A Few NanoComments on NanoScience *and* NanoTechnology

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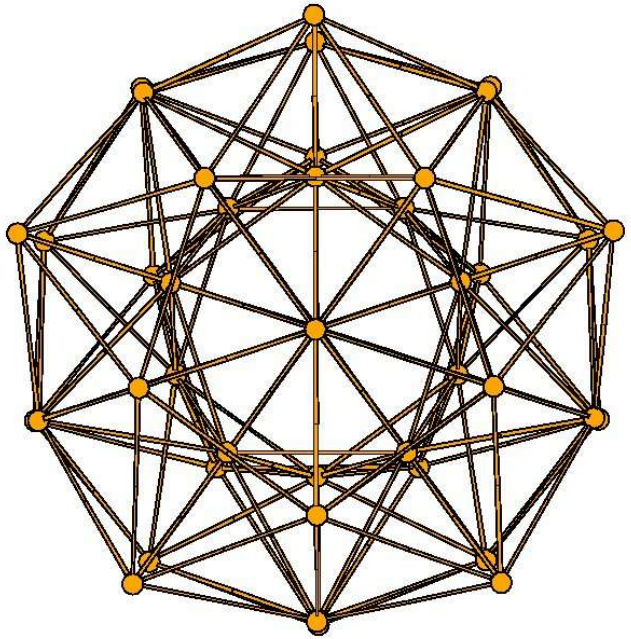


NANOME

MAPPING PROJECT

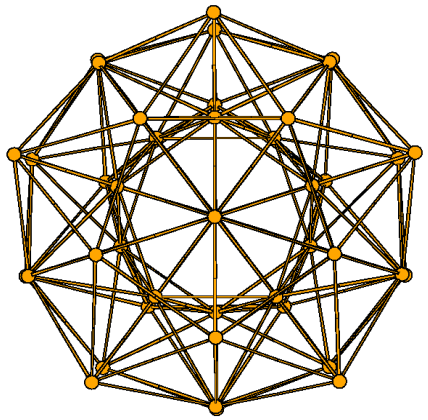
Mapping the NANOWORLD

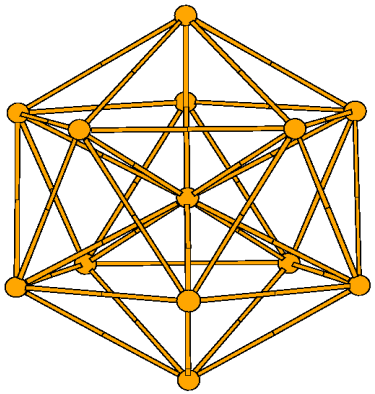
at

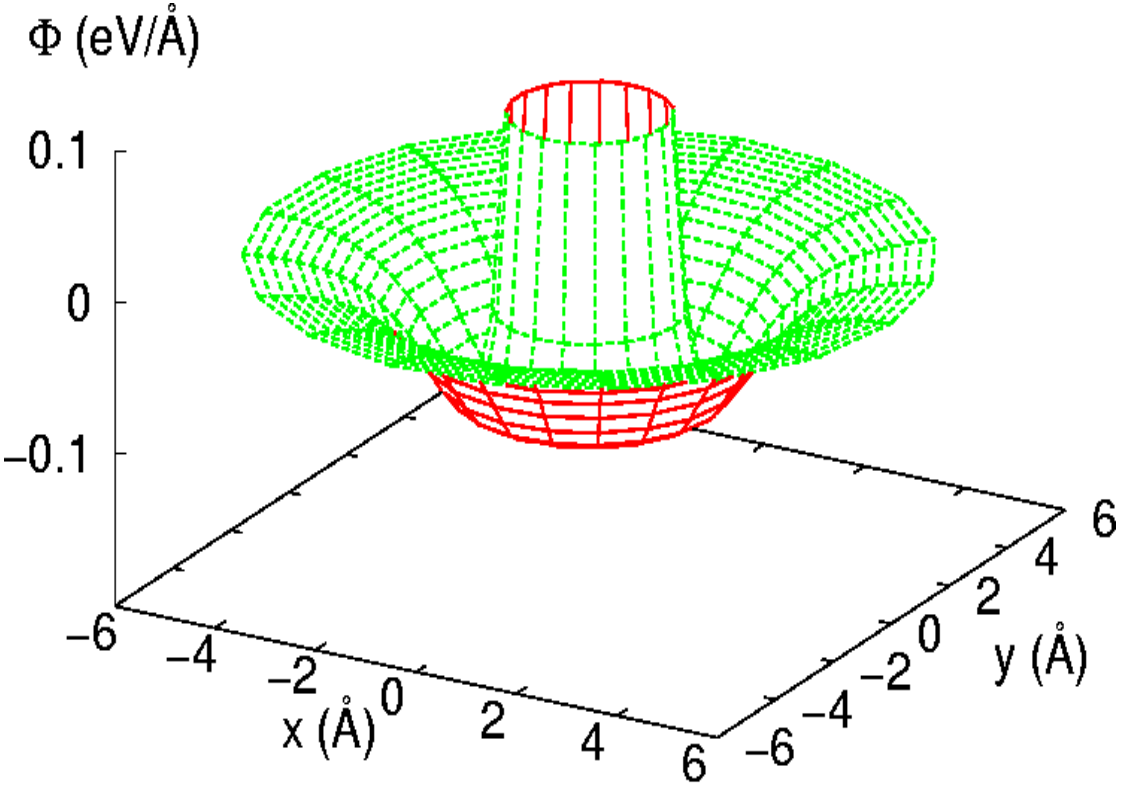
Magurele-Bucharest

We are making NANO at Magurele

(L. C. Cune)







Cune Potential

$$\Phi_{ij} = -\frac{1}{2} z_i^* z_j^* q \left(1 - \frac{2}{q\left|\mathbf{r}_i - \mathbf{r}_j\right|}\right) e^{-q\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

CONTENTS

Department of Energy, USA

Strategic Plan of Research 2005-2025

Priorities:

- **NanoSci & NanoTech (Electronization of Biology)**
- Complex Systems (Control of the Planet, Space, etc)
- Astrophysics & Cosmology (New Nuclear Weapons)

(USA's 21st Century Nano Res & Dev Act, 2003)

Hierarchy in Size

Atoms, Molecules <10Å

NanoStructures 10Å –1000-1500Å

Micro-, Mini- (lower bound of today ~900Å

MesoStructures (1μ)

MacroStructures (Avogadro's number 10^{23})
(Universe Age)

(1 nano=10Å=10^{-9}m)

Scale

Human Hair = 800 000Å (80µ)
Red blood cell = 70 000Å
Virus = 1000Å:

Here starts Nano down to

Fullerene molecule =7Å
DNA = 20Å (wide)
Water molecule=3Å

What we expect from Nano

- NanoElectronics (Moore's Law)
- Information & Communication (Nanonisation)
- Drug Development
- Water (Environment) Decontamination
- Stronger and Lighter Materials
- "Grey Goo" ?
- New Processes, Materials
- Functional Nanostructures (electronic, chemical, biological, ...)

Technological Matters
Investment: $5b ($2b private)

Etching Silicon Microchips (limited); Self-assembly (bottom-up)

Displays (Se), Paints, Batteries (Ni), Catalysts

Nanowires (carbon); Optical and magnetic NanoMemories

ZnO_2 (zirconia) – ceramic plastics; Al_2O_3 (aluminium oxide) – ceramic; SiO_2 (quartz) - microelectronics

Nano-Ag dresses wounds

Cosmetics (ZnO, TiO_2, FeO)

A few Examples

Nano-Au appear red, blue or gold in stained glass and ceramics, depending on its size

TiO_2-nanowires for (photo-) catalysis, *H, Li* storage (UV active, transparent)

Phosphorous algae

Proteins

Polymers

Romanian Advances

Cd/Se quantum nanowires (electrochemically, display)

Cu/Co multistrat nanowires (giant magnetoresistance)

Particulate alkali halogenides with Rare Earths (digital radiography)

3D Compact Disk of Ceramics with Rare Earths

NanoColoured optical crystals

Issues

-Health Risk, Social, Environmental, Safety, Regulatory, Ethical Issues

-Toxicity – NanoBomb (DustClouds), Explosion

-Dangerous Materials: Quartz, Asbestos, Air Pollutants *via* Combustion (1mg per cubic metre of breathing air)

-Human Enhancement (Commercialisation of Science)

Physics

Large Surface (Finite-Size Effects)

Quantum Effects (optical, electrical, magnetic)

(El Conductance quanta *vs* Mech Tension quanta in nanowires)

NanoTech: Size and Shape Matters (Quantum Dots Optics ~ Size)

New tools: STM, AFM (NanoMetrology); MBE

Chemical Binding

Dirac (~1930) (Hartree-Fock (HF), LCAO)

1. *Ab-initio* methods (LCAO) (Pople, 1940-1998) - configuration superposition (Slater, 1929, 1930)

2. Density functional (Kohn-Sham, 1964-1998)

H_2 - molecule (James-Coolidge, 1933) - energy vs size (*He* - Hylleraas, 1929, Pekeris, 1958)

Quasiclassical Description

THEORY

- Nanostructure (one-particle) orbital

$$\psi_s = \alpha_s \varphi_s + \beta_s \phi_s$$

(in contrast with *ab-initio* methods' φ_s only) - Mullikan (1928)

- Cores plus valence atomic-like orbitals (upper shells) $\varphi_s = \sum c_{ia}^s \chi_{ia}$

- Minimum of atomic energy $\rightarrow c_{ia}^s$

- Minimum of extended-orbital energy $\rightarrow \beta_s$

-Coupling $\sum |c_{ia}^s|^2 = 1$ and $\alpha_s^2 + \beta_s^2 = 1$ (self-cons; str dependent)

- binding effective charge z_i^* for each i-th ion

-binding ionic-hole density $\rho = \sum \beta_s^2 \left|c_{ia}^s\right|^2 \left|\chi_{ia}\right|^2$,

$z_i^* = \sum \beta_s^2 \left|c_{ia}^s\right|^2$: assume spherical symetric

$\sum z_i^* \delta(r - R_i)$ (more general $\rho = \sum \beta_s^2 c_{ia}^* c_{jb} \chi_{ia}^* \chi_{jb}$)

-s-like atoms: $z_{Na}^* = 0.44$, $z_K^* = 0.34$, $z_{Fe}^* = 0.57 (3d^6 4s^2)$

$z_{Ag}^* = 0.19 (4d^{10} 5s^1)$, $z_{Ba}^* = 0.34$

(quasiclassical description of heavy atoms; atomic screning)

-(magnetic momentum, structure dependent)

Binding (cohesion) Hamiltonian

(Liviu Cristian Cune)

$$H=\sum_{\alpha} p_{\alpha}^{2}/2m-e^{2}\sum_{i\alpha}\int dR\frac{\rho_{i}(R)}{|R-r_{\alpha}|}+\frac{1}{2}e^{2}\sum_{\alpha\neq\beta}\frac{1}{|r_{\alpha}-r_{\beta}|}+$$

$$\frac{1}{2}e^{2}\sum_{i\neq j}\int dRdR'\cdot\frac{\rho_{i}(R)\rho_{j}(R')}{|R-R'|}$$

$$\rho_{i}=\sum_{sa}\beta_{s}^{2}\left|c_{ia}^{s}\right|^{2}\left|\chi_{ia}\right|^{2}\rightarrow z_{i}^{*}\delta(R-R_{i})$$

Core-Electrons Equations

- (nano) structure orbitals

- solve iteratively for β_s and c_{ia}^{s} (corrections controlled by $a_{atom}/a_{structure}$, orbital-dependent)

- fractional β_s, theory of valence (donors, acceptors, etc)

-main role: actual atomic-like orbitals $\chi_{ia}(R)$ in upper shells

-(all for usual, relatively light, cohesion, upper shells!) *(Pd-H* problem!)

Hartree-Fock Equations (HF)

$$(p^2/2m)\phi_s - e\varphi\cdot\phi_s + \varepsilon_{ex}(\phi_s) = \epsilon\phi_s$$

$$\varphi = e\sum_i z_i^*/|r-R_i| - e\int dr'\cdot n(r')/|r-r'|$$

$$\varepsilon_{ex} = -e^2\int dr'\cdot 1/|r-r'|\sum_{s'}\phi_{s'}^*(r')\phi_{s'}(r)\cdot\phi_s(r')$$

$$n(r) = \sum_s |\phi_s(r)|^2 \quad , \quad n(r,r') = \sum_s \phi_s^*(r)\phi_s(r')$$

- eigenfunctions for ε_{ex} - plane waves

- unknowns: ϕ_s and number of s (non-linear!); local changes of electron density

- s - change in electron density: no change in ε_{ex} (rigidity, non-local; Slater, 1979; Seitz, Wigner, 1934) (functional of concentration, not of density!)

- screening the Hartree (1928) potential φ untill almost constant: plane waves as eigenfunctions almost everywhere

- slow spatial variations

Solution

Hartree (1928) - Fock (1930) energy functional - variation with respect to the s - number of states

Thomas (1927)-Fermi (1928) equations:

$$\hbar^2 k_F^2/2m - e\varphi = 0 \quad , \quad \Delta\varphi = -4\pi e \sum_i z_i^* \delta(r - R_i) + 4\pi e n$$

$$n = k_F^3/3\pi^2$$

plus LINEARIZATION! $n \sim \varphi$

- quasiclassical approximation $n \sim \varphi^{3/2}$ -valid for $z_i^* \to \infty$, no binding (Teller, 1962)

Linearization

$$k_F^n \to \bar{k}_F^{n-1} k_F \quad , \quad q^2 = (8/3\pi)\bar{k}_F$$

$\bar{k}_F$ to be compared with $k_{Fav} = (1/z_0)\int n k_F = (4/3\pi^2 z_0)\int \varphi^2$;

q^2 and q_{av}^2 $(z_0 = \sum_i z_i^*)$

-Poisson equation:

$$\varphi = \sum_i \frac{z_i^*}{|r - R_i|} e^{-q|r-R_i|}$$

- Thomas-Fermi screened potential

- HF energy functional (linearized):

$$E_{kin}=(27\pi^2/640)z_0 q^4 \quad , \quad E_{ex}=-(9/32)z_0 q^2$$

$$E_{pot}=-\frac{q}{4}\left\{3\sum_i z_i^{*2}+\sum_{i\neq j} z_i^* z_j^*\left[1-\frac{2}{q|R_i-R_j|}\right]e^{-q|R_i-R_j|}\right\}$$

-variational q from $E_q=E_{kin}+E_{pot}$

Cune potential

$$\Phi(R_i-R_j)=-\frac{qz_i^* z_j^*}{2}\left[1-\frac{2}{q|R_i-R_j|}\right]e^{-q|R_i-R_j|}$$

repulsive $R\to 0$, attractive $R\to\infty$, minimum at $qa\sim 2.73$

Recipee

- Minimization of E_{pot} with respect to $q|R_i - R_j|$

- Minimization of $E_q = E_{kin} + E_{pot}$ with respect to q

- Atomic positions (structure); vibration spectrum

- $q \simeq 0.77 z^{*1/3}$ and $q_{av} \simeq 0.9 z^{*1/3}$; 17%

- Electronic properties - "Quantum" corrections: HF eqs with screened potential (Clemenger-Nilson approximation, finite-size effects, etc)

- Correction for q (via linearized electron density)

- Maximal accuracy 3 % (one-particle functions; lifetime)

Full Recipee

- Start with actual atomic-like potentials and $z_i^* = 1$ (normalized)

- Minimization of E_{pot} with respect to $|R_i - R_j|$ and minimization of $E_q = E_{kin} + E_{pot}$ with respect to q simultaneously

- Correct for $z_i^* < 1$ by a_{at}/a_{str} -controlled core-electrons eqs (convergence)

- Structure (atomic positions); vibration spectrum

- Electronic properties - "Quantum" corrections: HF eqs with screened potential

-Refine everything by one more iteration with the corrected q (via linearized electron density) (convergence)

- Stop: at about 3% accuracy

Applications 1: Atomic Clusters

- homo-atomic (δ - cores, at screening z_i^*)

- structure, magic forms and magic numbers (symmetry and space economy; entropy economy?)

