Lecture 2

Atomic clusters (continuation)
Carbon nanosystems

Temperature properties (1)

Atomic clusters can exist in:

-- **liquid state (phase)** $t > t_m$ **without ionic lattice**

-- **solid state (phase)** $t < t_m$ **with ionic lattice**

Not crucial for quantum shells but important in other aspects

Valence electrons are in a heat bath of ions.

Melting temperature t_m **:**
Na: 371 K
Au: 1337 K

t^{o} C=(t+273.15) ^{o}K

Lord Kelvin: Does the melting temperature depends on the system size?

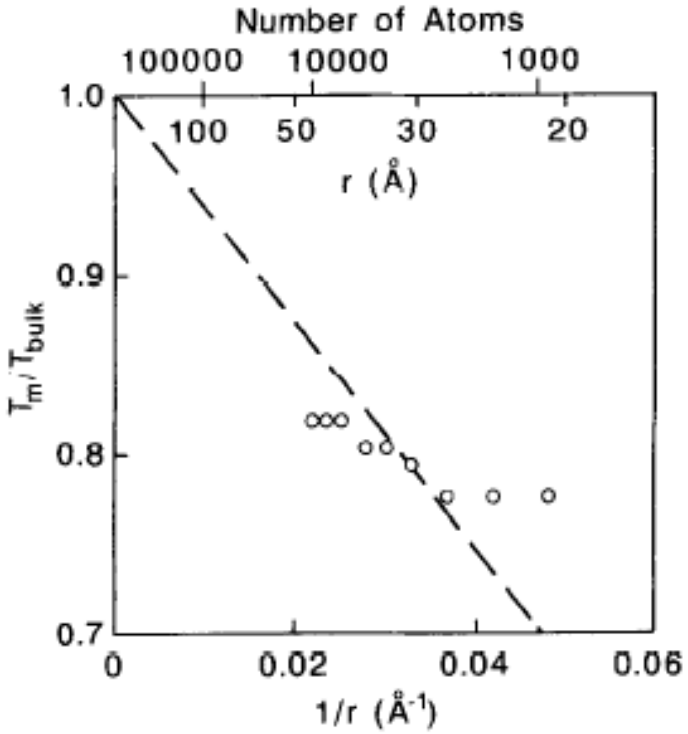
Yes!

$$t_m^{cl}/t_m^{bulk} = 1 + \frac{c}{R}$$

c > 0 or < 0?

Temperature properties (2)

Exper. for Na clusters: T. Martin (1996)



Melting temperature in clusters is lower than in the bulk:

$$t_m^{cl} / t_m^{bulk} \approx 0.8$$

Why?

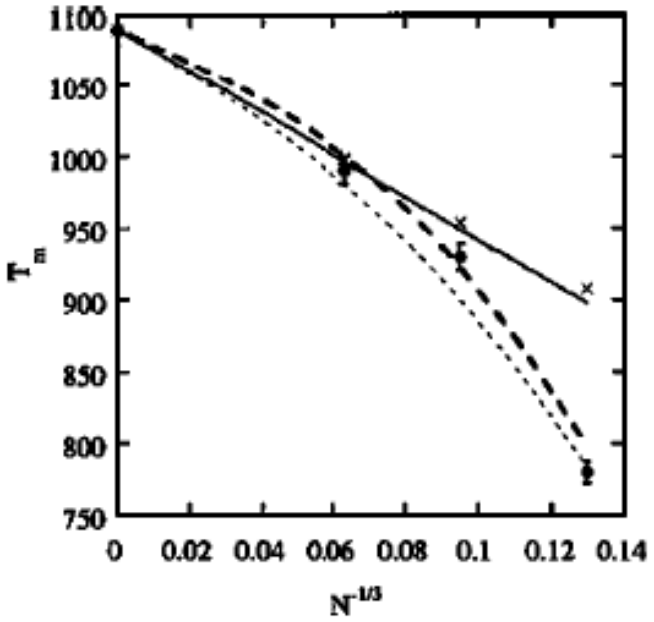
Lindemann criterion:
the matter will melt when the thermal fluctuations of the inter-nuclear distance become larger than 10-15%.

Atoms on the cluster's surface are less constrained in their thermal movement thus leading to lowering t_m **.**

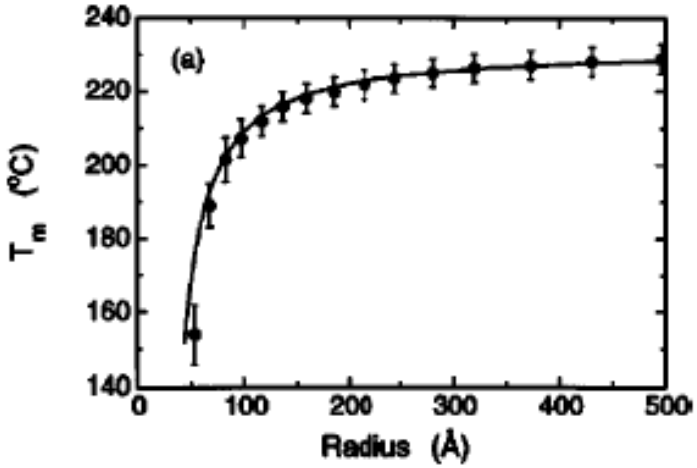
Phase transitions in clusters

-The transition does not take place sharply at a definite temperature but smoothly over a wide temperature range.
-Solid and liquid phases may coexist.
- Melting transition is preceded by premelting fenomena: isomerization in a limited part of configuration space

