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Phase transitions in metal clusters.

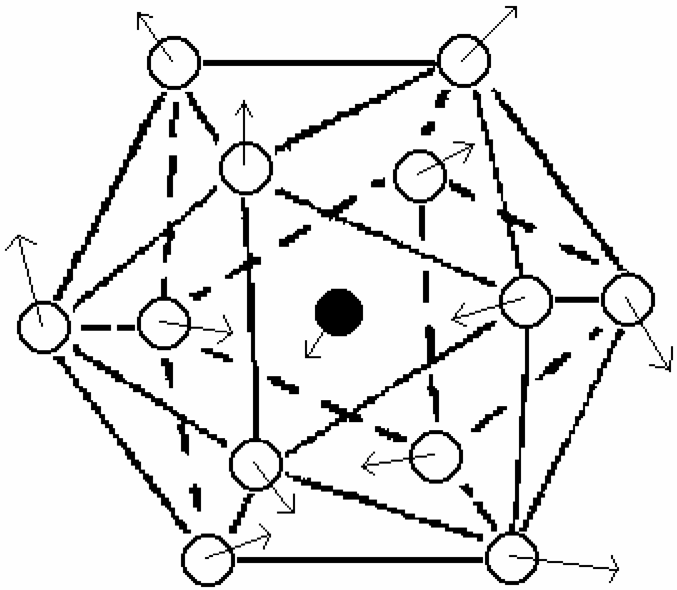
Contents.

Methods of description of cluster in a range of the phase transition.

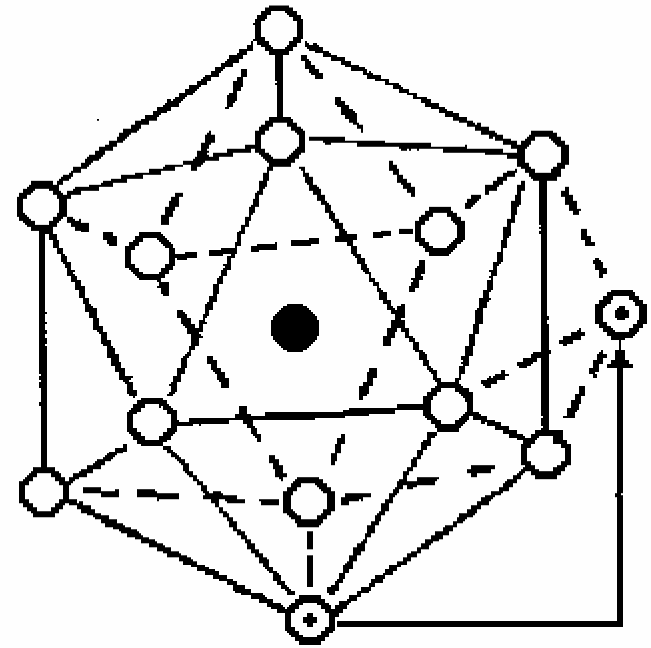
1. **Thermodynamic description** with thermodynamic parameters for each aggregate state.
2. **Computer simulation of clusters by methods of molecular dynamics.** Aggregate states behave to maxima of the probability of a given kinetic energy of atoms.
3. **Cross-saddle dynamics** based on local minima and saddles of the potential energy surface for atoms. Each aggregate state includes a group of local minima with nearby energies.

B.M.Smirnov, R.S.Berry. **Phase Transitions of Simple Systems. (Springer, Berlin, 2007)**

Types of cluster excitations.

