SIZE-DEPENDENT EMERGENCE OF CRYSTALINITY IN MOLECULAR CLUSTERS

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Sofia University St. Kliment Ohridski
1888

Laboratory complex, Sofia Tech Park
2016

Layout

Why clusters?

Production and experimental study

Computational methods and computers (clusters)

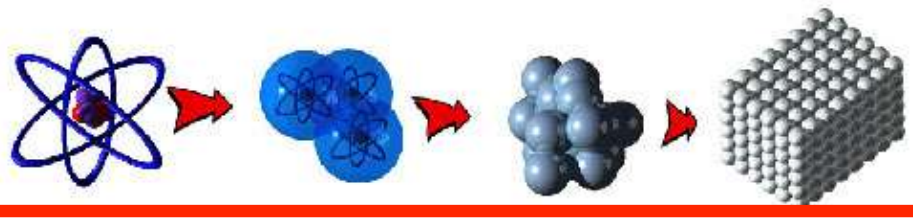
Phase transitions – disorder-order (cooling)

Phase coexistence (only clusters, not in bulk)

Topography of the potential energy surfaces

What can we learn when studying clusters

- 1960-1975: from atom to bulk



- 1975 – at present

Cluster physics to nanoscience

Clusters of atoms – stability and symmetry

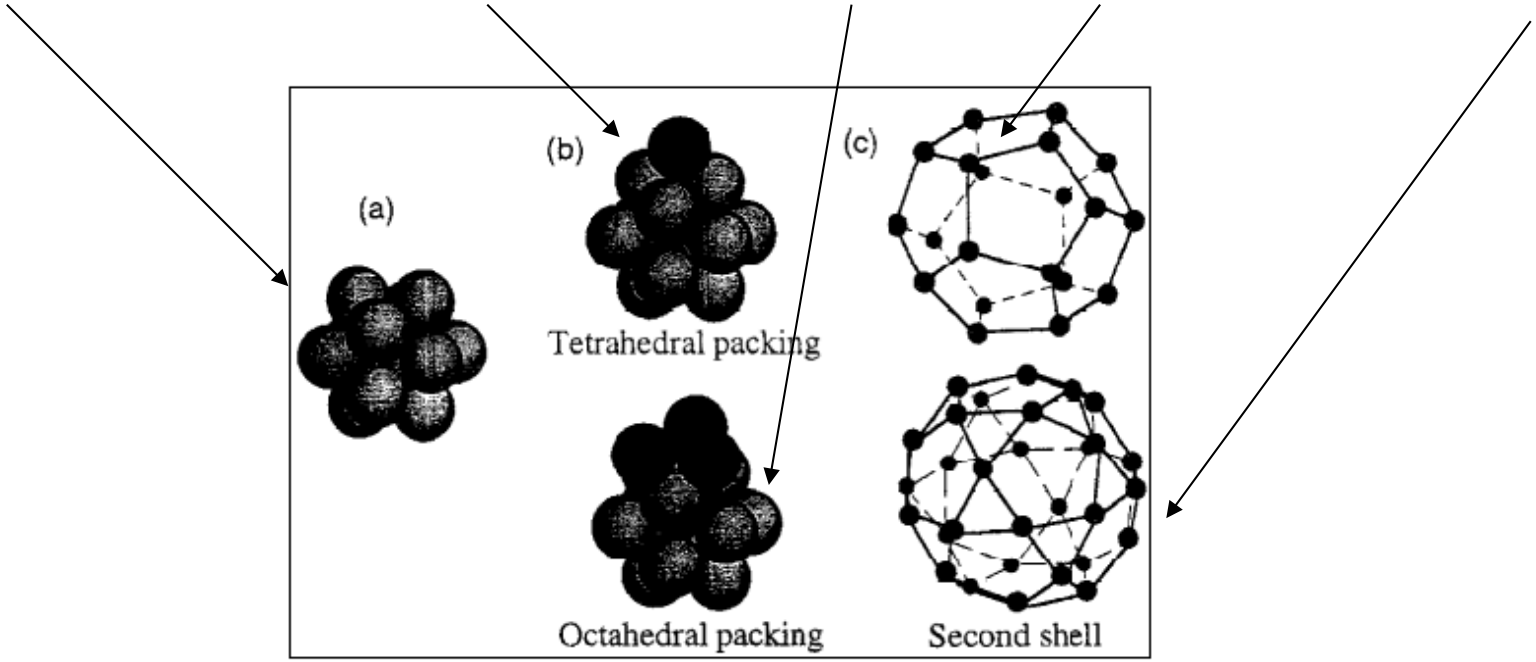
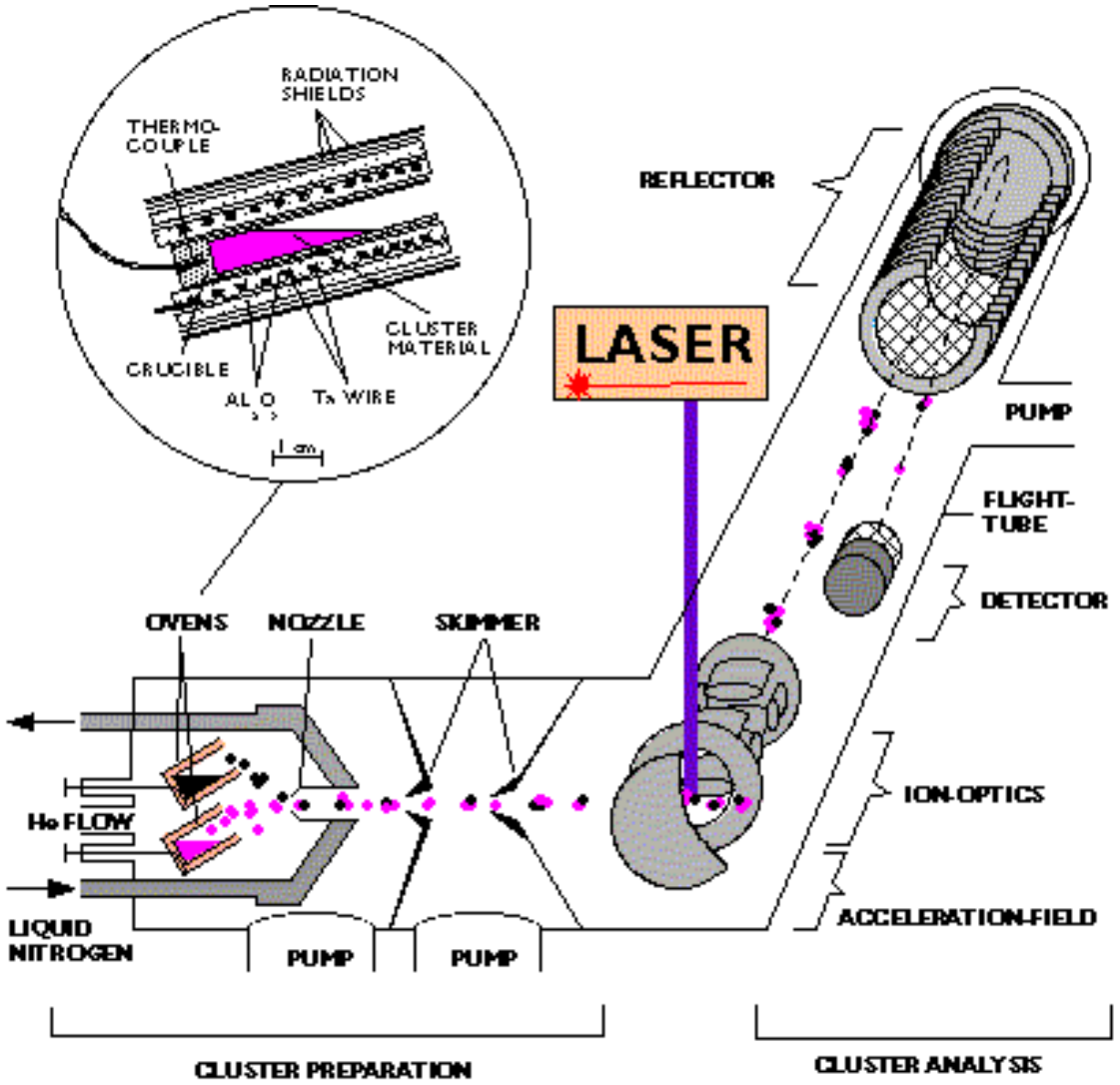


Fig. 3. (a); A fundamental atom cluster, (b); tetrahedral and octahedral packings of atoms on (a), and (c); second atom shells formed by tetrahedral and octahedral packings.