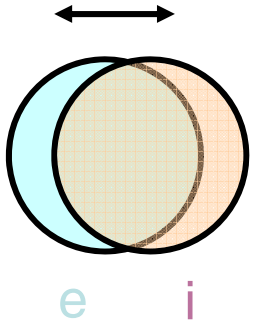
Au clusters



Sn clusters



Dipole plasmon



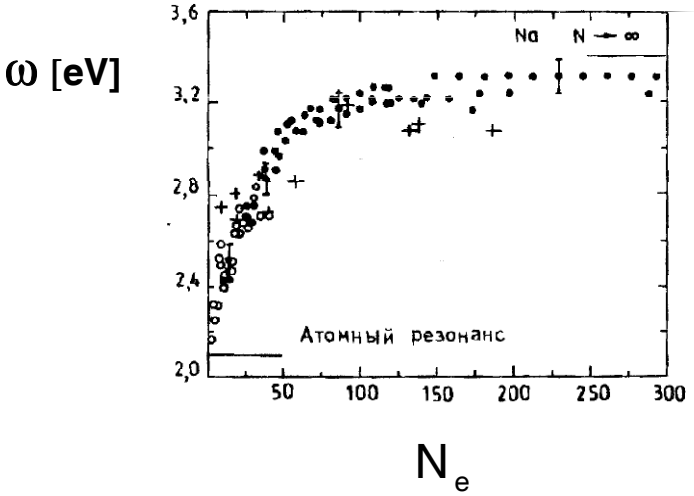
Dipole plasmon:

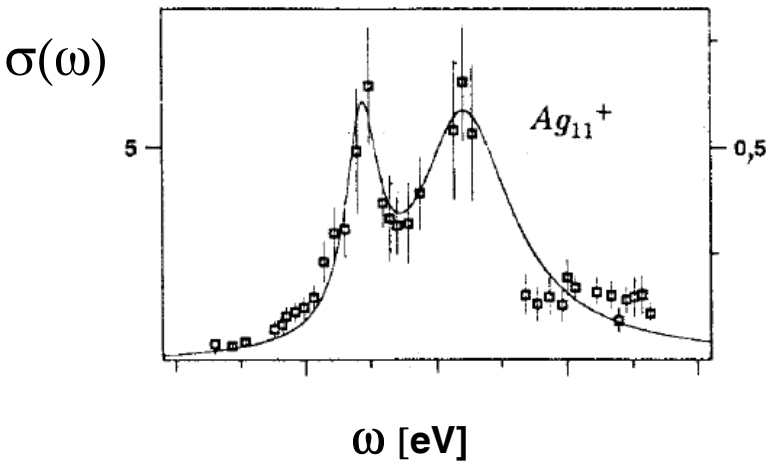
-- oscillations of valence electrons against ions,

-- the only collective mode still observed in atomic clusters,

-- one of the main sources of information about diverse cluster properties,

-- counterpart of E1 giant resonance in nuclei



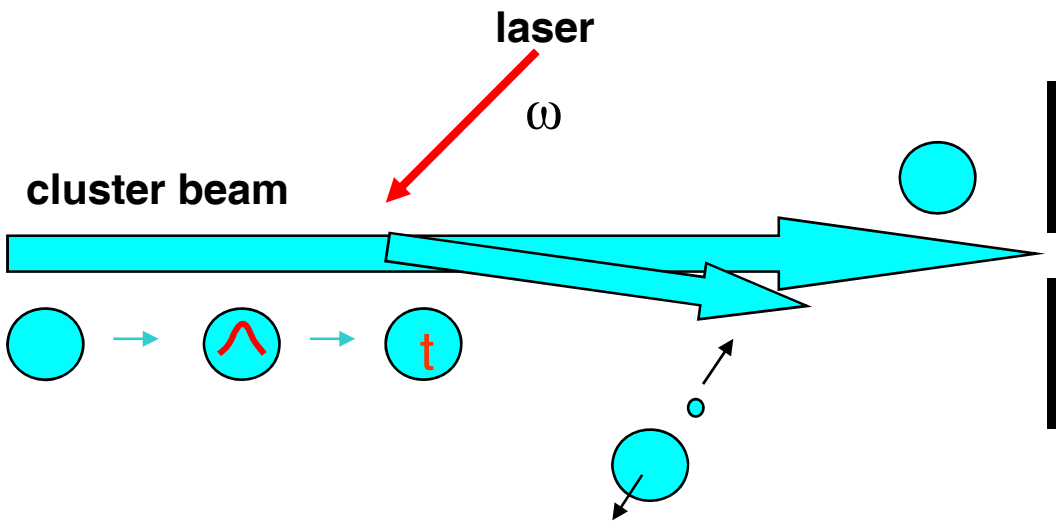


$$\omega_{E1} = \omega_{Mie}(1 - \frac{\delta N_e}{2N_e})$$

The only source of information on cluster deformation

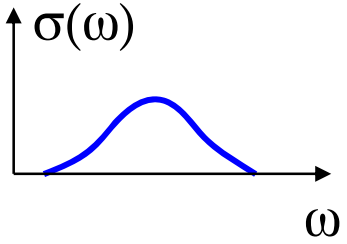
Numerous practical applications!