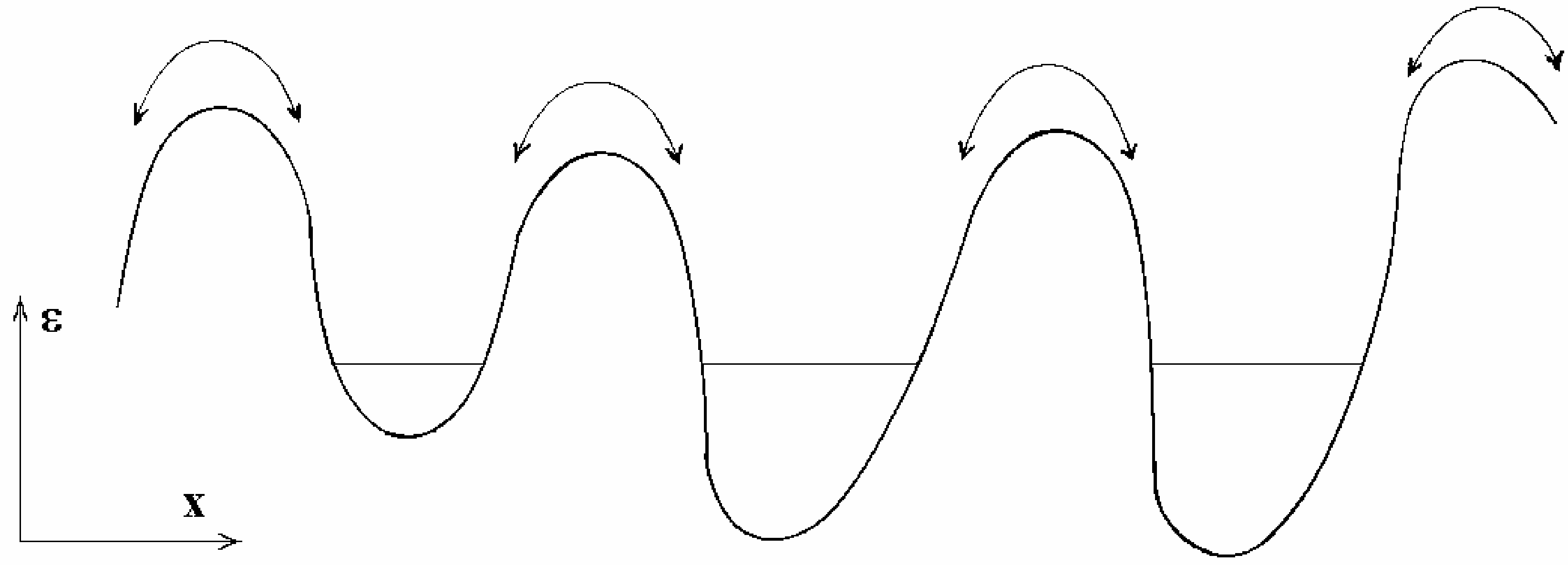


oscillations
or
thermal motion of atoms

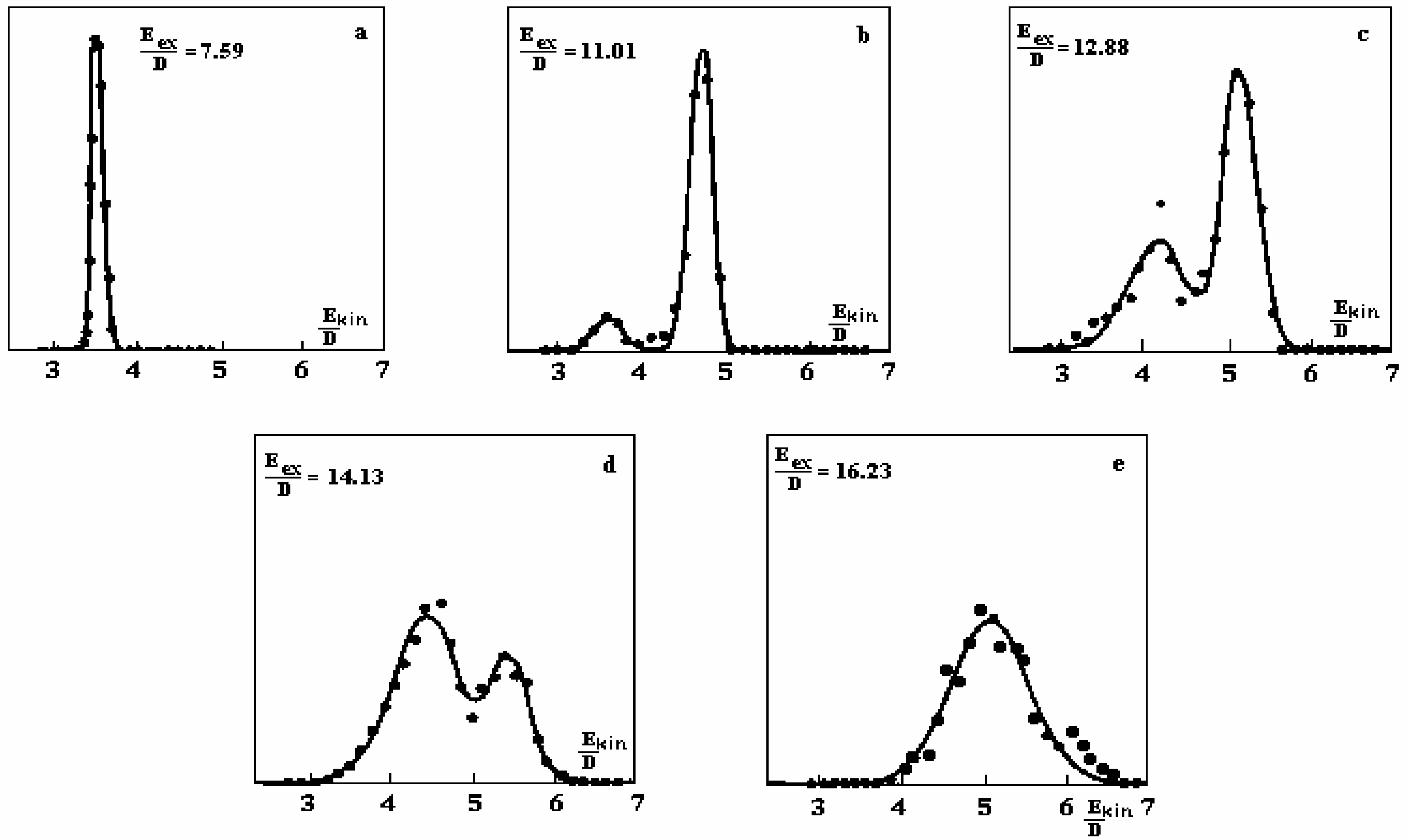


configuration excitation

Character of configuration transitions.

