, they could be unique materials!

How small does the collection have to become, before it fails to function in the same way as a bulk material?

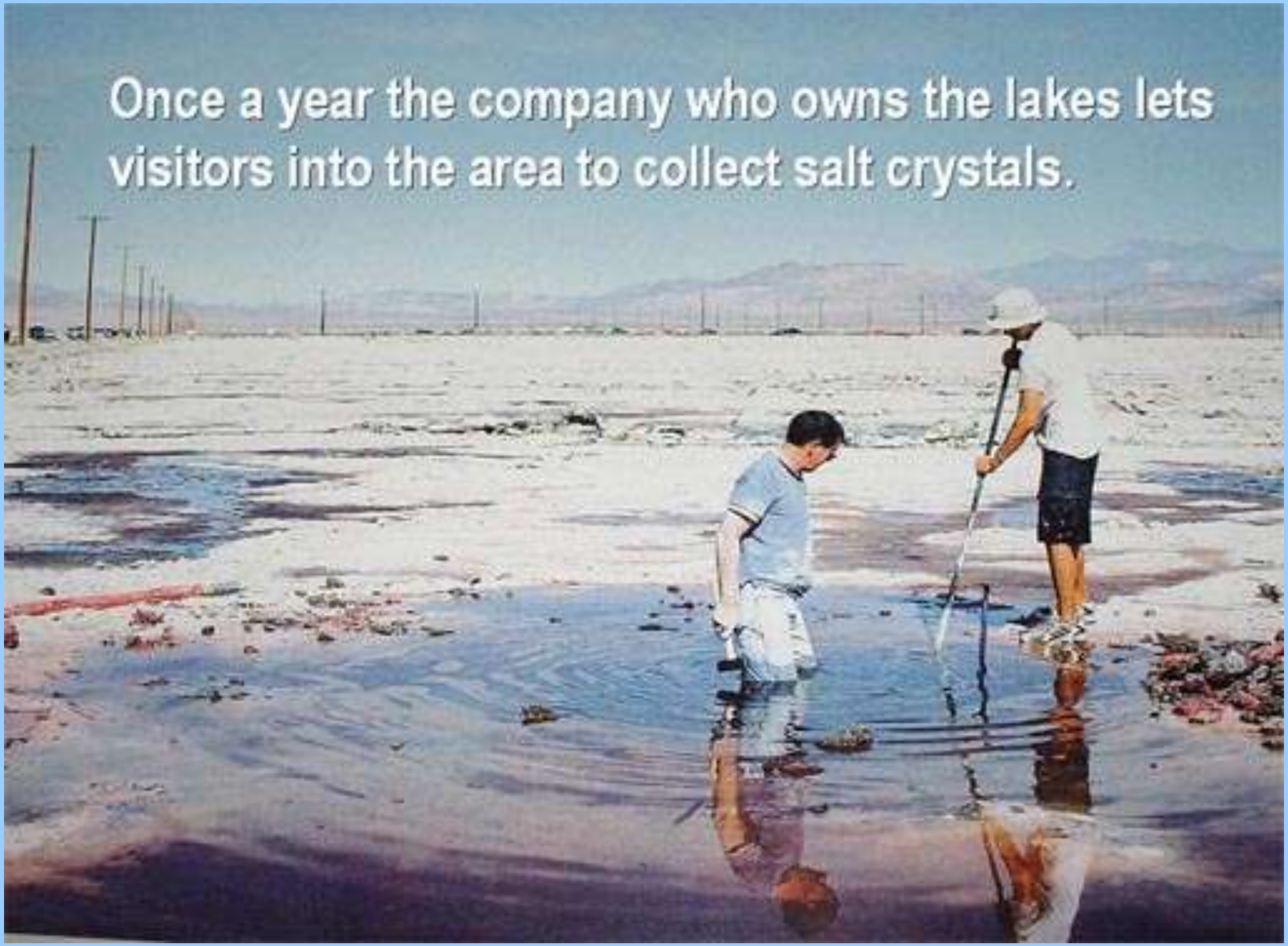
The types of questions we might seek answers to:

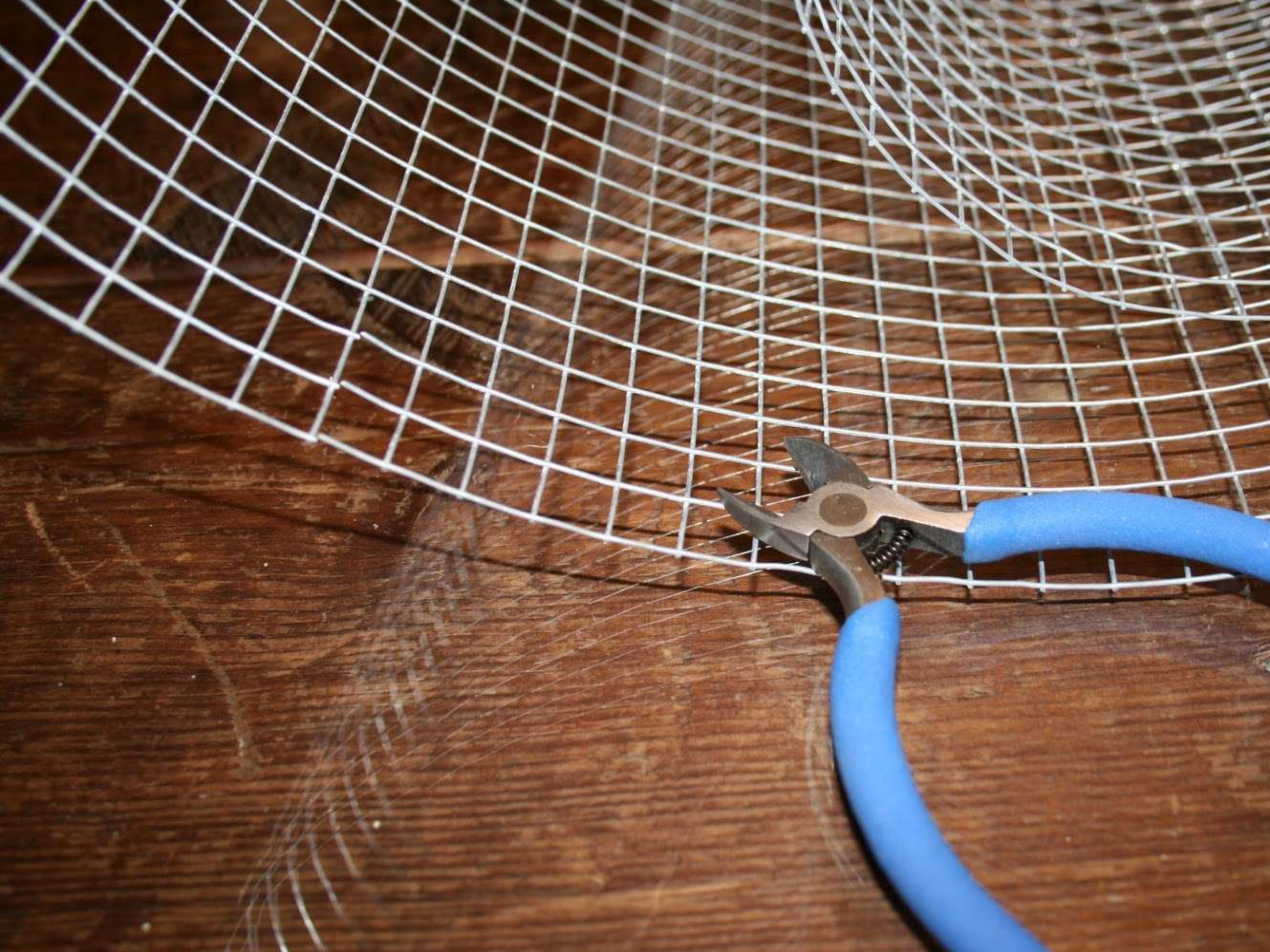
how many water molecules do we need to dissolve common salt (sodium chloride)?

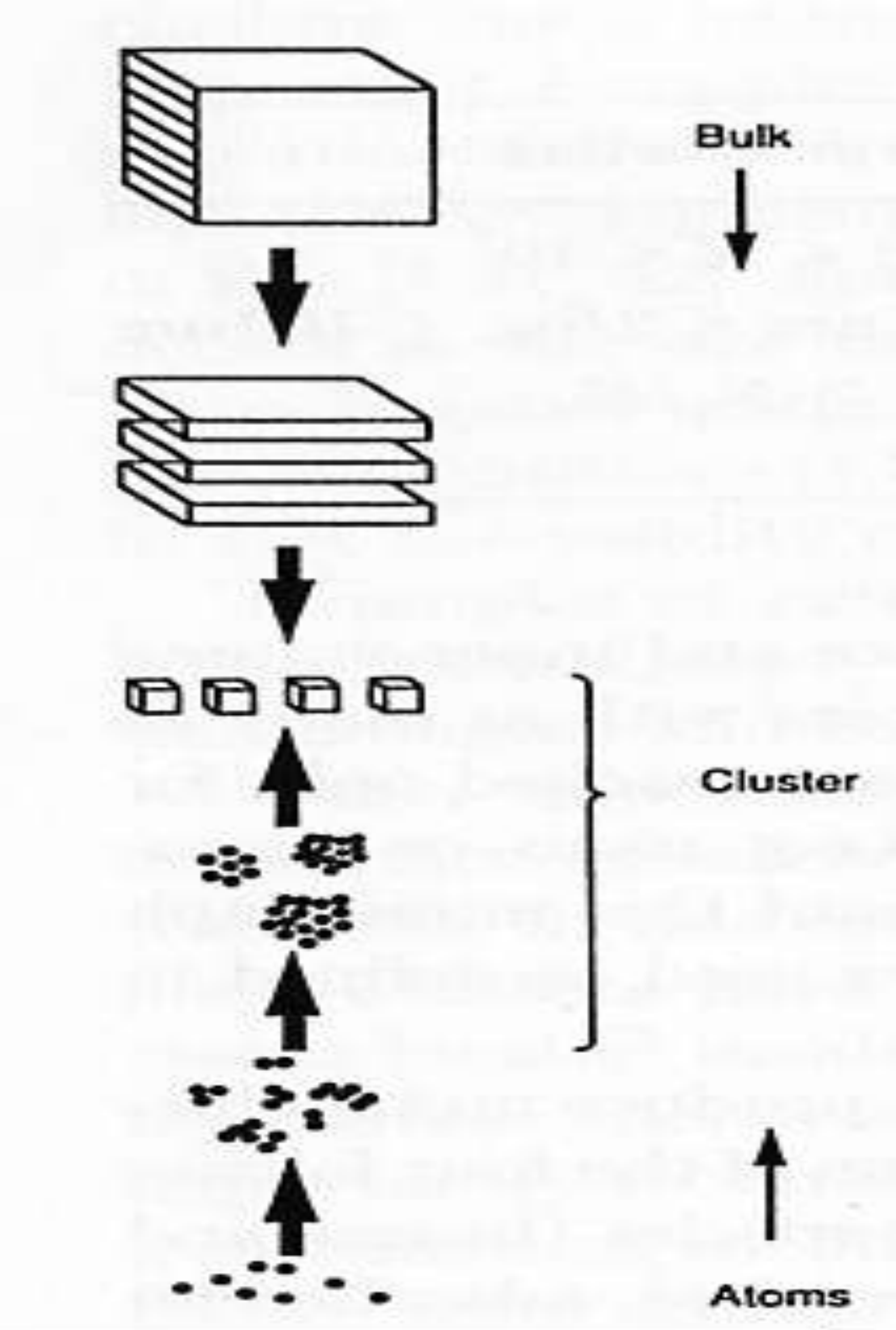
or

how many metal atoms do we need to make a piece of copper wire?


50 ml
PYREX


Once a year the company who owns the lakes lets visitors into the area to collect salt crystals.




