CLUSTERS: CHEMISTRY AND PHYSICS IN A FINITE WORLD

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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?
Once a year the company who owns the lakes lets visitors into the area to collect salt crystals.
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 $\propto (R_c/R_a)^3$ \hspace{1cm} $R_c = R_a N^{1/3}$

Scaling cluster properties: \( X_N = X_{\text{bulk}}(1 \pm \beta/N^{1/3}) \) 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.
<table>
<thead>
<tr>
<th>no. of atoms</th>
<th>radius $R_c(\text{Å})$</th>
<th>$N_s/N$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N 125</td>
<td>4</td>
<td>80</td>
</tr>
<tr>
<td>1000*</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>10,000</td>
<td>22</td>
<td>10</td>
</tr>
<tr>
<td>1m</td>
<td>100</td>
<td>4</td>
</tr>
</tbody>
</table>

* start of nanotechnology

1 $\text{Å} = 0.0000000001 \text{ m} = 0.1 \text{ nm}$
Production of clusters
Temperature: \( 300 \text{ K} \rightarrow 1 \text{ K} \)

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

Rate of cooling: \( >10,000,000 \text{ K per second} \)
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

$T_M = 1336.15 - 5543.65/R$ (Å)

Smaller clusters are icosahedra.
Melting is initiated by the presence of mobile atoms or molecules on surfaces.

On a piece of metal 1\(\text{cm}^3\) 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

- Ionisation energy
- Work function ($\varphi$ or $\omega$)

**Single metal atom**

**Metallic solid**

metal surface
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 $1/radius$

Collection of $\sim 100$ atoms

Starting to look metallic

$\phi$, $\omega$

Ionisation energy of mercury clusters as a function of $1/radius$
Solubility
Sodium chloride (salt) in water
Entropy is also important under certain circumstances.
Na^+ + 2\delta^- + \delta^+ + H = O
Gas phase experiment

$\text{Na}^+ + \text{H}_2\text{O} \rightarrow \text{Na}^+(\text{H}_2\text{O}) \quad \Delta E$

$\text{Na}^+(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightarrow \text{Na}^+(\text{H}_2\text{O})_2 \quad \Delta E'$

$\text{Na}^+(\text{H}_2\text{O})_2 + \text{H}_2\text{O} \rightarrow \text{Na}^+(\text{H}_2\text{O})_3 \quad \Delta E''$

$\text{Na}^+ + n\text{H}_2\text{O} \quad (\Delta E + \Delta E' + \Delta E'' + ...)$
## Ion hydration energies / kJ mol\(^{-1}\)

<table>
<thead>
<tr>
<th>Ion</th>
<th>6 water molecules</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>1123</td>
<td>1129</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>515</td>
<td>520</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>403</td>
<td>405</td>
</tr>
<tr>
<td>K(^+)</td>
<td>333</td>
<td>321</td>
</tr>
</tbody>
</table>
Solventation

For singly-charged metal ions it is possible to reproduce the essential energetics of ion solvation with \( \sim 6 \text{ - } 10 \) molecules.

To dissolve sodium chloride, we need approximately \( 12 \) water molecules 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:

\[ \text{Ca}^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+} \text{ and } \text{Fe}^{2+/3+} \]

Experiments suggest that these ions need 20 – 30 water molecules to dissolve.
$[\text{Ca(H}_2\text{O)}_{10}]^{2+}$
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$_2$O)$_n$H$^+$ 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.
The diagram shows the variation of ion density with altitude (km) in the ionosphere. The ion density is given in ions cm\(^{-3}\). The graph includes several markers and lines representing different ion species:

- $M^+$: Na\(^+\), Mg\(^+\), Al\(^+\), Fe\(^+\)
- $\Sigma H^+ (H_2O)_{n<12}$
- $\Sigma H^+ (H_2O)_{n<12}$
- $19^+ + 37^+ + 55^+ + 73^+ + \ldots$

The lines and markers indicate the density changes at various altitudes.
Ionosphere (90 km)

Need a chemical route for the transition:

$$\text{NO}^+ \rightarrow (\text{H}_2\text{O})_n\text{H}^+$$

Suggested pathway:

$$\text{NO}^+.\left(\text{H}_2\text{O}\right)_3 + \text{H}_2\text{O} \rightarrow (\text{H}_2\text{O})_3\text{H}^+ + \text{HONO}$$

Cluster equivalent

$$\text{NO}^+.\left(\text{H}_2\text{O}\right)_4 \rightarrow (\text{H}_2\text{O})_3\text{H}^+ + \text{HONO}$$
Decomposition of NO+(H2O)n clusters

loss of HONO

Relative intensity

$n$, number of water molecules
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.

$\text{Co}_{55}$
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
<table>
<thead>
<tr>
<th>Description</th>
<th>Number of Atoms/Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure (regular)</td>
<td>~13 atoms</td>
</tr>
<tr>
<td>Structure (bulk)</td>
<td>~2000 atoms</td>
</tr>
<tr>
<td>Melting</td>
<td>~1,000,000 atoms</td>
</tr>
<tr>
<td>Becoming a metal</td>
<td>~200 atoms</td>
</tr>
<tr>
<td>Solvation</td>
<td>~6 molecules (Na^+)</td>
</tr>
<tr>
<td></td>
<td>~30 molecules (Cu^{2+})</td>
</tr>
</tbody>
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