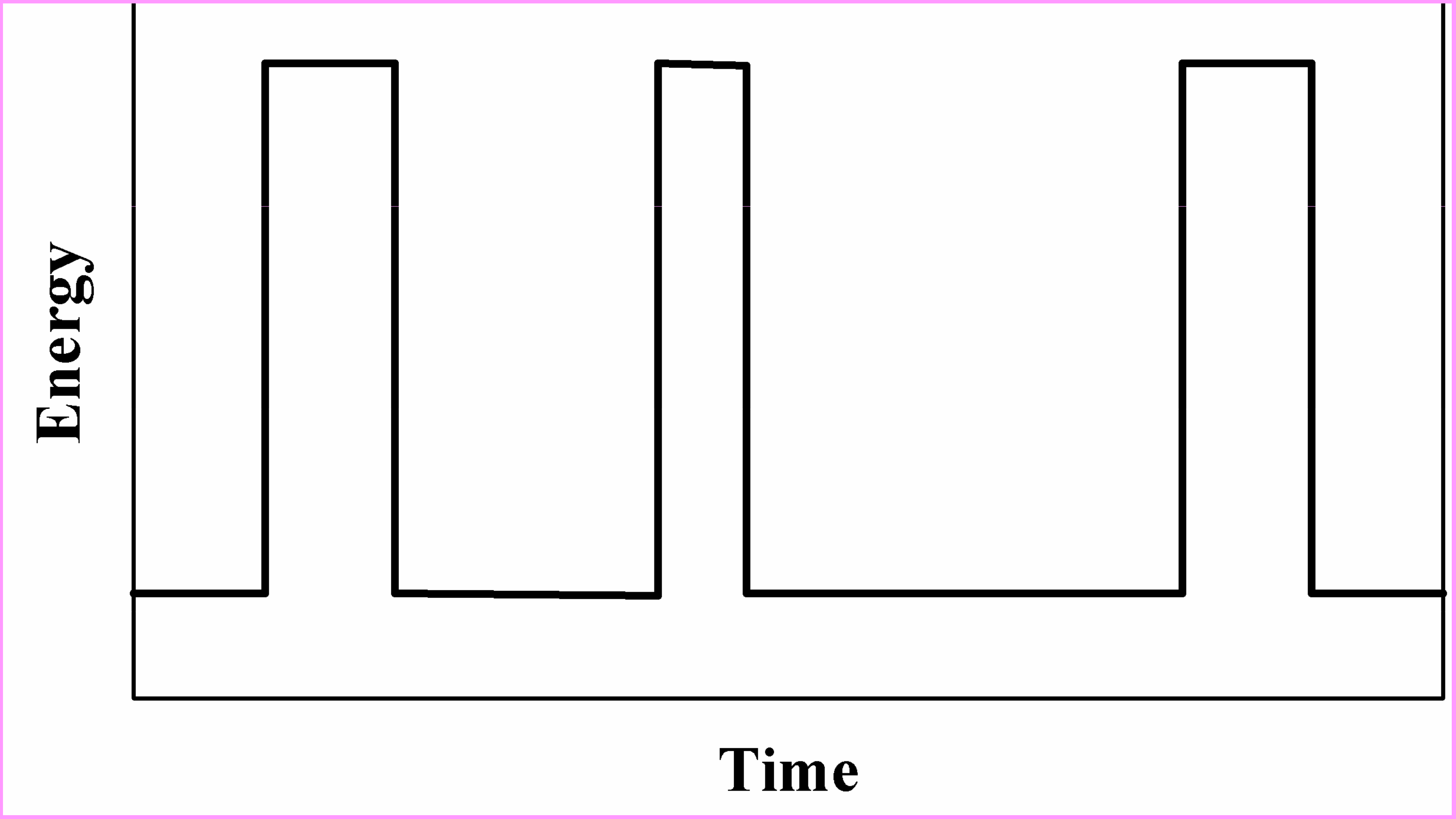


Distribution on kinetic energies isolated 13- atom Lennard- Jones cluster.