Bulk
Cluster
Atoms

Important physical and chemical properties of bulk materials:

Structure	diamond
Melting	ice cube
Conduction of electricity	copper wire
Solubility	salt in water
Magnetism	???????
Chemistry	combustion

Size effects (bulk): **(spherical cluster model)**

R_a radius of a single atom

R_c radius of cluster

Volume of 1 atom – $4/3\pi R_a^3$

Volume of a cluster – $4/3\pi R_c^3$

no. of atoms (N) is $\propto (R_c/R_a)^3$ $R_c = R_a N^{1/3}$

Scaling cluster properties: $X_N = X_{bulk}(1 \pm \beta/N^{1/3})$ or $(1 \pm \alpha/R)$

Melting temperature of N atoms of gold $T_M / K = 1336.15 - \beta/N^{1/3}$

Size effects (surface):

No. of atoms on the surface (N_s) is $\propto 4(R_c/R_a)^2 = 4N^{2/3}$

Fraction of surface atoms $F_s = N_s/N = 4/N^{1/3}$

$F_s < 0.01$ (1%) for N > 64,000,000 atoms

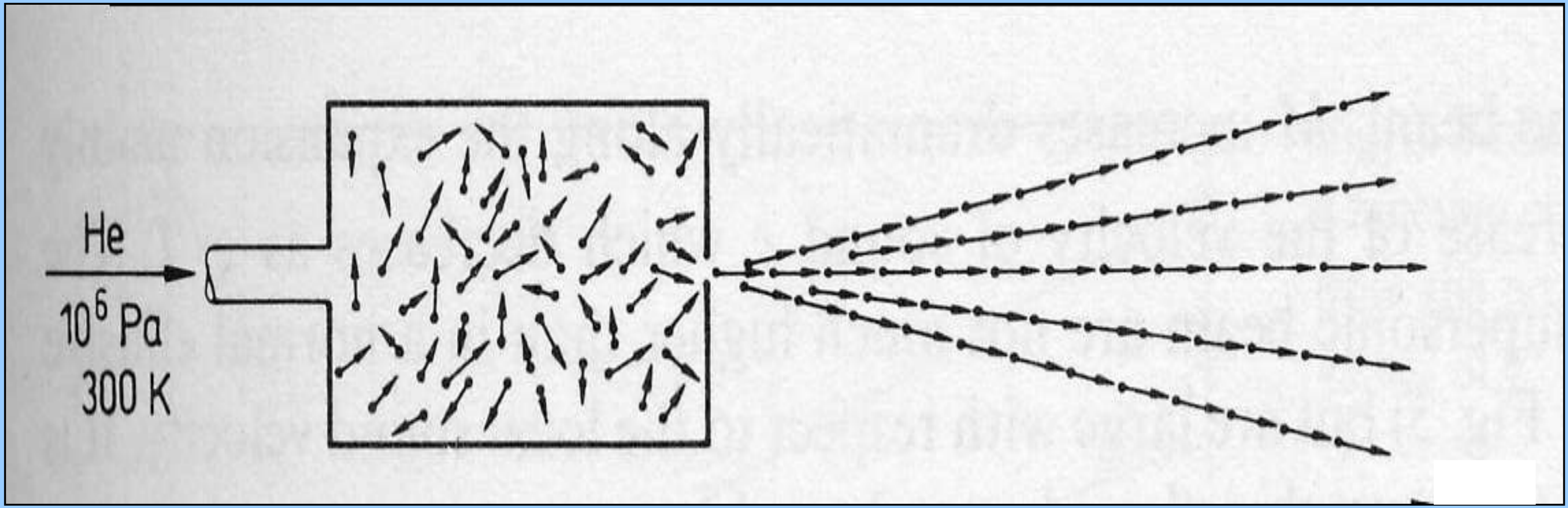
The significance of surface atoms is that when F_s is large, surface energy (surface tension) becomes as important as bulk binding energy in determining the properties of a material.

no. of atoms	radius	atoms on the surface
N	R_c(Å)	N_s/N (%)
125	4	80
1000*	10	40
10,000	22	10
1m	100	4

