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Stability of metal nanoclusters - shells of atoms and electrons

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Cluster science – at the heart of "Nano"!

- Thermodynamics of small systems
- Nanocatalysts
- Understanding the size-dependent properties of clusters in vacuum
- Cluster materials
- Supported nanoparticles
- Reaction centers in enzymes
- Passivated nanoparticles
### Some literature

Cluster sources

- Seeded supersonic nozzle source
- Gas-aggregation source
- Laser vaporization source
- Sputtering source
- Liquid-metal ion source

Cluster sources – overview

- Seeded supersonic nozzle source: intense continuous beams, low-boiling-point materials, evaporative cooling -> structured mass spectra (magic stabilities visible), temperature not well controlled
- Gas-aggregation cluster source: efficient for production of large clusters (up to 20,000+), low intensity, low-to-medium boiling point materials (< 2000 K), low cluster temperature (< 100 K)
- Laser vaporization source: pulsed beams from any material, cluster temperature near the source temperature
- Sputtering source: energetic heavy inert-gas ion sputtering beam (Kr+, Xe+, 10 – 20 keV) -> continuous beam of singly ionized (hot) clusters, cooling by evaporation
- Liquid-metal ion source: singly and multiply ionized (hot) clusters of low-melting point metals
Analysis techniques

- Wien filter
- Quadrupole mass filter
- Time-of-flight mass spectrometry
- Ion cyclotron resonance mass spectrometry in ion trap
- Molecular-beam mobility analysis
- Electron diffraction in ion trap (structure factor)
- Photoelectron spectroscopy

Cluster mass analysis
Example of a full setup

Gas-aggregation source

Photoionization by laser

Time-of-flight mass analysis


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Photoelectron spectroscopy

O. Kostko, PhD Thesis Freiburg 2007

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Cluster stability: atomic and electronic shells

Sodium

Aluminium
Cluster stability – atomic shells

T.P. Martin
Physics Reports
273, 199 (1996)

Delocalized-electron shell model
Spherical clusters

FIG. 1. Selfconsistent effective potential of jellium sphere corresponding to Na_{10}, with the electron occupation of the energy levels. After Chen et al., 1984.

3D isotropic anharmonic oscillator

- Single-particle Hamiltonian
  \[ H = \frac{p^2}{2m} + \frac{m\omega_0^2q^2}{2} - U\hbar\omega_0(t^2 - n(n + 3)/6) \]
  \[ R_0 = r_0N^{1/3} \quad \hbar\omega_0 = E_F/N^{1/3} \]

- Eigenvalue spectrum
  \[ E_n = \hbar\omega_0\left(n + \frac{1}{2}\right) - U[1^2 - n(n + 3)/6] \]

Electron shells - Effect of deformations

- Clemenger (1985) <- Nilsson (nuclear physics, 1955 !) model: for a fixed volume, the cluster shape adjusts to minimize the total energy
- Deformation \( \rightarrow \) cluster radii \( R_x, R_y, R_z \) \( \rightarrow \) tri-axial oscillator
  \[ E(n_x, n_y, n_z) = \hbar\omega_0 \left( \left(n_x + \frac{1}{2}\right) \frac{R_0}{R_x} + \left(n_y + \frac{1}{2}\right) \frac{R_0}{R_y} + \left(n_z + \frac{1}{2}\right) \frac{R_0}{R_z} \right) \]
- Spheroid \( (R_x = R_y) \), distortion parameter
  \[ \eta = \frac{R_x - R_z}{R_x + R_z} \]
- Total energy for spheroids
  \[ E_{\text{tot}}(\eta, N) = \frac{1}{2} \sum E(n_x, n_y, n_z) \]
Clemenger – Nilsson diagram

Cluster stability – electron shells

FIG. 1. Sodium cluster abundance spectrum: (a) Experimental (after Knight et al., 1984); (b) dashed line, using Woods-Saxon potential (after Knight et al., 1984); solid line, using the ellipsoidal shell (Clemenger-Nilsson) model (after de Heer, Knight, Chiu, and Cohen, 1987).

W.A. deHeer
Rev. Mod. Phys
85, 611 (1993)
Photoabsorption spectroscopy detects the joint density of occupied and unoccupied states.

Photoemission spectroscopy detects the occupied states.

In the simplest approximation the spectrum is proportional to the density of states of the filled levels.

Measured (kinetic energy) spectrum:

- $E_1$
- $E_2$
- $E_3$

Energy levels:
- Fermi level
- Vacuum level
- Optical excitations
- Detached electrons

Binding energy
- $h\nu - E_1$
- $h\nu - E_2$
QUANTUM-SIZE EFFECTS (QSE) IN METALLIC NANOPARTICLES?

Free-electron model of metal: density of electron states $D(\varepsilon) \propto \sqrt{\varepsilon}$

Mean spacing of electron levels at the Fermi level $\varepsilon_F$:
$$\delta (\varepsilon_F) = \frac{1}{D(\varepsilon_F)} - 2 \varepsilon_F / 3 N z$$  $(N = \text{number of atoms}, z = \text{valence number})$

QSE observable when $\delta > kT$  $(kT = 0.025 \text{ eV at } 300 \text{ K})$

E.g. for Au, $\varepsilon_F = 5.5 \text{ eV}, z = 1 \rightarrow$

$$\delta > kT \quad \text{when} \quad N < 150 \text{ atoms} \rightarrow \text{diameter} < 1.7 \text{ nm}$$

QSE $\rightarrow$ stabilization of the nanoparticle structure by electronic effects
$\rightarrow$ opening of the energy gap at the Fermi level (HOMO-LUMO gap)
$\rightarrow$ "metallic" $\rightarrow$ "semiconductor" behaviour

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Experiment vs. theory: Na clusters from 4 to 350 atoms
Na cluster anions I: optimised structures at T=0 from density functional theory (DFT)


Na cluster anions II: Cluster shapes from DFT

Cluster radii from GS (T=0)

Radii from RT DFT-MD

Na cluster anions III: Photoelectron spectroscopy vs. electron density of states

Na\textsubscript{13}\textsuperscript{−} is oblate!

Na cluster anions IV: Photoelectron spectroscopy vs. electron density of states

55 → 147 → 309: Icosahedral growth via overlayers