- energy

- abundance $\ln(I_N^2/I_{N-1}I_{N+1}) = E_{N+1} + E_{N-1} - 2E_N$

- vibrations spectrum

- isomers

- quantum corrections (electronic), deformed cluster potentials, finite-size effects included (ionization potential, electron affinity, reactivity)

Electronic Properties

$$\varphi = \sum_i \frac{z_i^*}{|r - R_i|} e^{-q|r-R_i|}$$

$$\varphi = \frac{4\pi z^*}{a^3 q^2}(1 - F e^{-qR}) \;,\; F = (1+qR)\frac{\sinh qr}{qr} \;,\; r < R$$

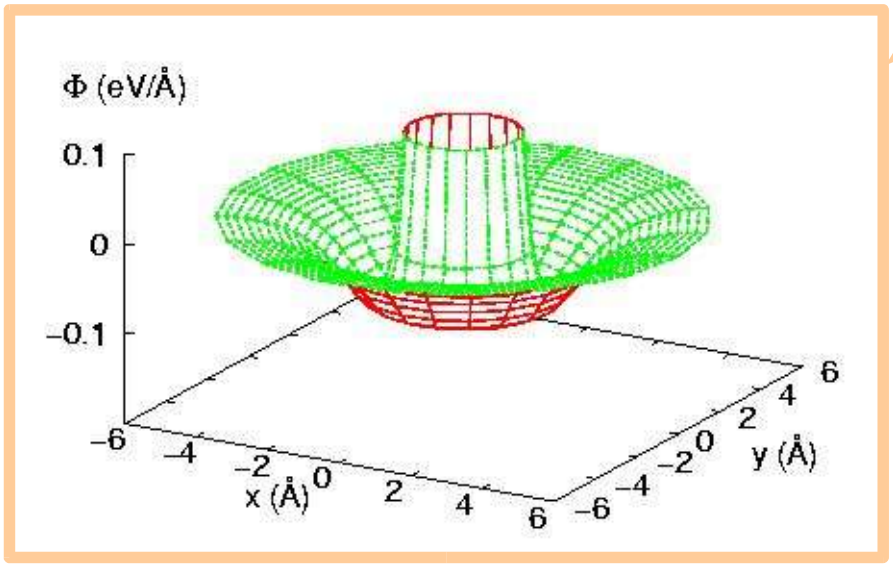
$$(\text{harm osc } \omega^2 \text{ controlled by } a/R)$$

$$\varphi = \frac{4\pi z^*}{a^3 q^2}(qR\cosh qR - \sinh qR) e^{-qr}/qr \;,\; r > R$$

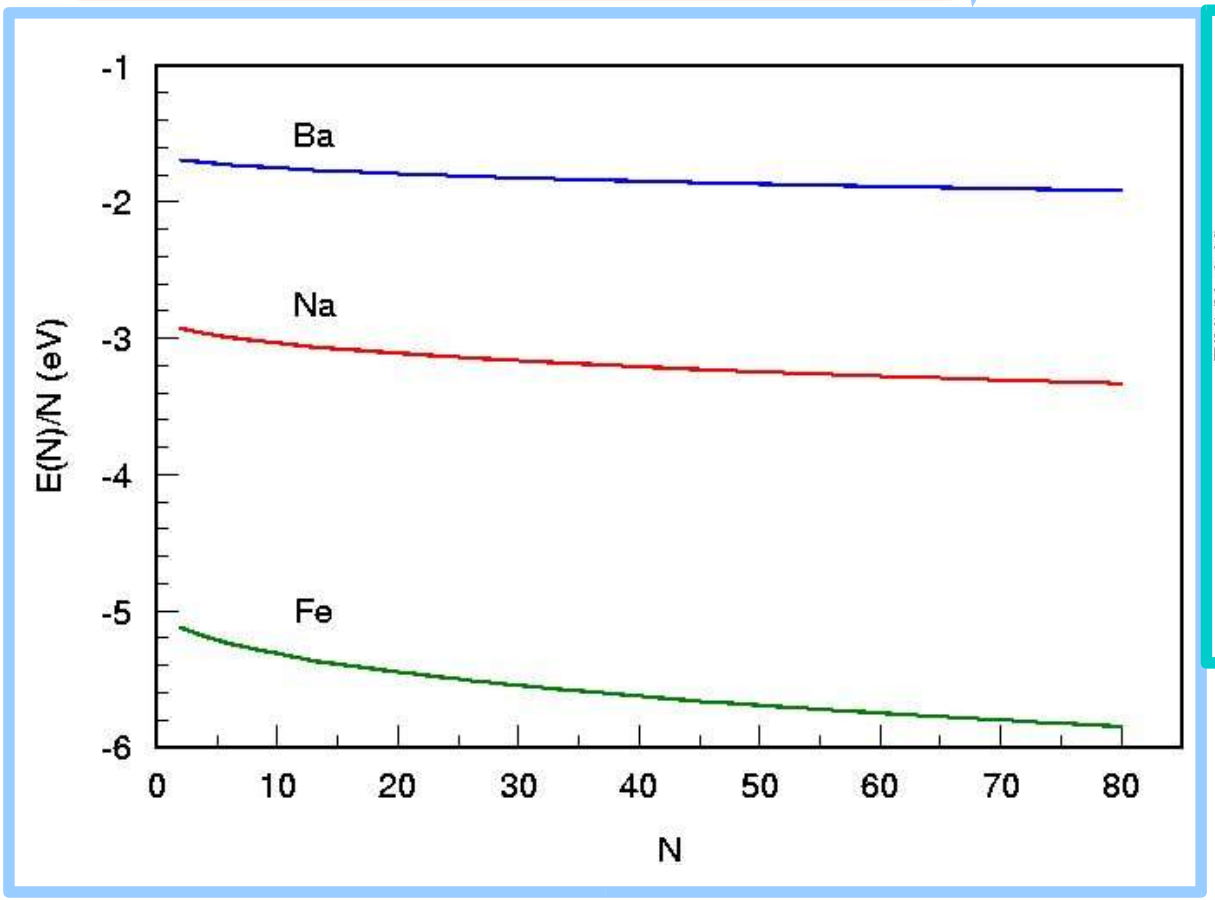
$$E_{pot} = -\frac{3}{4} q N z^* \left(1 - \frac{2\pi}{(aq)^3} \cdot \frac{1}{qR}\right)$$

(surface tension)

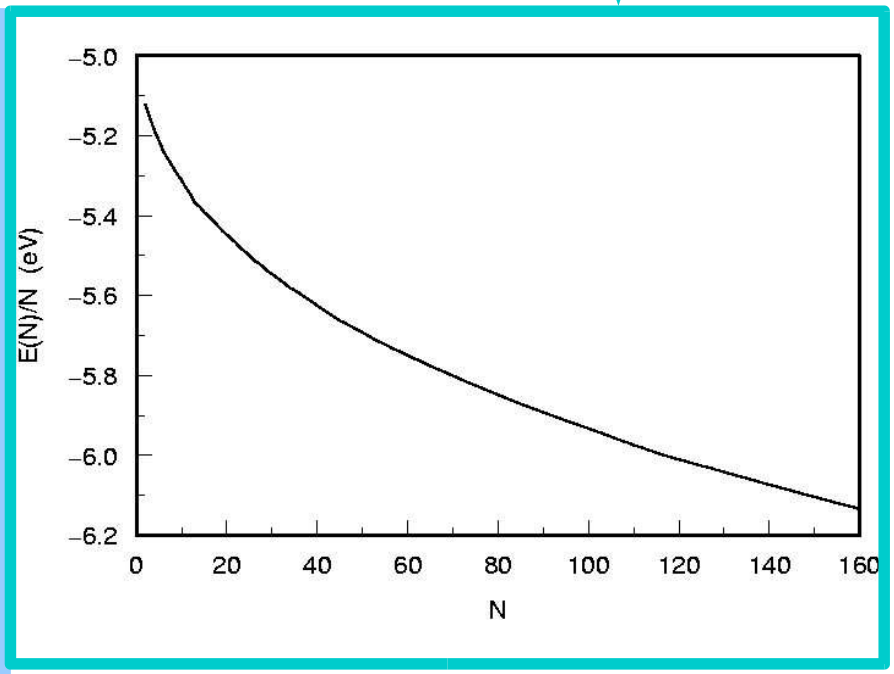
Effective inter-atomic potential



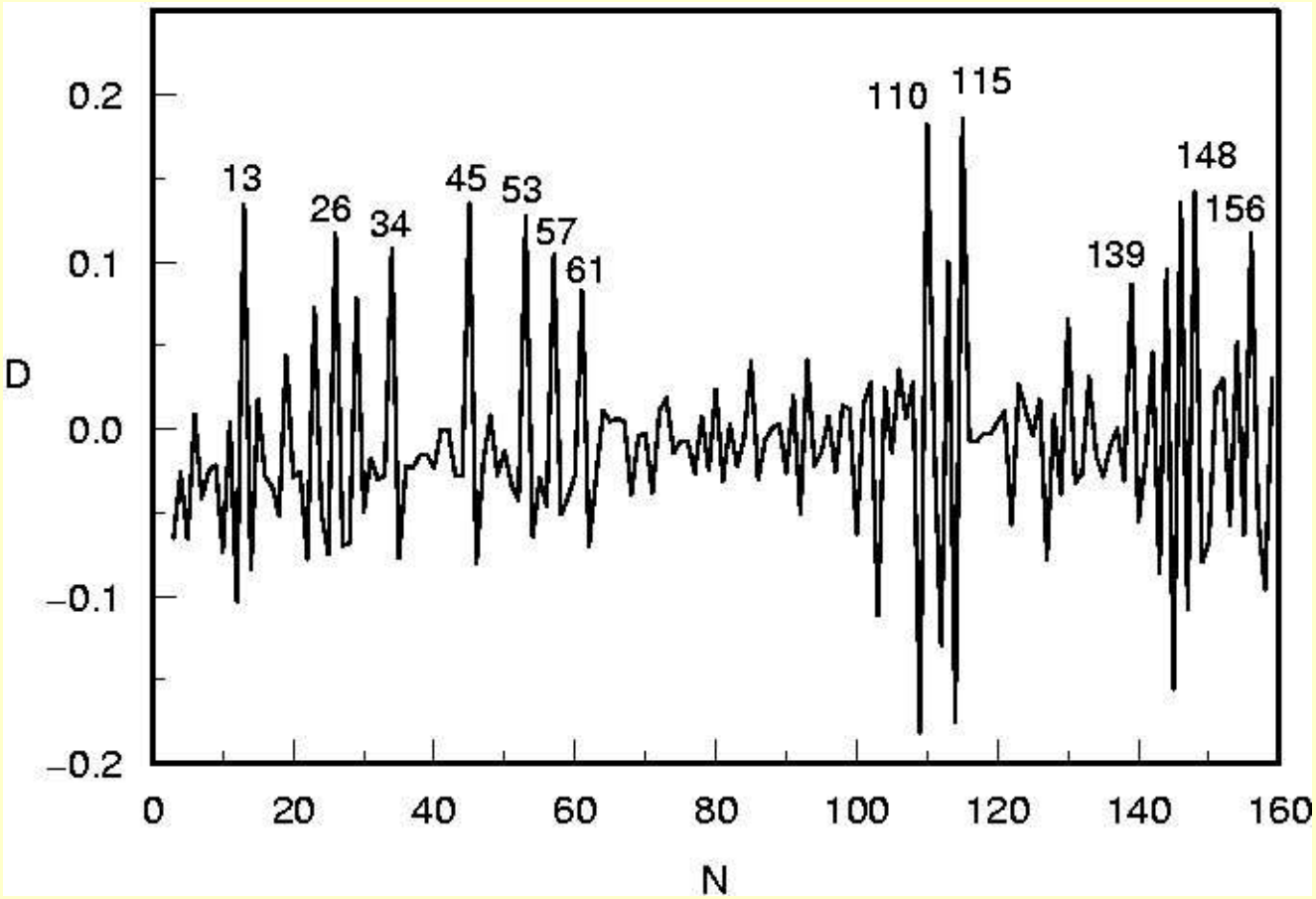
Energy per atom *vs* N for Ba-, Na-, and Fe-clusters (N<80)

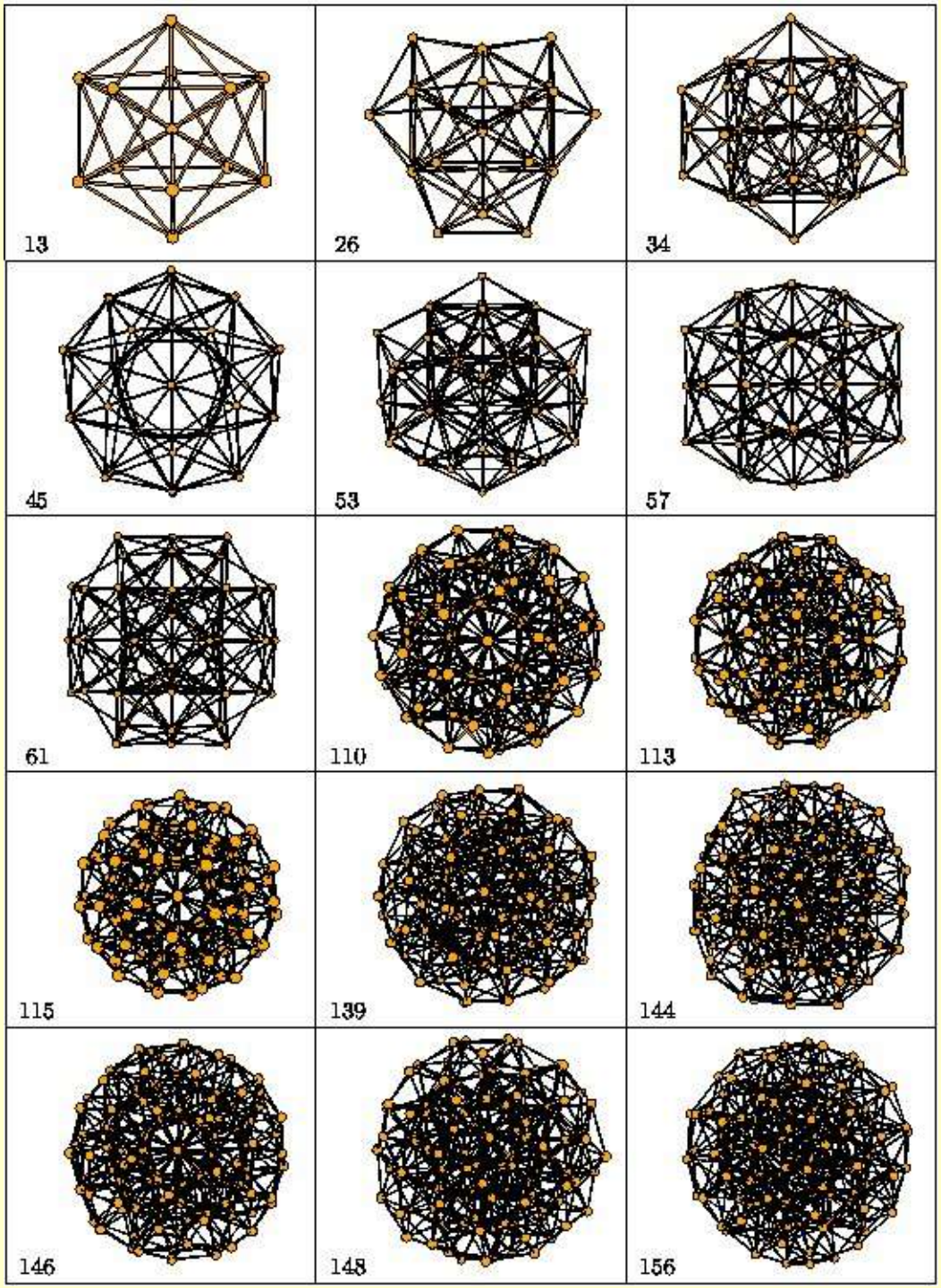


Energy per atom *vs* N for Fe-clusters (N<160)

