# Melting at nanoscale

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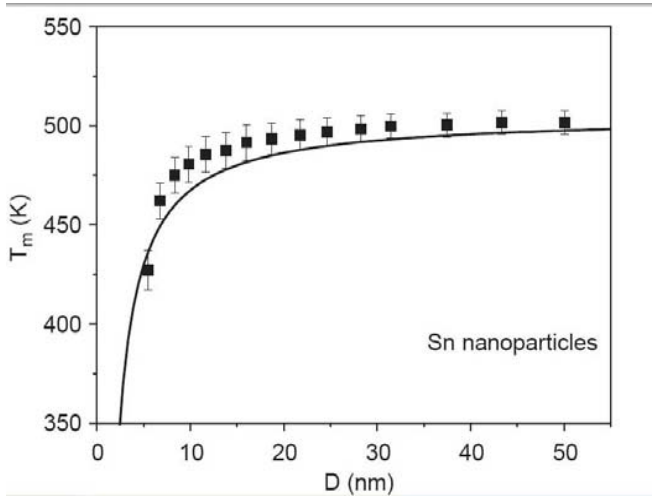
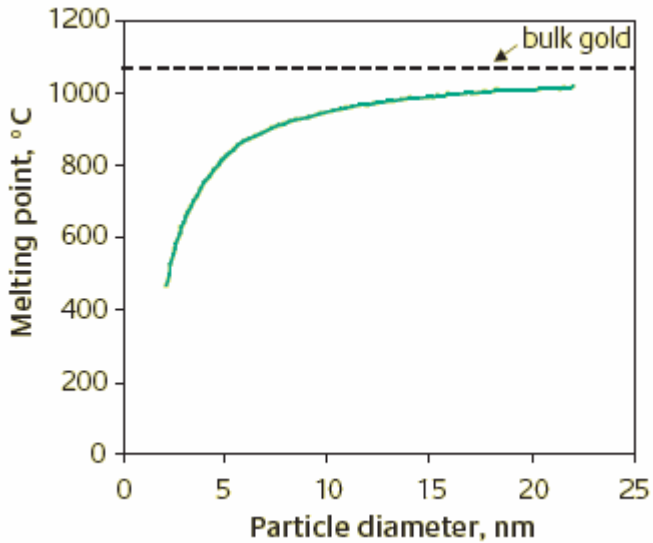
# Melting at nanoscale

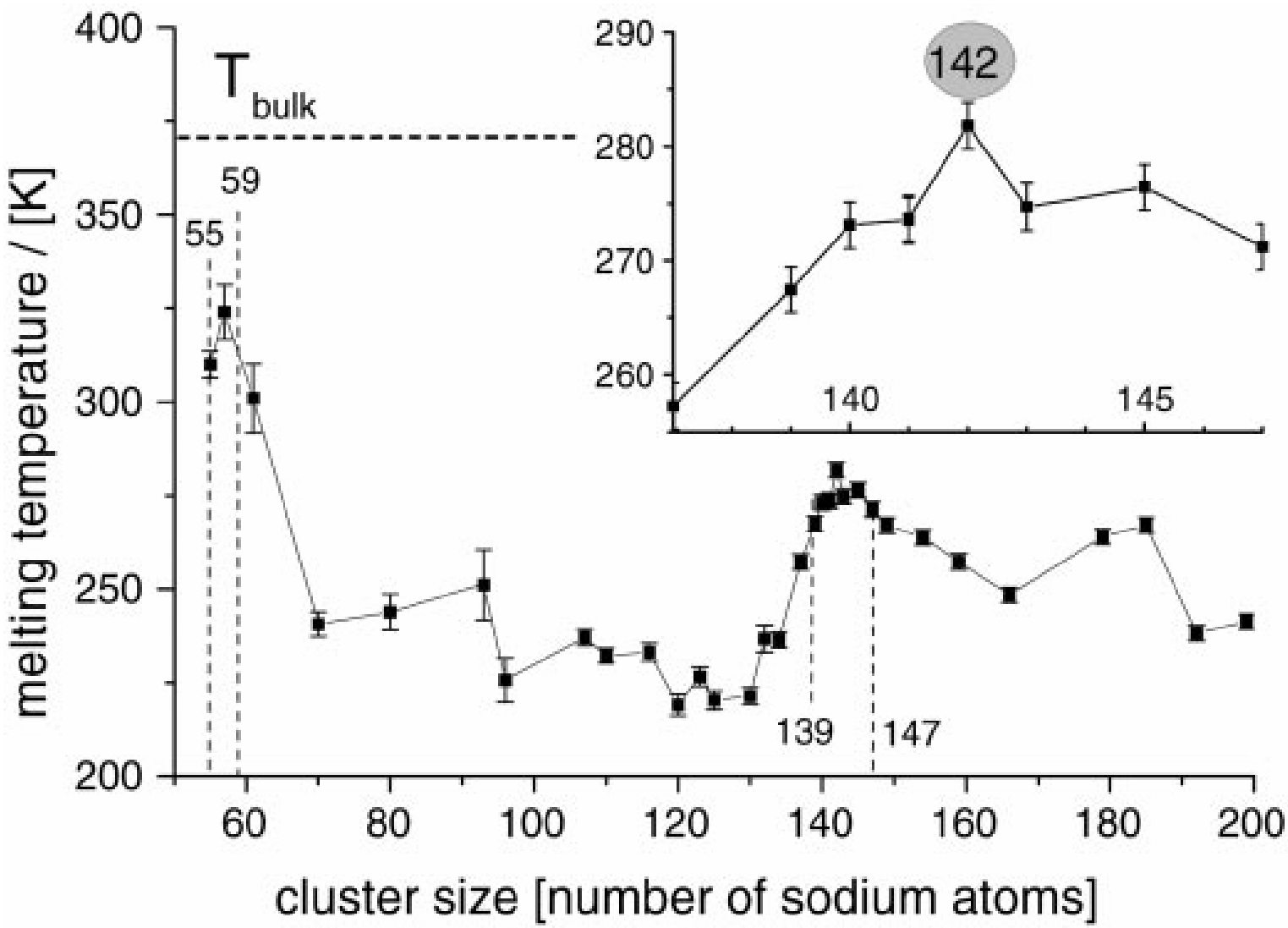
- Crystals at Nanoscale have been found to melt at temperatures lower than that at the bulk.
- Melting at nano scale occurs over a broad range of temperature unlike the bulk material where melting occurs at a particular temperature.
- Surface to volume ratios