Dipole plasmon: experiment



Depletion spectroscopy

$$\sigma(\omega) = \sigma_{no\ laser} - \sigma_{laser}(\omega)$$

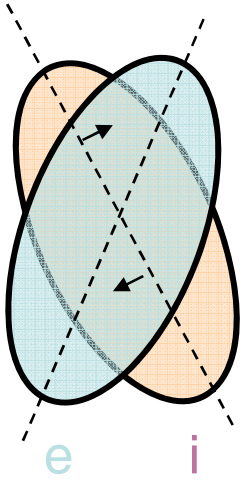


Main steps:

-- excitation of dipole plasmon by laser;
-- transformation of the plasmon energy into heat,
-- evaporation of atom(s) from cluster,
-- change of direction of cluster flight due to the recoil.

M1 scissors mode

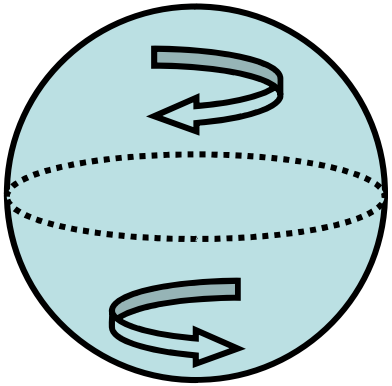
Predictions for metal clusters:



General feature of any finite deformed two-component Fermi and Bose systems
[nuclei, clusters, Bose-Einstein condensate, …]

V.O. Nesterenko, W. Kleinig, F.F. de Souza Cruz and N. Lo Iudice, "Orbital Magnetic Dipole Mode in Deformed Clusters: Fully Microscopic Analysis", Phys. Rev. Lett., 83, 57 (1999)

M2 twist mode



Most strong magnetic orbital mode in spherical metal clusters

V.O. Nesterenko, J.R. Marinelli, F.F. de Souza Cruz, W. Kleinig and P.-G. Reinhard, "Twist Mode in Spherical Alkali Metal Clusters", Phys. Rev. Lett., v.85, p.3141 (2000).

KS: Kohn-Hohenberg theorem

P. Hohenberg and W. Kohn, Phys. Rev., 136 (1964) B864

1) Inhomogeneous system of interacting electrons in external field $v_{ext}(\vec{r})$.

2) Theorem (a): the ground state energy has a form

$$E[\rho] = \int v_{ext}(\vec{r})\rho(\vec{r})d\vec{r} + F[\rho(\vec{r})]$$

where $F[\rho(\vec{r})]$:

- is a functional of one density $\rho(\vec{r})$ only!

- is independent on $v_{ext}(\vec{r})$.

Theorem (b): minimum of $E[\rho]$ is exact ground state energy if $\rho(\vec{r})$ is exact ground state density.

Therefore, if we know $F[\rho(\vec{r})]$ then we can find exact $E[\rho]$ and $\rho(\vec{r})$!

W. Kohn and L.J. Sham, Phys. Rev., 140 (1965) A1133

Kohn-Sham functional : explicit expression

$e = m_e = \hbar = c = 1$

$$E[\rho_e] = T_{kin}[\tau_e] + E_{Coul}[\rho_e] + E_{xc}[\rho_e]$$

$$T_{kin}[\tau_e] = -1/2 \int d\vec{r}\, \tau_e(\vec{r},t)$$

- kinetic energy

$$E_{Coul}[\rho_e] = 1/2 \iint d\vec{r} d\vec{r}_1 \frac{(\rho_e(\vec{r},t) - \rho_i(\vec{r}))(\rho_e(\vec{r}_1,t) - \rho_i(r_1))}{|\vec{r} - \vec{r}_1|}$$

- Coulomb energy

(e-i, i-i $\longrightarrow$ V_{ext})

$$E_{xc}[\rho_e] = \int d\vec{r}\, \varepsilon_{xc}[\rho_e(\vec{r},t)]\rho_e(\vec{r},t)$$

- exchange-correlation energy (use of KS theorem)

$$\rho_e(\vec{r},t) = \sum_j^{occ} |\varphi_j(\vec{r},t)|^2$$

- density of valence electrons

$$\tau_e(\vec{r},t) = \sum_j^{occ} |\nabla\varphi_j(\vec{r},t)|^2$$

- kinetic energy density of valence electrons

$\rho_i(\vec{r})$ - density of ions

$\varepsilon_{xc}[\rho_e]$ -density of exchange-correlation energy (to be determined !!!!!)