Molecular clusters

- Clusters consisting of N octahedral molecules AF_6 exhibit several structural phase transformations under the temperature of solidification – this is shown with Monte Carlo simulations, Molecular Dynamics calculations, and quantum computations (density-functional theory) and experiments.

Laser production of clusters (nozzle-jet) & analysis with electron diffraction



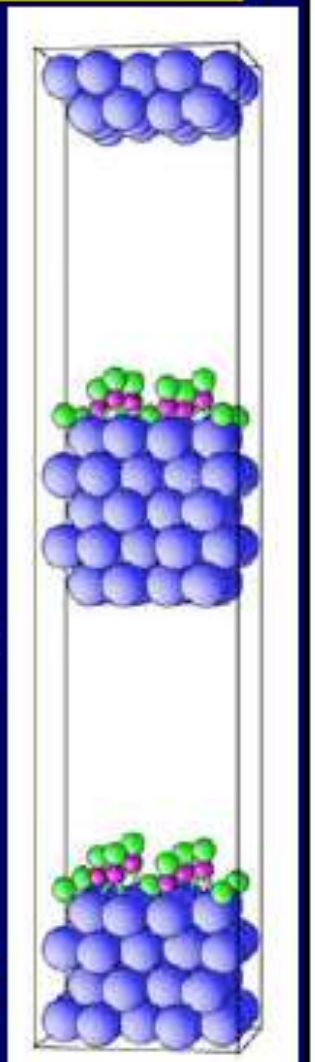
Methods

I

- **Density functional theory**
  - **-- *ab initio* pseudopotentials**
    (the fhi98md - code ---
    www.fhi-berlin.mpg.de/th/th.html)
  - **-- FP-LAPW**
    (the WIEN - code by
    P. Blaha, K. Schwarz, et al.;
    *M. Petersen et al., CPC **126** (2000)*)

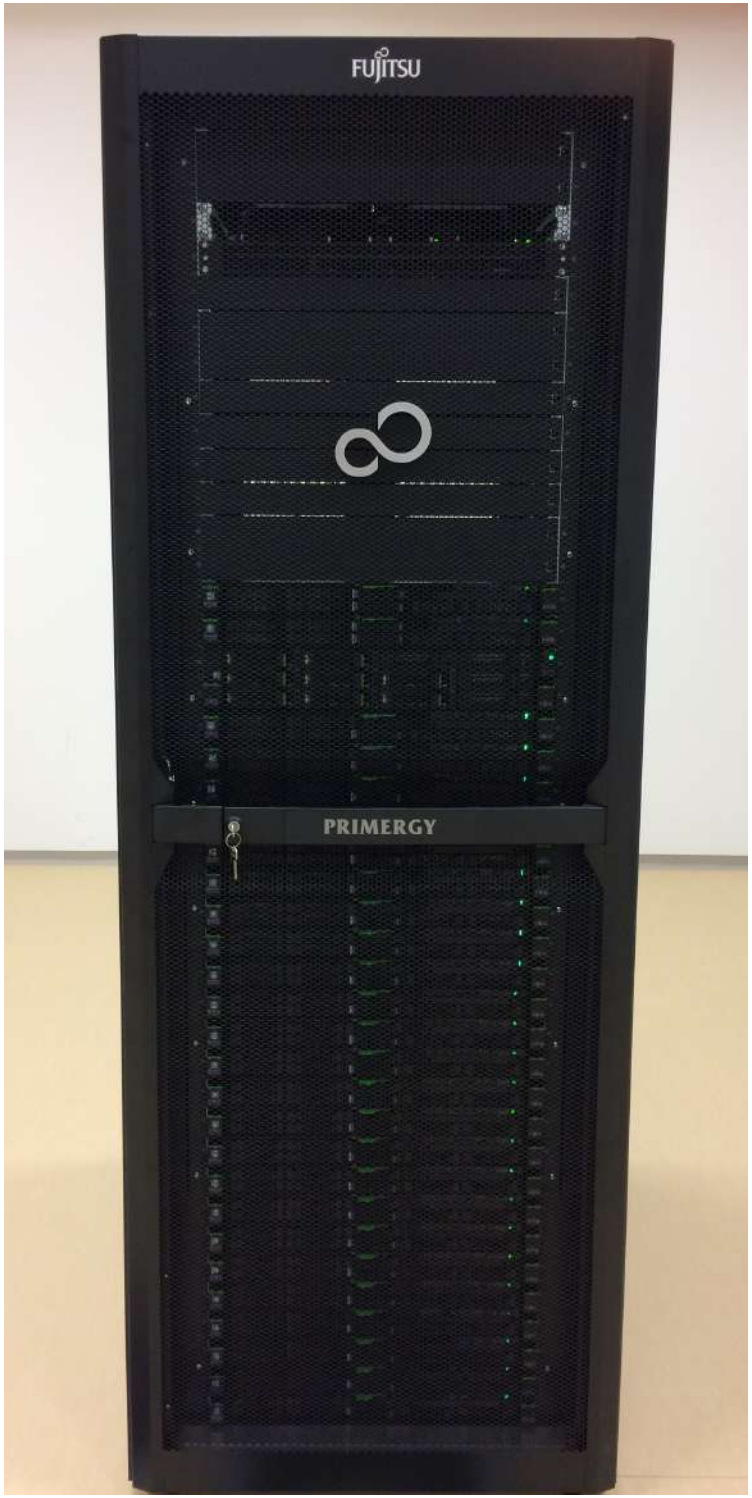
II

- ***ab initio* Molecular Dynamics**
- ***ab initio* Quantum Dynamics**
- ***ab initio* Lattice Gas Hamiltonian**
- ***ab initio* kinetic Monte Carlo**



PhysOn Cluster
http://physon.phys.uni-sofia.bg

PhysOn – initial stage



Nestum Cluster

- A homogeneous cluster based on Intel Xeon Haswell (22 nm processes) architecture
- 24 nodes with two 16-core processors Intel Xeon E5-2698 v3 @ 2.3 GHz
- Infiniband with 56 Gbps
- SAN (storage area network) subsystem with 10 TB; Raid 50
- Dynamical memory 3TB

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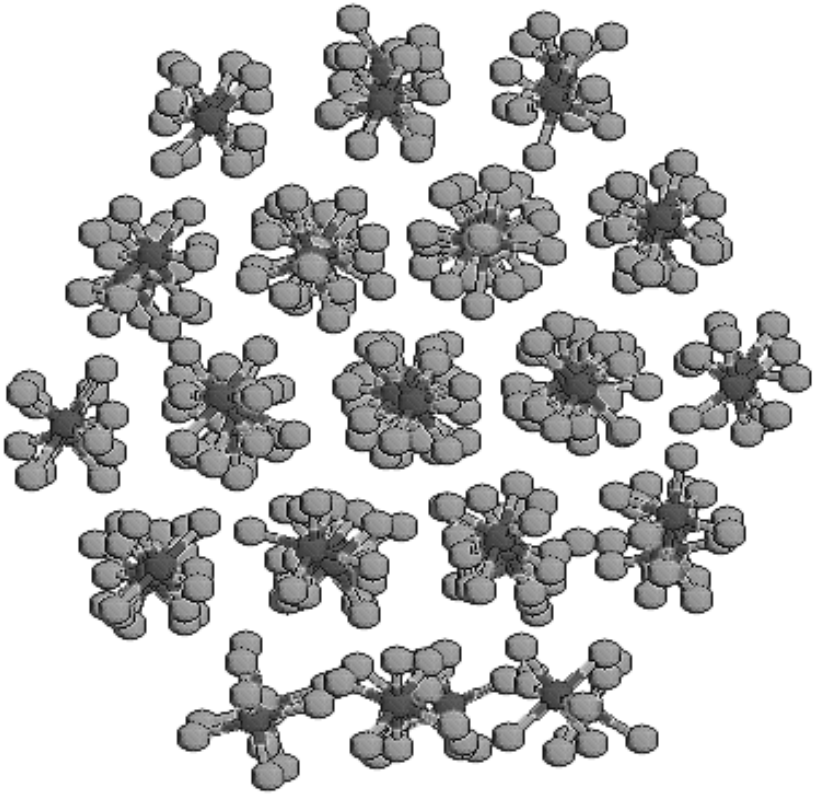
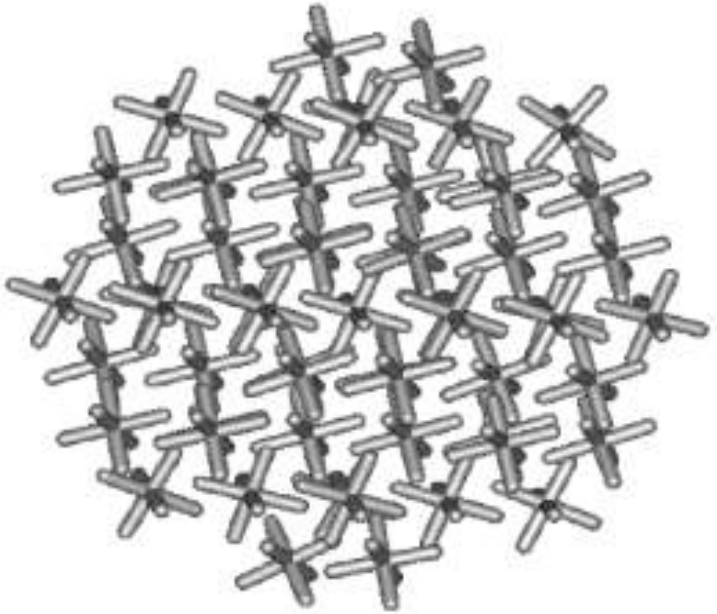
Cluster of 59 octahedral molecules – molecular dynamics simulations ate different temperatures