***Size dependence of melting point of Sn particles***



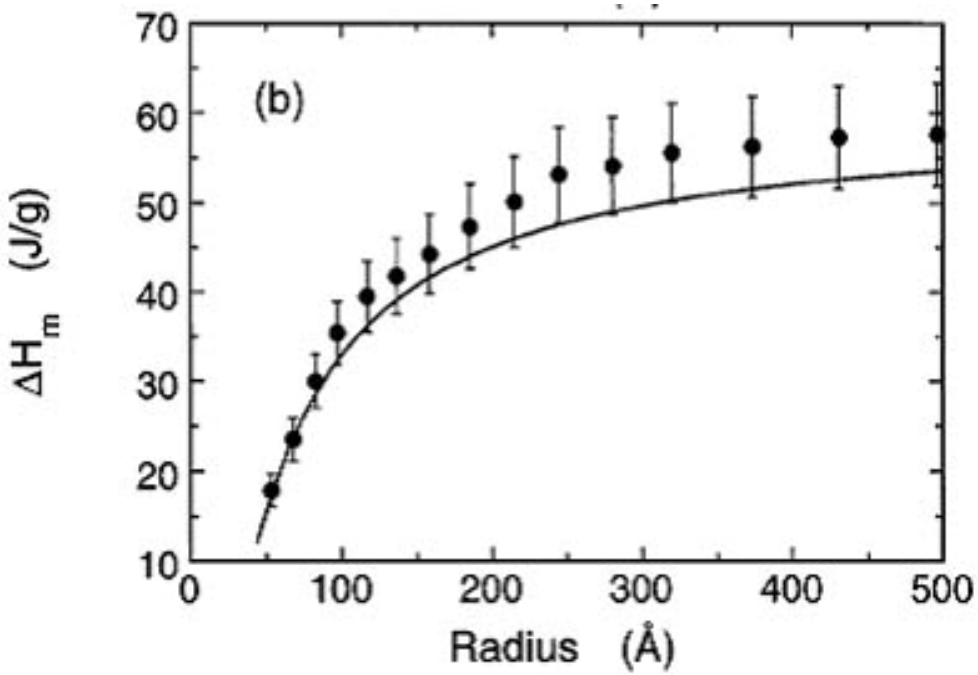

*Size dependence of melting point for gold*


400
350
300
250
200
melting temperature / [K]
T bulk
59
55
290
280
270
260
142
140
145
139
147
60
80
100
120
140
160
180
200
cluster size [number of sodium atoms]

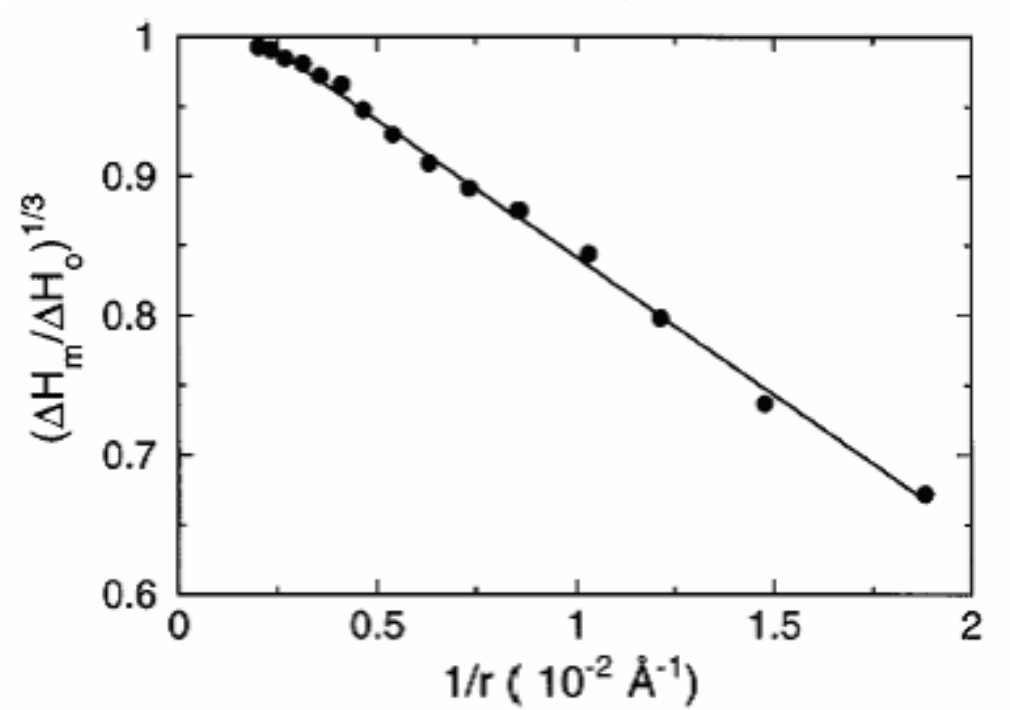
# Latent Heat of Fusion

- Experimentally it is found that Latent heat of fusion value is size-dependent and monotonously drops as dimension of the crystal decreases.
- Experiments to study the latent heat values was done using nano calorimetric measurements made by ultra fast scanning calorimetric technique.
- Considering latent heat of fusion per volume of the bulk like solid core is independent of temperature, the expression for the normalized heat of fusion is obtained in terms of the original particle size *r*, as shown in the following equation:

$\Delta H_m = \Delta H_o (1 - t_0/r)^3$ where $t_o$ is an adjustable parameter in accordance with experimental results.




Change in heat of fusion with size for Sn




Normalized heat of fusion as a function of size for Sn

# Influence of Shape

- The decrease in the melting temperature occurs due to the large surface to volume ratio.
- Even if the Nano particles have same volume they differ in surface areas owing to the differences in particle shapes and the area difference is large in case of small particles.
- Particle shapes play a major role in the decrease of the melting temperature of nano particles when compared to the bulk.
- The particle shape difference can be taken into consideration with the new parameter i.e., the shape factor $\alpha$ which is given by the following equation:

$$\alpha = S/S_0$$

- Using this shape factor temperature dependence of dimension has been calculated as:

$T_{mp} = T_{mb}(1 - 6\ \alpha r/d)$ where d is size of crystal and r is atomic radius.

The calculated shape factor for different particle shapes

| Particle shape | Shape factor ($\alpha$) |
|---|---|
| Spherical | 1 |
| Regular tetrahedral | 1.49 |
| Regular hexahedral | 1.24 |
| Regular octahedral | 1.18 |
| Disk-like | >1.15 |
| Regular quadrangular | >1.24 |

The cohesive energy of metallic crystal in any shape (*E*p) can be written as

$$E_{\mathrm{p}} = \frac{1}{2} n\beta E_{\mathrm{bond}} \left(1 - 6\alpha \frac{r}{D}\right)$$

Rose and Debye model :

$$T_{\mathrm{mb}} = \frac{0.032}{k_{\mathrm{B}}} E_0$$

Using this shape factor temperature dependence of dimension has been calculated as:

$T_{mp} = T_{mb}(1 - 6\ \alpha r/d)$ where d is size of crystal and r is atomic radius.