* start of nanotechnology

1 Å = 0.0000000001 m = 0.1 nm

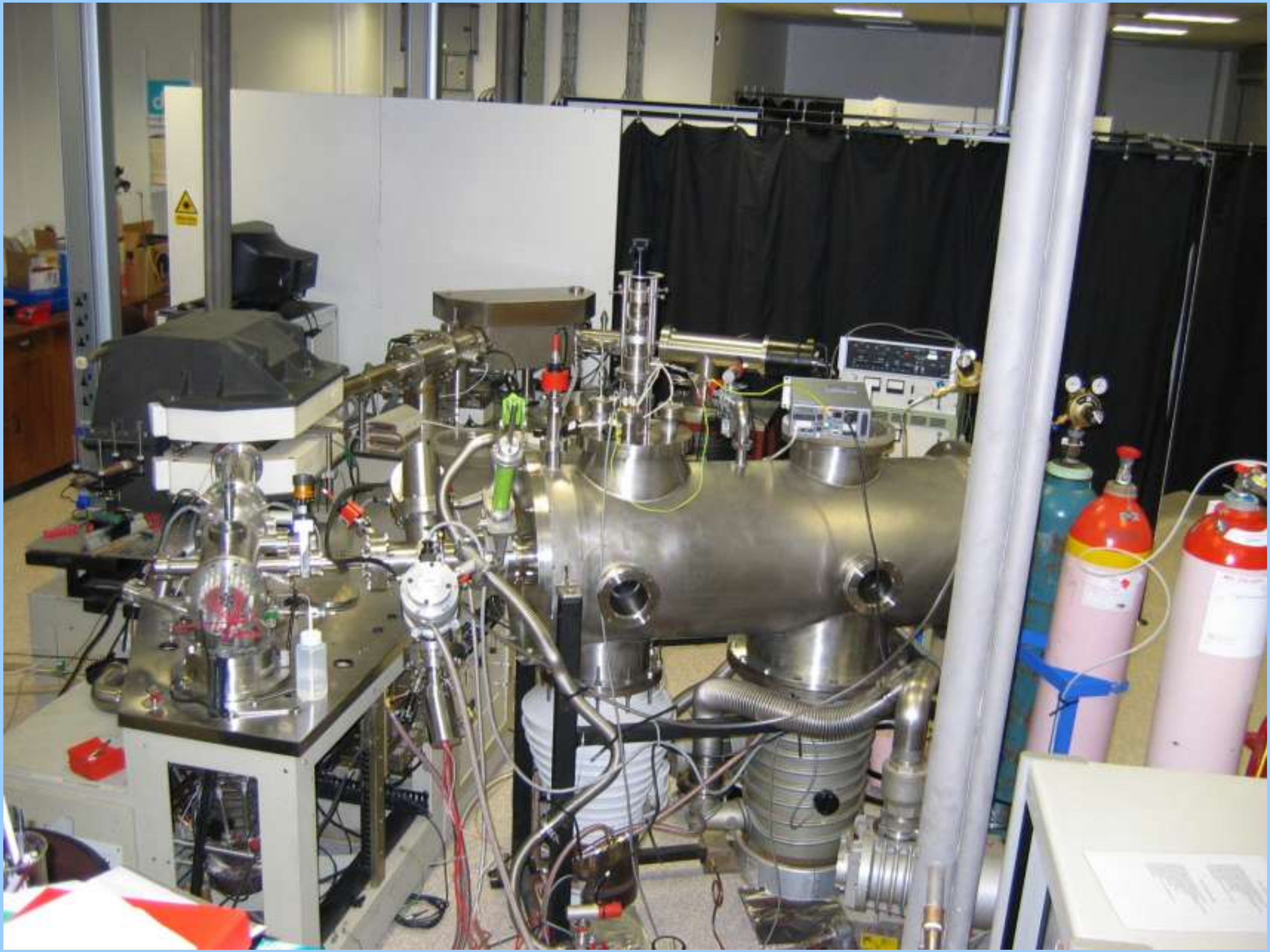
Production of clusters

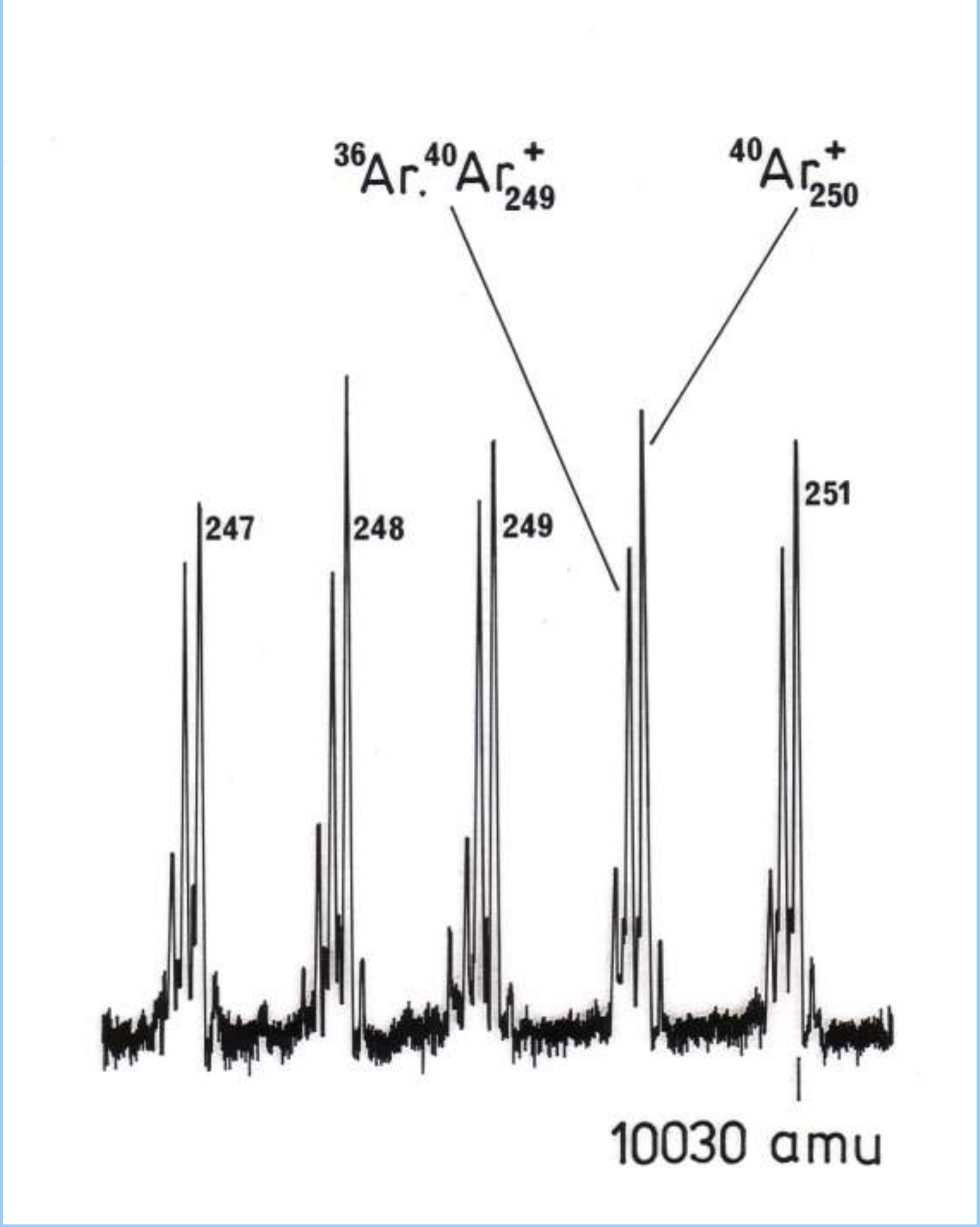


Temperature: 300 K → 1 K

Time taken for an atom to reach the vacuum is 0.000001 s

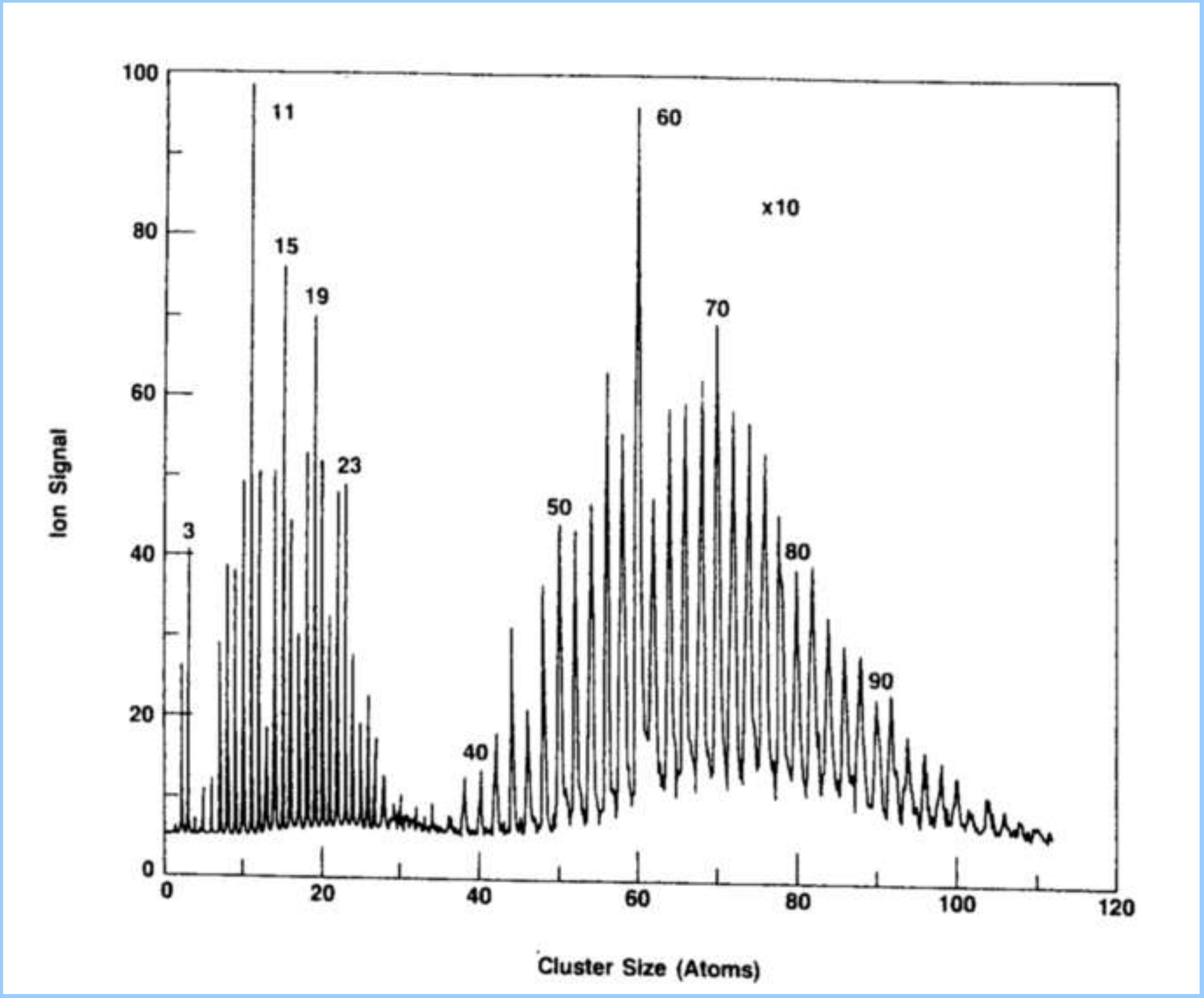
Rate of cooling: >10,000,000 K per second





Pure argon

Carbon clusters and fullerenes

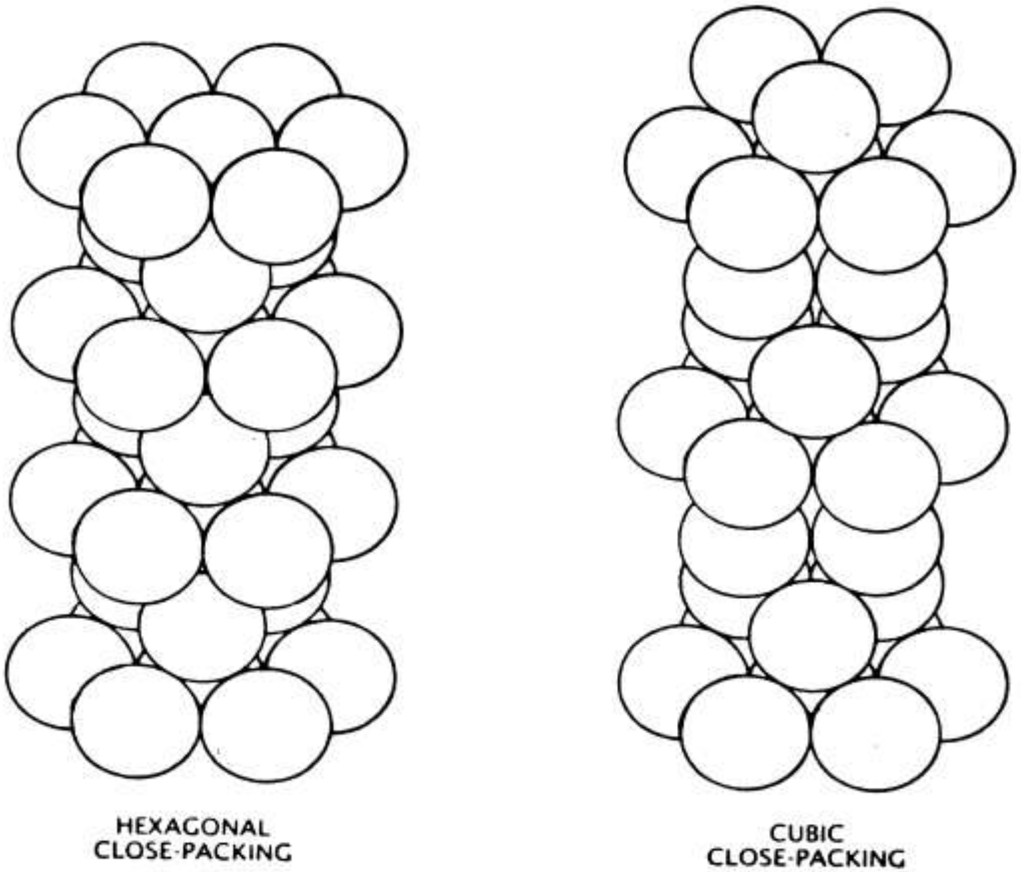


Kaldor *et al* 1984

Kroto *et al* 1985

How Nobel Prizes are won and lost!!

Structure



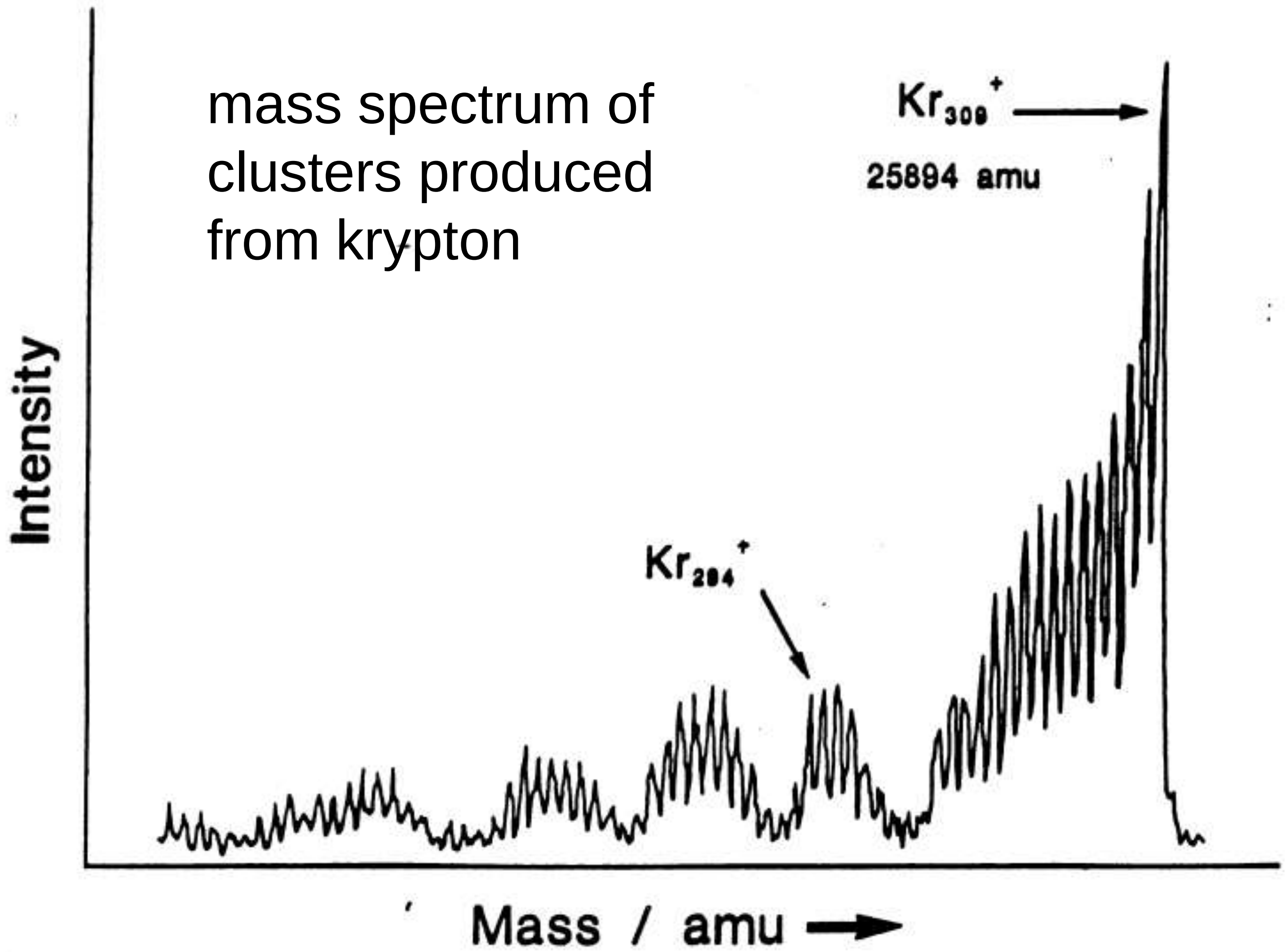
Be, B, Cd, Co, Ru, Sc, Re

For clusters, one way to investigate structure is to look for stable collections of atoms in a mass spectrum –

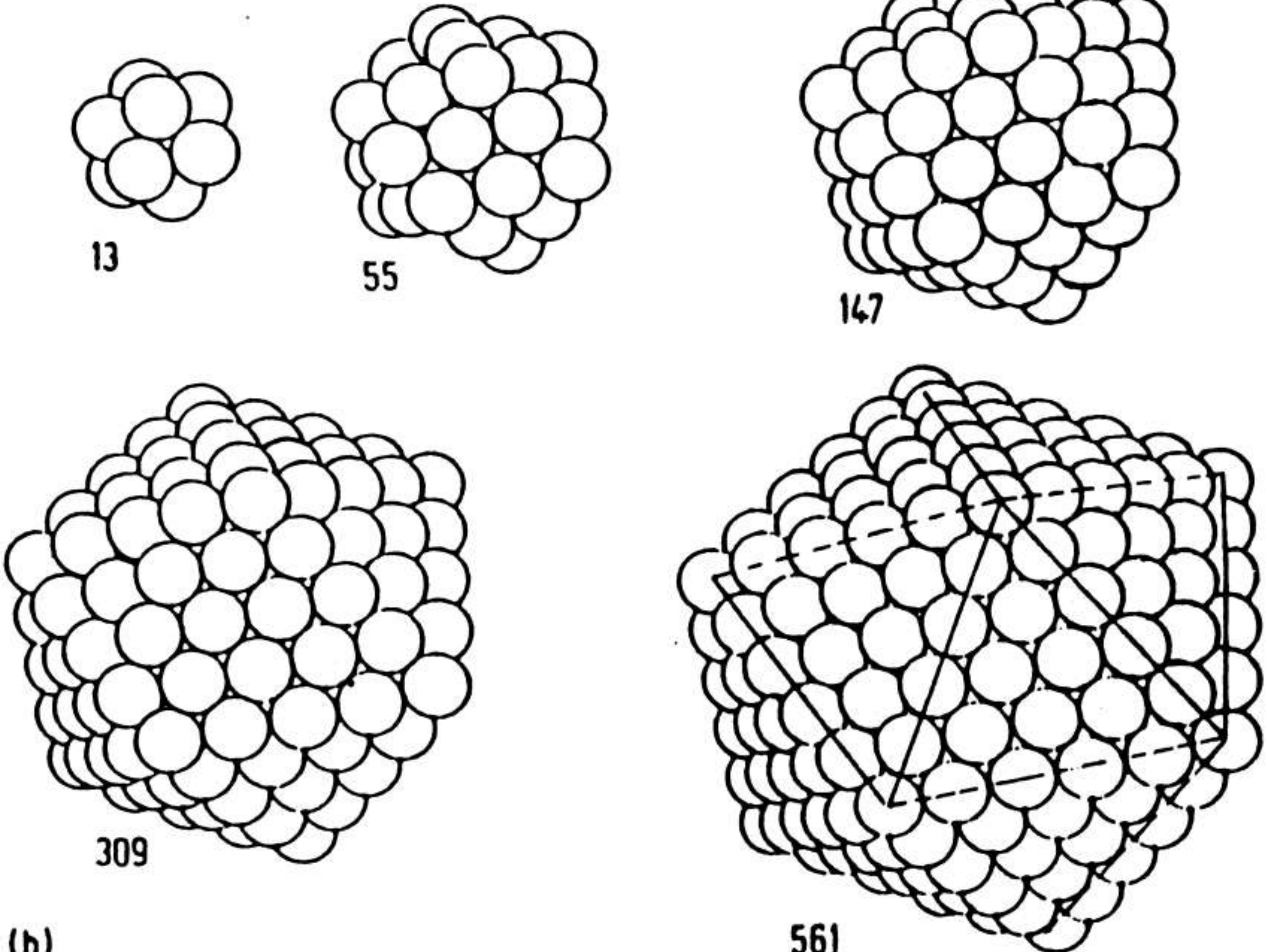
- a stable structure will be strongly bound and so will give a comparatively intense signal.