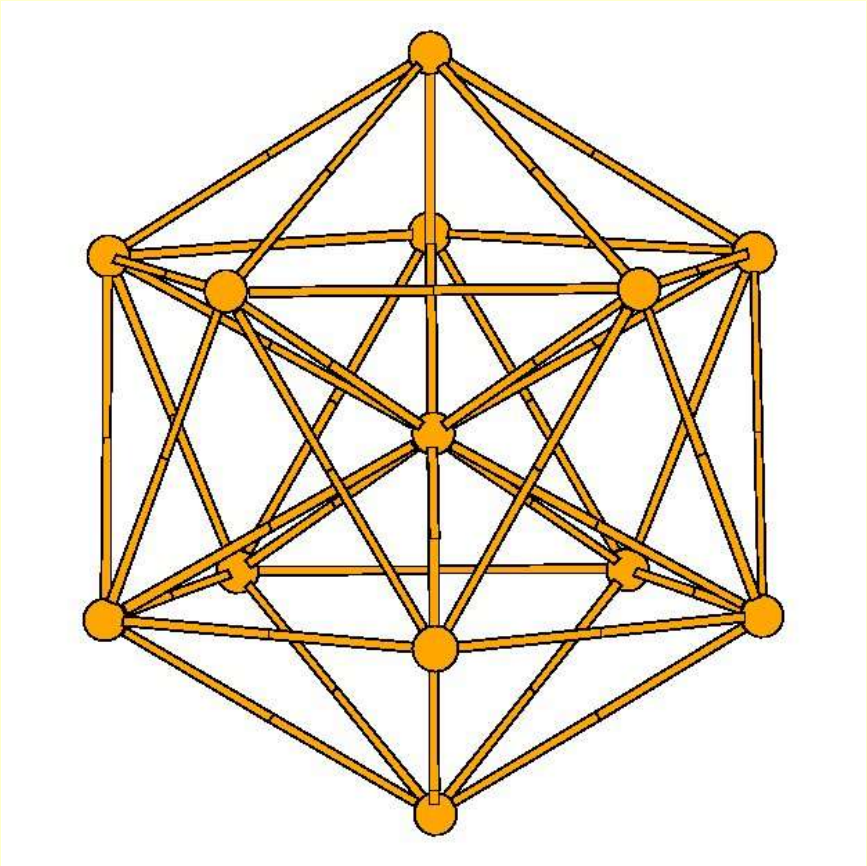


Magic numbers

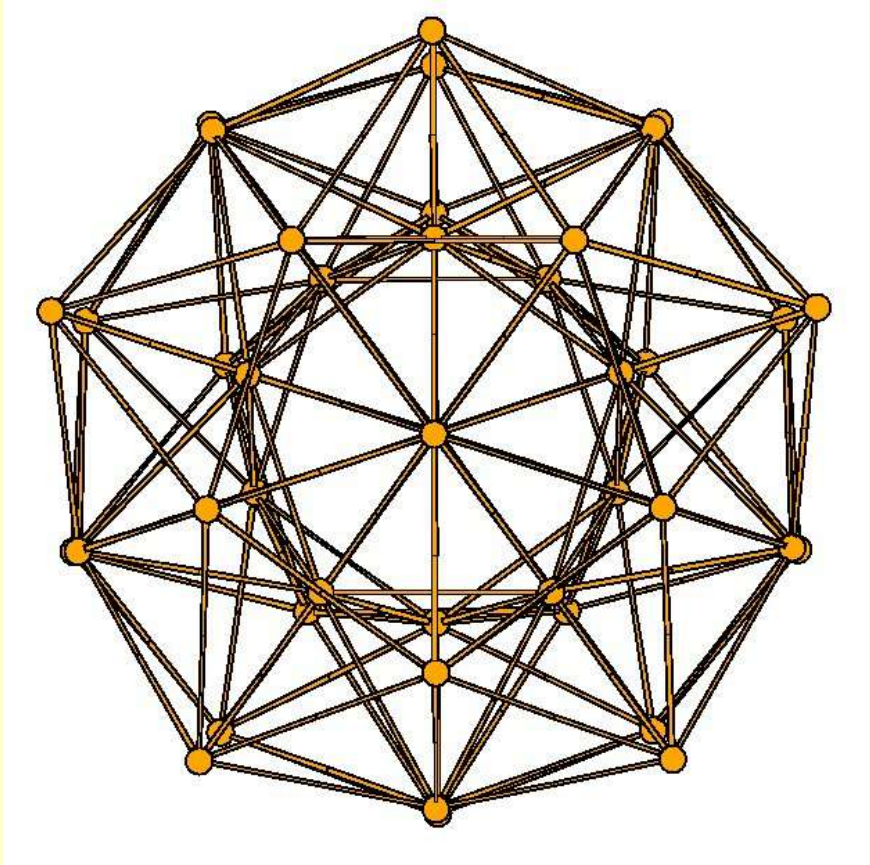




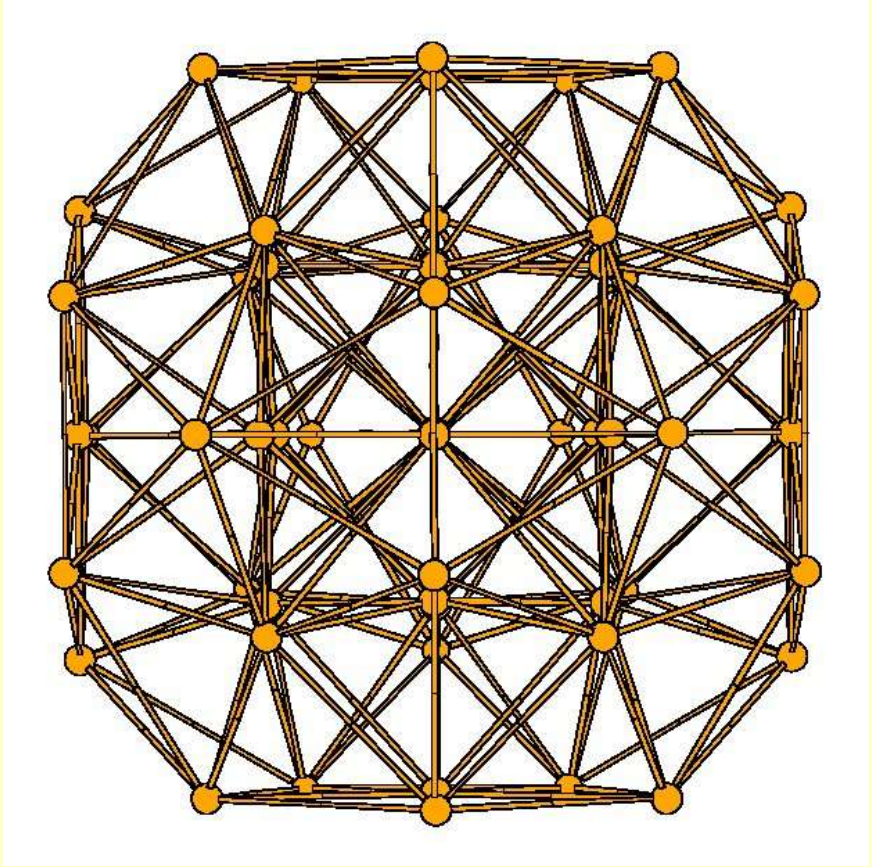
Magic homo-atomic metallic clusters



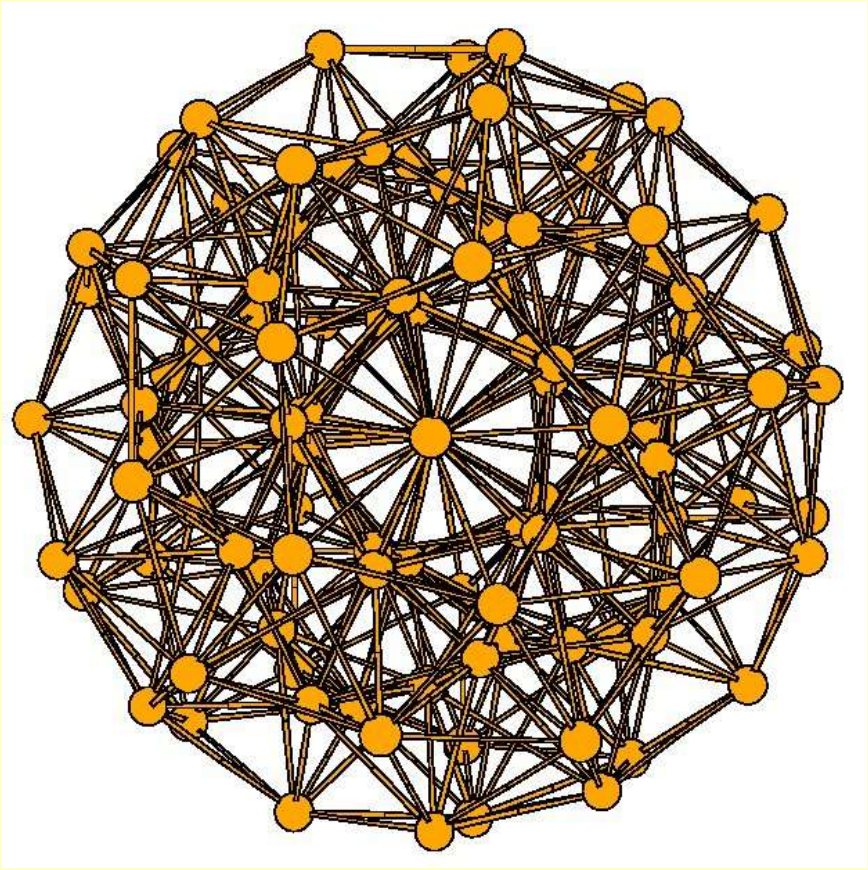
Fe_{13}



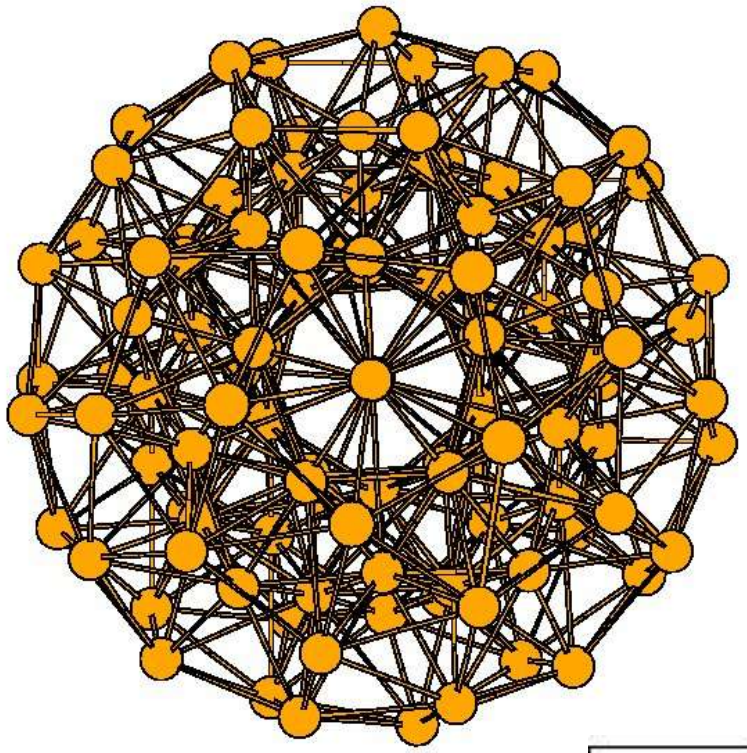
Fe_{45}



Fe_{55}

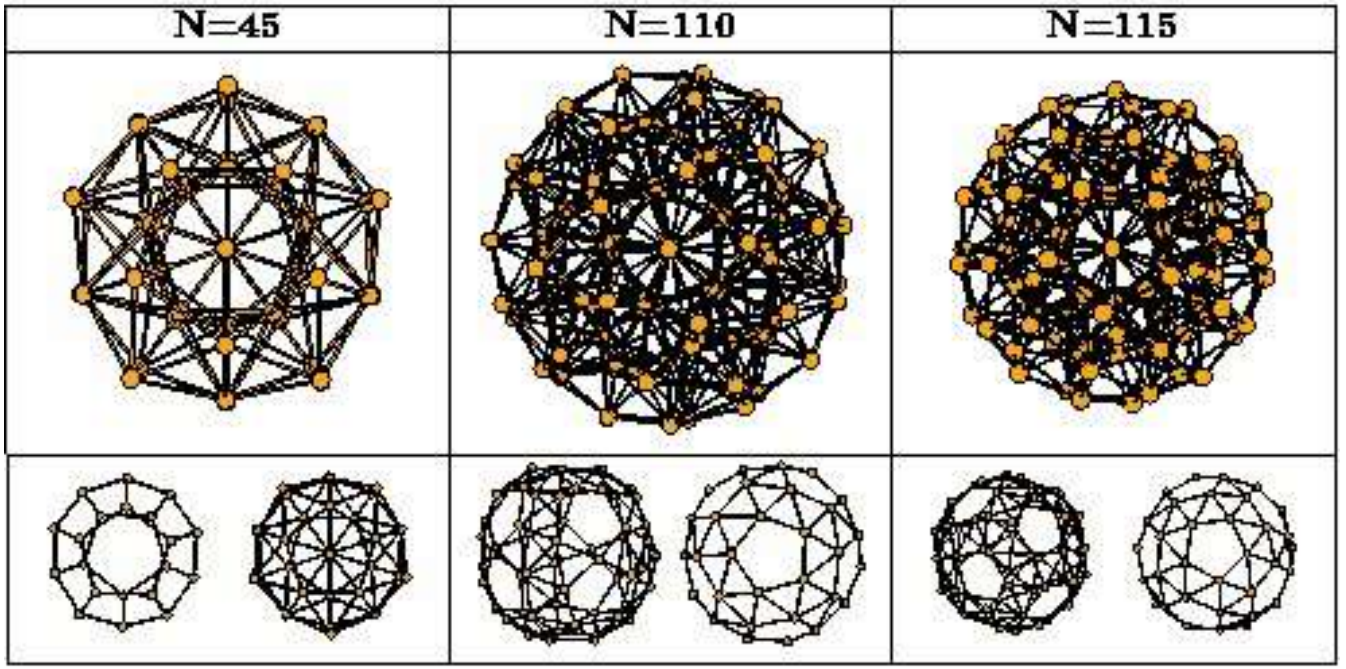


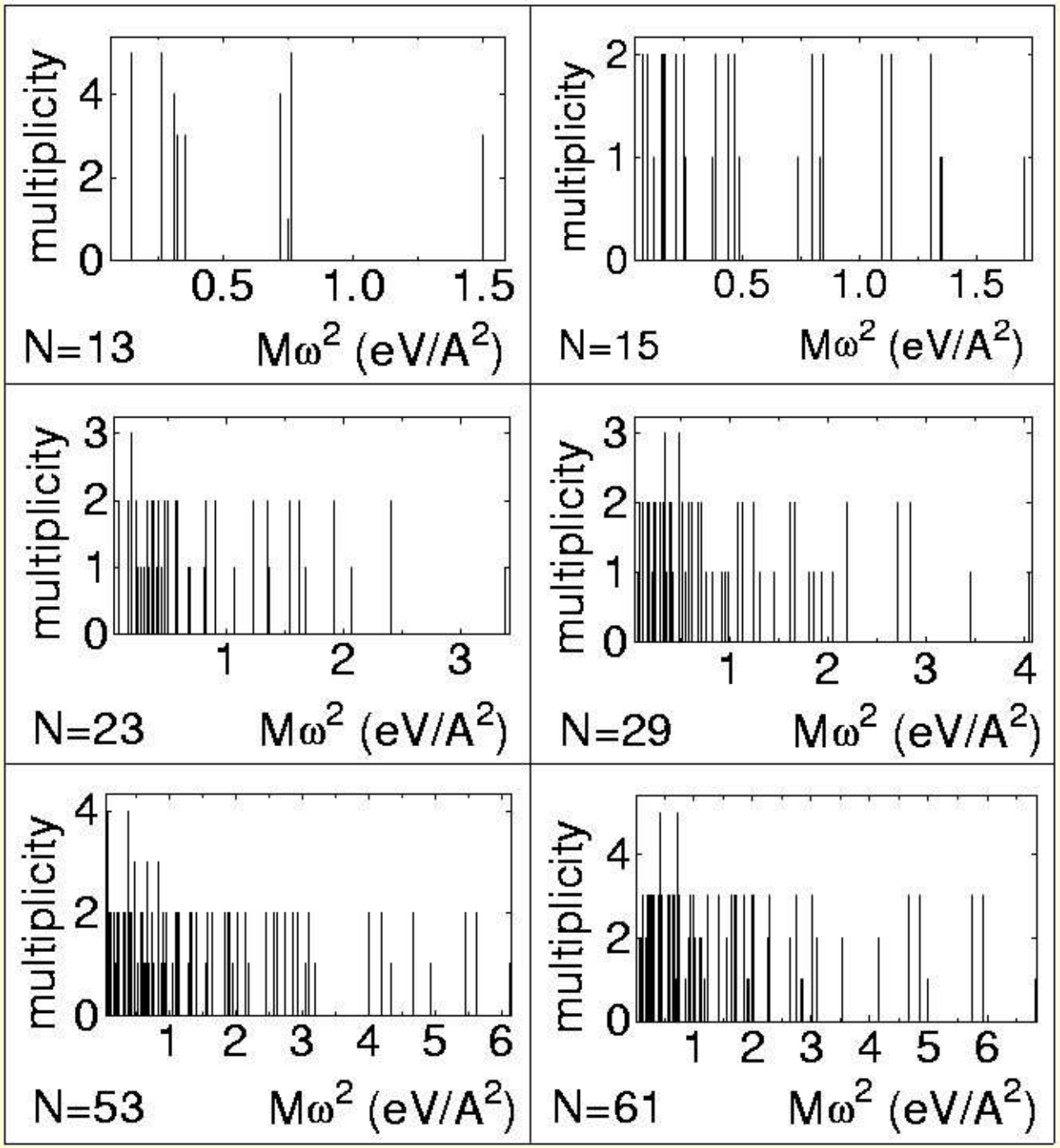
Fe_{110}



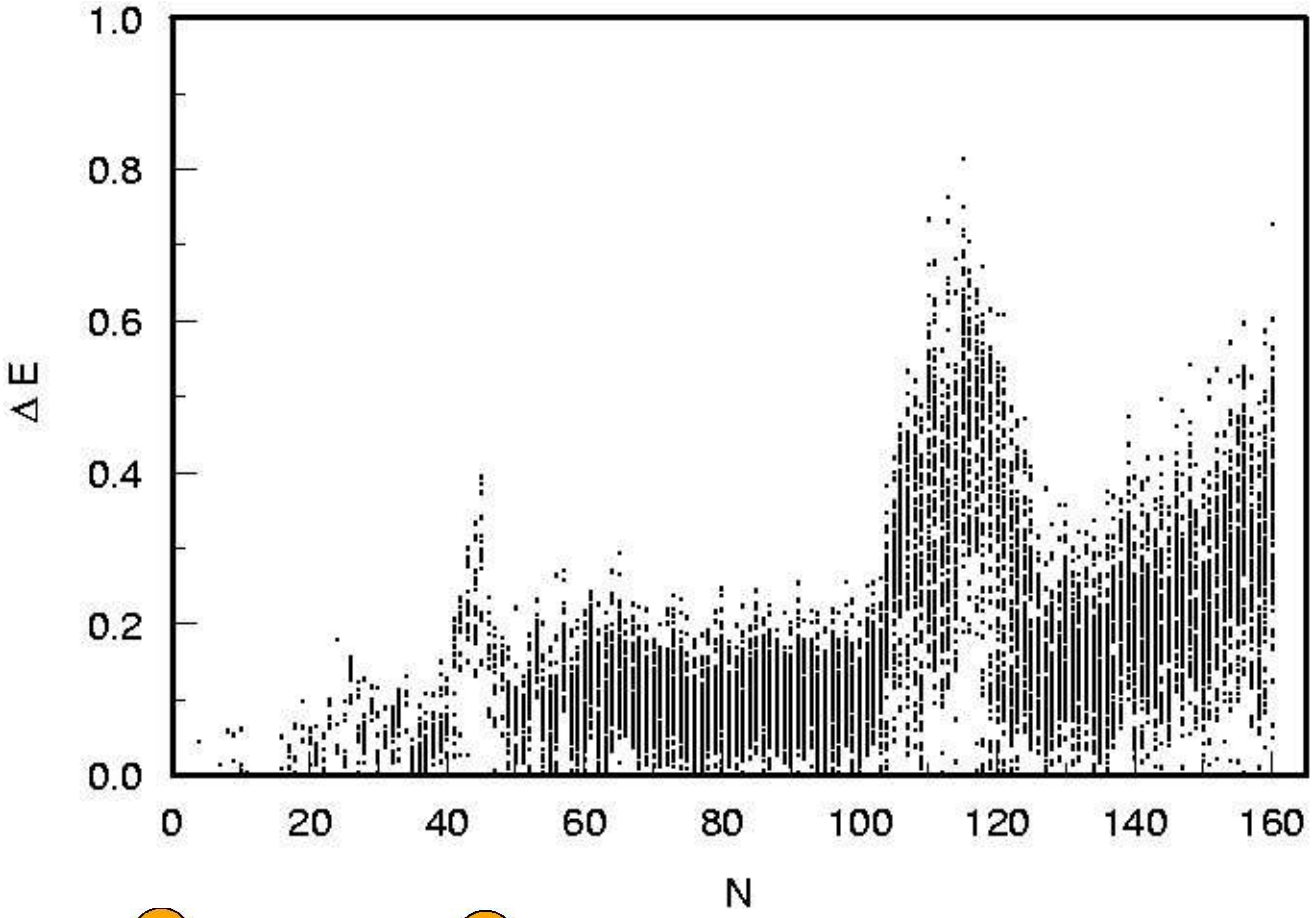
Fe_{115}

Outer atomic shells

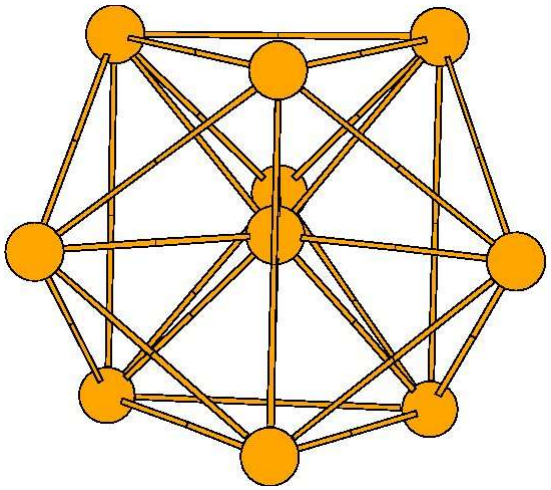