Involves Pauli principle and all the correlations beyond the classical Coulomb interaction.

KS: equations for electronic mean field

W. Kohn and L.J. Sham, Phys. Rev., 140 (1965) A1133

$$\hat{h}_0(\vec{r})\varphi_j(\vec{r}) = \frac{\delta E[\rho_e]}{\delta \varphi_j^*}\Big|_{\rho_e=\rho_e^0} = \frac{\delta E[\rho_e]}{\delta \rho_e}\Big|_{\rho_e=\rho_e^0} \frac{\delta \rho_e}{\delta \varphi_j^*}$$

Kohn-Sham equations:

$$\hat{h}_0(\vec{r})\varphi_i(\vec{r}) = e_i\varphi_i(\vec{r})$$

$$\hat{h}_0(\vec{r}) = -\frac{\nabla^2}{2} + U_{Coul}(\vec{r}) + U_{xc}(\vec{r})$$

$$U_{Coul}(\vec{r}) = \int d\vec{r}_1 \frac{\rho_e^0(\vec{r}) - \rho_i(\vec{r})}{|\vec{r} - \vec{r}_1|}$$

$$U_{xc}(\vec{r}) = \varepsilon_{xc}[\rho_e^0(\vec{r})] + \rho_e^0(\vec{r})\frac{\delta \varepsilon_{xc}[\rho_e^0(\vec{r})]}{\delta \rho_e^0}$$

$$\rho_e^0(\vec{r}) = \sum_j^{occ} (\varphi_j(\vec{r}))^2$$

- **KSE reduce the correlated many-body problem to a self-consistent mean-field problem of Hartree type**

- **solutions by iterations**

$$\varphi_i \rightarrow \rho_e^0 \rightarrow \hat{h}_0 \rightarrow KSE$$

- **quasi-vanishing U_{Coul} domination of U_{xc}**

- **ionic density**

$$\rho_i(\vec{r}) = \begin{cases} [\frac{4\pi}{3} r_s^3]^{-1}, & r \le R \\ 0, & r > R \end{cases}$$

KS: Thomas-Fermi approximation

How to treat large electronic systems (N > 1000) where KS calculations are too time consuming?

Is it possible to avoid calculation of $\varphi_i(\vec{r})$ and to deal directly with $\rho(\vec{r})$?

$$\frac{\delta}{\delta\rho}\left(E[\rho(\vec{r})] - \lambda\int\rho(\vec{r})d\vec{r}\right) = 0 \qquad (1)$$

Yes, in Thomas-Fermi approximation for $T_{kin} = -\frac{\hbar^2}{2m}\int d\vec{r}\sum_i |\nabla\phi_i(\vec{r})|^2$**:**

$$T_{kin} = \frac{\hbar^2}{2m}k\int\rho^{5/3}(\vec{r})d\vec{r}, \quad k = \frac{3}{5}[3\pi^2]^{2/3}$$

from Fermi-gas model with constant density

Then (1) gives well-known Thomas-Fermi equations:

$$\frac{5}{3}\frac{\hbar^2}{2m}k\rho^{2/3}(\vec{r}) + \int d\vec{r}\,'\frac{\rho_e(\vec{r}\,') - \rho_I(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} + xc = \lambda$$

- **no: quantum shells**
- **yes: trends with N**

(total energy, density and its moments, ioniz. potential , polarizability, plasmon energy, …)

$$T_{kin} = \frac{\hbar^2}{2m}k\int[\rho^{5/3}(\vec{r}) + \frac{1}{36}\frac{(\nabla\rho)^2}{\rho} + \ldots]d\vec{r}$$

from expansion in powers of $\hbar$ or in terms of $\nabla\rho$

KS: progress in density functional theory (DFT) for electronic systems

- **Hohenberg, Kohn (1964): theorem for non-degenerate ground state**

- **Kohn, Sham (1965): mean field equations**

- **Mermin (1965) : theorem for temperature**

- **Gunnarsson, Lundqvist (1976) : xc for spin densities** $\sigma\downarrow$ **and** $\sigma\uparrow$

- **Levy (1979): general ground state**

- **Runge, Gross (1984): time-dependent DFT: TD-DFT**

- **Vignale, Kohn (1996): current TD-DFT**

Outlook for fundamental physics

-Comparison of processes in clusters and bulk (photoionization, …)