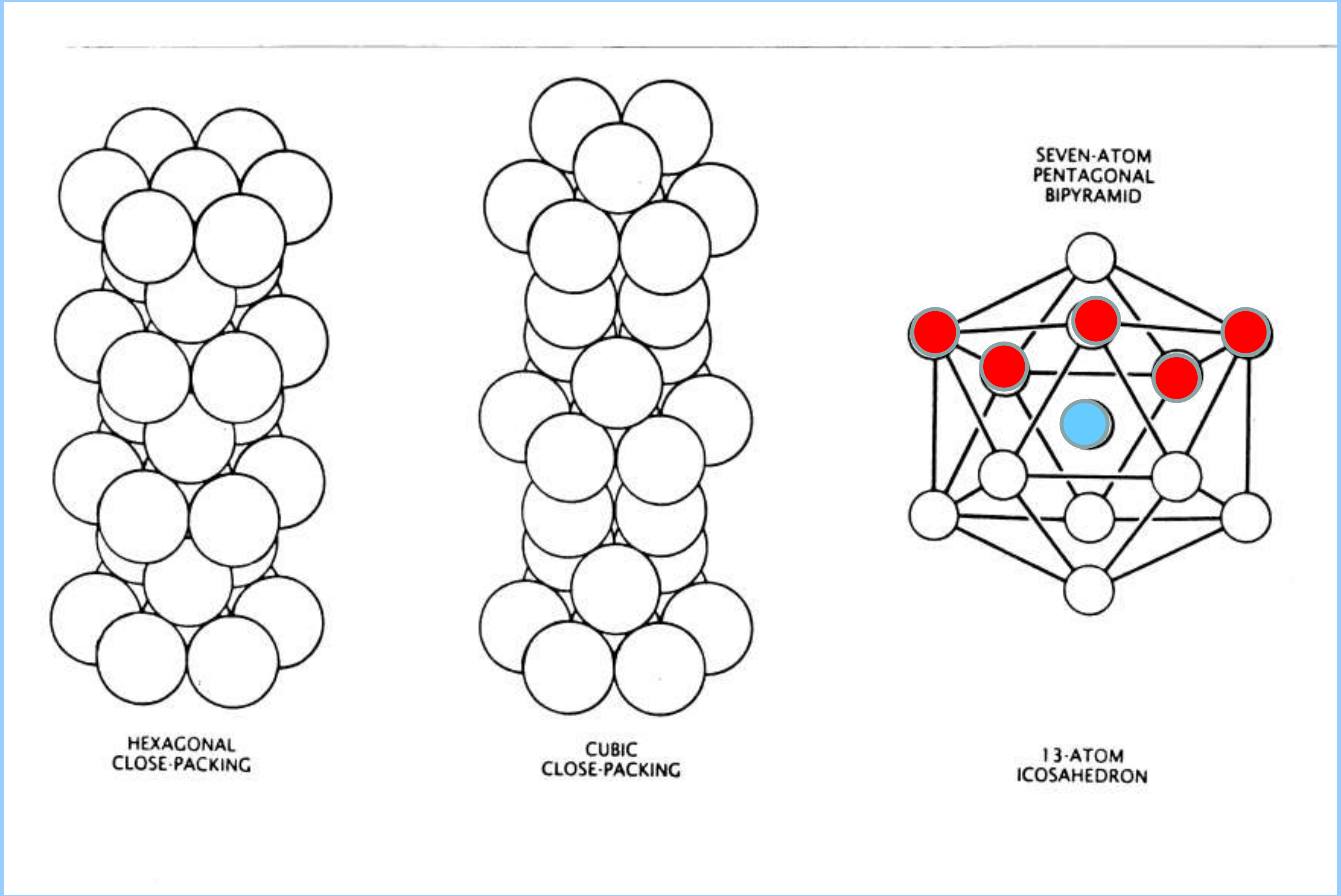
- structures that are less stable will yield weaker signals .

mass spectrum of clusters produced from krypton



All stable icosahedra



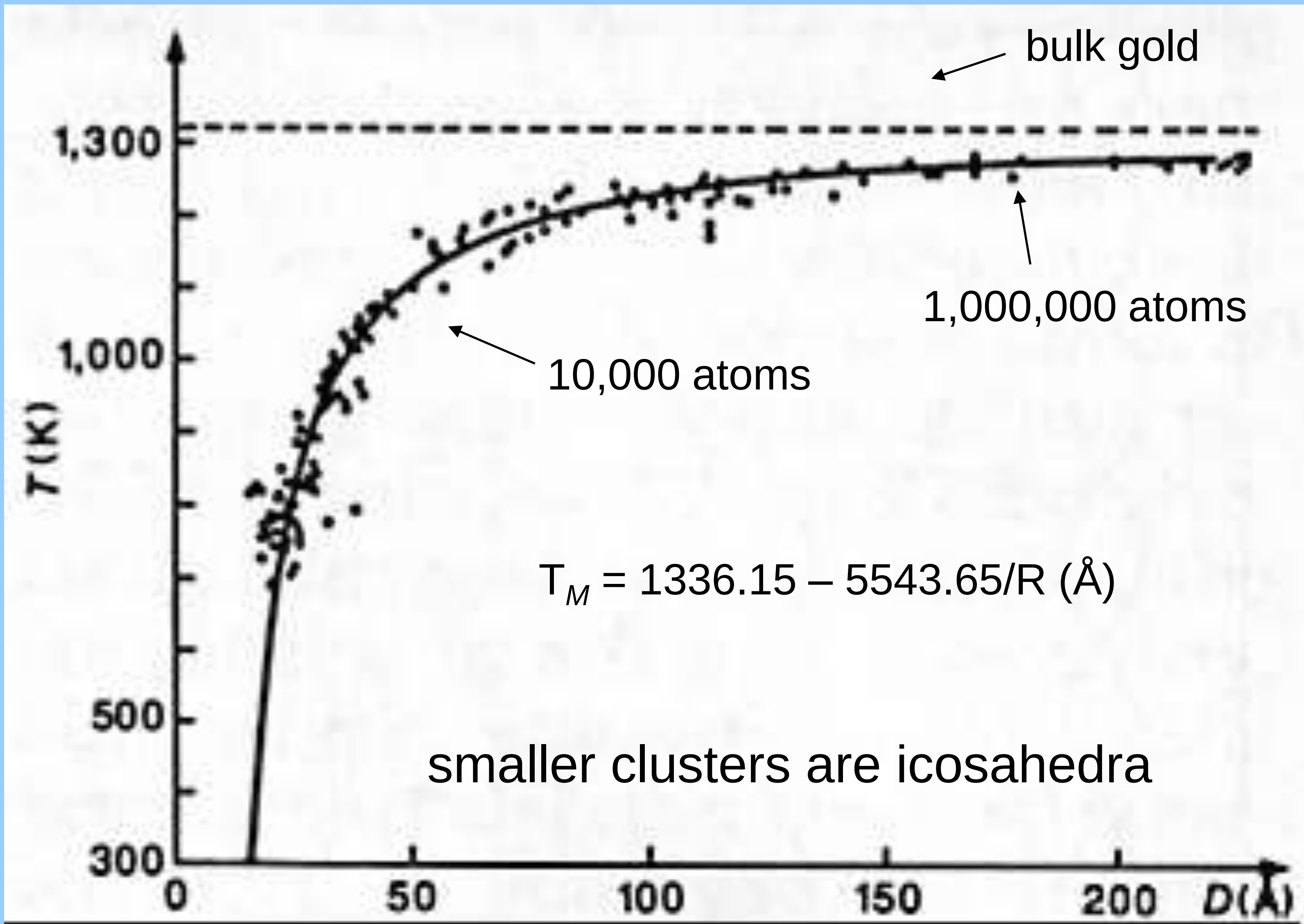


For single-atom systems there is no bulk equivalent – the structure is only stable because of surface energy.

The driving force for this effect in small clusters is surface energy, and a cluster needs to contain about 2000 atoms before the bulk binding energy is high enough for them to adopt stable close-packed structures.

Melting

Melting in deposited gold nanoparticles

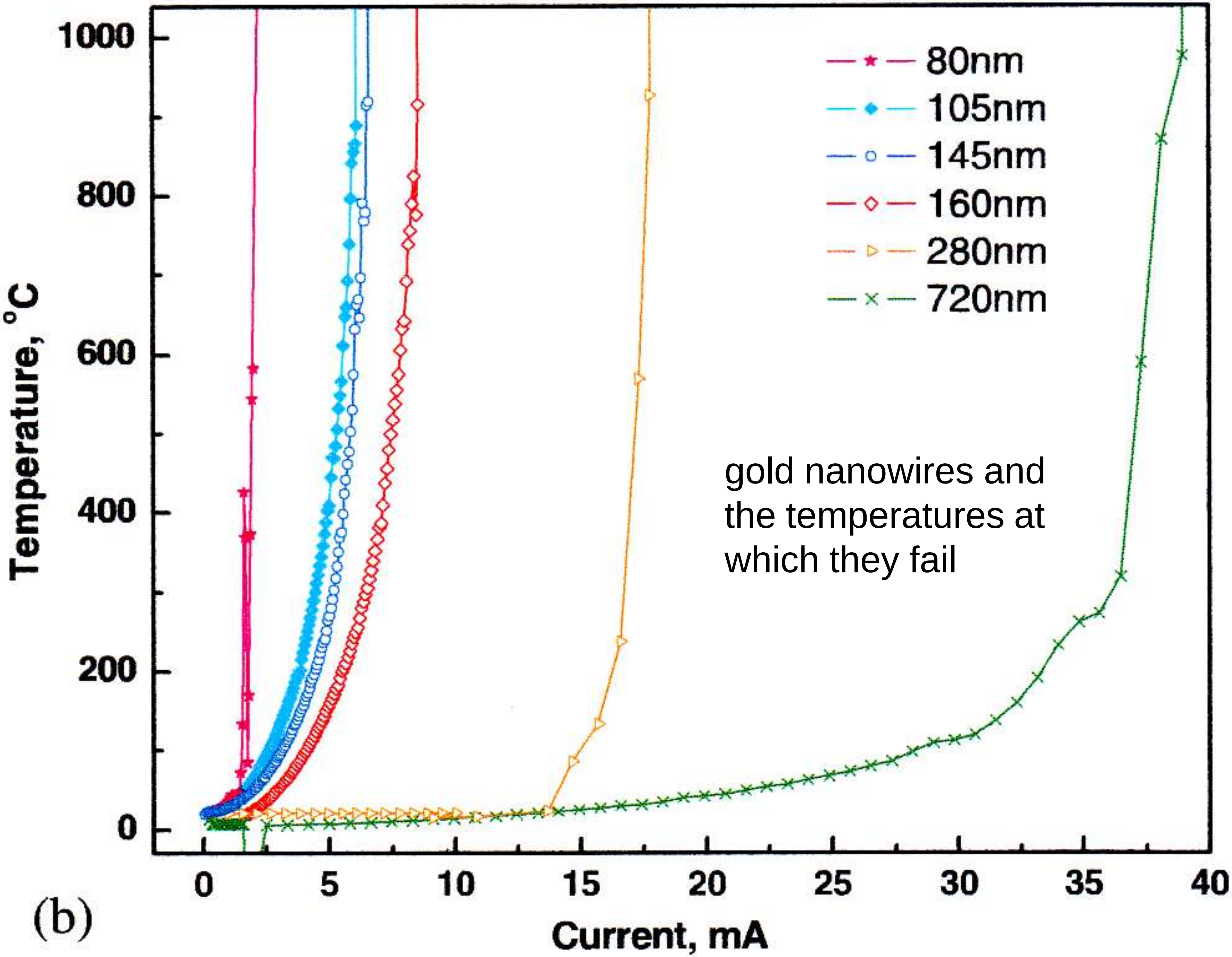


Melting is initiated by the presence of mobile atoms or molecules on surfaces.