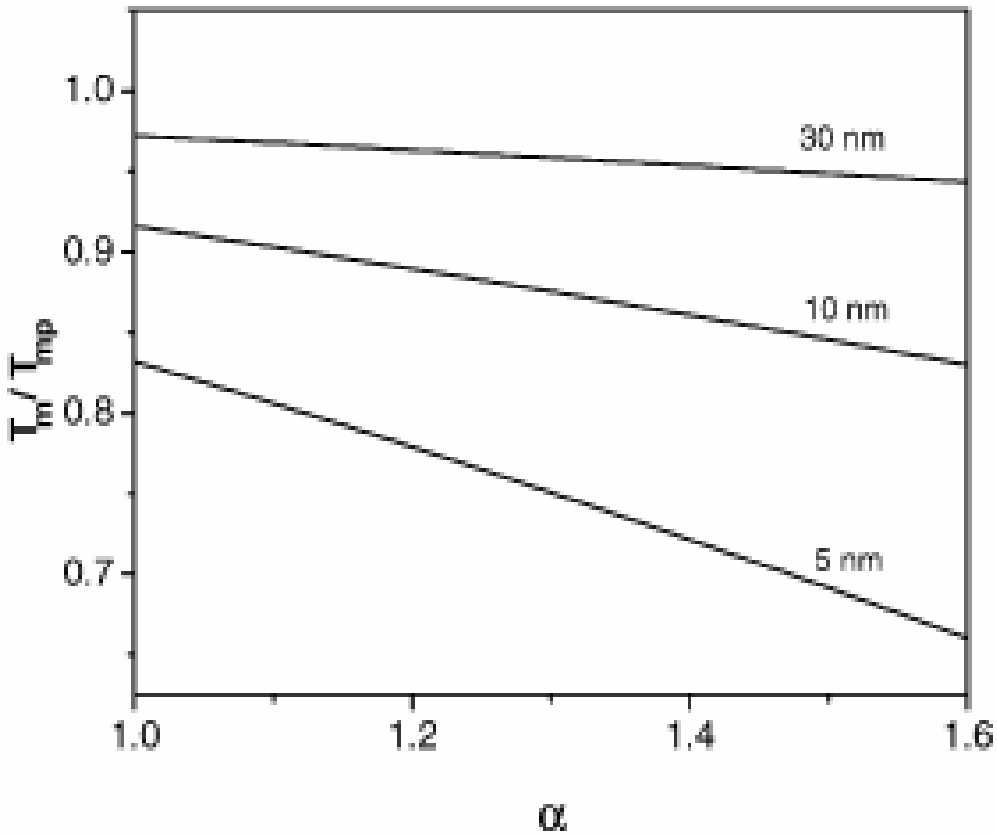



Fig. 1. Variation of the relative melting temperature of Sn nanoparticles as a function of shape factor. The solid lines are the results calculated from Eq. (10).

# Surface melting

- The Radial Distribution Function (RDF) for the spherical shells is defined by

$$g(r) = \langle n(r)/(\rho 0 * 4\pi r2*\Delta r)$$

where $\Delta r$ is the width of the shell at a distance r , n(r) =number of atoms in this shell , $\rho 0$=mean atom density of a perfect lattice

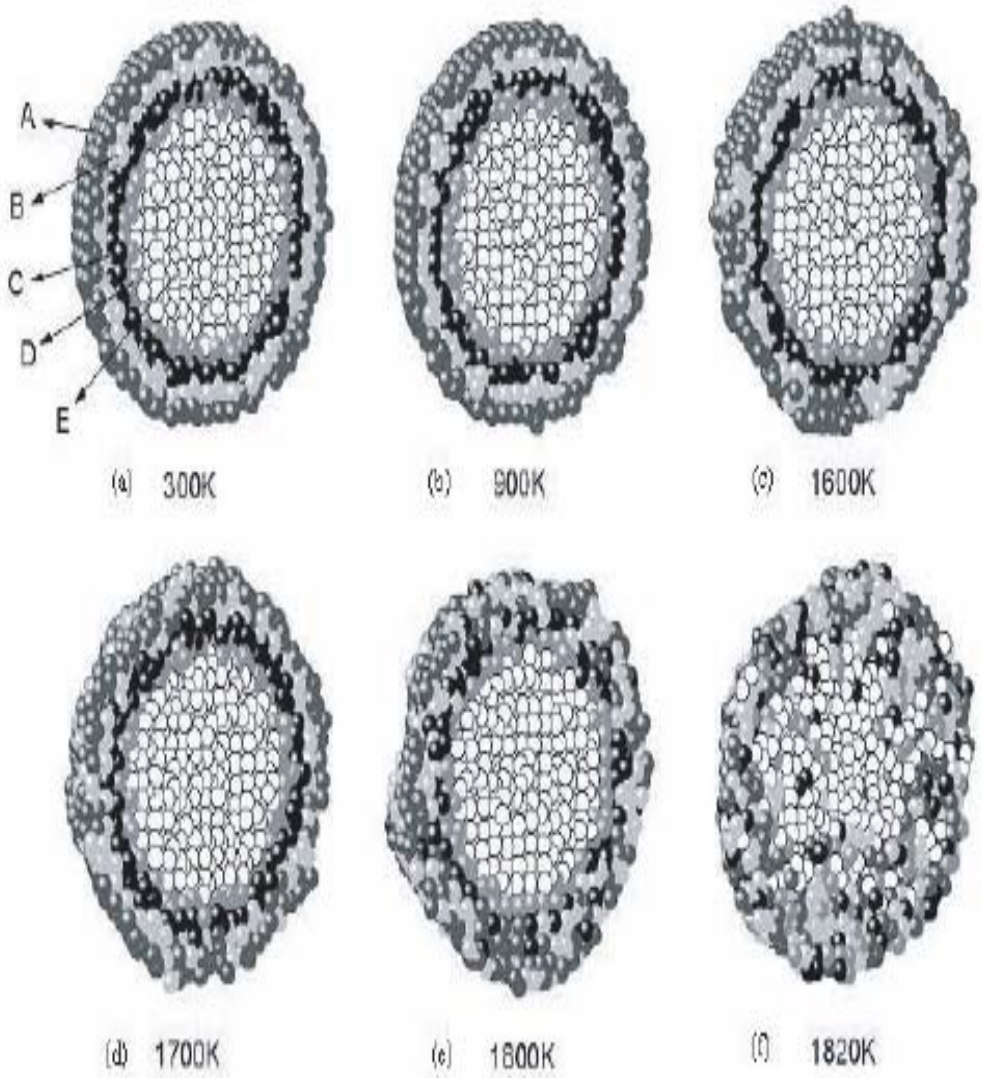



Fig. 2. Section snapshot views of the MD sample with $N = 8393$ ($D \approx 6$ nm) at a series of temperatures during heating.