at T = 100 K (bcc)



at T = 20 K (bcc)



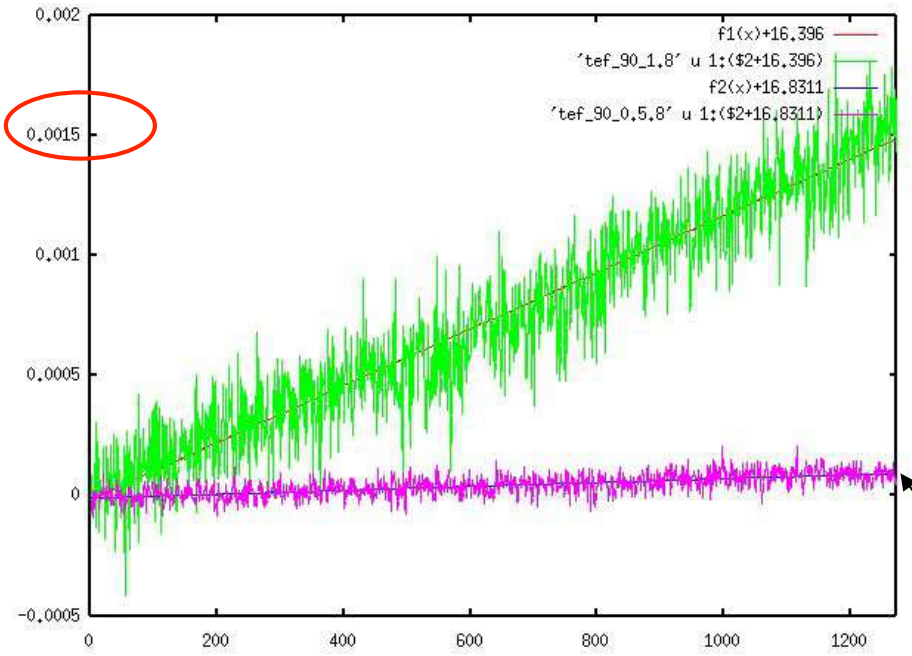
Molecular dynamics – equivalent to solving the Hamilton equations
6(N-1), 7<N<300

$$dr_i/dt = \partial E/\partial p_i$$

$$dp_i/dt = -\partial E/\partial r_i$$

a) E = U(r) + Ekin(p) = const

- Microcanonical ensemble



10 fs

5 fs

Temperature – kinetic energy

- Linear and angular velocity – re-scaling with **s;**

  g – degrees of freedom

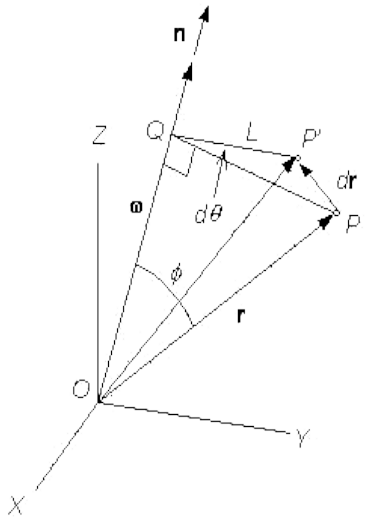
S

$$s^2 \sum_i 0.5 m_i \left[v_i(t + \Delta t/2) \right]^2 = (g/2) k_B < T_{vib} >$$

$$s^2 \sum_i 0.5 m_i \left[\omega_i(t + \Delta t/2) \right]^2 = (g/2) k_B < T_{rot} >$$

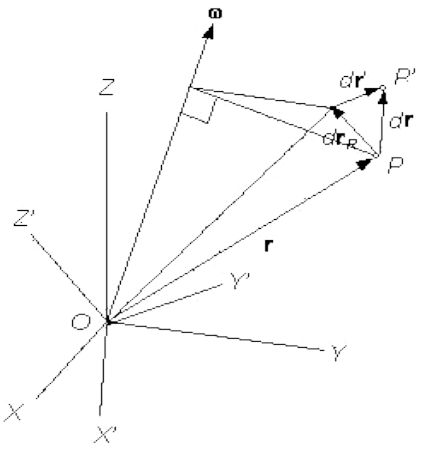
Transfer between two coordinate systems
b- molecular s - cluster

$$\tau_i = \sum_a (\mathbf{r}_{ia} - \mathbf{r}_i) \times \mathbf{f}_{ia} = \sum_a \mathbf{d}_{ia} \times \mathbf{f}_{ia}.$$



$$\begin{aligned} \tau^b &= A \cdot \tau^s \\ \omega^s &= A^{-1} \cdot \omega^b = A^T \cdot \omega^b \end{aligned}$$

$$A = \begin{pmatrix} q_0^2 + q_1^2 - q_2^2 - q_3^2 & 2(q_1 q_2 + q_0 q_3) & 2(q_1 q_3 - q_0 q_2) \\ 2(q_1 q_2 - q_0 q_3) & q_0^2 - q_1^2 + q_2^2 - q_3^2 & 2(q_2 q_3 + q_0 q_1) \\ 2(q_1 q_3 + q_0 q_2) & a(q_2 q_3 - q_0 q_1) & q_0^2 - q_1^2 - q_2^2 + q_3^2 \end{pmatrix}.$$

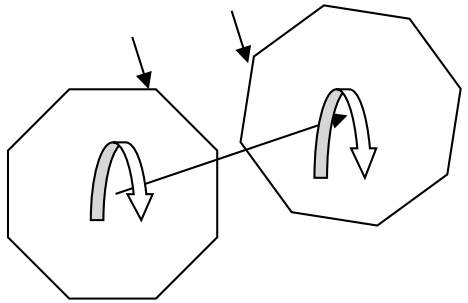


Total angular momentum J of a plastic cluster made of octahedral molecules that rotate and vibrate

- J= $\sum_i mr_i \times v_i + \sum_i I w_i = L_{clust} + \sum_i I w_i$

- w_i Angular velocity of the i-th molecule in the molecular system
- The lab (space) coordinate system is centered in the cluster center of mass with a fixed orientation

Let us consider two points of the molecules which come nearer as a result of interaction; the molecules rotate with w_i and wj, respectively



Total angular momentum (2)

- The vector of the relative velocity is

$$v_{ij}^{imp} = v_i^{imp} - v_j^{imp} = (v_i - v_j) - 1/2(\omega_i + \omega_j) \times r_{ij}$$

- Each 'bumpy' molecule reverses the sign of velocity as a result of collision:

$$\delta v_{ij}^{imp} = v_{ij}^{imp}(after) - v_{ij}^{imp}(before) = -2v_{ij}^{imp}(before)$$