On a piece of metal $1cm^3$ in size, fewer than 0.000000001% of the atoms are on the surface and so they have almost no influence on how the metal behaves at low temperature.

However, in a cluster F_s is large and so melting can take place at much lower temperatures.


LEAD

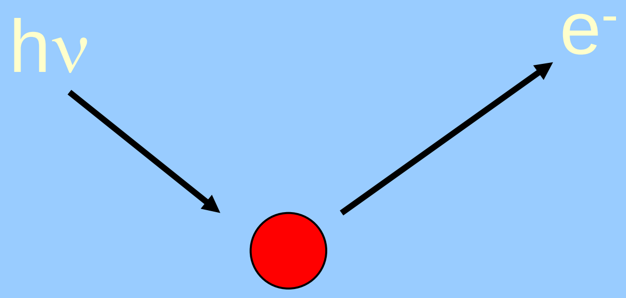


gold nanowires and the temperatures at which they fail

Electrical conductivity

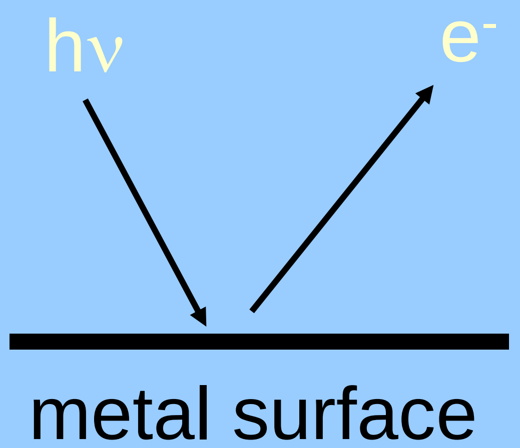
How small is a piece of wire?

Electrical Properties



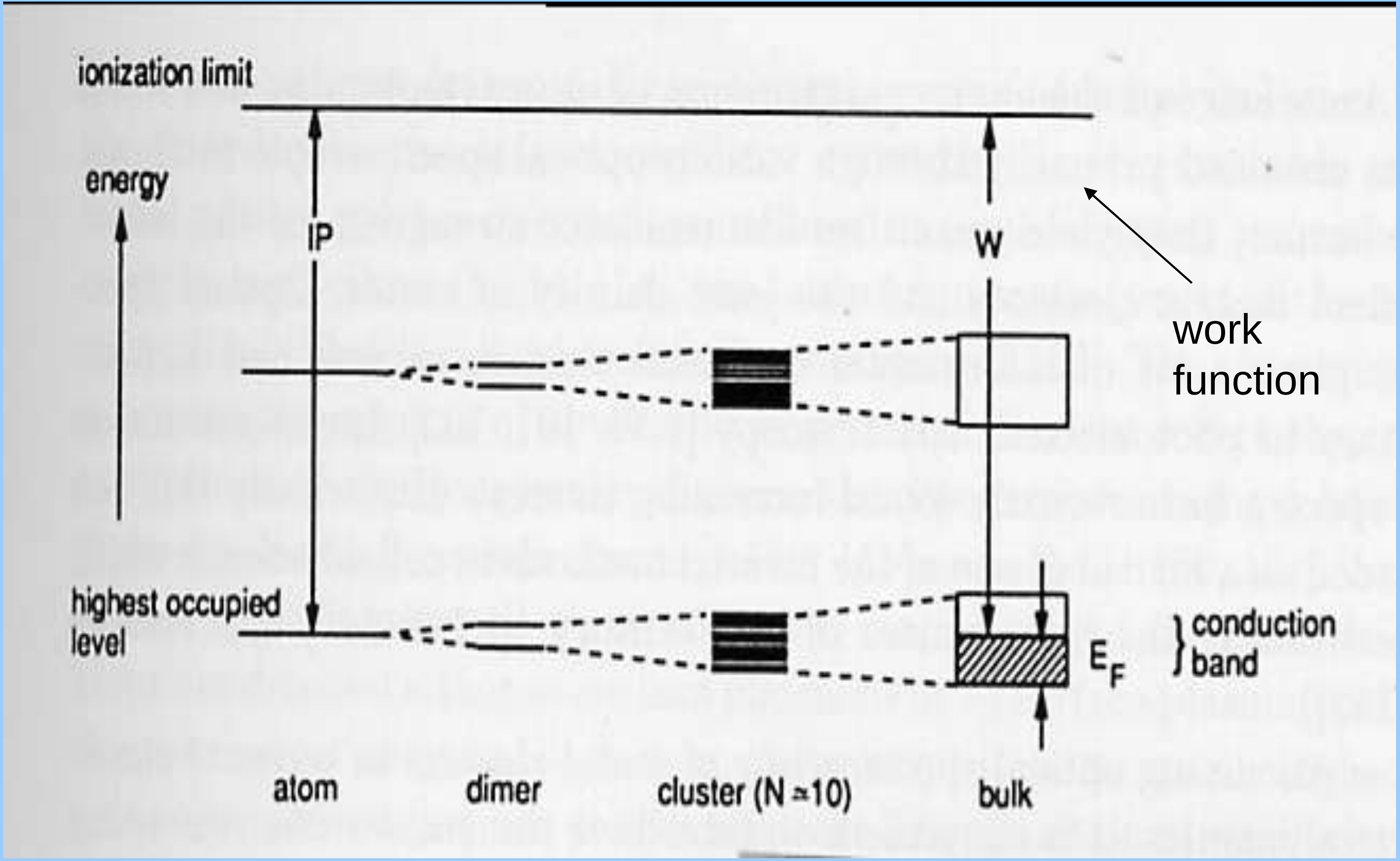
single metal atom

ionisation energy



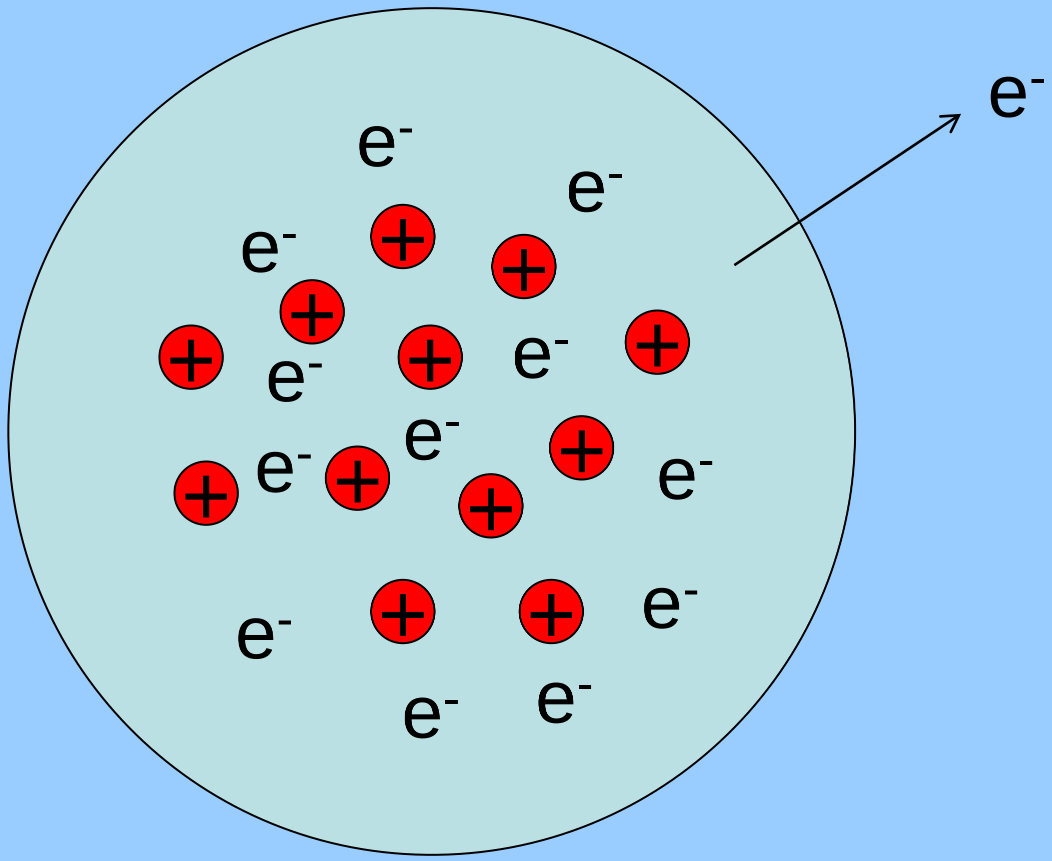
metallic solid

work function (φ or ω)