# Dynamic Coexistence

- Three regions occur before the cluster melts into liquid, low temperature solid phase region before the coexistence region, the coexistence region and the high temperature liquid phase region above this coexistence region.

- This back and forth fluctuations between solid and liquid states has been observed with some clusters (like N= 7,9,11,13,19,25,33,44,55,147). For medium sized clusters (N>55) the low energy solid and high energy liquid groups lead to the dynamic coexistence.

- Solid clusters expand on temperature rise and energy gap between solid state and liquid state decreases. The cluster starts fluctuating between solid and liquid states; the dynamic coexistence. On further heating, the instability of the solid states results in meting of clusters into liquid states.

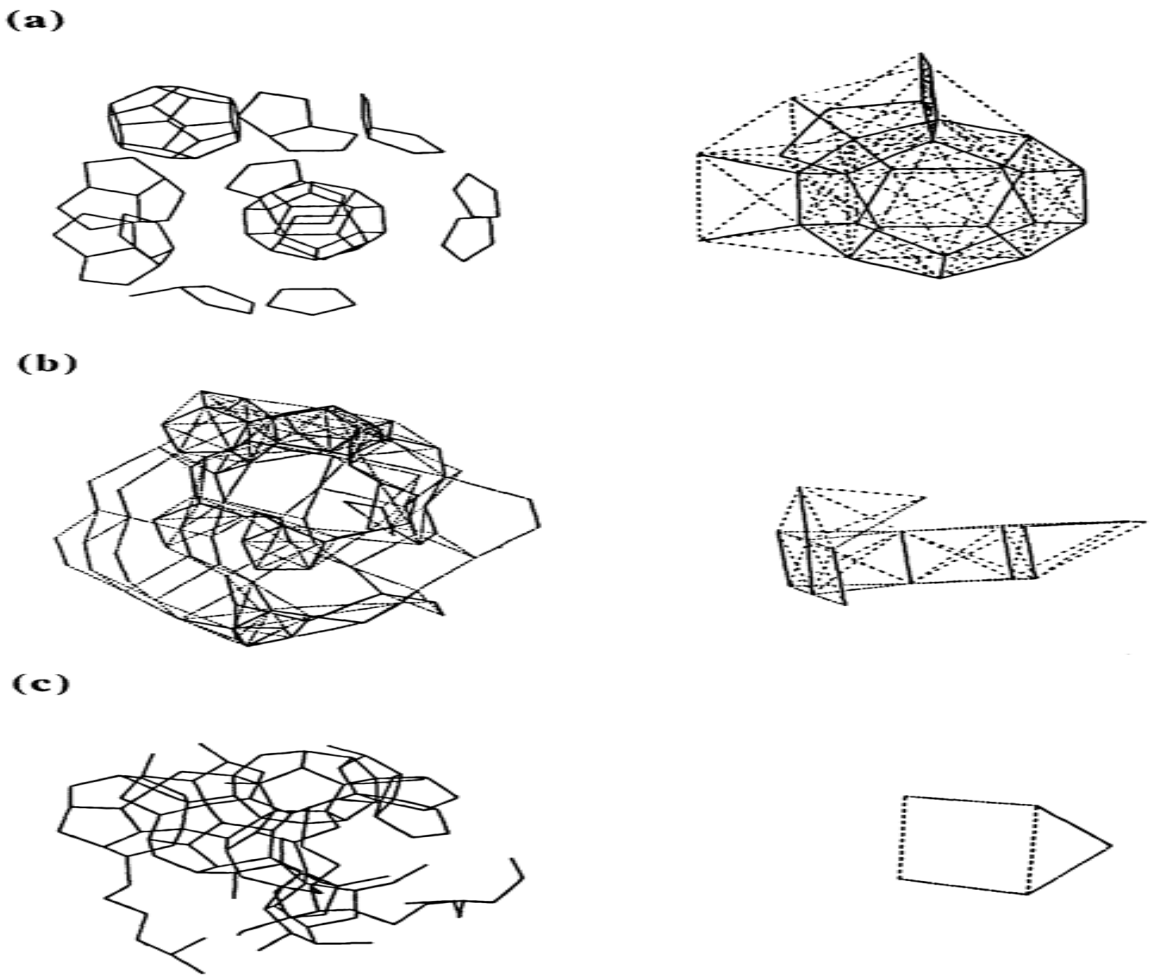



FIG. 2. The tetrahedral (right) and octahedral connectivity diagrams for the structures inside the coexistence range (at $E = -709.6 \times 10^{-16}$ erg/atom). (a) A solid structure at 180000 time steps. (b) A solid structure at 300000 time steps. (c) A liquid structure at 330000 time steps.

- The equilibrium behavior of gold nano particles was studied using clusters of sizes N=55,177,381,725.The empirical potential was given by:

$$V = -\frac{1}{2} V_0 \sum_{i=1}^{N} \left[ \left[ \sum_{j \neq i} \exp[-2q(r_{ij} - 1)] \right]^{1/2} - A \sum_{j \neq i} \exp[-p(r_{ij} - 1)] \right],$$

- The solid phase atoms at low temperatures start oscillating with amplitudes comparable with atomic separations. Even below the melting point of the cluster it is observed that surface atoms are active on the large clusters