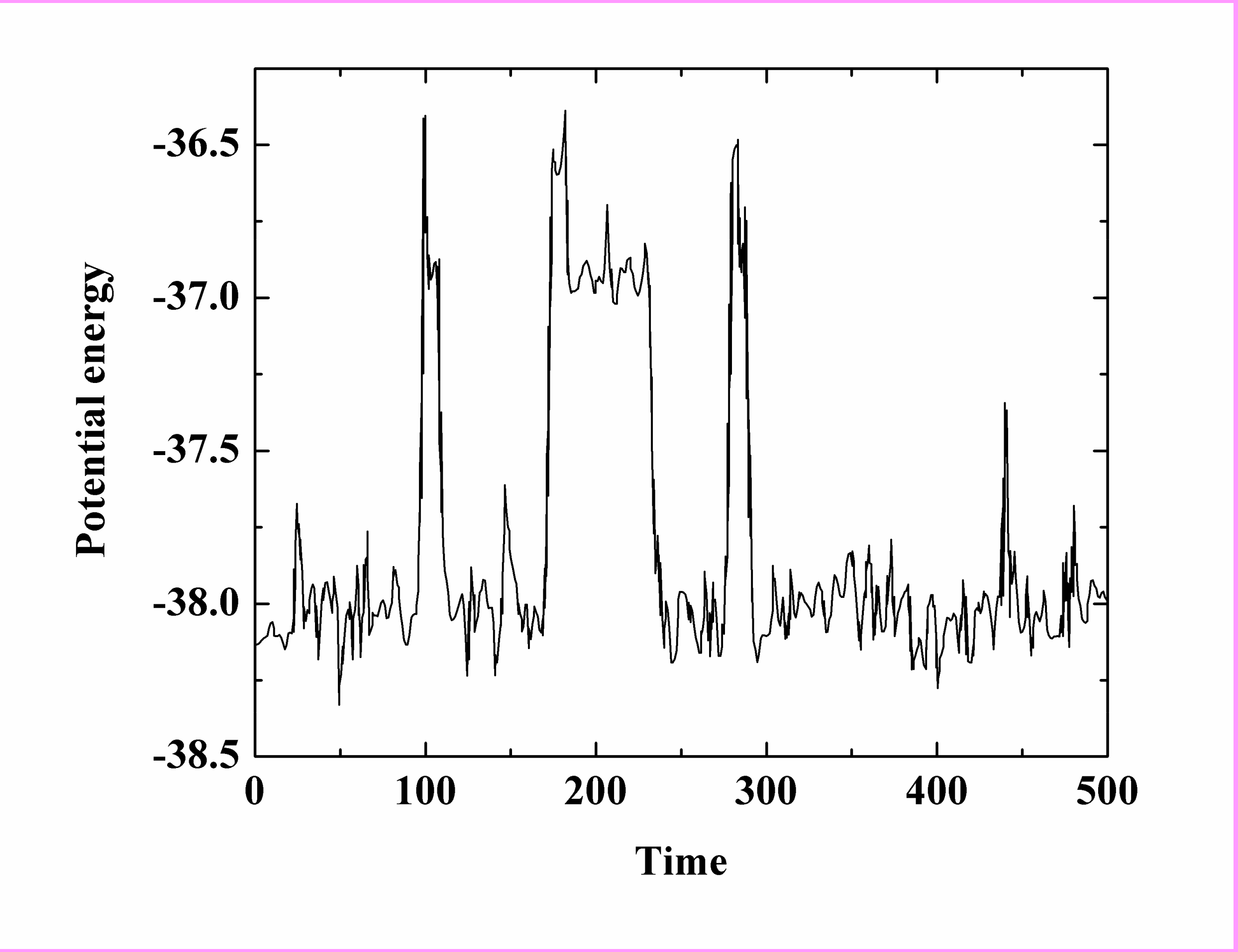


Jellinek,Beck,Berry 1986

Time variation of the cluster energy.



Time variation of the cluster energy (experiment)



Energy of the phase transition under adiabatic conditions.

The energy is $$E_{ex} = U_{sol} + K_{sol} = \Delta E + U_{liq} + K_{liq}$$