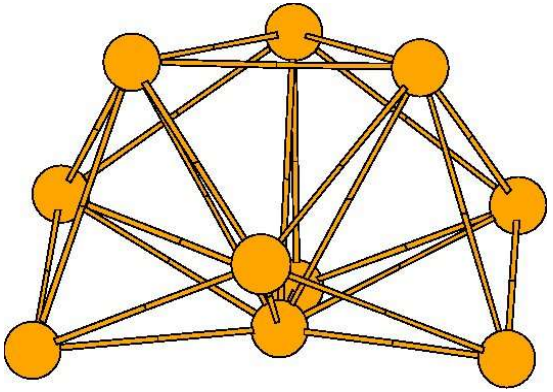
Vibration spectra for ground-state Fe-clusters

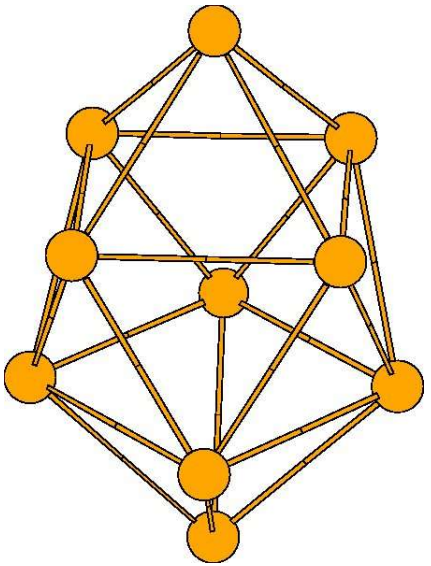


Isomers



Fe_{10} ground-state





Fe_{10} isomers

Applications 2: Exotic Structures

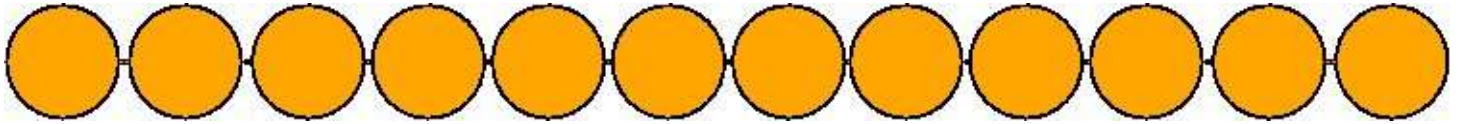
- nanowires (metallic, unstable)

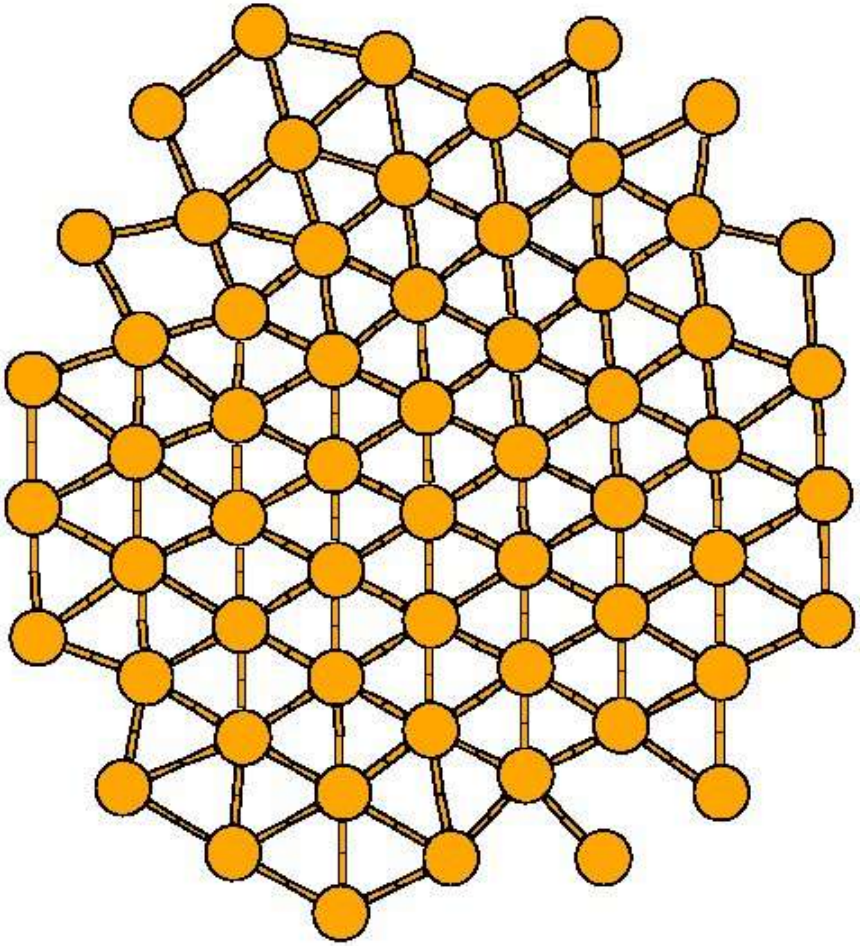
- 2D atomic sheets (unstable)

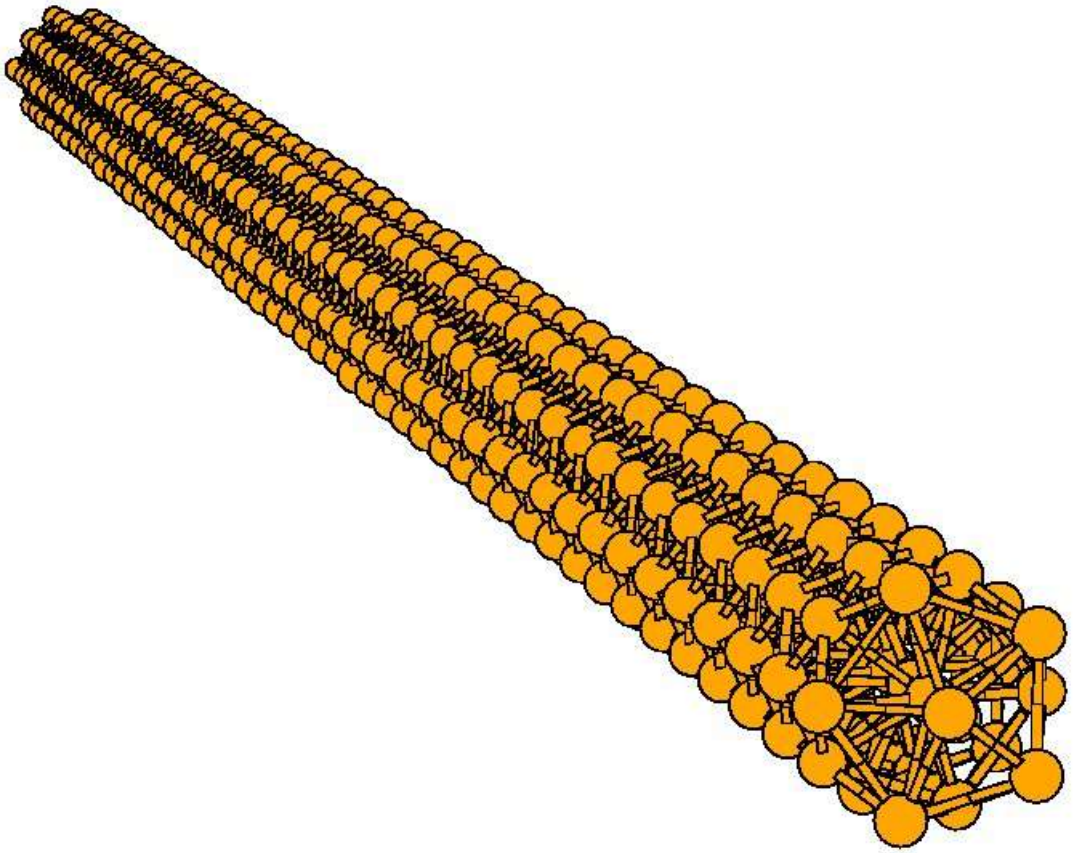
- discontinuos clusters, metastability, clusters of clusters