- Impulse changes to:

$$\delta p_i = \frac{1}{2} m(\delta v_{ij}^{imp\parallel} + \frac{k}{1+k} \delta v_{ij}^{imp\perp})$$

$$k = 4I / 2mR$$

$$v_{ij}^{imp} = v_{ij}^{imp\perp} + v_{ij}^{imp\parallel}$$

Angular momentum (3)

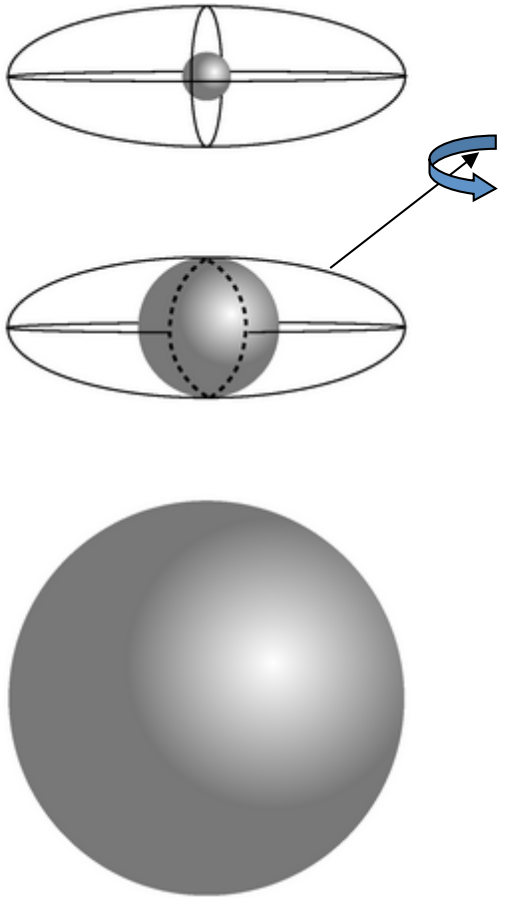
- The total energy

$$E_L^{"rb"}(t) = E_L^{"rb"}(\{r_i(t)\})$$

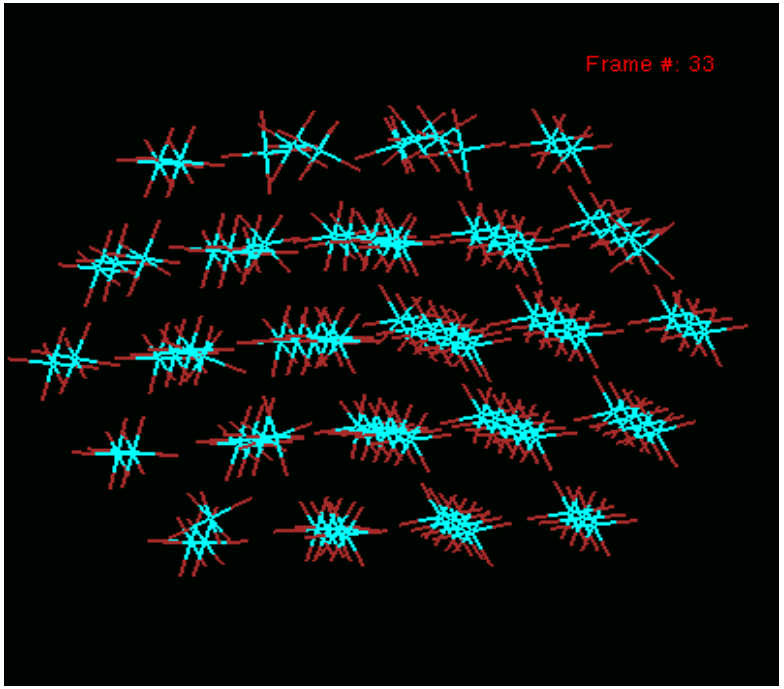
$$\sum_i \frac{p_i^2}{2m_i} = E_L^{"rb"} + \sum_i \frac{(\Delta p_i)^2}{2m_i}$$