The anharmonism parameter is $$\eta = \frac{K}{K + U}$$

U is the potential energy, K is the kinetic energy of atoms.

The transition energy is

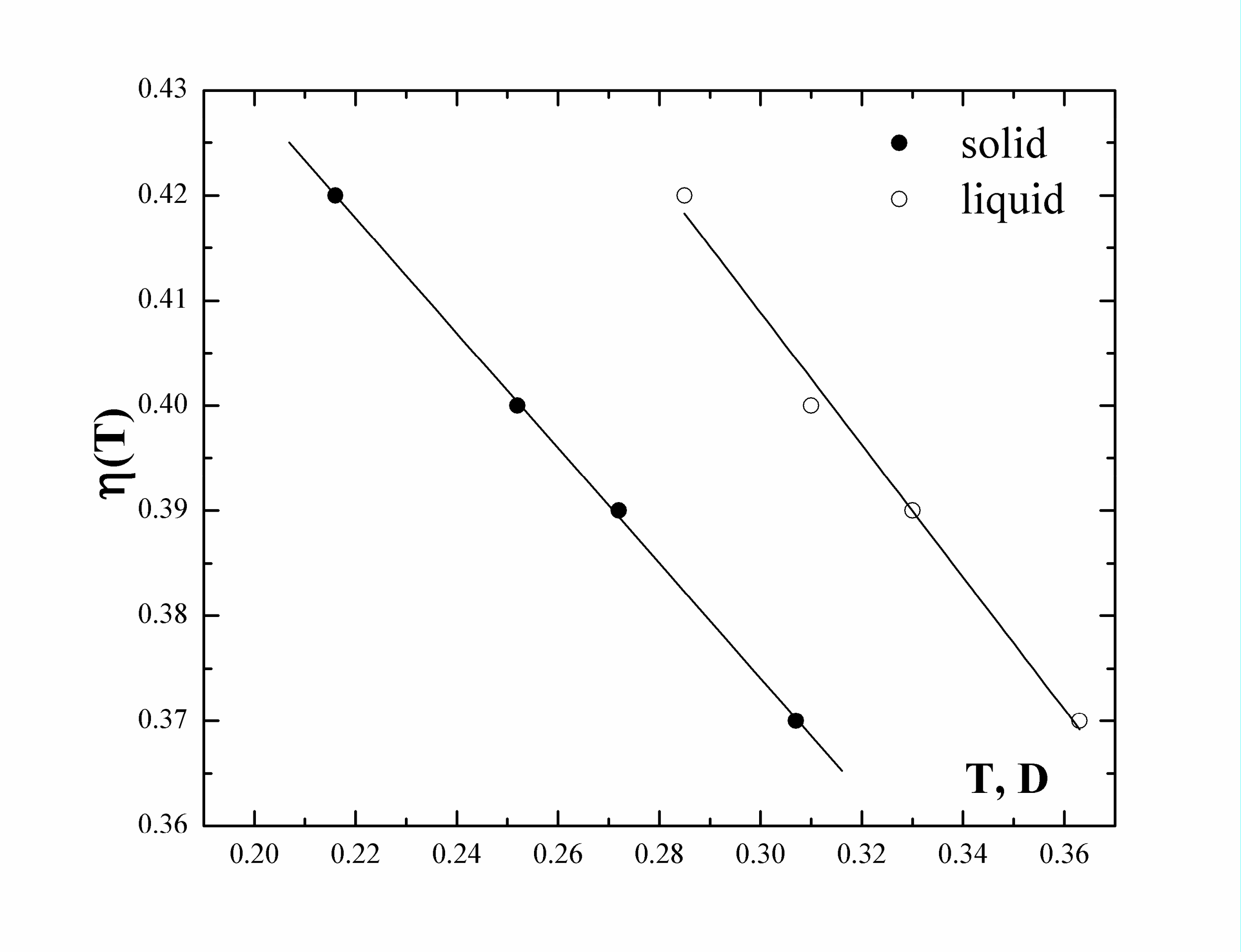
$$\Delta E = \frac{K_{sol}}{\eta_{sol}} - \frac{K_{liq}}{\eta_{liq}} = E_{ex}\left(1 - \frac{K_{sol}}{K_{liq}}\right)$$