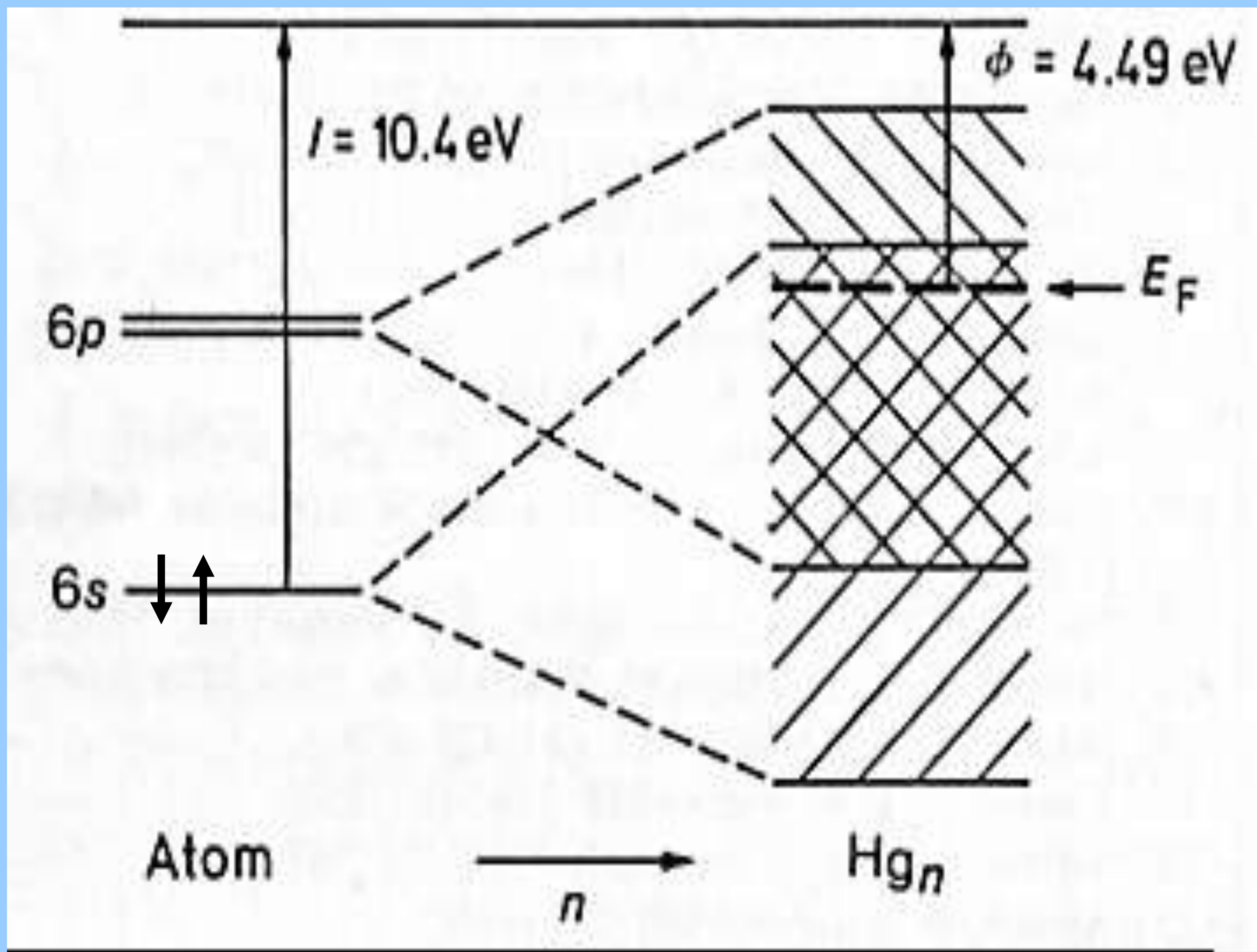
work
function

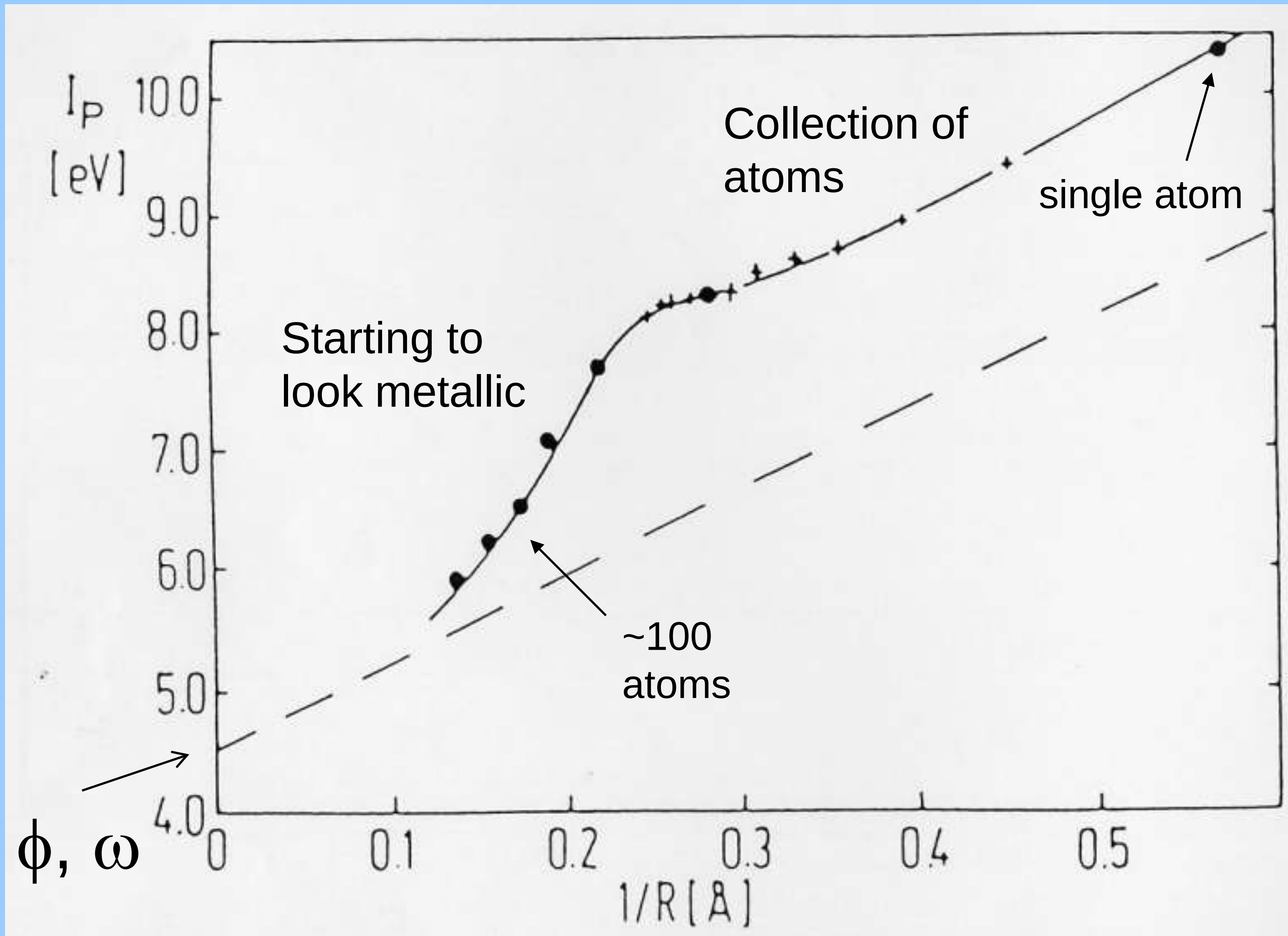
Metal cluster



None of the electrons are associated with any particular atom

Measuring the ionisation energies of mercury clusters

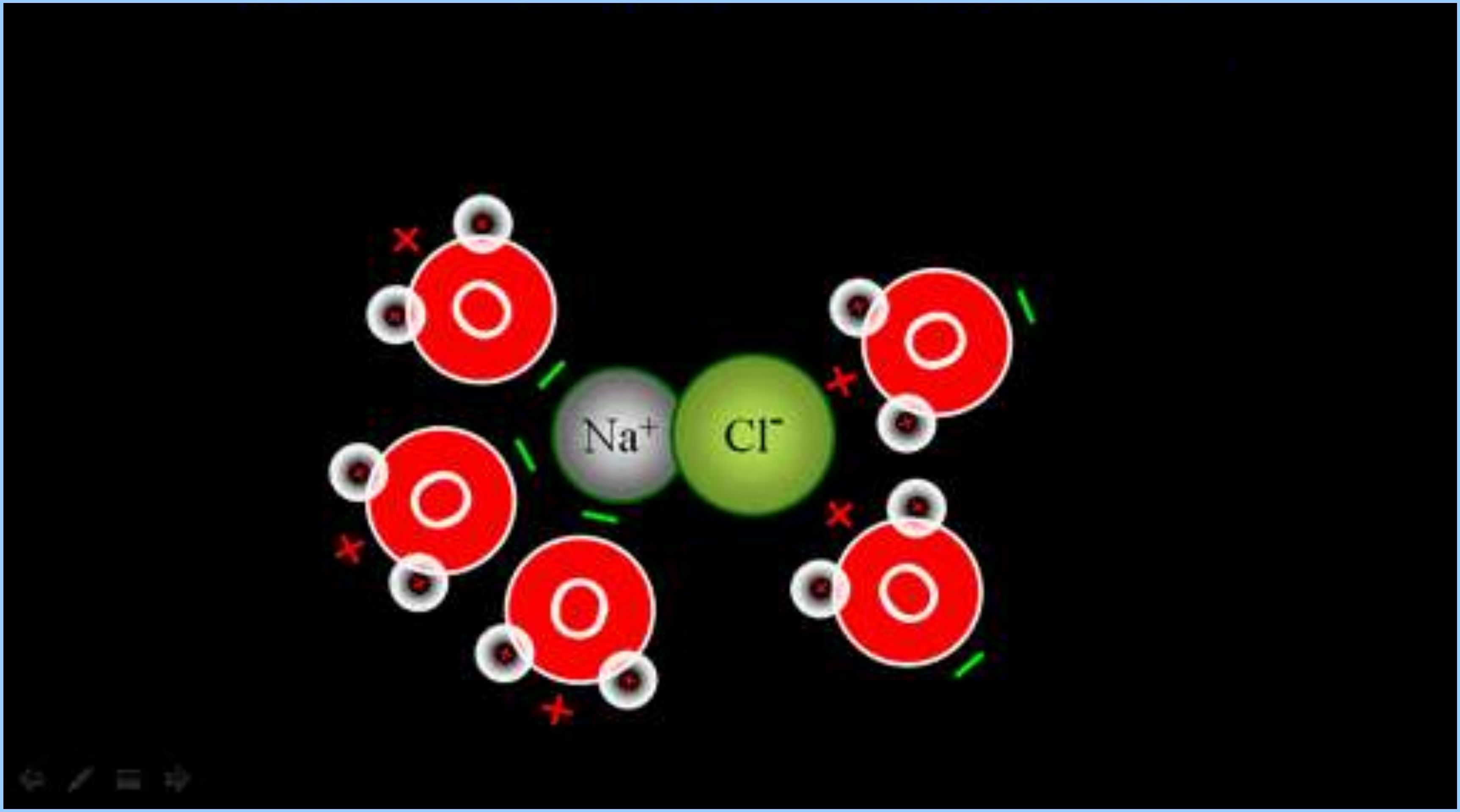


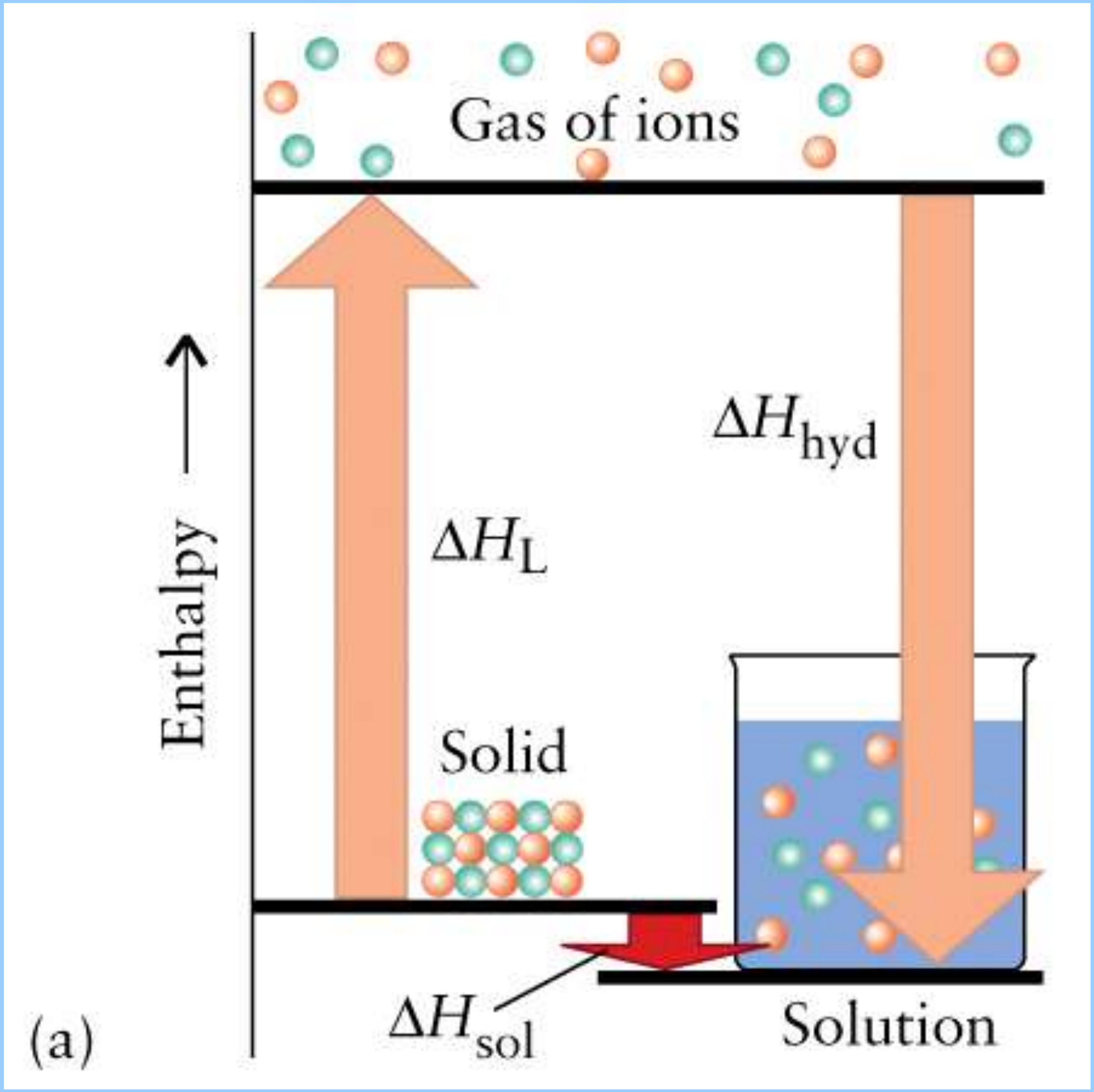


Ionisation energy of mercury clusters as a function of 1/radius

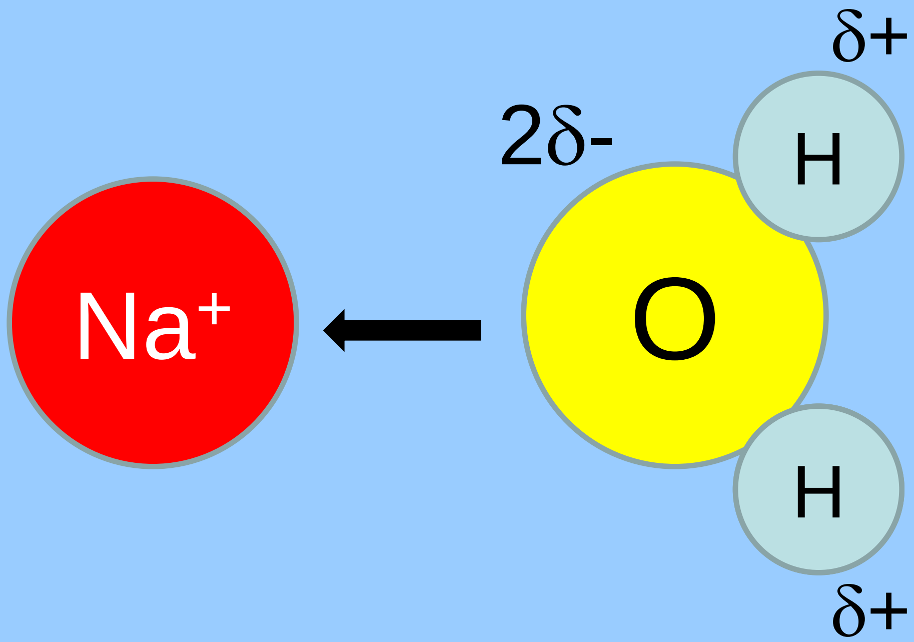
Solubility

Sodium chloride (salt) in water





Entropy is also important under certain circumstances


δ+
2δ-
H
Na+
O
H
δ+

Gas phase experiment

$Na^+ + H_2O \longrightarrow Na^+(H_2O)$ ΔE

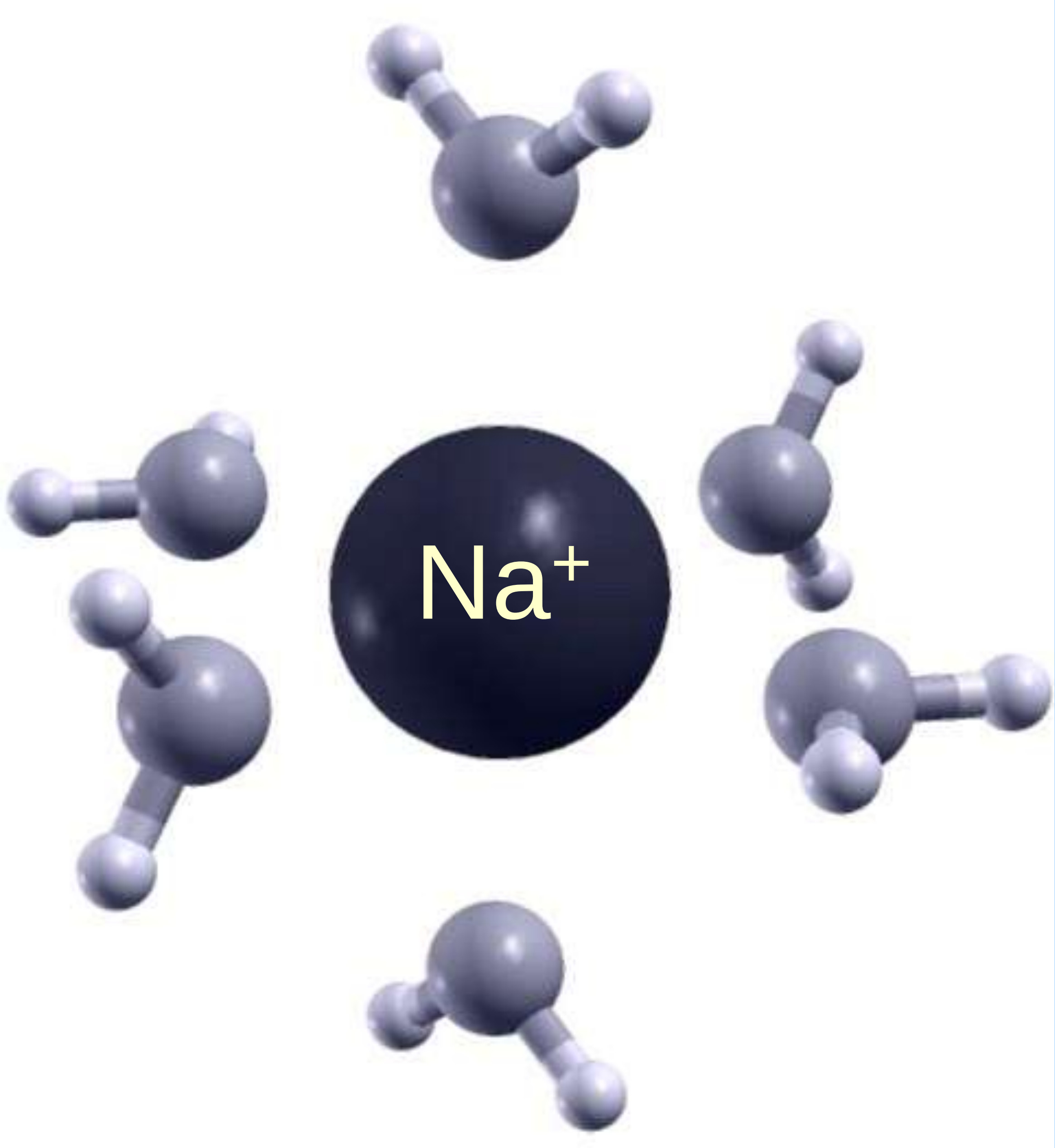
$Na^+(H_2O) + H_2O \longrightarrow Na^+(H_2O)_2$ $\Delta E'$

$Na^+(H_2O)_2 + H_2O \longrightarrow Na^+(H_2O)_3$ $\Delta E''$