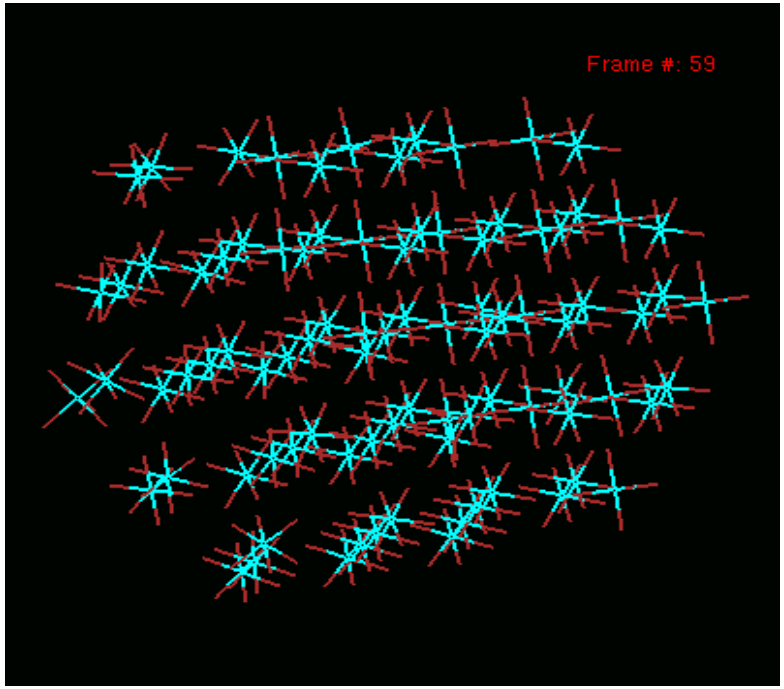
- Rotation-vibration potential

$$V_L(\{r_i\}) = E_L^{"rb"}(\{r_i(t)\}) + V(\{r_i\})$$

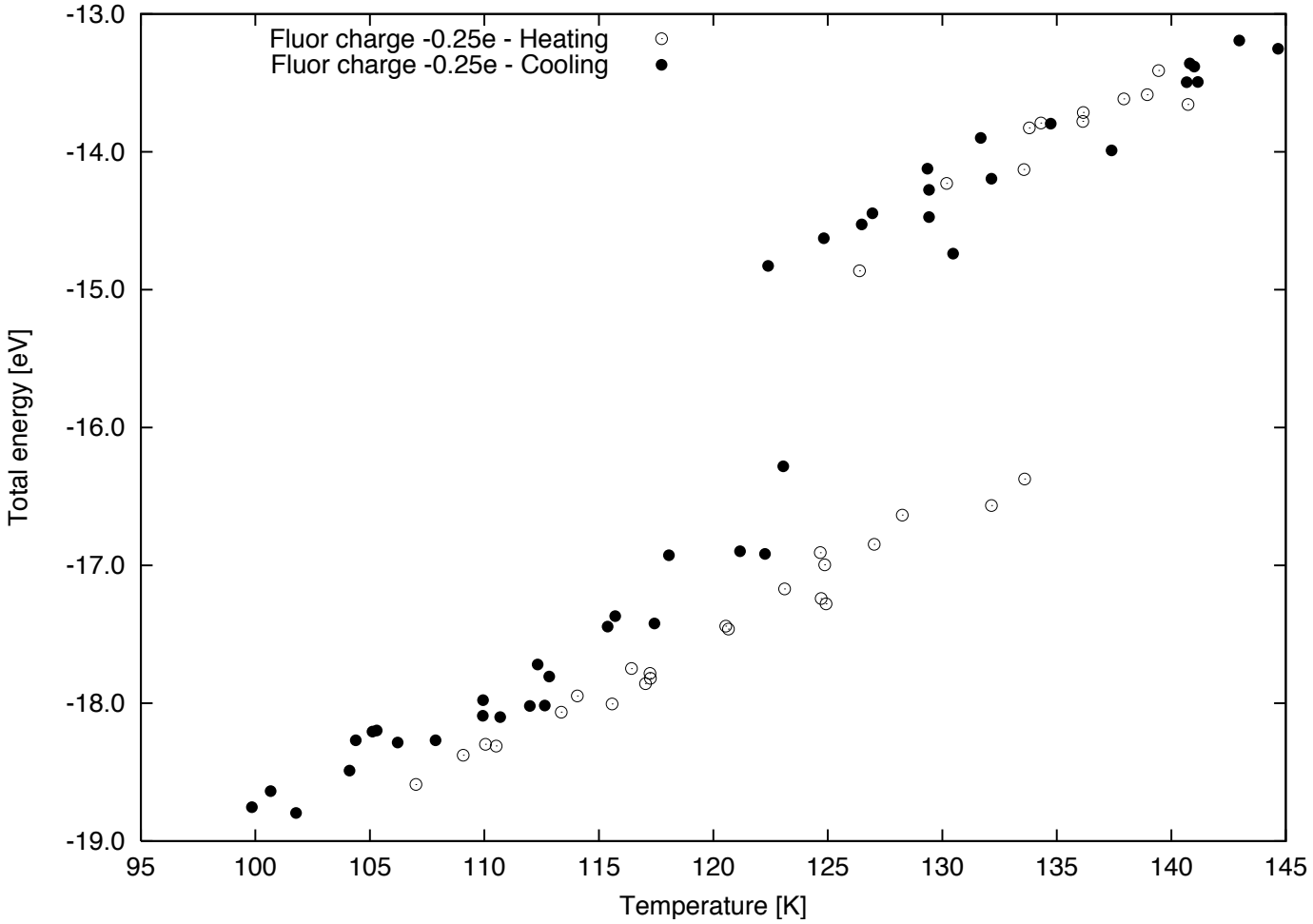


Coexistence of different crystal phases

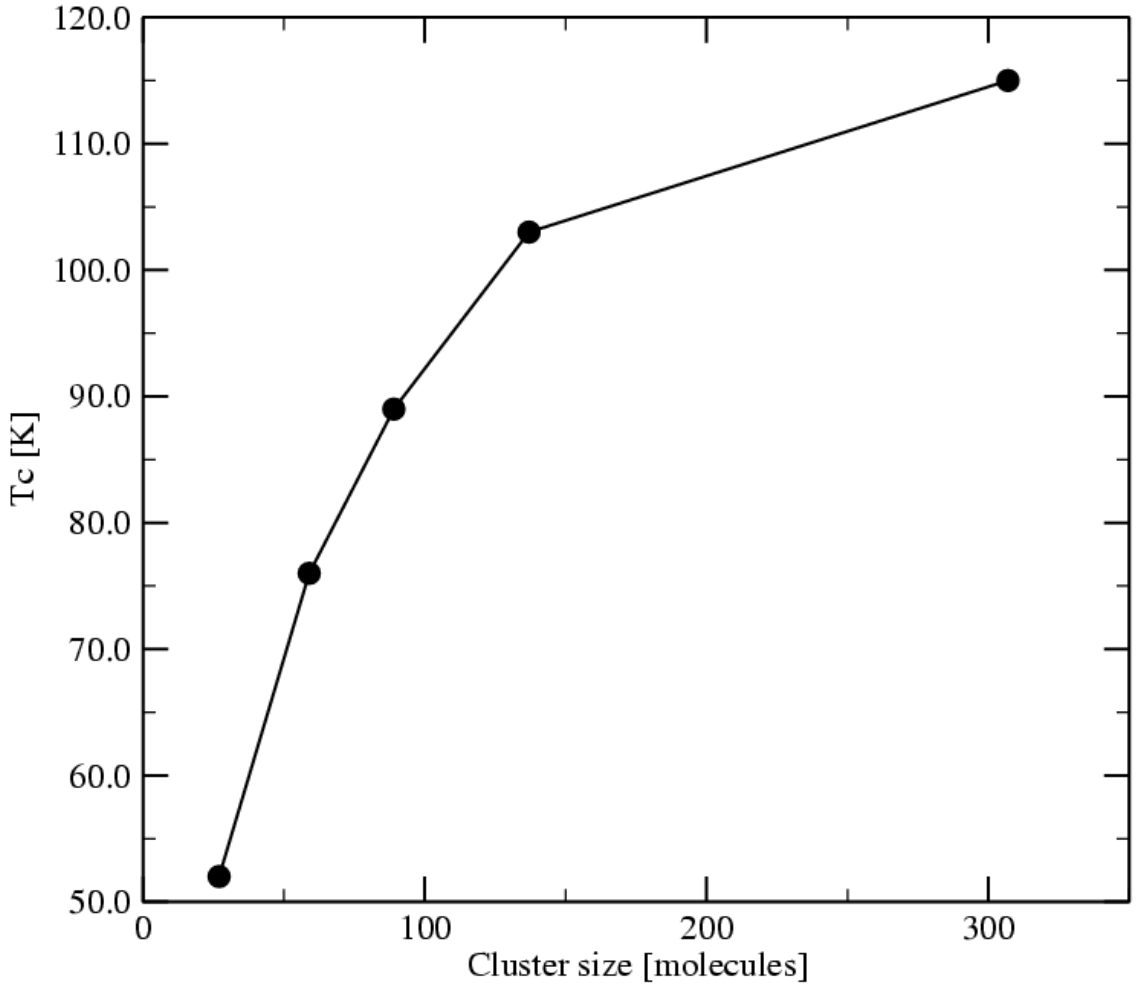




Phase transformations – latent heat



Size-dependent critical temperature



Potential energy surface - resonant inelastic X-ray scattering (RIXS)

https://www.tandfonline.com/doi/full/10.1080/08940886.2017.1289799#

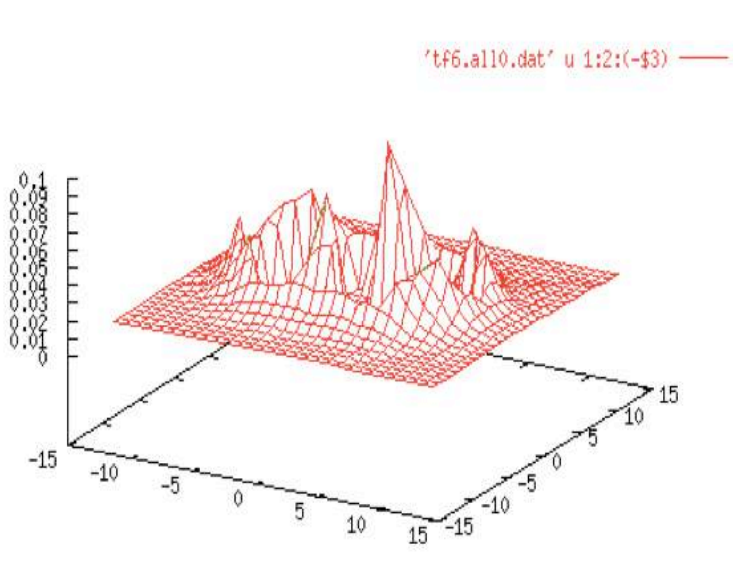
Potential energy surfaces are a central tool to rationalize, in a multidimensional system, how distortions along defined degrees of freedom link conformation and structural modifications to energy. The local and global minima define stable conformations and the ground state.

Optically excited or spin-excited states live on different potential energy surfaces.