- Dynamics of clusters in intense femtosecond lasers fields

- Clusters at surface, embedded clusters

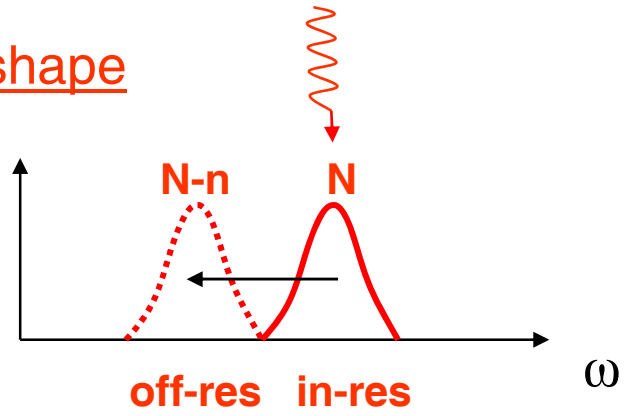
- Exotic clusters (C20), …

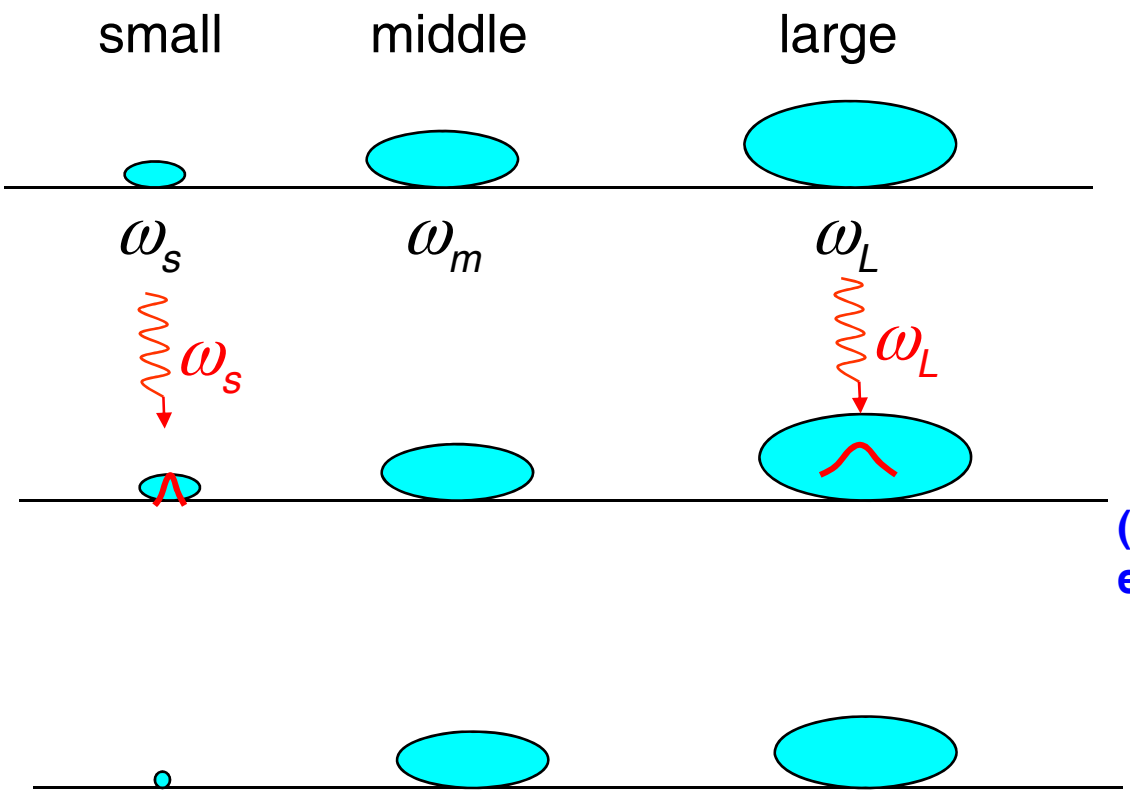
- Thermodynamics, phase transitions in small systems

Applications

Dipole plasmon: monitoring cluster size and shape

Experiment: F. Trager et al (1999)





Initial set of very different clusters.

Irradiation by laser beams with ω_s and ω_L in resonance with DP of small and large clusters.

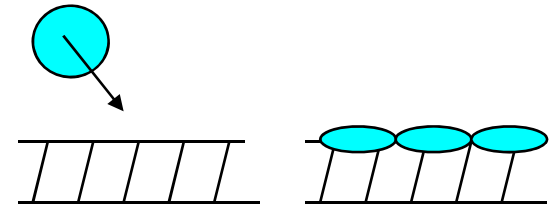
(excitation of DP, heating, evaporation, decreasing the size)

Final set of more uniform clusters.

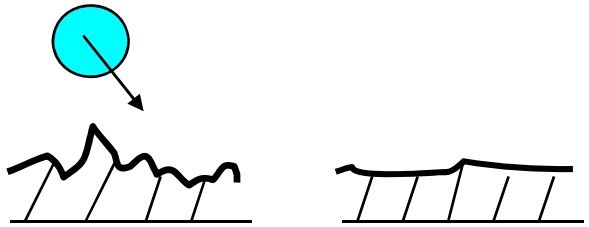
Applications of atomic clusters (1)

✓ **Medicine:**
- **-- cluster beams to treat caner,**
- **-- cluster biosensors for diagnostics,**
- **-- drug delivery**
- **-- fototermolise of tumors**

✓ **Creation of new materials by cluster beams. Soft deposition.**



✓ **Flattening hard surfaces by cluster beams.**



✓ **Catalysis:**
- **-- sodium clusters, large ratio surface/volume,**
- **-- strongly depends on the size and surface preparation of nanoparticles.**