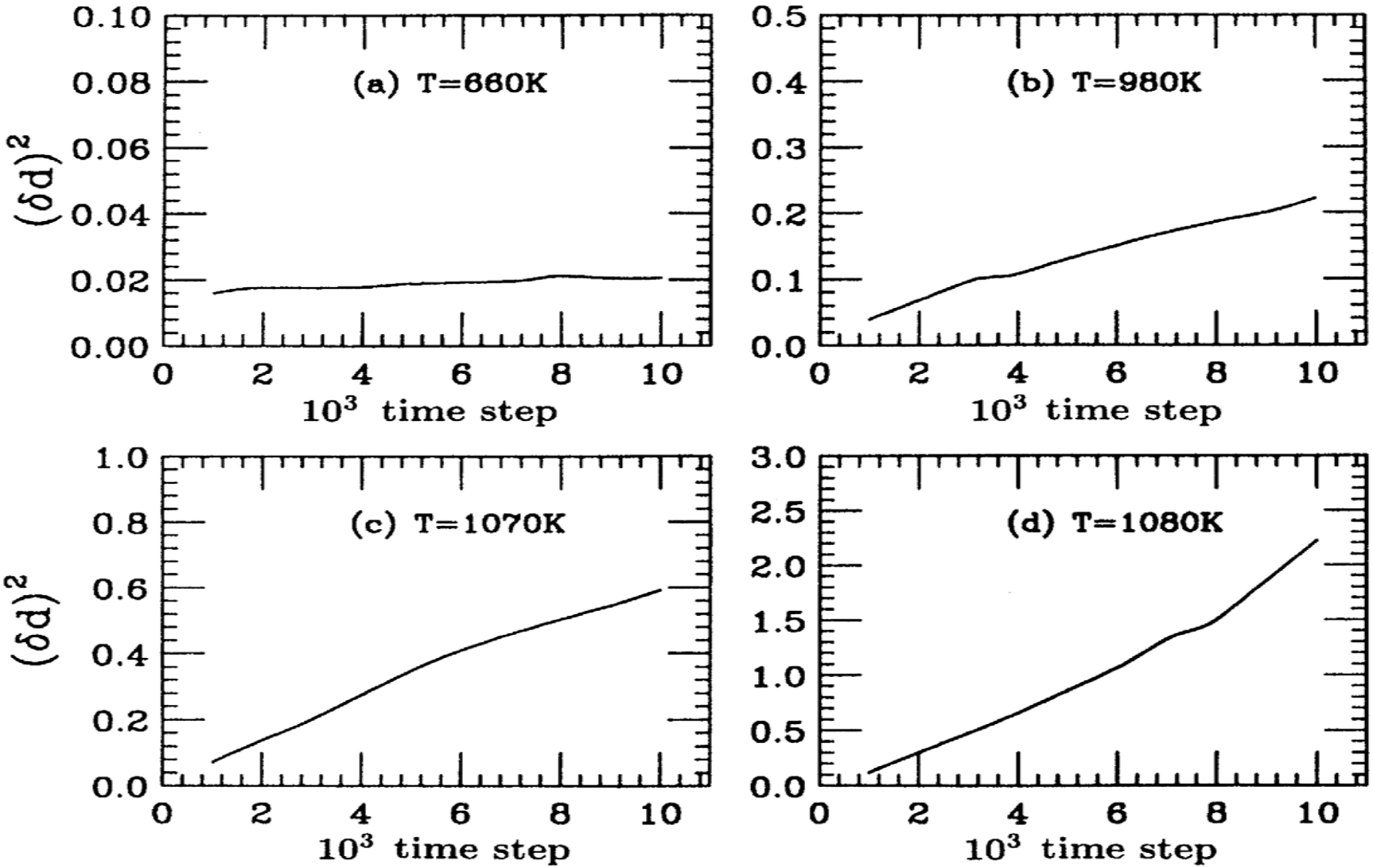
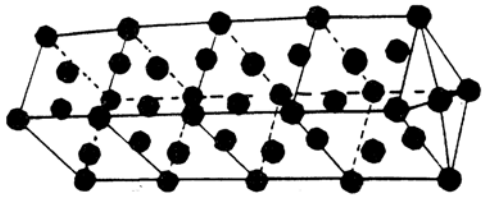


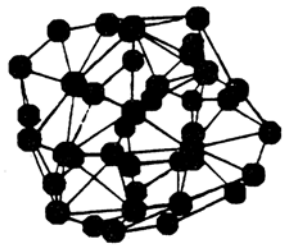

FIG. 2. The average mean-square displacement as a function of time for atoms in a $N = 725$ cluster for various temperatures.

- For small clusters there is not much difference between the bulk and the surface atoms and surface diffusion below melting point is absent. This leads to qualitatively different behavior in their non-equilibrium shape change dynamics.
- The melting scenario described here for gold nanoclusters differs from the previously mentioned surface premelting one.
- Precursor to melting these clusters undergo at elevated temperatures solid-to-solid transformations from the low-temperature optimal structural motifs (truncated decahedra, Dh, for n, 250, and truncated octahedra, TO, for larger clusters) to an icosahedra, Ih, structure, with eventual melting of the latter below the bulk melting temperature.



(a)

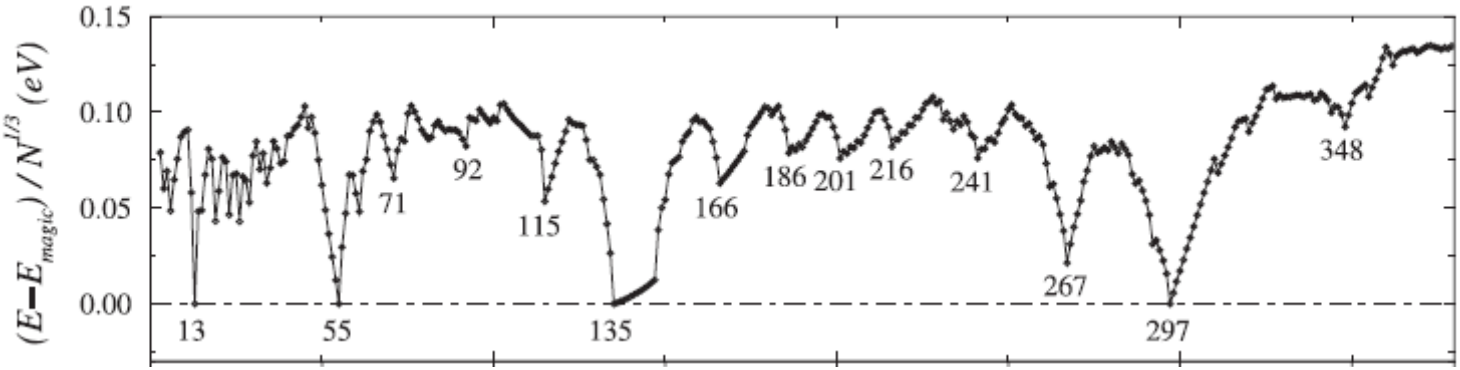
N=41,$r_g$=1.43



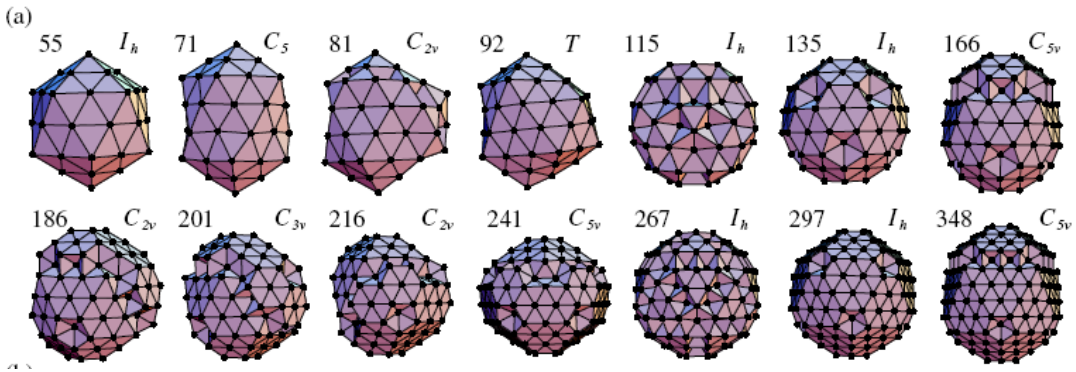
(b)

FIG. 5. (a) The initial fcc structure of an $N=41$ cluster and (b) the compact shape found after 500 000 time steps.