Topography - computed

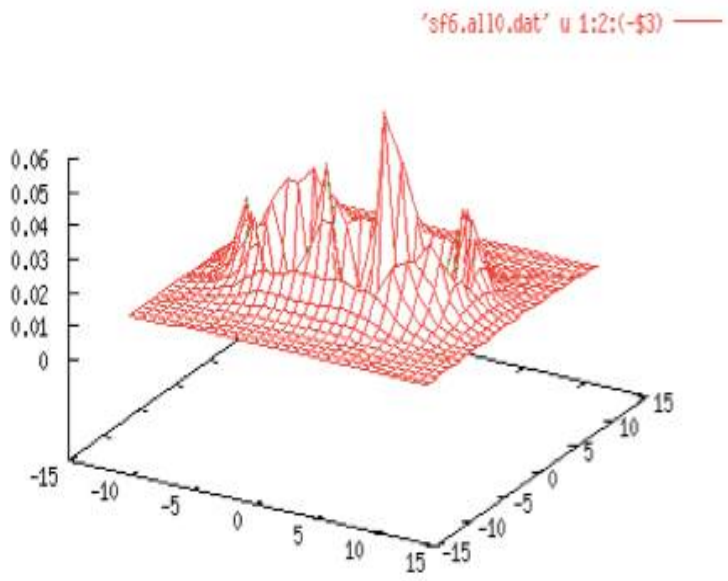
TeF6

- Max 0.1

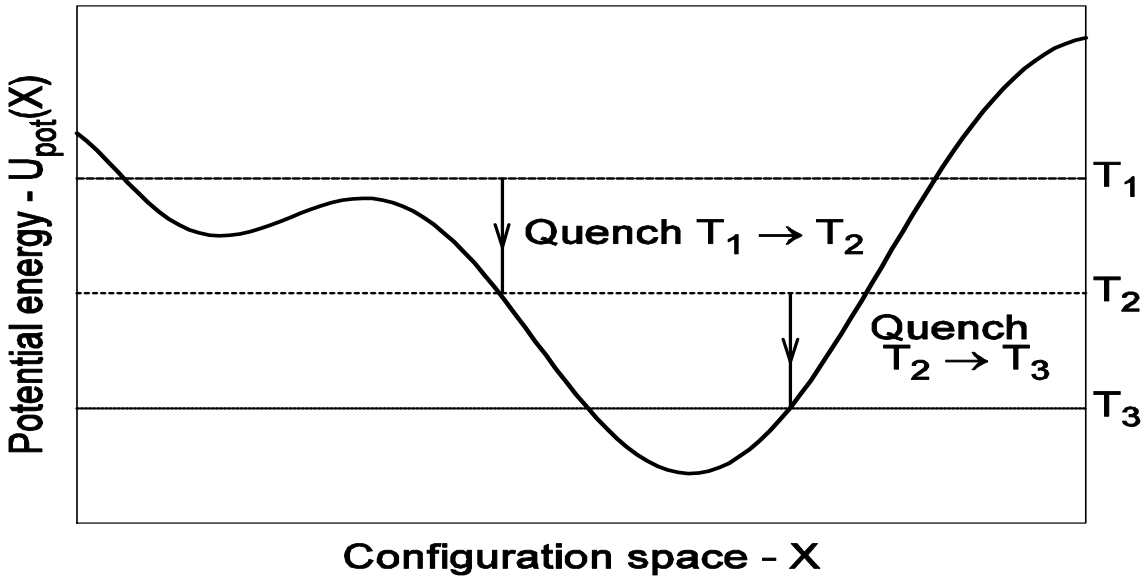


SF6

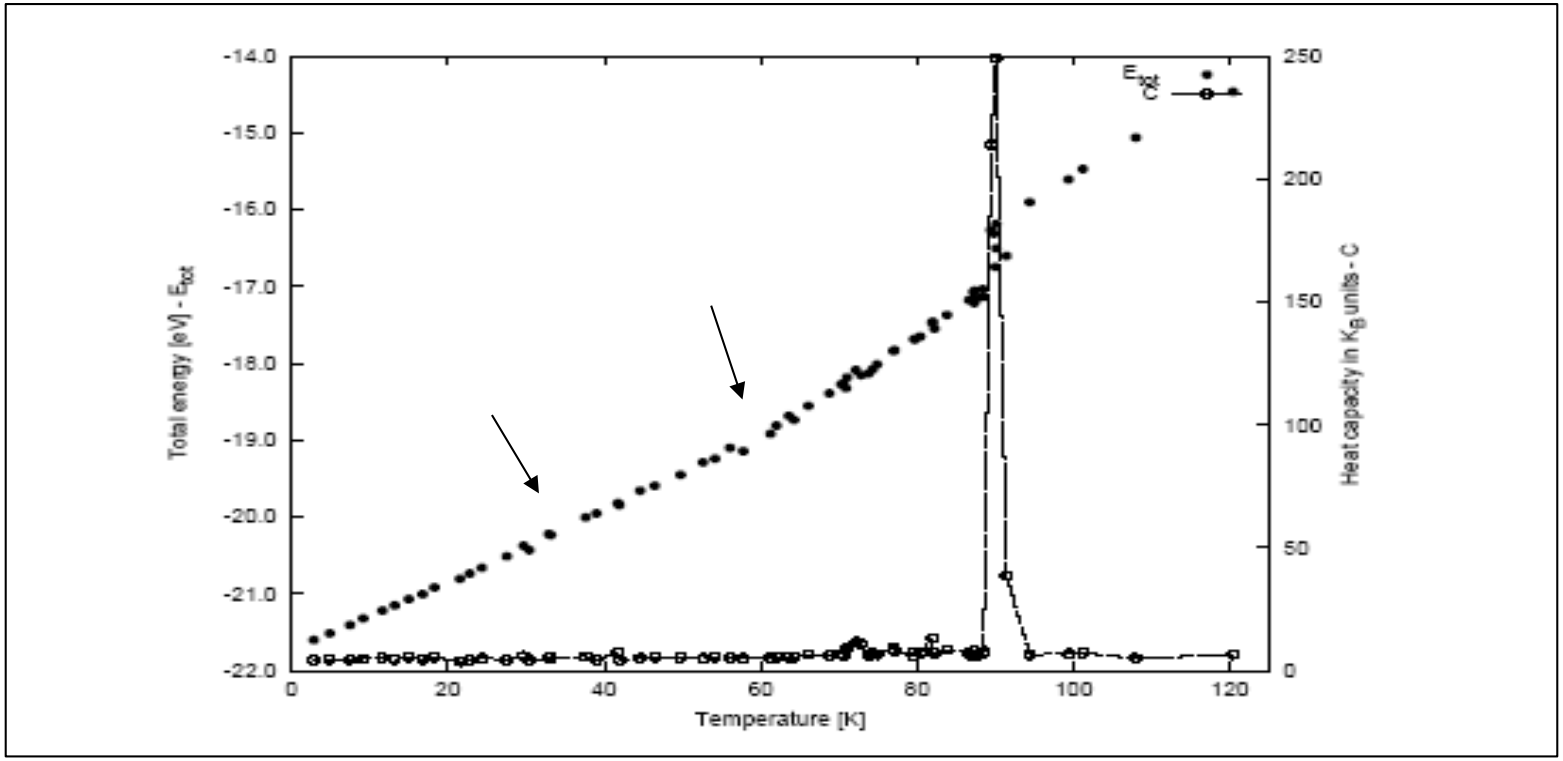
- Max 0.06



Local minima search - quenching



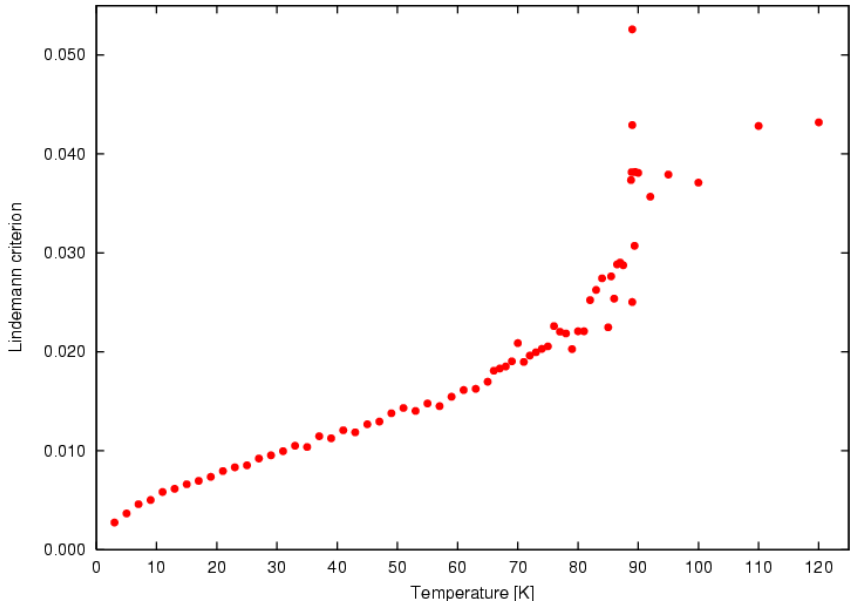
$$\frac{\langle (\delta K)^2 \rangle}{\langle K \rangle} = \frac{N}{N-1} k_B T \left(1 - \frac{3k_B}{2C} \right)$$