- megaclusters

- constrained clusters

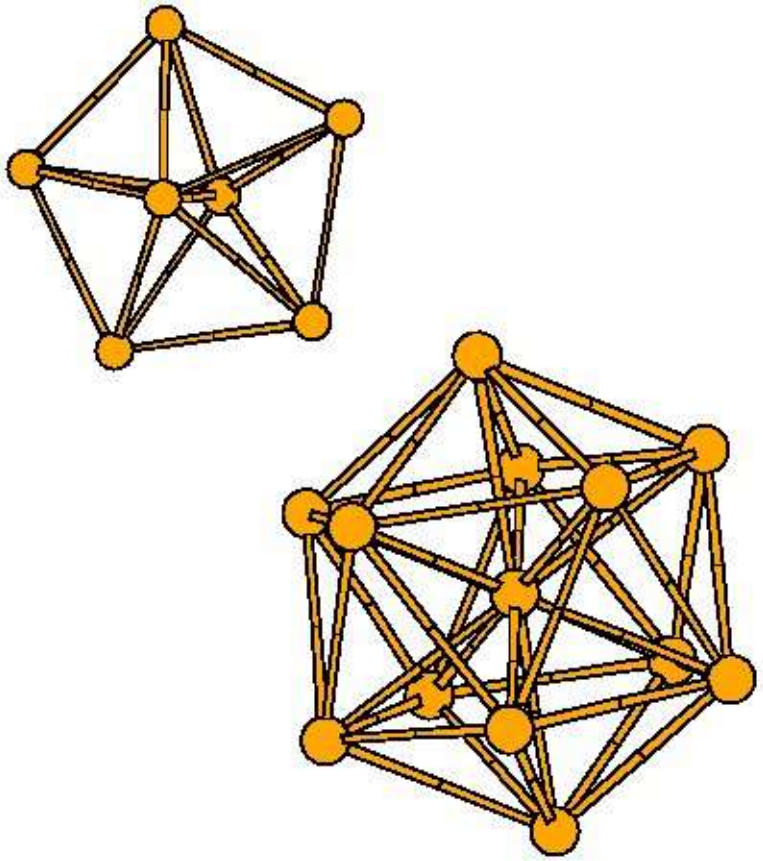




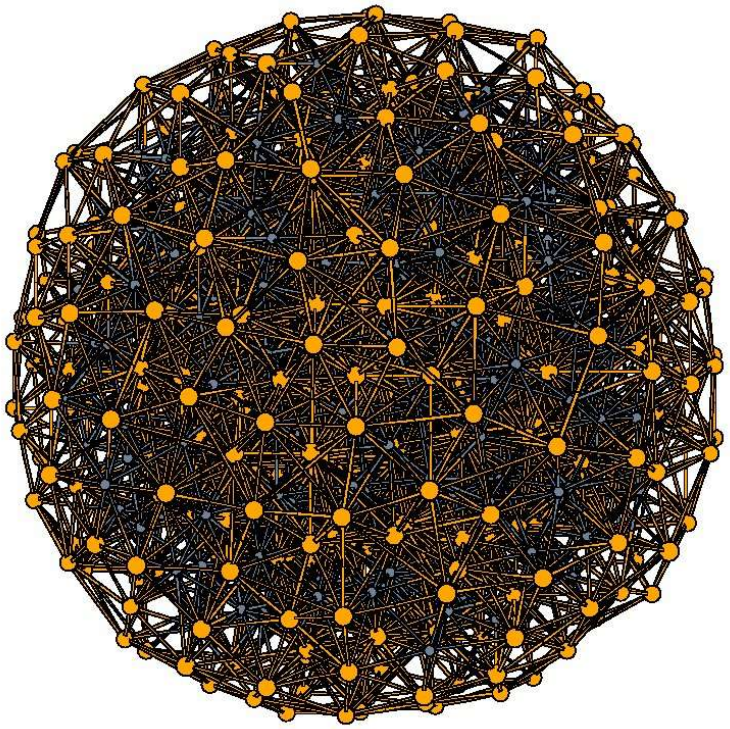


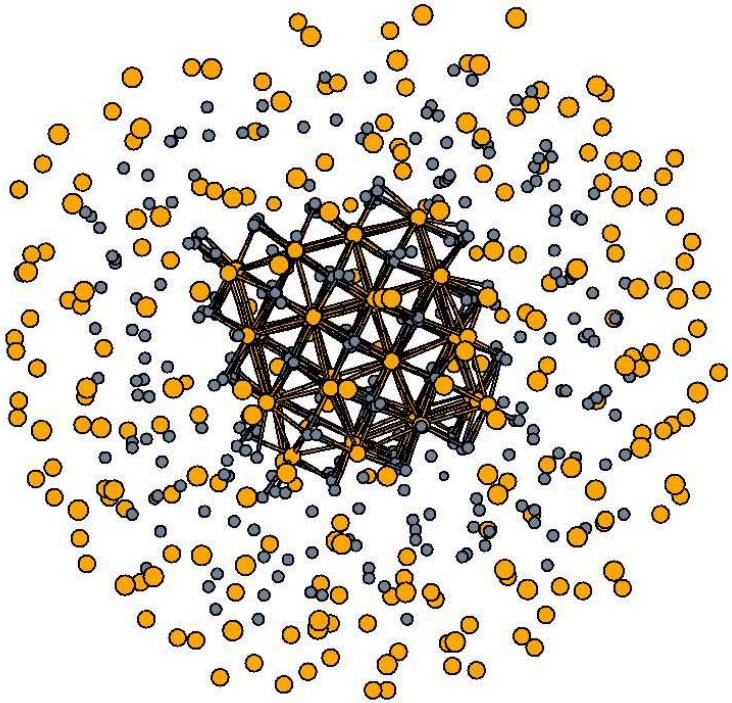
Exotic structures

Two weakly interacting metallic clusters



An 855-atoms bit of metal
with a bcc-core





Applications 3: Heavy Atoms

- Experimental $E=-16Z^{7/3}$ eV (empirical)

- TF model $E=-20.8Z^{7/3}+13.6Z^{2}(b)-5.98(7.3)Z^{5/3}(ex)+...$ (Schwinger, 1980, 1981)

- $Z \longrightarrow \infty$ (no-binding, classical atoms)

- Linearized TF $-11.78Z^{7/3}-4.56Z^{7/3}=-16.34Z^{7/3}$, ($-4.53Z^{5/3}$ or $-5.52Z^{5/3}$ ...)

- Quantum corrections

- (Virial theorem); molecules (statistics because linearization)

Applications 4: Universal Solid

– $E = Aq^4/4\,(\mathrm{kin}) - Bq + q\sum_{i\neq j} F(qr_{ij})\,(\mathrm{pot}) + E_{ex}$

– $F = \frac{1}{2q}\Phi \;,\; \Phi = \frac{-qz_i^* z_j^*}{2}(1 - 2/qr_{ij})e^{-qr_{ij}}$

- continuum approximation $E = -0.43Nz^{*7/3} - 0.17Nz^{*5/3}$

- Wigner universal metal; energy bands; universal solid

- compressibility $(aq = \mathrm{const},\; \delta a \sim \delta q)$, sound waves $v_s(z^*)$; thermodynamics

- δq (δn), δR_i $\longrightarrow$ vibrations ($\delta R_i \delta R_j$), el-phonon int ($\delta n \delta R_i$), el-el residual int ($\delta n \delta n$) (plasmons lifetime)

- plasmons (fractional occupancy)

-electrons: excitations (quasi-particles), $m^* = m(1+0.39 z^{*1/3})$, lifetime, etc, all by the self-consistent potential φ

- polarizability and diamagnetic susceptibility (δn changes in energy); response in general

Applications 5: Surfaces

- Self-consistent electron potential

$$\varphi = \sum_i \frac{z_i^*}{|r - R_i|} e^{-q|r-R_i|}$$

- Continuum half-space (semi-infinite) solid

$$\varphi = \frac{4\pi z^*}{q^2 a^3}\left(1 - \frac{1}{2}e^{qx}\right), \quad x<0; \quad \varphi = \frac{2\pi z^*}{q^2 a^3} e^{-qx}, \quad x>0$$

$$(q = 0.77 z^{*7/3}, \; aq = 2.73)$$

- surface double layer; electrons overspill (Bardeen, transistor, 1947)

- work function φ (semi-empirical); boundary effects (finite-size quasiparticle lifetime)

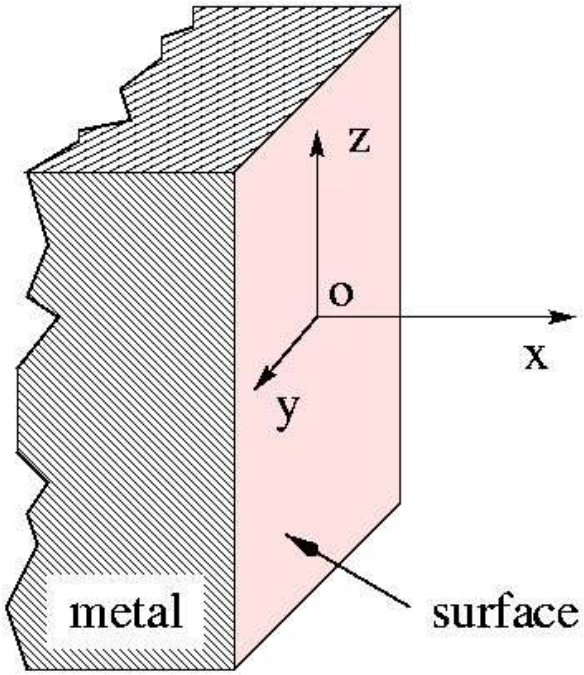
- Potential energy

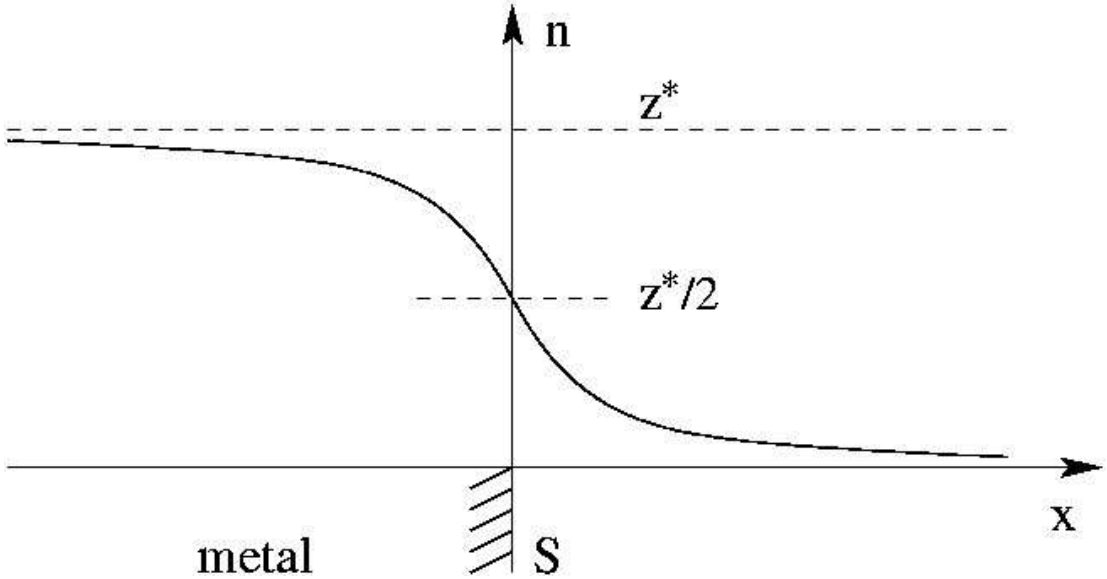
$$E_{pot} = -\frac{3}{4} q \sum_i z_i^{*2} + \frac{1}{2} \sum_{i \neq j} \Phi(R_{ij})$$

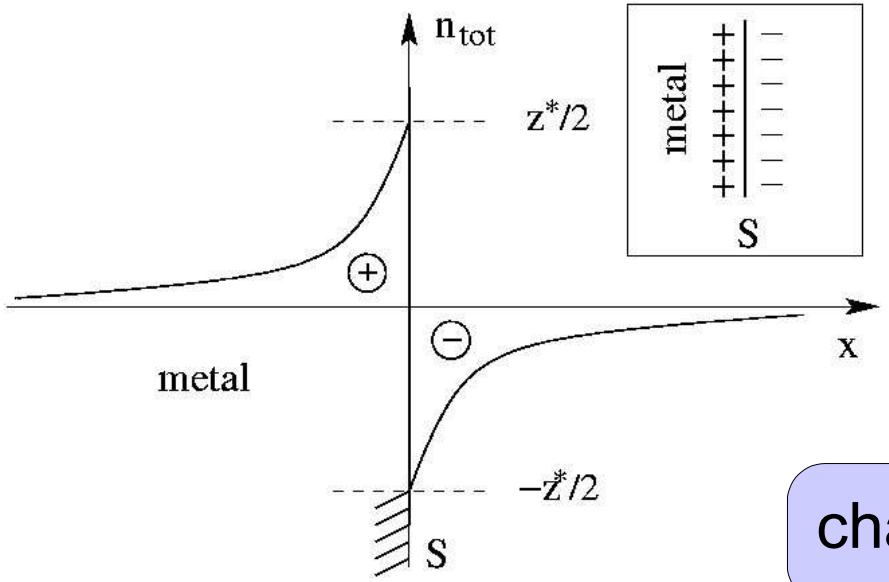
$$\Phi(R_{ij}) = -\frac{1}{2} q z_i^* z_j^* \sum \left(1 - \frac{2}{q|R_i - R_j|}\right) e^{-q|R_i - R_j|}$$

- Semi-infinite continuum: surface energy, surface tension (solid breaking energy)

electron density







charge distribution

Applications 6: Clusters Deposited on Surfaces, Contacts, Junctions and Interfaces

- Solid (surface) + clusters

$$E_{pot} = E_s - \frac{3}{4} q \sum_i z_i^{*2} + \frac{1}{2} \sum_{i \neq j} \Phi(R_{ij}) - \frac{\pi z^*}{q a^3} \sum_i z_i^* X_i e^{-q|X_i|}$$

- Cluster-surface interaction energy

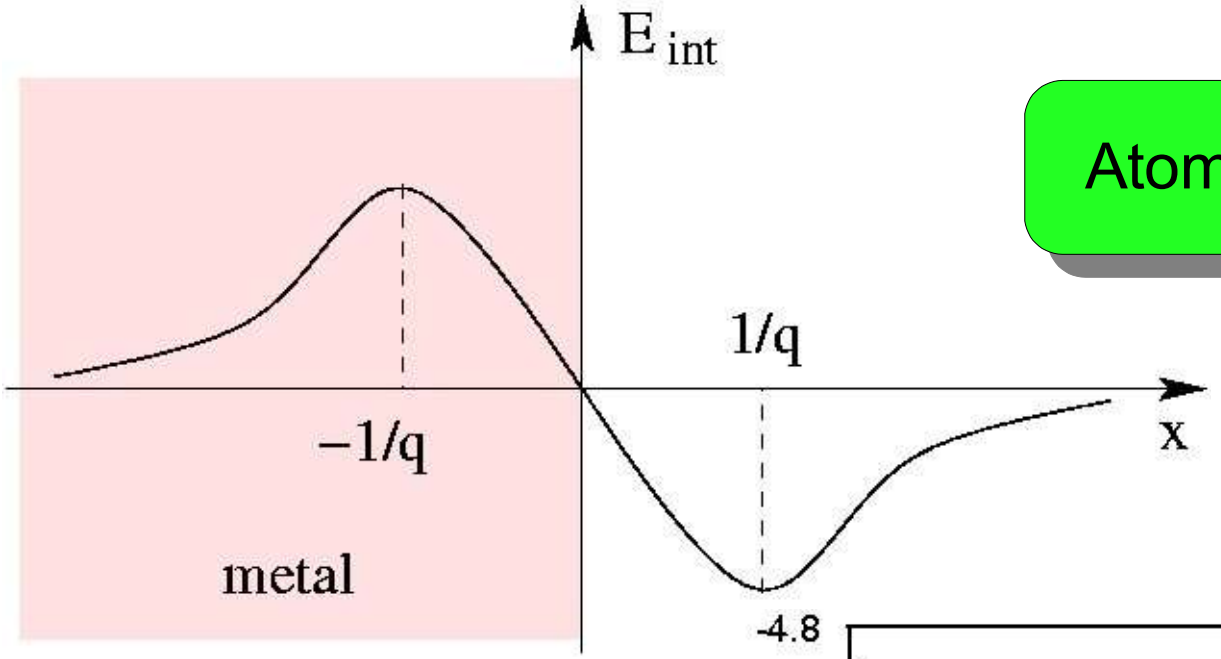
$$E_{int} = -\frac{\pi z^*}{q a^3} \sum_i z_i^* X_i e^{-q|X_i|}$$

- Two interacting semi-infinite solids: surface energy

- Clusters deposited on surfaces (Fe on Na): energy, magic forms and numbers, isomers