✓ **Nanostructures at the surface**

Applications of atomic clusters (2)

- ✓ **Embedded clusters, magneic liquids**

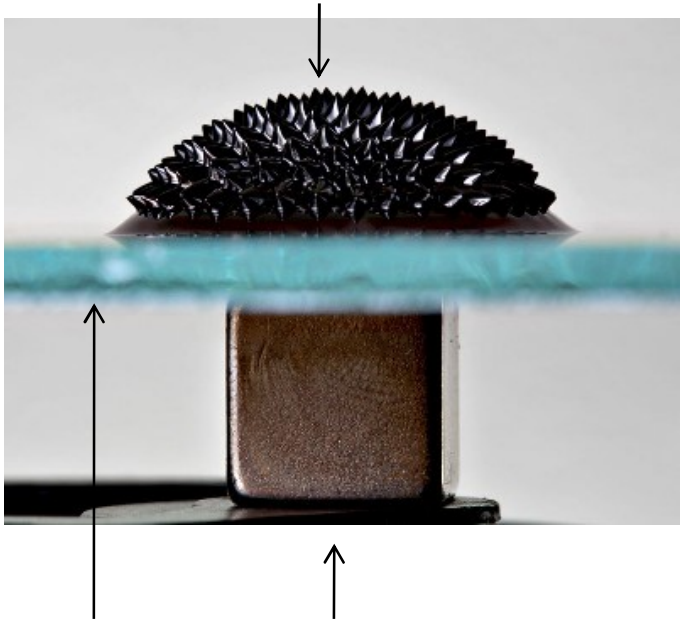
- ✓ **New alloys: combination of materials not mixed in bulk.**

- ✓ **New magnetic materials:**
  -- transformation of magnetic properties due to distorted ionic lattice.

- ✓ **Molecular and cluster nanoelectronics and nanodevices:**
  -- circuits, switches, transistors, ...
  -- ultrahigh density magnetic recording devises,
  -- nanotermometers, microcoolers, ...

- ✓ **Helium clusters as nanoscale cryostats:**
  -- $t < 0.37$ K,
  -- creation of cold clusters inside He droplets.

Magnetic fluids



Mixture of magnetic nanoparticles (~ 10 nm)
and liquid carrier with a sufractant.
Usually (in volume units):
5% - nanoparticles (e.g. of magnetite, **atomic clusters**, …)
10% - sufractant (e.g. oleic axid)
85% - liquid carrier (e.g. kerosene)

- ML is a usual liquid without magnetic field
- can accept fantastic shapes in external magnetic fields
- used since 1960 years in:
  - cosmonaut helmets, …

and later in:

- laser heads in CD and DVD players,
- low-friction seals,

New perspectives with magnetic atomic clusters!

References: atomic clusters

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"Oscillations in Finite Quantum Systems",
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2) W.A. de Heer,
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experimental aspects and simple models",
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"The physics of simple metal clusters:
self-consistent jellium model
and semiclassical approaches",
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4) C. Binns,
"Nanoclusters deposited on surfaces",
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5) F. Boletto and R. Ferrando,
"Structural properties of nanoclusters: energetic,
thermodynamical and kinetic effects",
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Физика элементарных чачстиц и атомного ядра,
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7) V.P. Krainov and M.B. Smirnov,
"Cluster beams in the super-intense femtosecond
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8) В.П. Крайнов, Б.М. Смирнов, М.Б. Смирнов,
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Springer series in chem. physics, vol. 52,
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9) F. Calvayrac et al,
Phys. Rep., 337, 493 (2000).

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"Introduction to Cluster Dynamics",
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CARBON NANOSYSTEMS

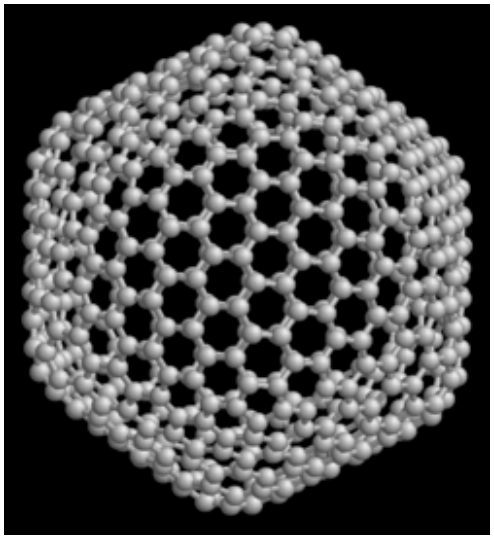
macrosystems

- **diamond**
- **graphite**
- **soot**

nanosystems

- **fullerenes**
- **graphene**
- **nanotubes**

Fullerenes (1): definitions



icosahedral fullerene C_{540}

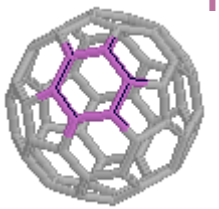
Definition:

Fullerenes (Buckminster Fuller) are systems composed entirely of carbon atoms in the form of a hollow sphere (buckyball), ellipsoid or tube (buckytube).