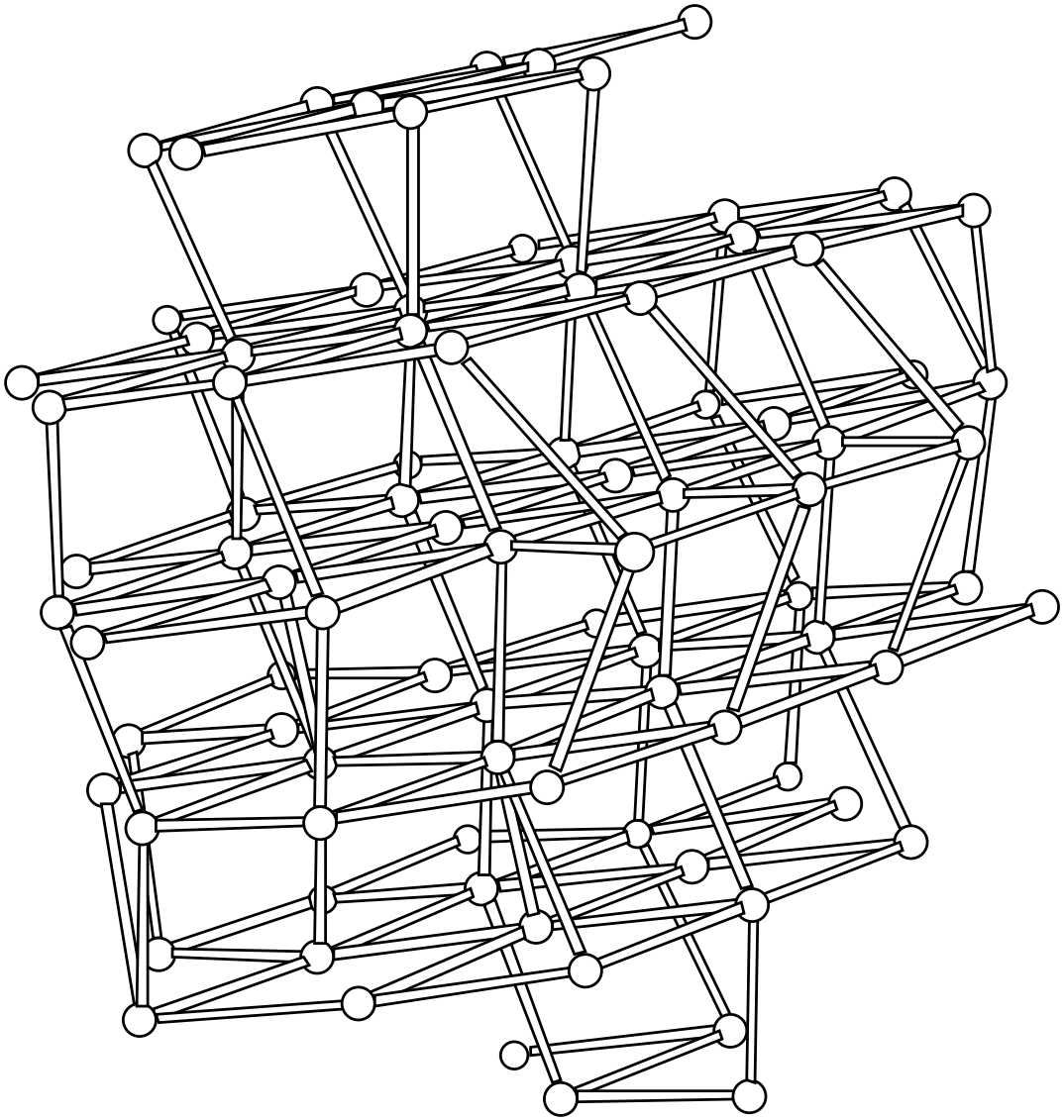
Liquid-like or solid-like

- Lindeman criterion

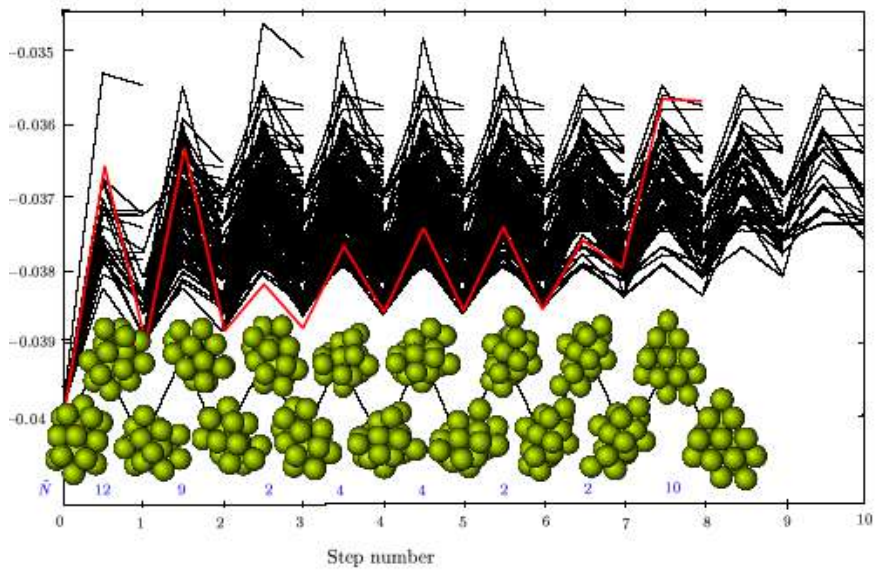
$$\delta_{lin} = \frac{2}{N(N-1)} \sum_{i,j(>i)=1}^{N} \frac{\sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}}{\langle r_{ij} \rangle}$$

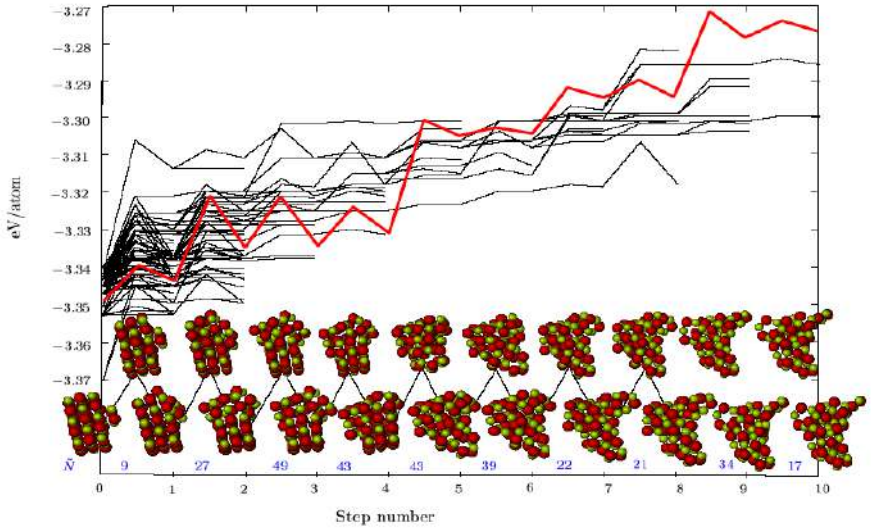


Centers of Te (TeF6) – T = 20 K



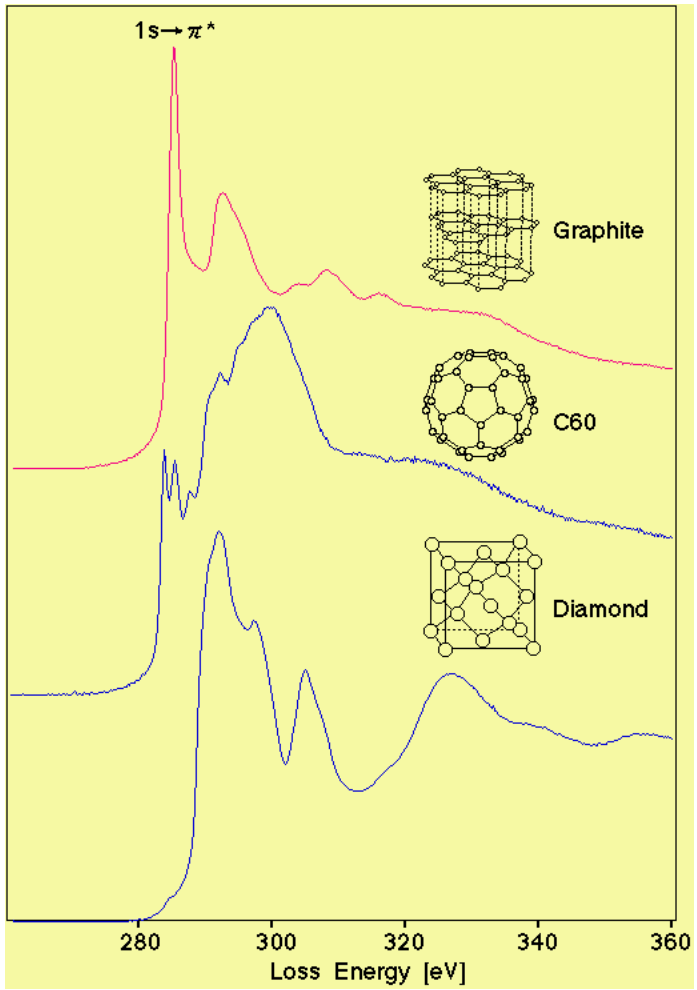
The topography of the potential energy surface determine the lowest energy state: glass or crystal