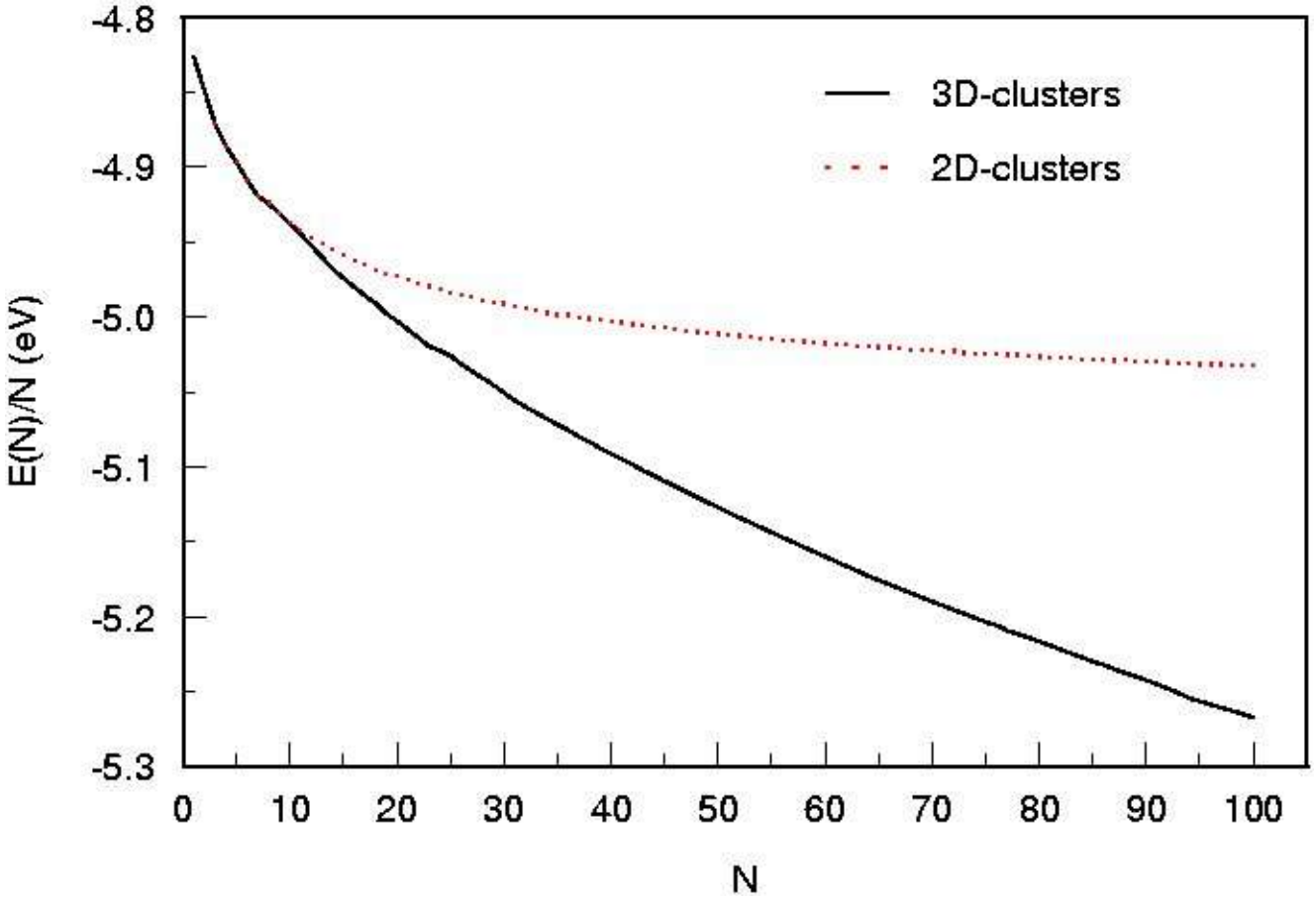
- monolayers, multilayers

- diffusion: contacts, junctions, interfaces

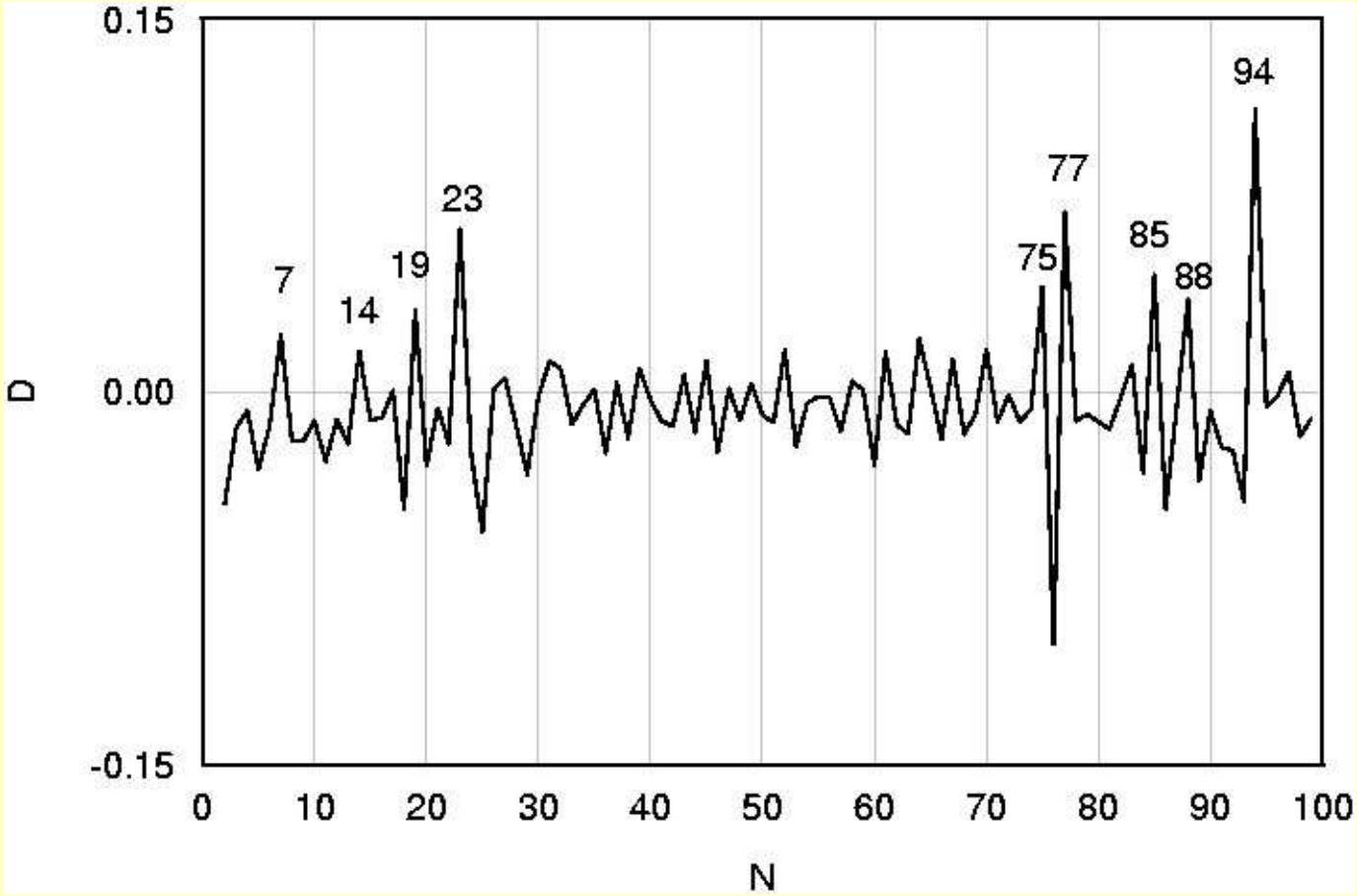


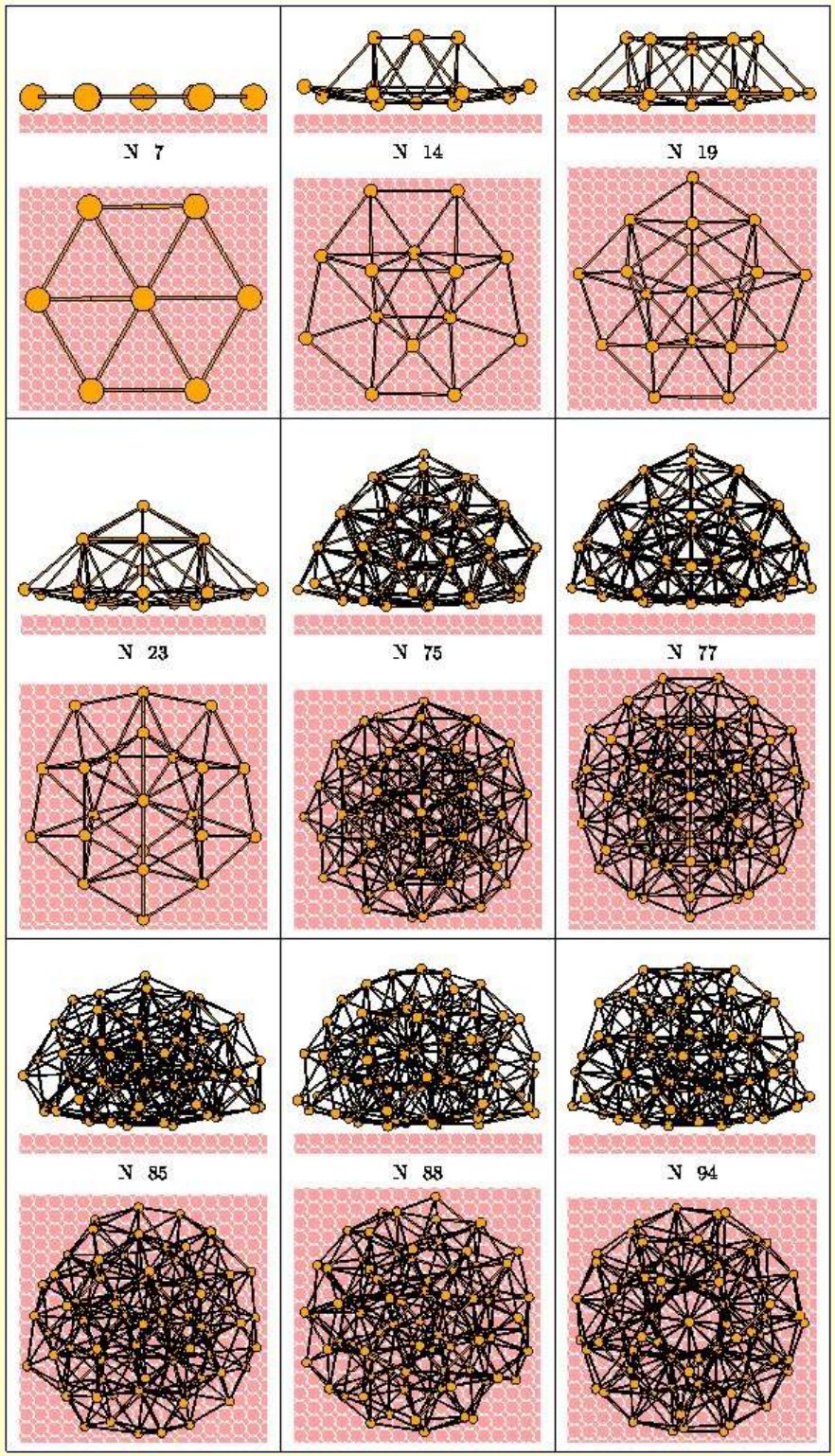
Atom-surface interaction

Binding energy

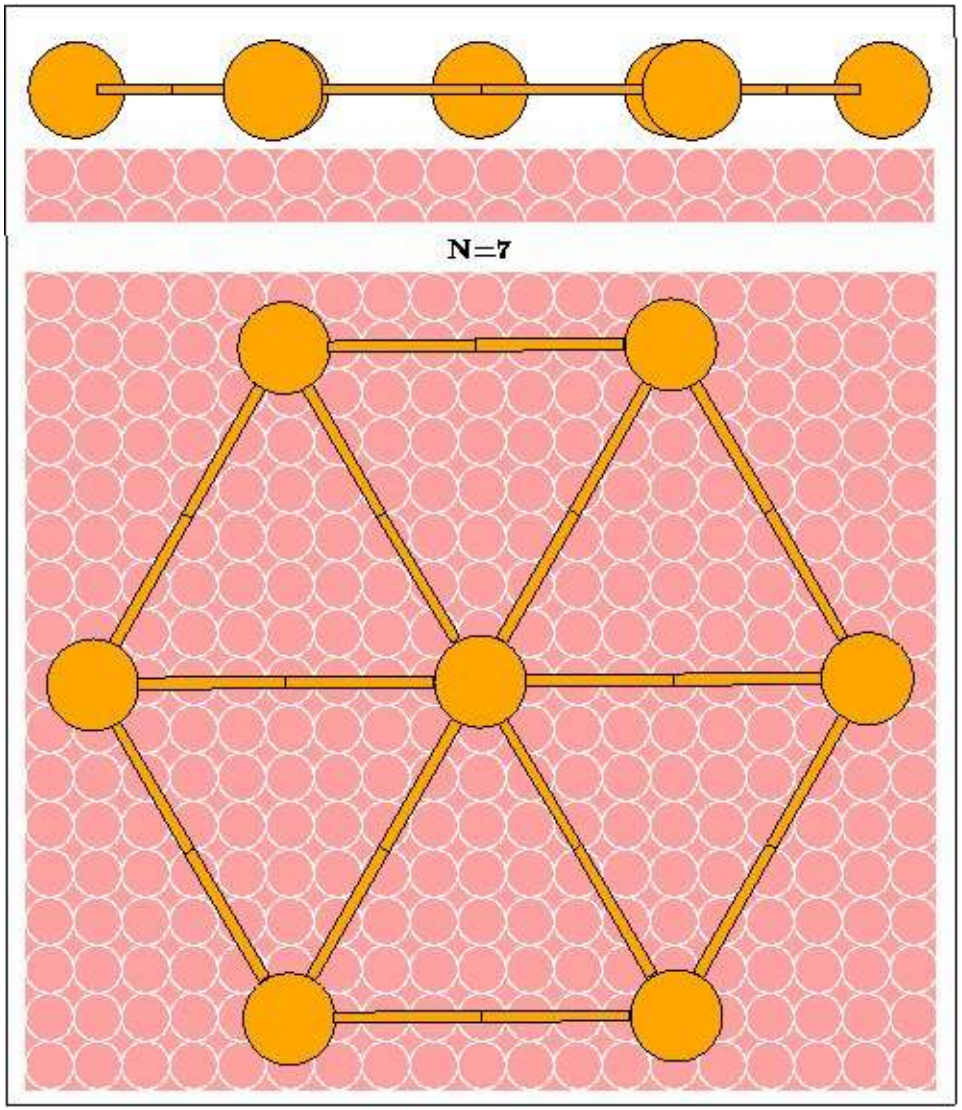


Magic numbers





Magic clusters
deposited on a surface



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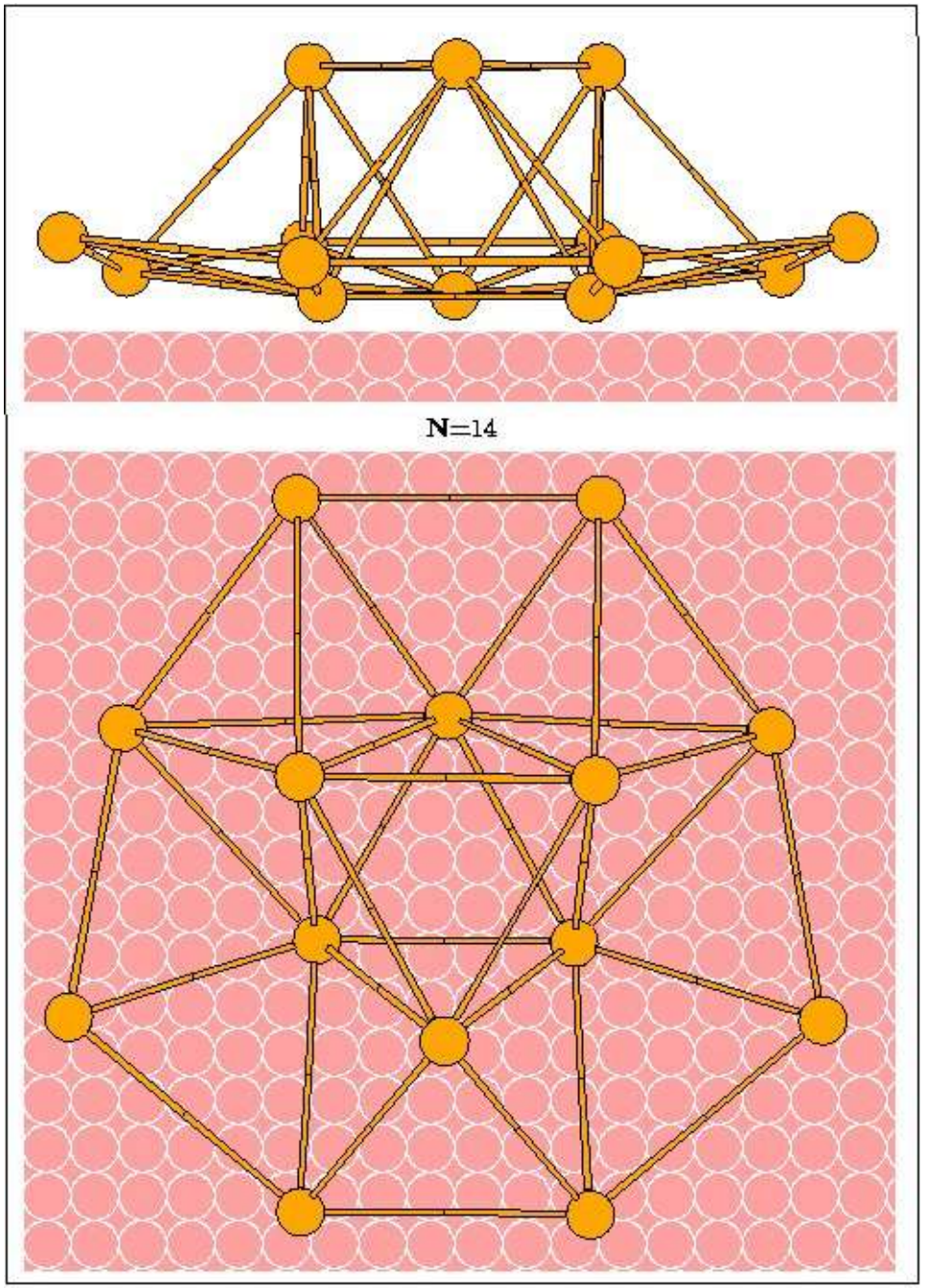