# Geometric magic numbers




**Energies of the putative global minima for gupta potencial.-Cambridge Cluster Database**



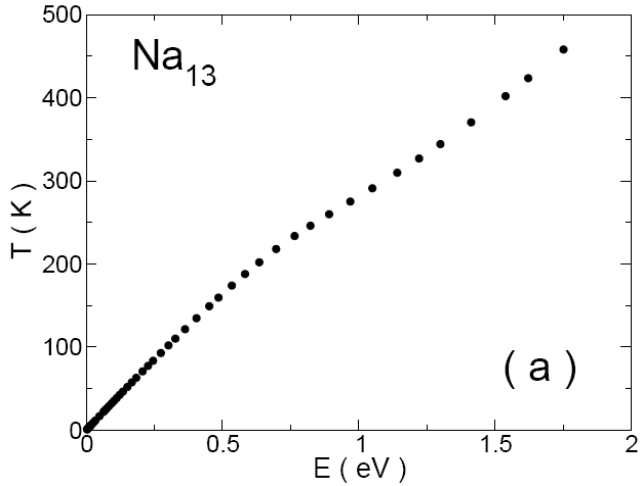

Juan A. Reyes-Nava[1], Ignacio L. Garzón[1], Marcela R. Beltrán[2], and Karo Michaelian[1] **-2002**

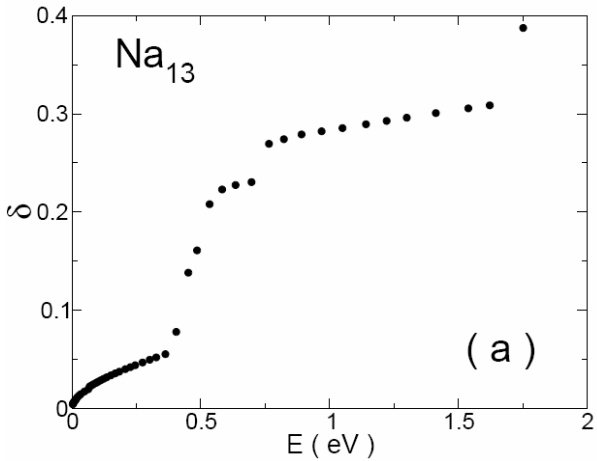
- **1. Caloric curves.**
- **2. Specific heat curves**
- **3. their RMS bond length fluctuations**
- **many-body Gupta potential and simulation**

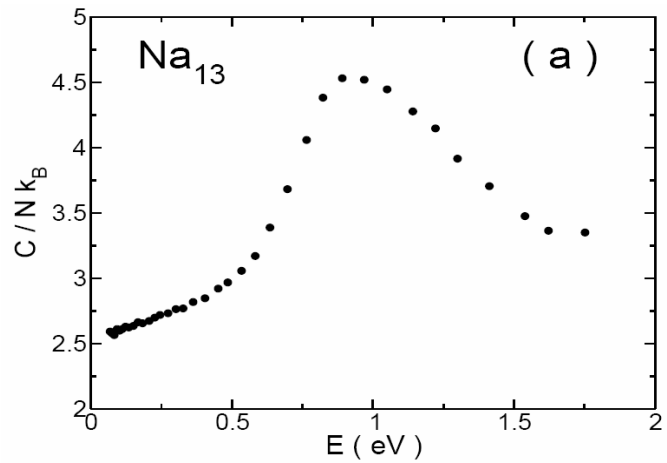
**times of 50 nanoseconds**

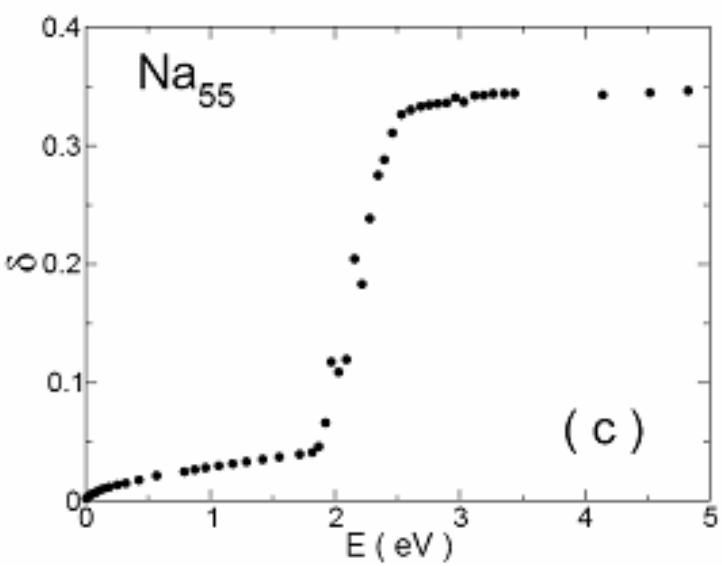
$$V = \sum_{i=1}^{N} V_i$$

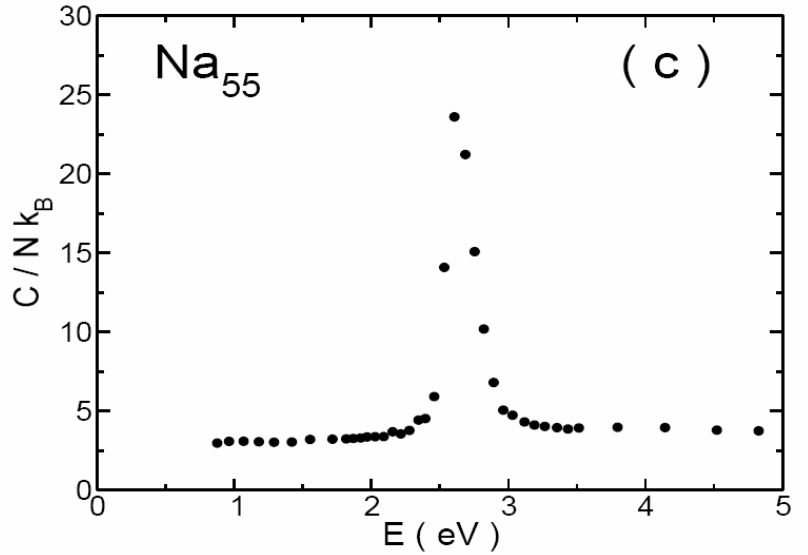
$$V_i = A \sum_{j \neq i} e^{-p\left(\frac{r_{ij}}{r_0} - 1\right)} - \xi \left( \sum_{j \neq i} e^{-2q\left(\frac{r_{ij}}{r_0} - 1\right)} \right)^{\frac{1}{2}}$$