$Na^+ + nH_2O$ $(\Delta E + \Delta E' + \Delta E'' + ...)$

Ion hydration energies / kJ mol^{-1}

Ion	6 water molecules	Bulk
H^+	1123	1129
Li^+	515	520
Na^+	403	405
K^+	333	321


Na^+

Solvation

For singly-charged metal ions it is possible to reproduce the essential energetics of ion solvation with ~ 6 - 10 molecules.

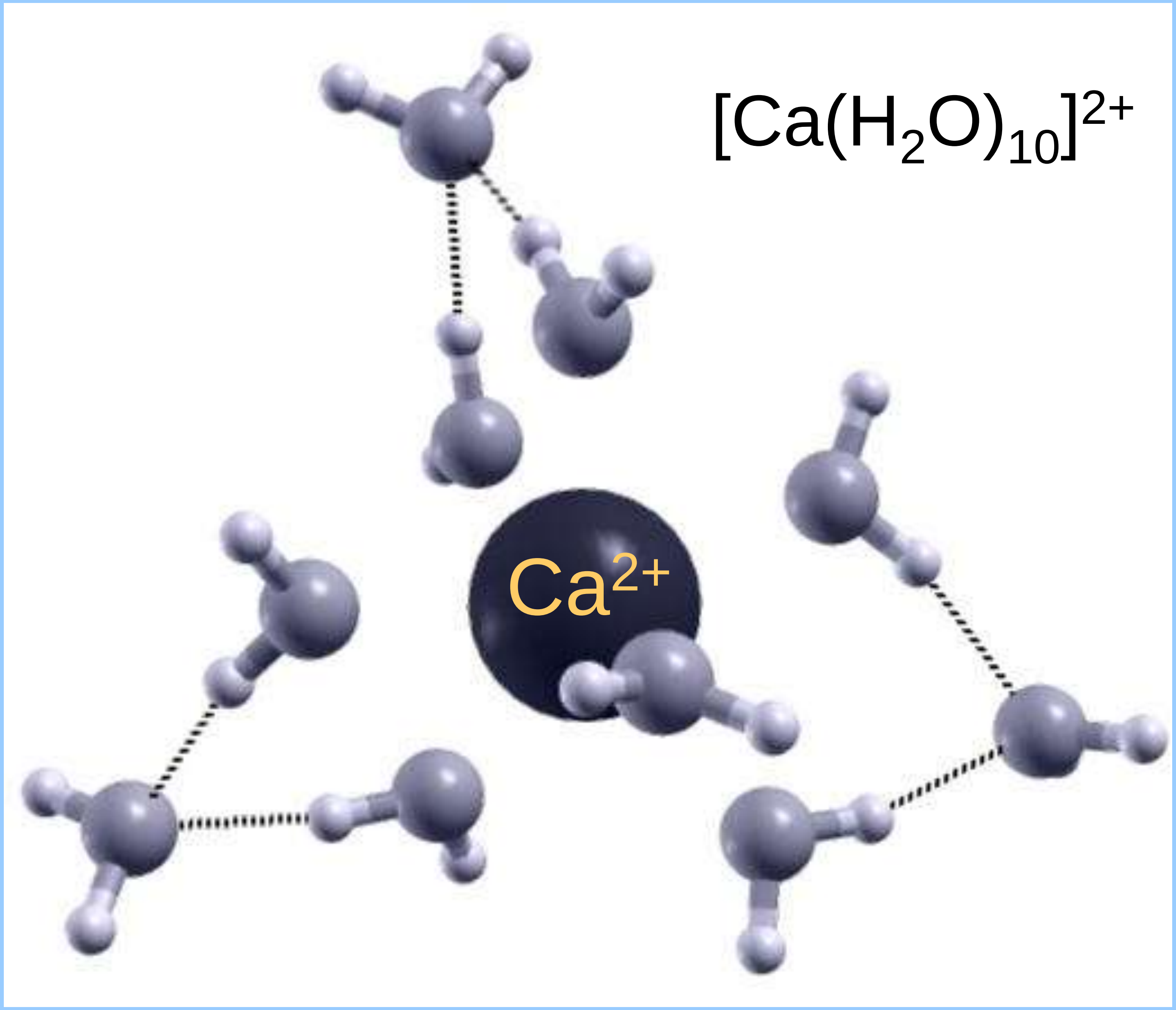
To dissolve sodium chloride we need approximately 12 water molecule for each NaCl unit

No comparable data on how metal ions carrying more than one charge dissolve.

Almost all of the metals that are important for our existence and quality of life carry more than one charge:

Ca^{2+}, Cu^{2+}, Ni^{2+} and $Fe^{2+/3+}$

Experiments suggest that these ions need 20 – 30 water molecules to dissolve.



$[Ca(H_2O)_{10}]^{2+}$
Ca^{2+}

Chemistry

Ionosphere (100 km)