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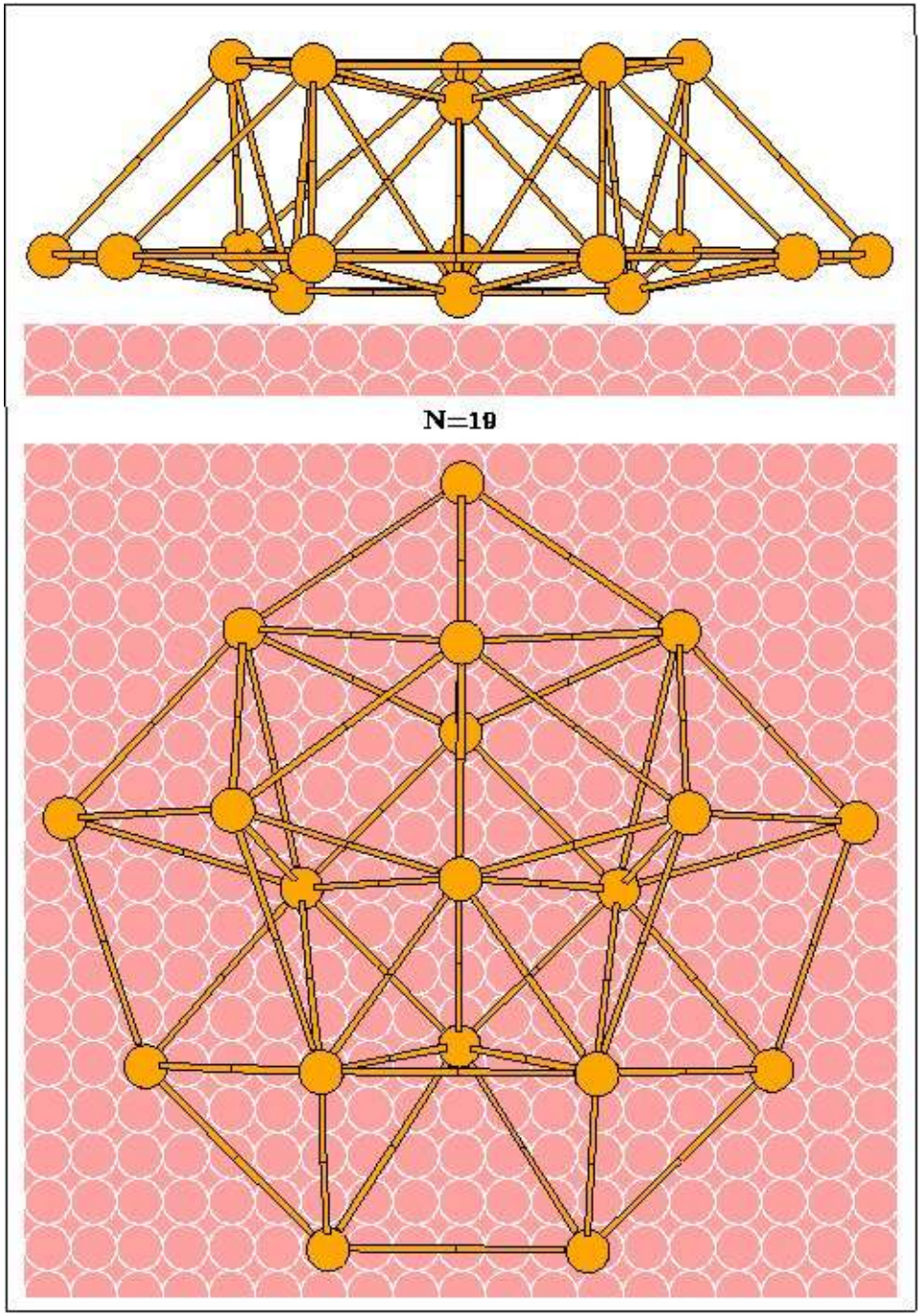

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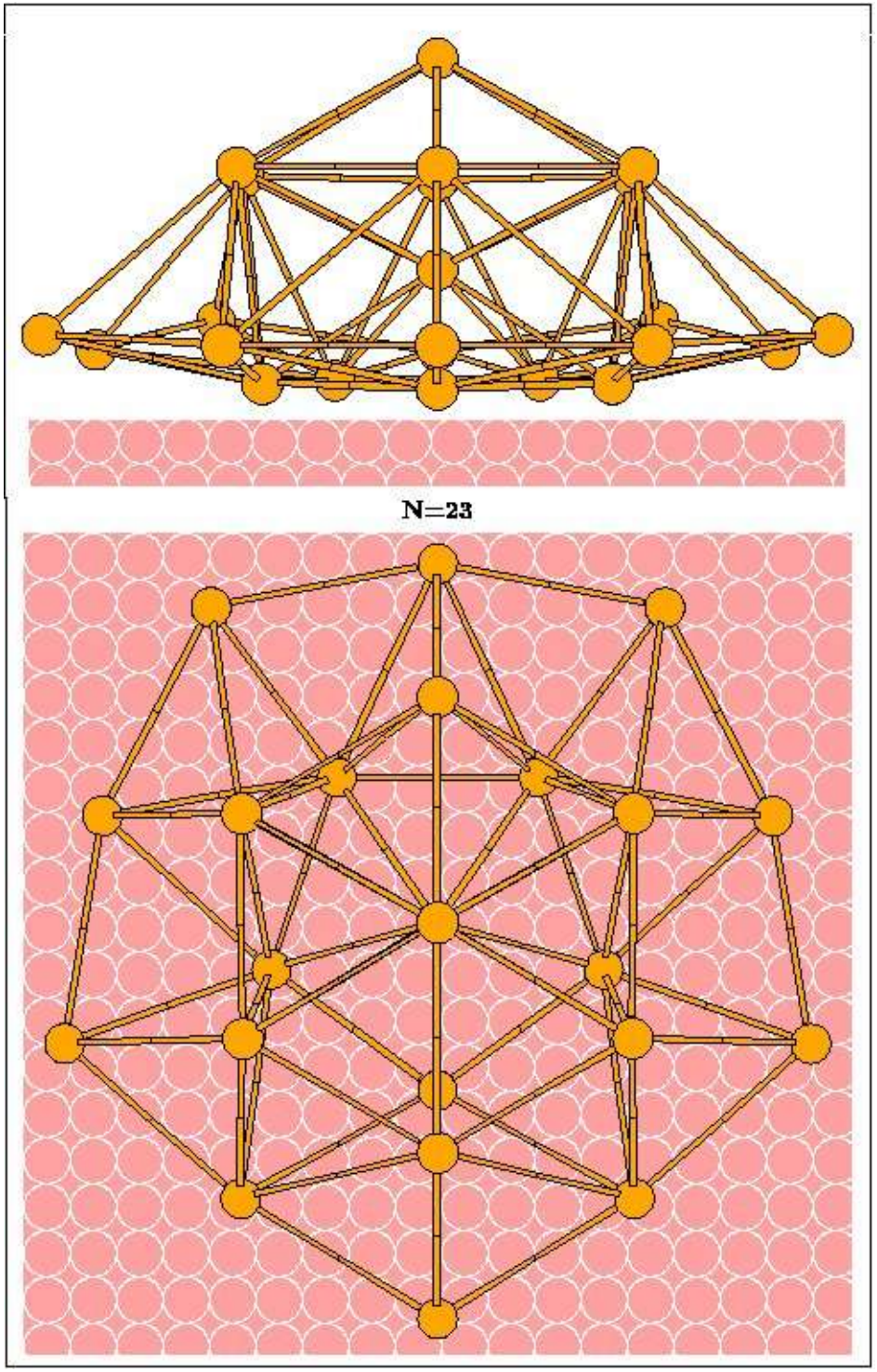

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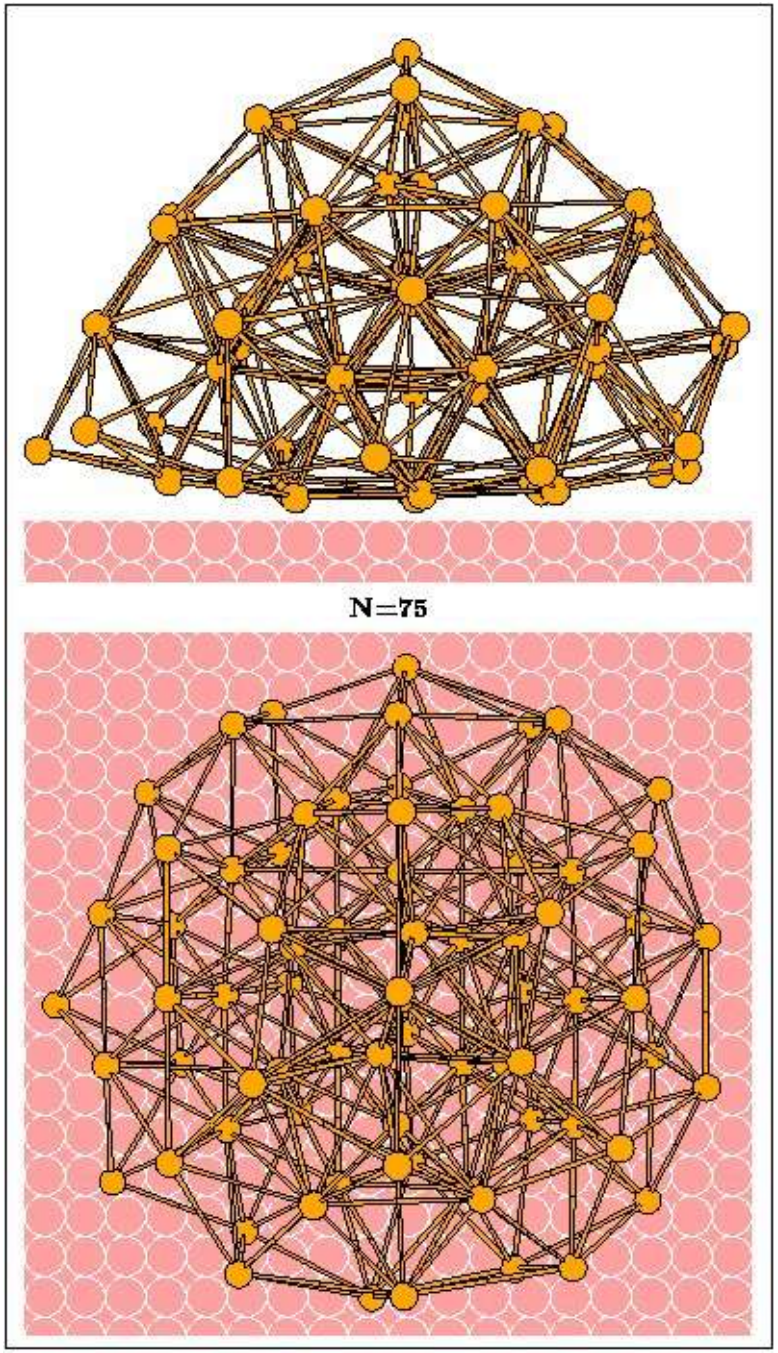

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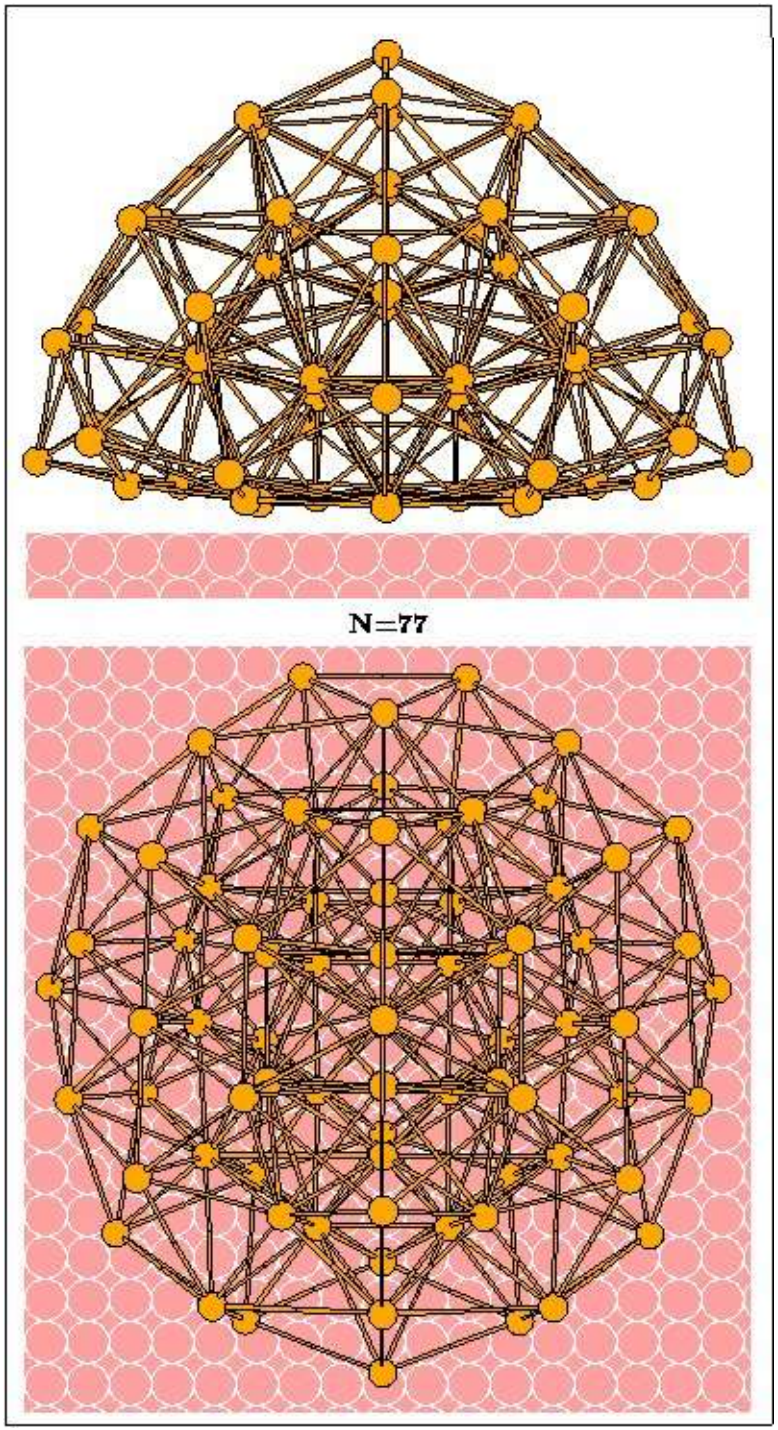