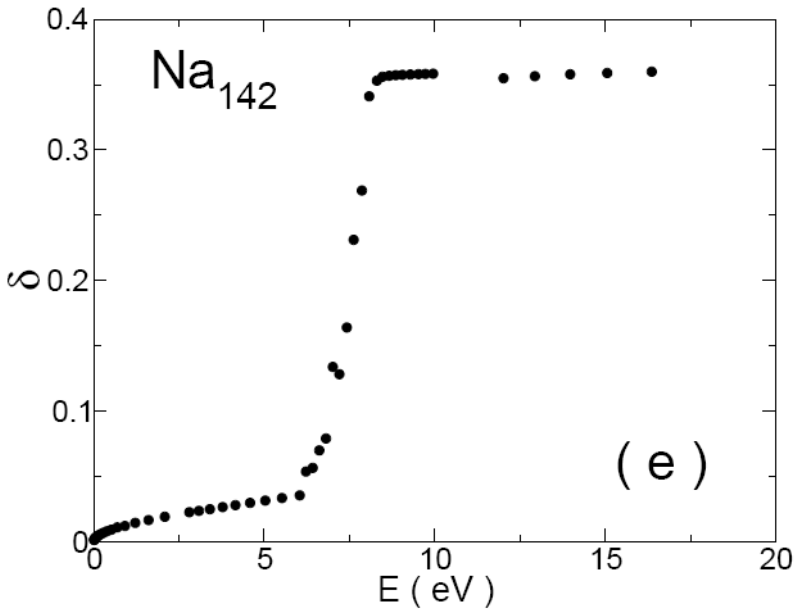


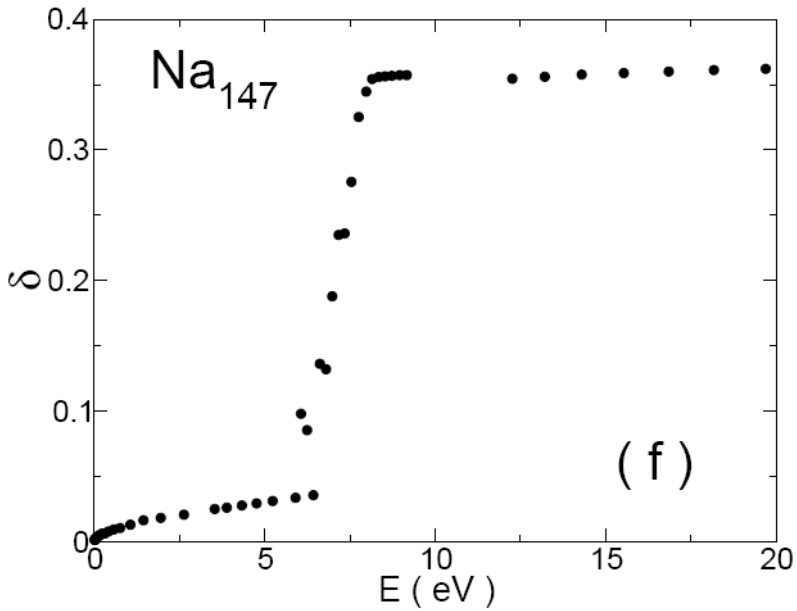




Na55
( c )
δ
E ( eV )


Na55
( c )
C / N kB
E ( eV )


Na142
( e )
δ
E ( eV )


Na147
( f )
δ
E ( eV )

# Qualitative features

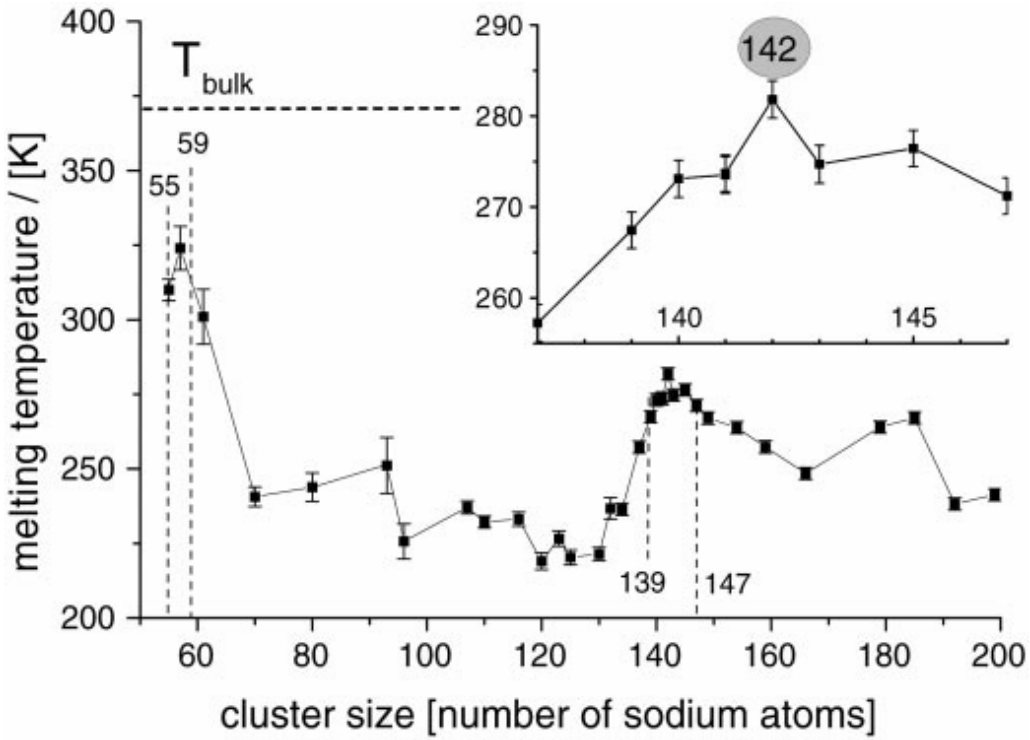
- The melting temperatures calculated from the maxima of the specific heats are systematically higher than the values obtained using the Lindemann criterion.
- The calculated melting temperature for the Na55 cluster is about 40 % lower than the reported experimental value

| $N$ | BE | Maximum in $C$ | Lindemann criterion |
|---|---|---|---|
| 13 | 0.684 | 260 | 149, 226 |
| 20 | 0.734 | 220 | 57, 157 |
| 55 | 0.855 | 166 | 151 |
| 135 | 0.929 | 181 | 135 |
| 142 | 0.933 | 189 | 190 |
| 147 | 0.935 | 180 | 171 |