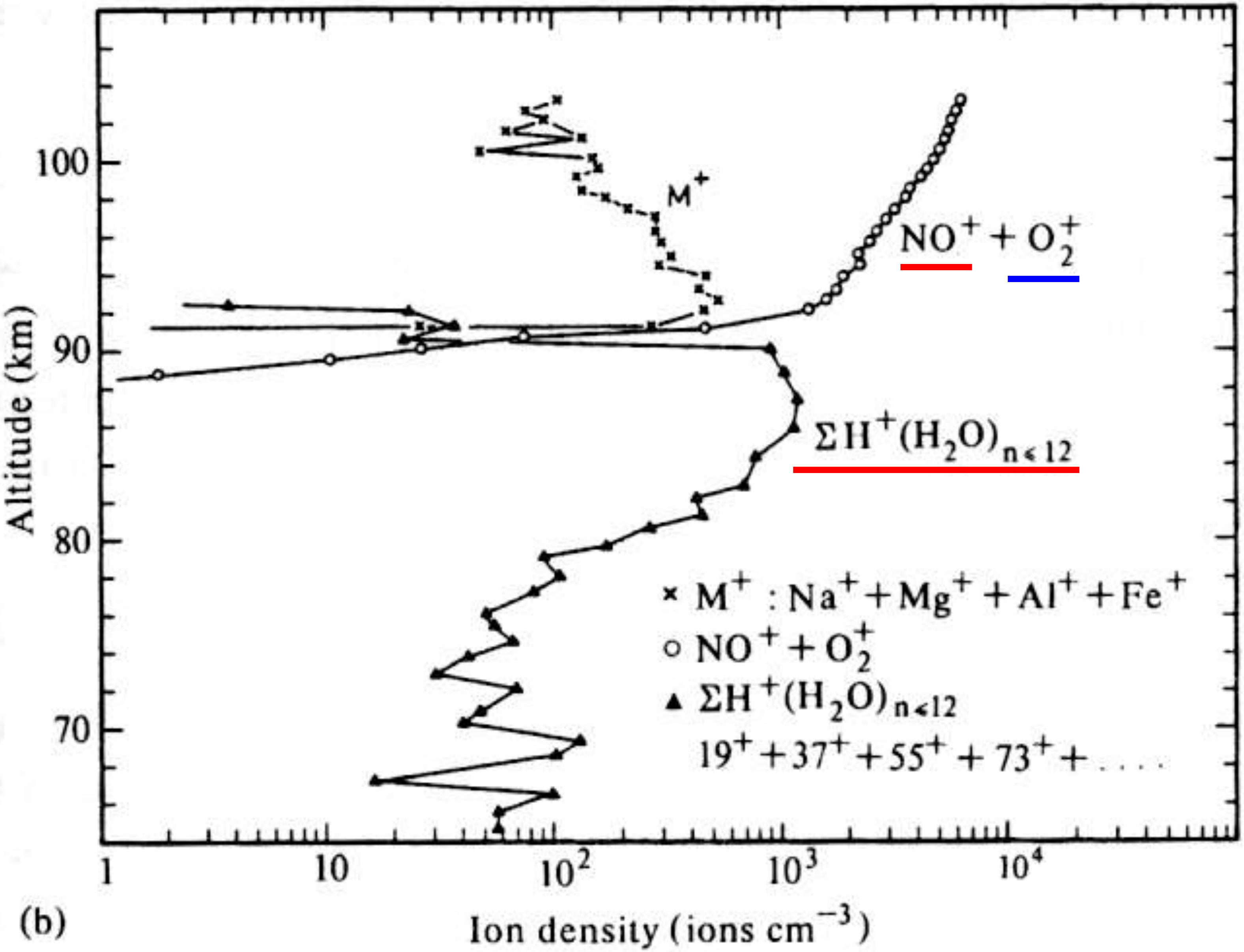
Most abundant species is NO^+

NO originates from activities on the surface of the Earth and because it has a low ionisation energy, it acts as a charge sink. Neutral O_2 and N_2 are far more abundant, but have much higher ionisation energies.

As the altitude drops, ions of the form $(H_2O)_nH^+$ begin to appear and these are thought to be precursors to cloud formation.

The clouds that are formed are often referred to as "night-shining" or Noctilucent clouds.

They form in an upper layer of the Earth's atmosphere called the mesosphere during the Northern Hemisphere's summer season, and they are also seen during the summer months in the Southern Hemisphere.



M+
NO+ + O2+
ΣH+(H2O)n<12
Altitude (km)
100
90
80
70
× M+ : Na+ + Mg+ + Al+ + Fe+
○ NO+ + O2+
▲ ΣH+(H2O)n<12
19+ + 37+ + 55+ + 73+ + ...
1
10
10²
10³
10⁴
(b)
Ion density (ions cm⁻³)

Ionosphere (90 km)

Need a chemical route for the transition:

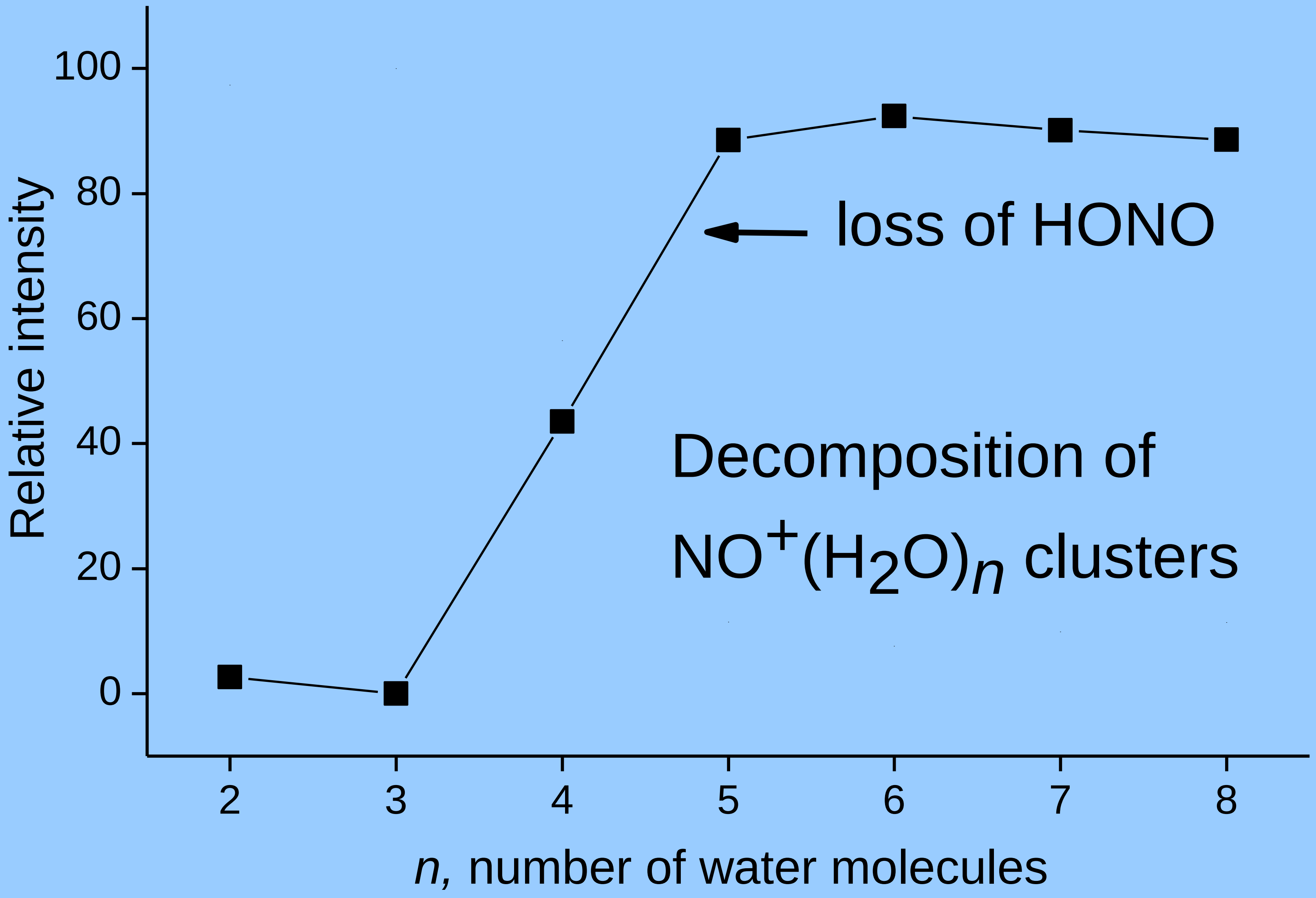
$$NO^+ \rightarrow (H_2O)_nH^+$$

Suggested pathway:

$$NO^+.(H_2O)_3 + H_2O \rightarrow (H_2O)_3H^+ + HONO$$

Cluster equivalent

$$NO^+.(H_2O)_4 \rightarrow (H_2O)_3H^+ + HONO$$

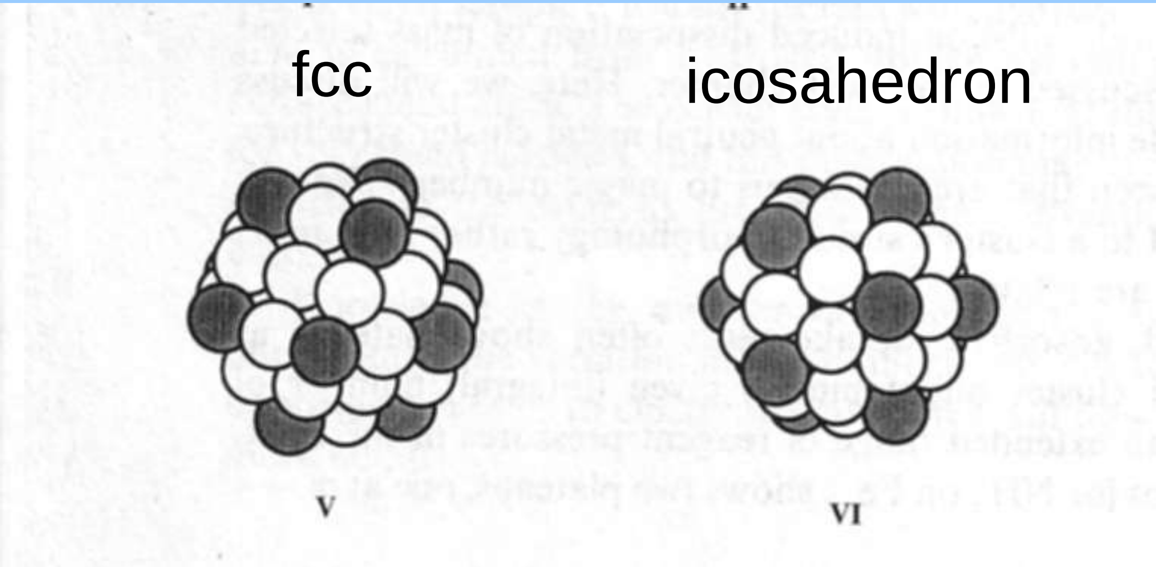


Relative intensity
100
80
60
40
20
0
2
3
4
5
6
7
8
n, number of water molecules
loss of HONO
Decomposition of
$NO^+(H_2O)_n$ clusters

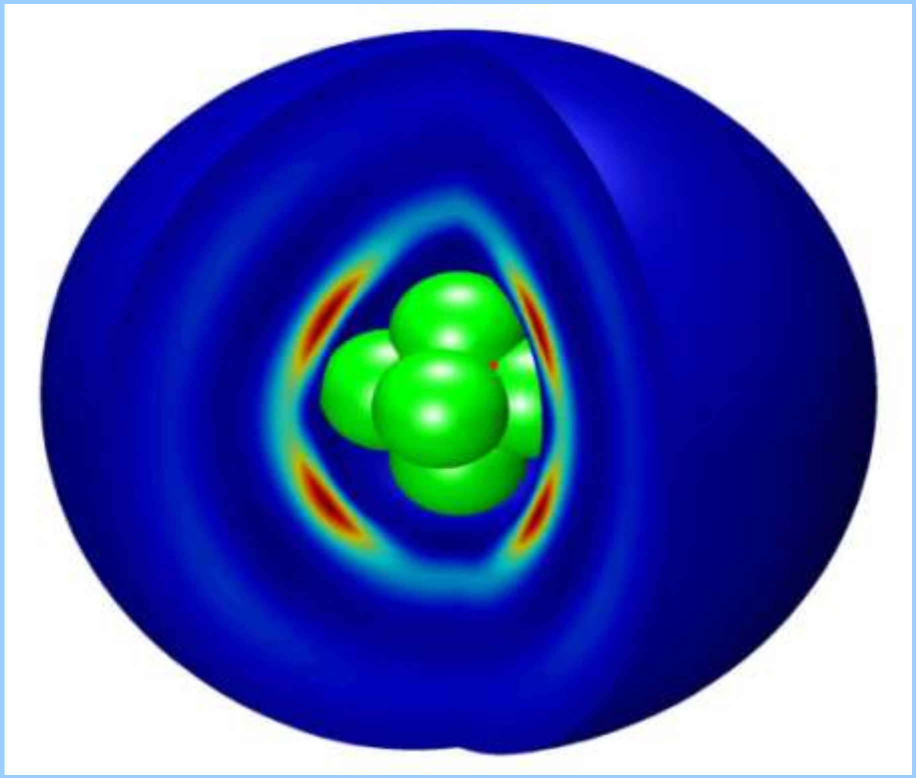
Where is cluster science going?

Metal clusters and the possibility of creating new catalysts – reactions take place on the surface and clusters offer a high surface to volume ratio.

Co_{55}



Helium Nanodroplets
(10^3 – 10^6 atoms)



Internal temperature of 0.38 K

Helium nanodroplets (superfluid!):

1 Chemical Reactions at 0.38 K

2) Magnetic behaviour

3) Superconductivity

4) Spectroscopy

How small is a solid or a liquid?

Structure (regular)	~13 atoms
Structure (bulk)	~2000 atoms
Melting	~1,000,000 atoms
Becoming a metal	~200 atoms
Solvation	~ 6 molecules (Na^{+}) ~ 30 molecules (Cu^{2+})