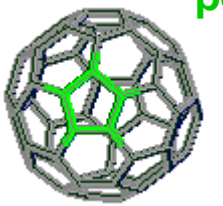
4th carbon state in addition to graphite, diamond, soot.

Fullerenes are similar in structure to graphite (composed of a sheet of hexagonal rings) but contain also pentagonal rings that prevent them from being planar.

hexa

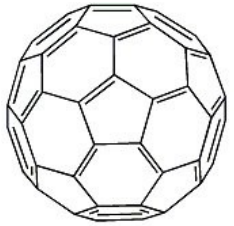


penta



Fullerenes (2): discovery, name

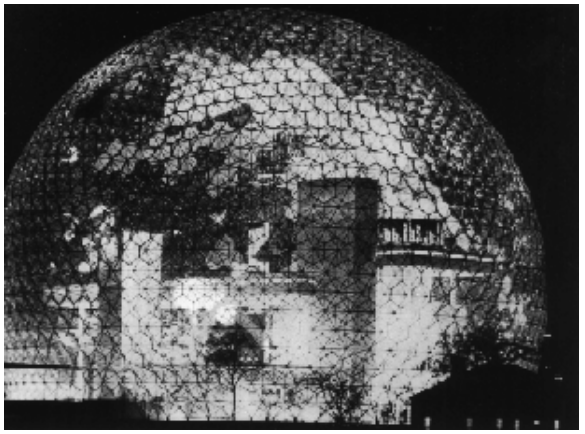
Fullerenes (C_{60} , …) were discovered in molecular beam experiments in 1985 (Rice University, US).



C_{60}
"Buckminster-Fulleren"

Later fullerenes were found in a candle soot.

H. Kroto, R. Curl, R. Smalley:
Nobel price in chemistry, 1996



Buckminster Fuller's Dome
Expo' 67, Montreal

Name from a US architect, writer and inventor Richard Buckminster Fuller (1885-1983) who propagated the geodesic dome.

D. Huffman and W. Kratschermer (1991): invention of easy production of fullerene powder.

Fullerenes (2): Buckminsterfulleren C_{60}

-- constructed from 60 carbon atoms,
-- truncated icosahedron,
-- resembles a soccer ball,
-- 12 pentagons, each completely surrounded by a ring of hexagons

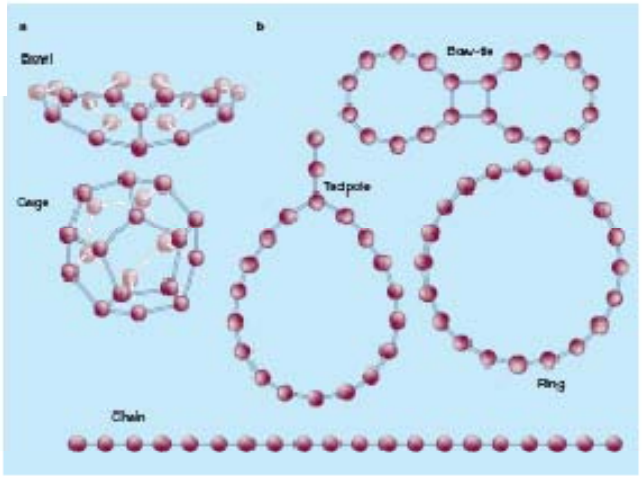
C_{60}

"Buckminster-Fulleren"

-- 60*4=240valence electrons,
-- σ- and π- electrons,
-- mean field,
-- quadrupole deformation: C_{70}
-- two dipole plasmons, for σ and π electrons
-- …

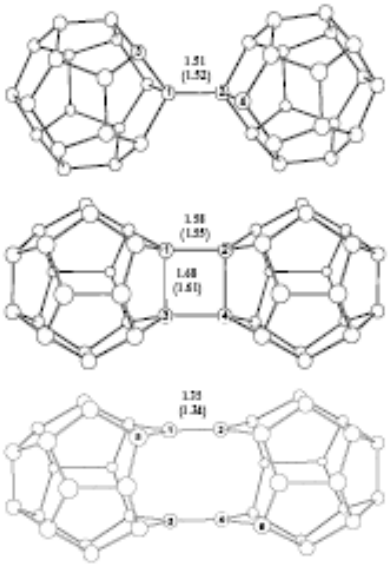
Lightest fullerene C_{20}

-**produced in 2000 (cage and bowl),**
- **cage: 12 pentagons only,**
- **bowl: 1 pentagon surrounded by 5 hexagons,**
- **few forms,**
- **perspectives for creation of fullerite with high-T superconductivity**



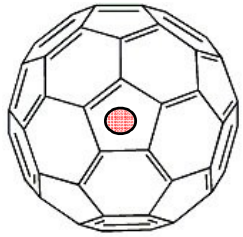
C_{20}

-prefers less compact ring and chains geometries (first observed),
-formation through the precursor: carbon skeleton of the fullerene cage capped with hydrogen and bromine atoms
-identification of the form: by photo-electron spectra



Two conflicting explanations how fullerenes are made from small carbon fragments: "fullerene" and "pentagon" roads.