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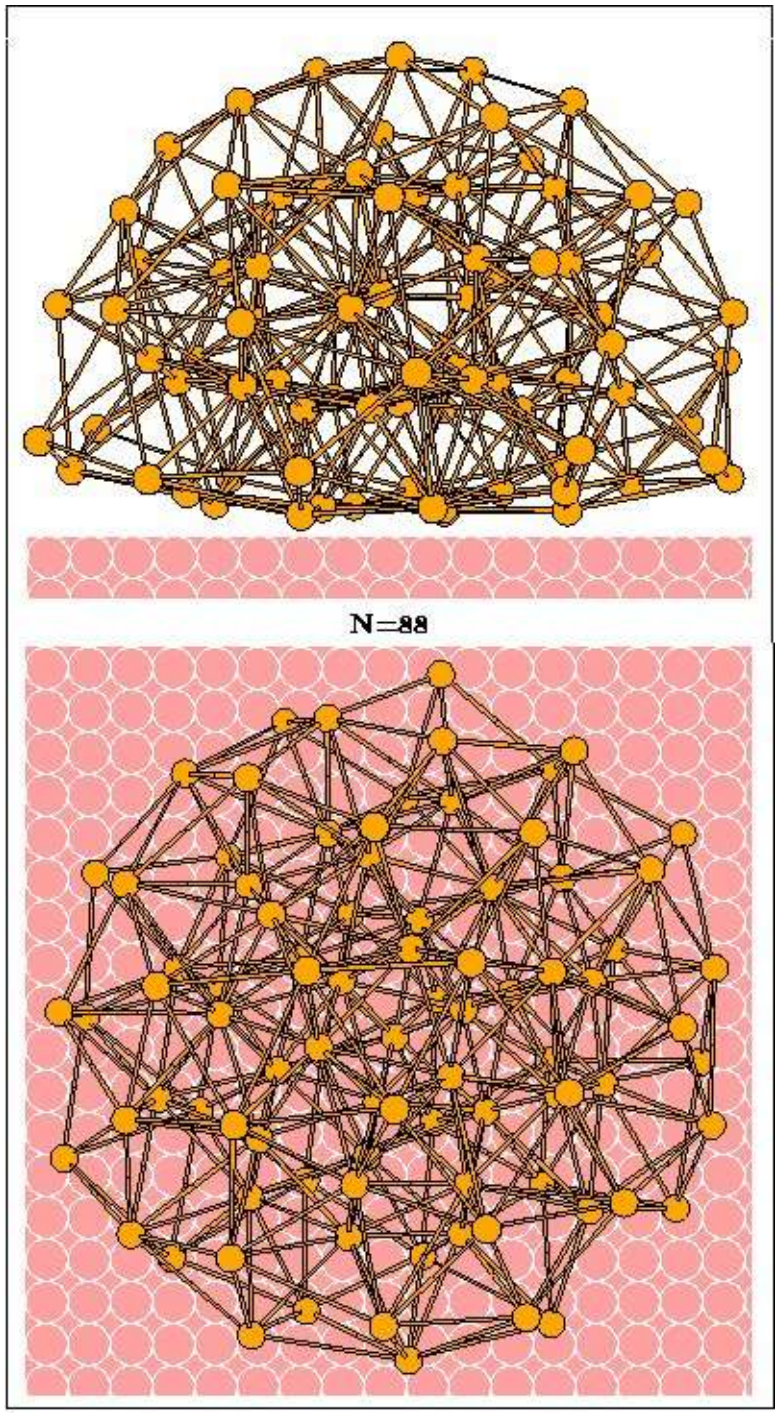
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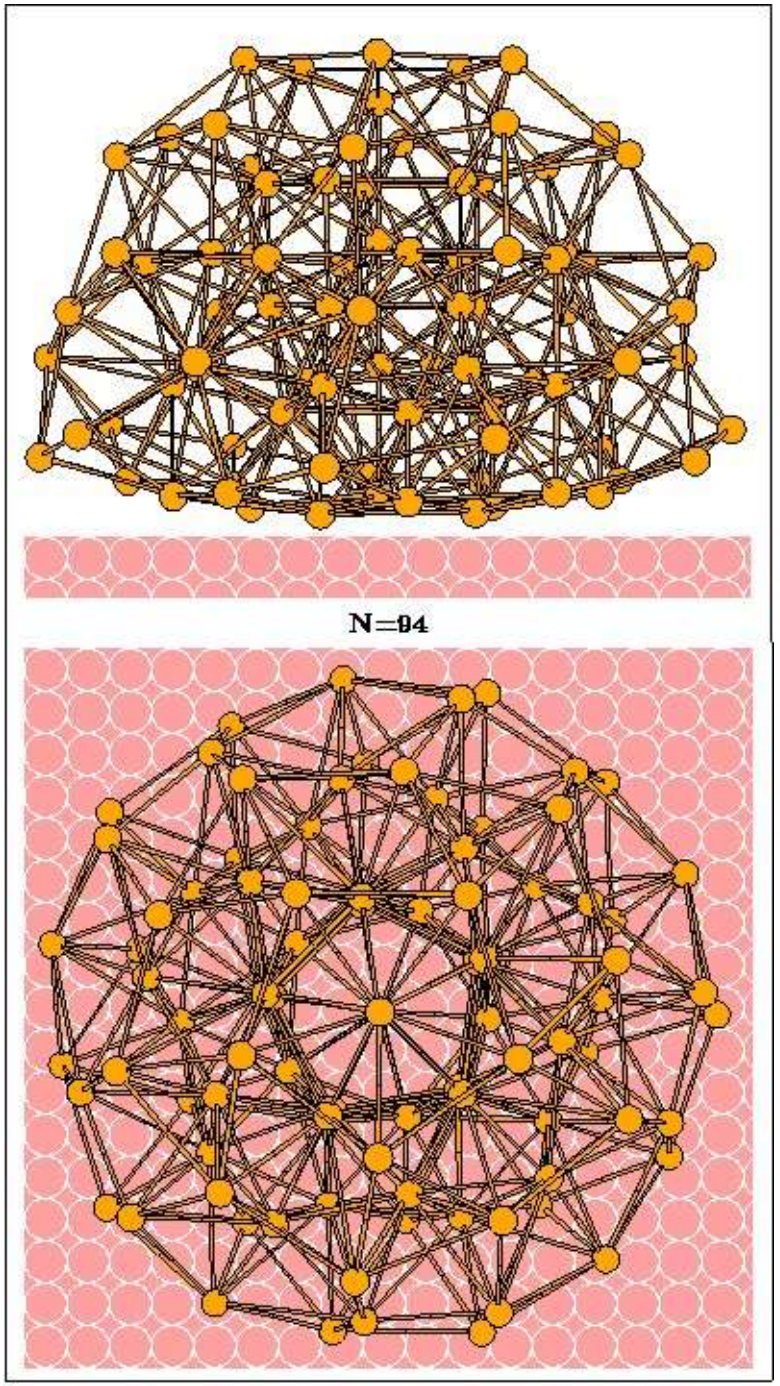
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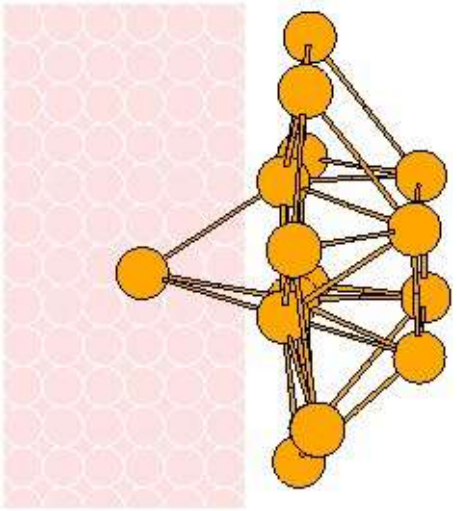
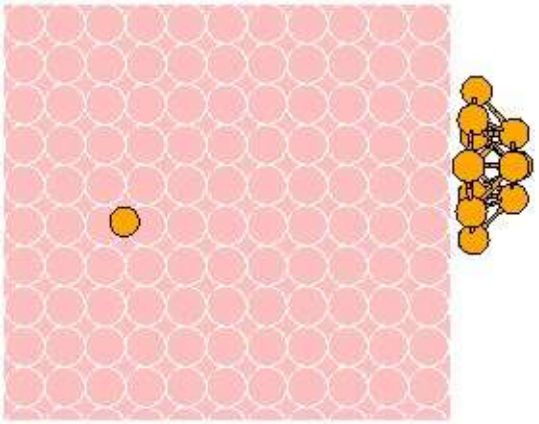
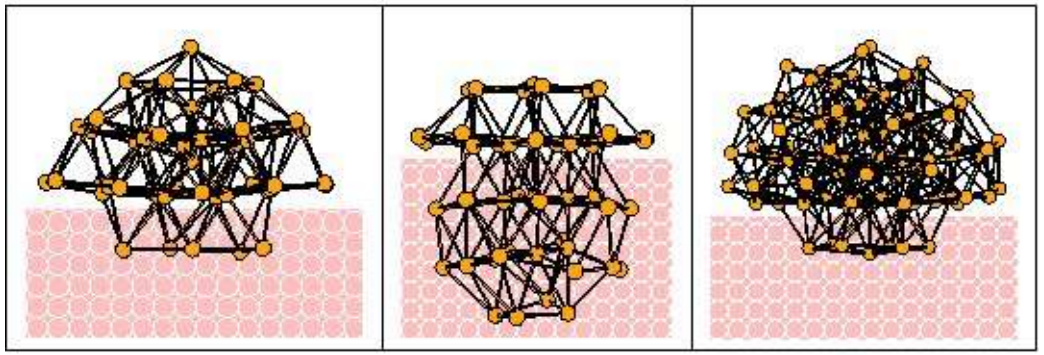






Clusters developing an interface with the solid

Applications 7: $Fe_{13}(C_2H_2)_6$

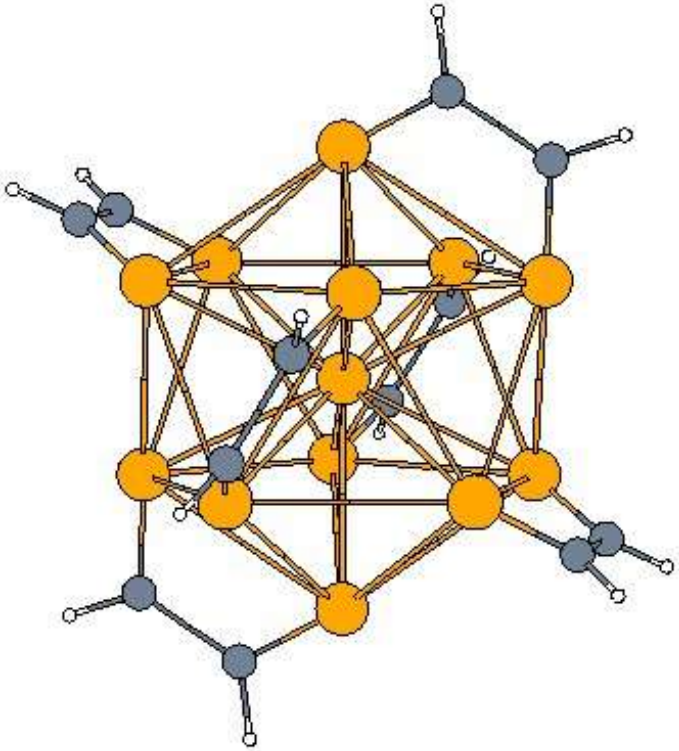
(Huysken & Morjan, 2003)

- Fe - core

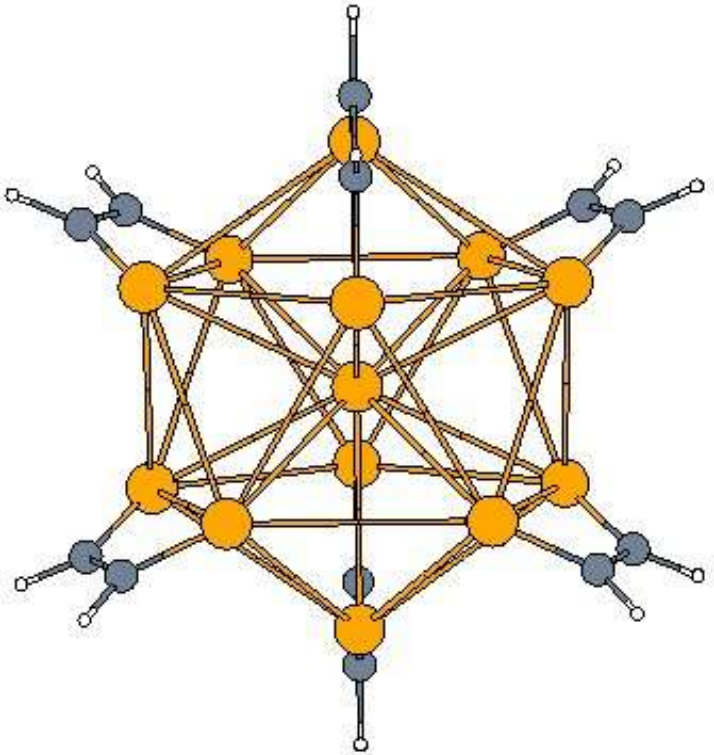
- C_2H_2 - ethylene clasps

- core energy, structure and vibration spectra

$Fe_{13}(C_2H_2)_6$

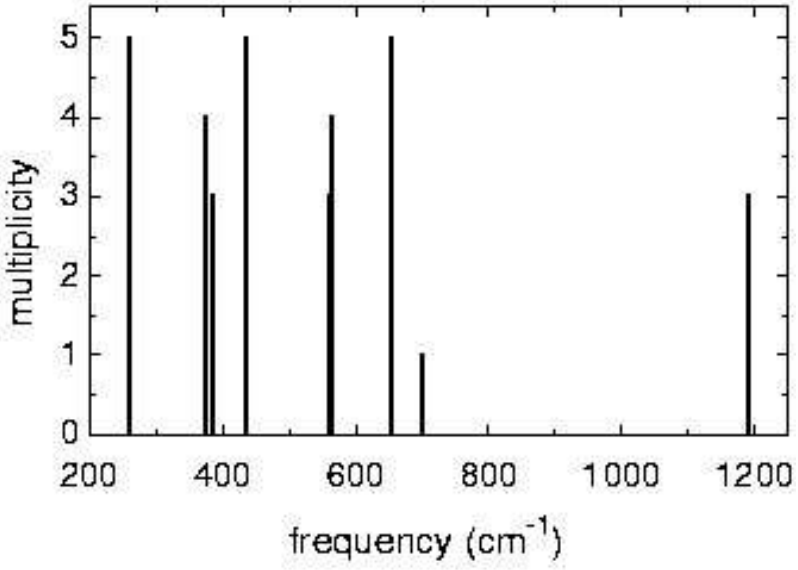


ground-state

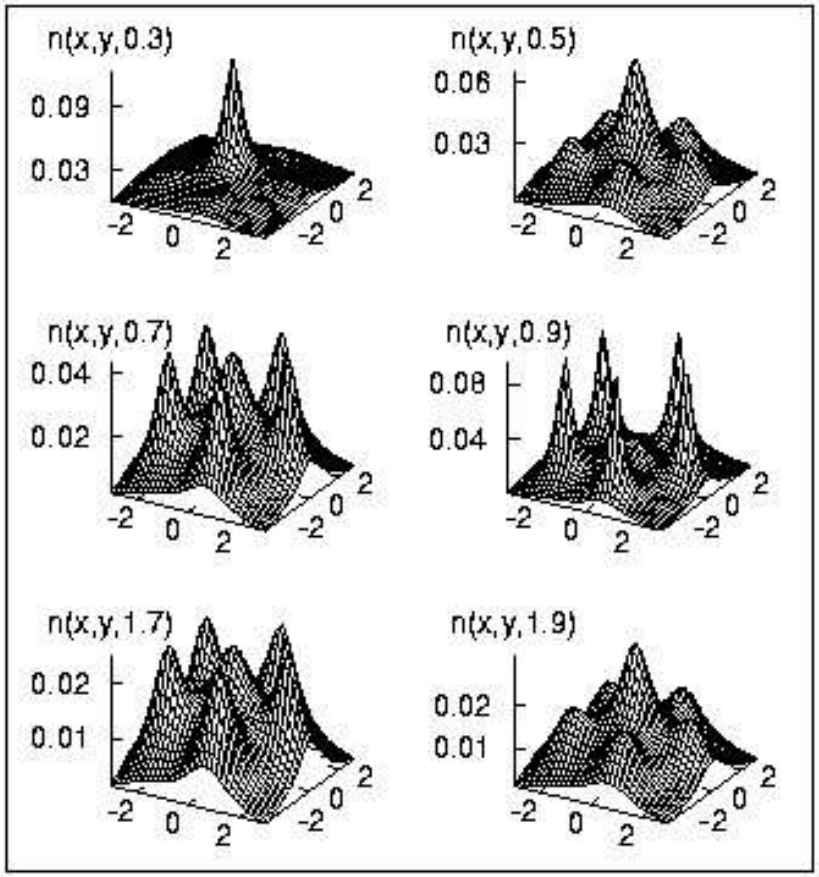


isomer

$Fe_{13}(C_2H_2)_6$



vibration spectrum



electron density