M. Schmidt, R. Kusche, B. von Issendorff, and H. Haberland, Nature **393**, 238 (1998).

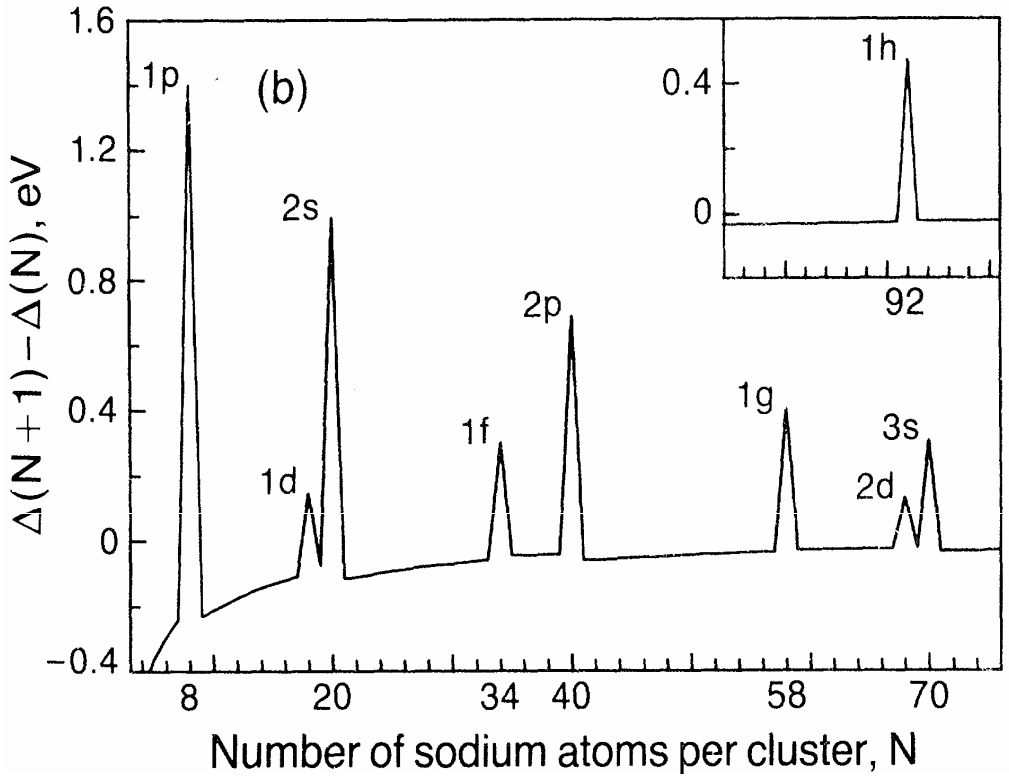
# Electronic shell theory

- *Magic Numbers*: For certain crystal sizes at nano scale abnormally higher melting points are observed for the crystal. These sizes are called magic numbers




- The Jellium model (1984 – 86) and the electronic shells (1994-96)

- **Jellium** model: In this model the cluster is treated as a uniformly positively charged sphere filled with an electron gas. The schrödinger equation is solved for an electron constrained to move within this positive sphere under a potential.



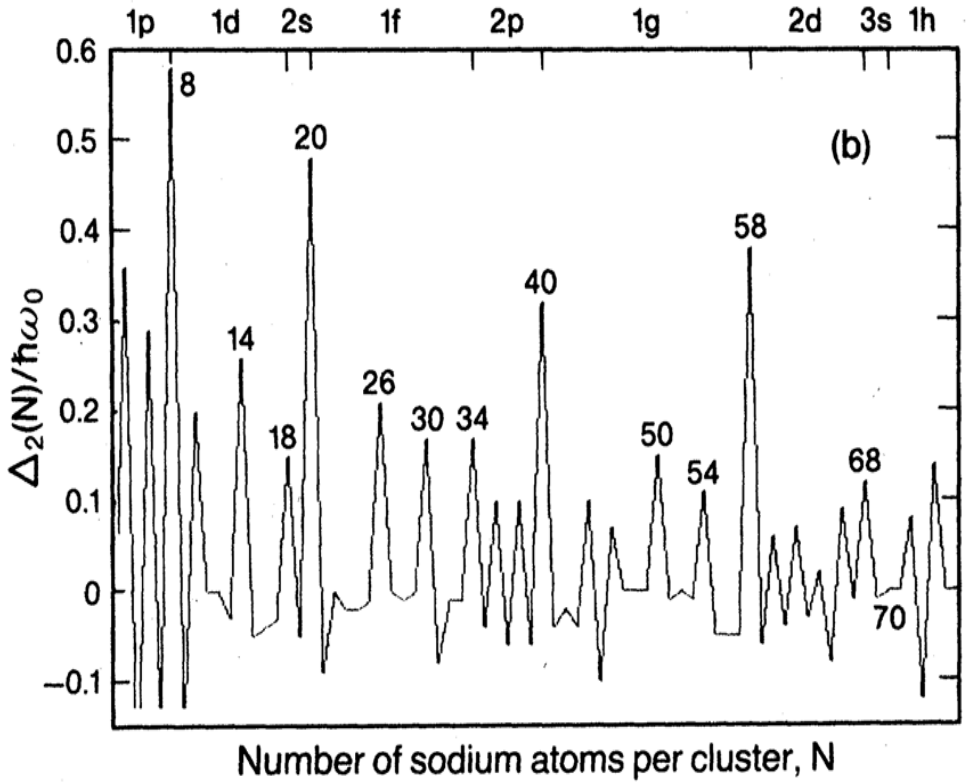

$$U(r) = -\frac{U_0}{\exp[(r - r_0)/\epsilon] + 1},$$

$U_0$ is the sum of fermi energy and work function in bulk.

$r_0$ is the effective cluster radius. $r_0 = 3.93N^{1/3}$ a.u

$\varepsilon$ depends on the variation of potential at the edge of the sphere. $\varepsilon$ = 1.5 a.u

- Bulk crystals : structures with largest possible nearest neighbors are favored
- Nanoclusters: Jahn Teller effect.
- Ellipsoidal jellium model: the second difference energies vs. N



•For clusters smaller than 2000 atoms, the frequency of peaks (indicating magic numbers) is considerable.

•Magic numbers in this range have been explained by invoking electron shell theory.

•Electronic shells are formed by bunching of Jellium orbitals. Closing of these shells result in a magic number cluster.

**Competition between electronic and geometric magic numbers**

•Do the clusters numbers where both electronic and geometric shell closings occur, exhibit exceptionally high stability and hence high melting point?

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