Fullerenes (5): endohedral fullerenes



C_{60}
"Buckminster-Fulleren"

Endohedral fullerenes incorporate in their inner sphere intruder atoms, ions or clusters.

The first complex La@Ca60 was synthesed in 1985.

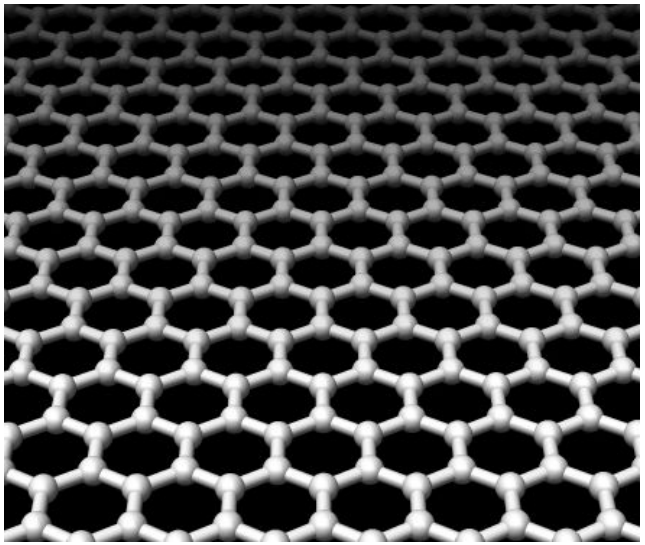
Two types:

- **-- endohedral metallofullerenes: La@Ca60, …**
- **-- non-metal doped fullerenes: He@C60, Ne@C60, … .**

New kind of atomic trap:

- **-- room temperature,**
- **-- arbitrary long trapping,**
- **-- no any reciprocal effect from the environment,**
- **-- investigations: compression of atomic wave function, …**

Graphene



- theoretical studies at least since 1947
- first obtained in 2004 ← **Novoselov K.S. + Manchester Univ.**
-exclusively hexagonal cells
- single planar sheet of carbon atoms
  (one graphite layer with the thickness of one atom)
- semimetal, zero forbidden zone, linear spectrum
- can be used for:
  - planar field-effect transistors,
  - quantum interference devises
  - …
- high mechanical rigidity and heat conductance

- Electrons obey a massless relativistic Dirac equation

$$E=\hbar v_F k$$

like photons with $v_F \sim 10^6\, ms^{-1}$ instead of speed of light.

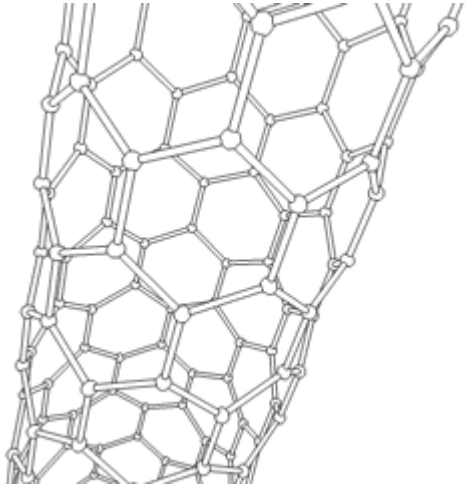
Charged massless fermions!
No analogs?

- Mobility μ up to 104 $cm^2V^{-1}s^{-1}$ is reported:
  - almost independent of temperature,
  - electrons in graphene can move easier than in any other known material at room temp.

- test for relativistic theory
- new (relativistic) version of quantum Hall effect

$v = \mu E$

Fullerenes (4): carbon tubes



-- observed accidentally in 1991,
-- cylindrical fullerenes,
-- few nm wide but μm – mm in length,
-- can be single- and multi-walled,
-- quantum physics of one-dimensional systems,

-- unique macroscopic properties:
- high tensile strength
  (63 GPa ⟷ high-carbon steel: 1.2 GPa)
- multi-walled NT: striking telescopic property,
- high plastic deformation,
- high electrical conductivity:
  - can be metallic or semiconductor,
    (in metallic CT electrical current density 1000 times lager than in Cu or Ag!)
- high heat conductance along the tube,
- high lateral heat resistance,
- chemical inactivity,
- can merge at a high pressure thus forming unlimited length wires,
- easily soluble in most solvents.

Applications of nanotubes:

Structural:
- **waterproof tear-resistant clothes,**
- **combat jackets,**
- **sports equipment,**
- **ultra-high speed flywheels.**

Chemical:
- **water filter,**
- **air-pollution filter**

Electromagnetic:
- **artificial muscles,**
- **bucky-paper (250 times stronger, 100 times lighter),**
- **computer circuits (two joined CT of a different diameter act as diode)**
- **conductive films for liquid screens, photovoltaic devices, etc,**
- **brushes for commercial electric motors,**
- **light filaments,**
- **optical ignition for explosives,**
- **solar cells,**
- **superconductor at low temperature,**
- **ultracapacitors,**
- **displays,**
- **transistors.**

References: carbon nanosystems

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Thank you for your attention!