Example

EELS = electron energy loss spectroscopy:



- Low energy electrons: scattering with carbon objects

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NESTUM cluster

- Calculations of unusual magnetic and electronic properties of carbon materials
- Studying peculiarities of crystal growth
- Climate change predictions
- Big Data for Smart Society
- Big Data Analytics – Financial market

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Thank you for listening!

Благодаря за вниманието!

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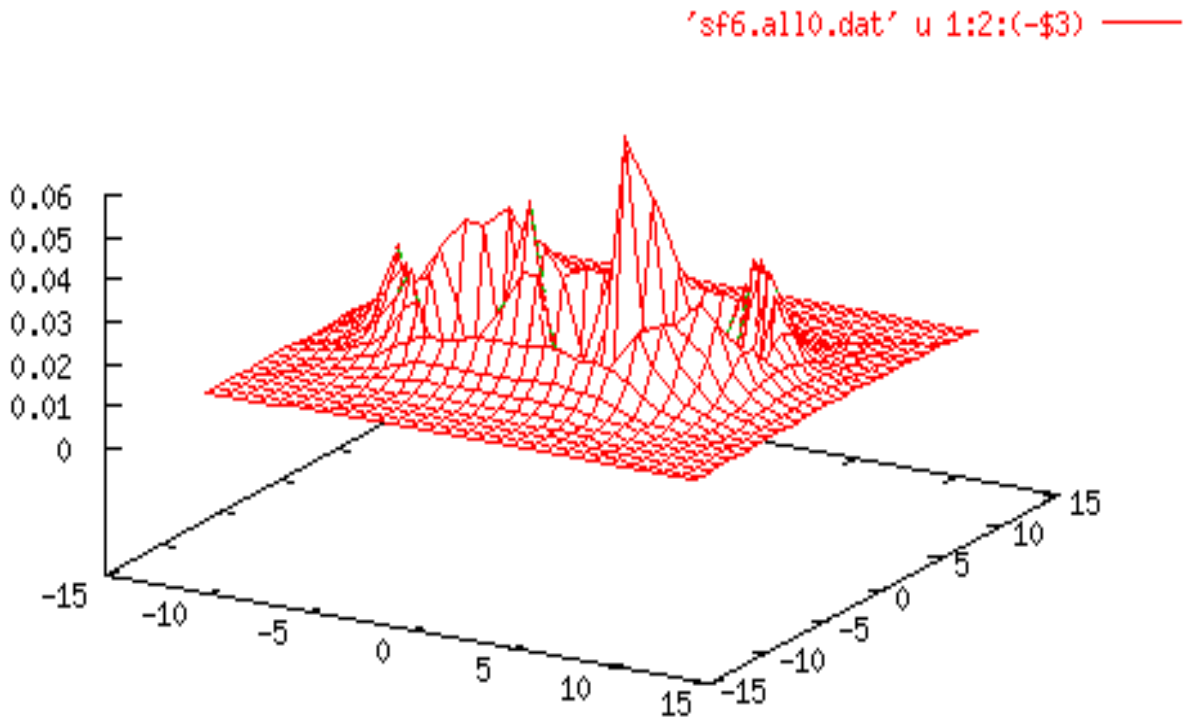
SF6 surface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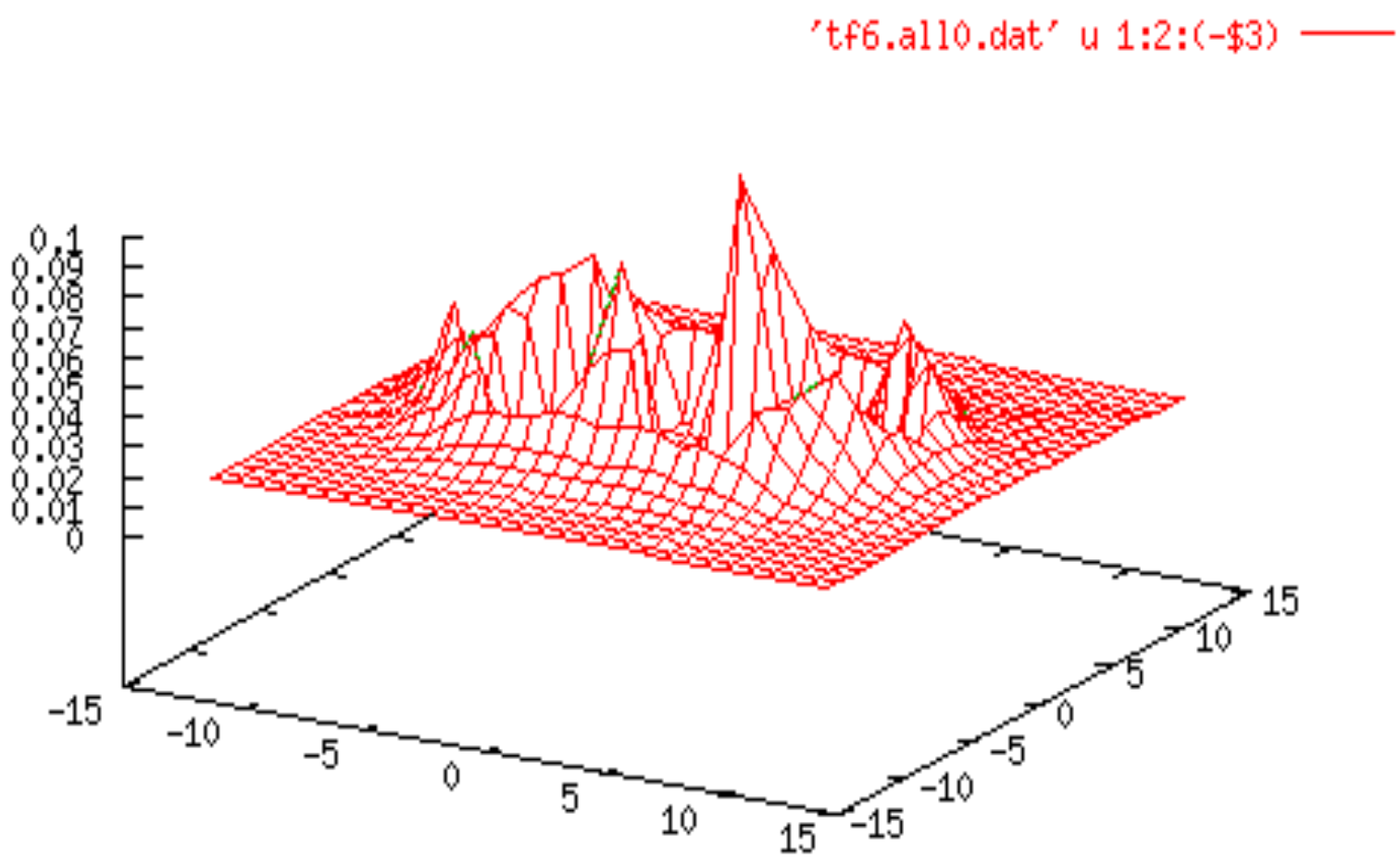
10
15

TeF6 surface



Methane cluster (computed)