For 13-atom Lennard-Jones cluster

$$\Delta E = (2.47 \pm 0.03)D$$

The anharmonicity parameter.

$$\eta = \frac{K}{K+U}$$



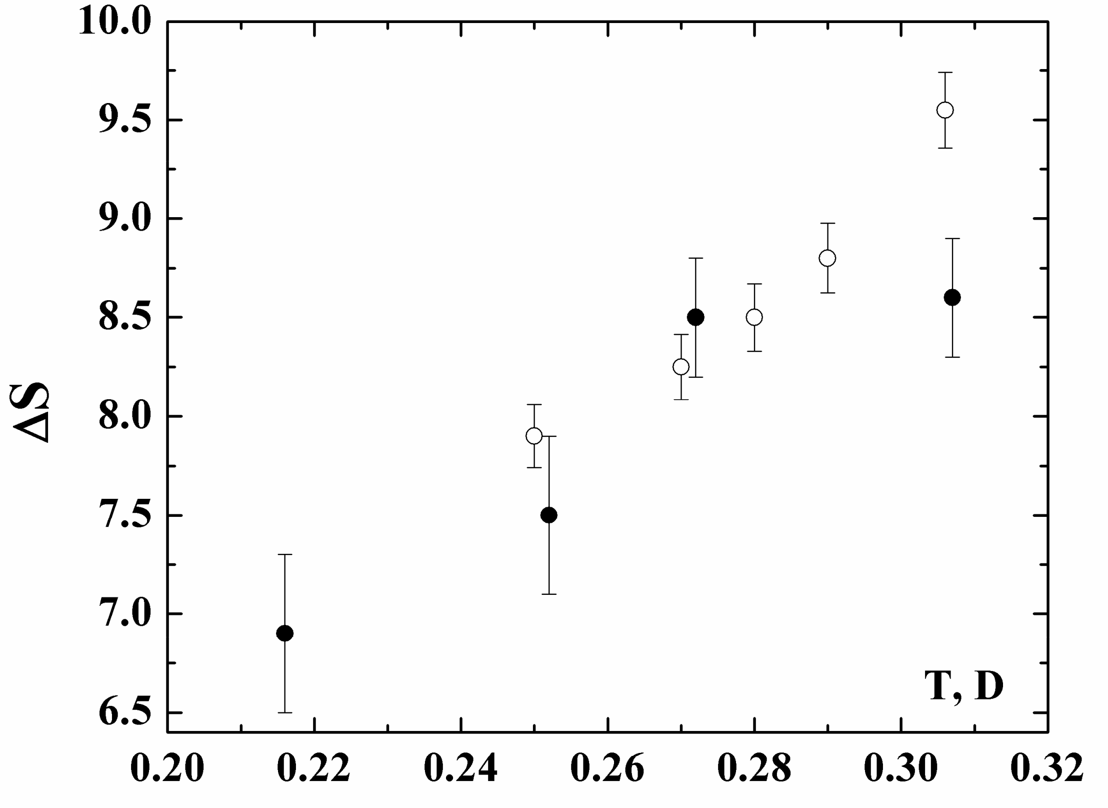
Parameters of the phase transition in the adiabatic case for 13-atom Lennard-Jones cluster.

$$T_{sol}^{m} = \frac{2\eta E_m}{33} = (0.33 \pm 0.01)\, D$$

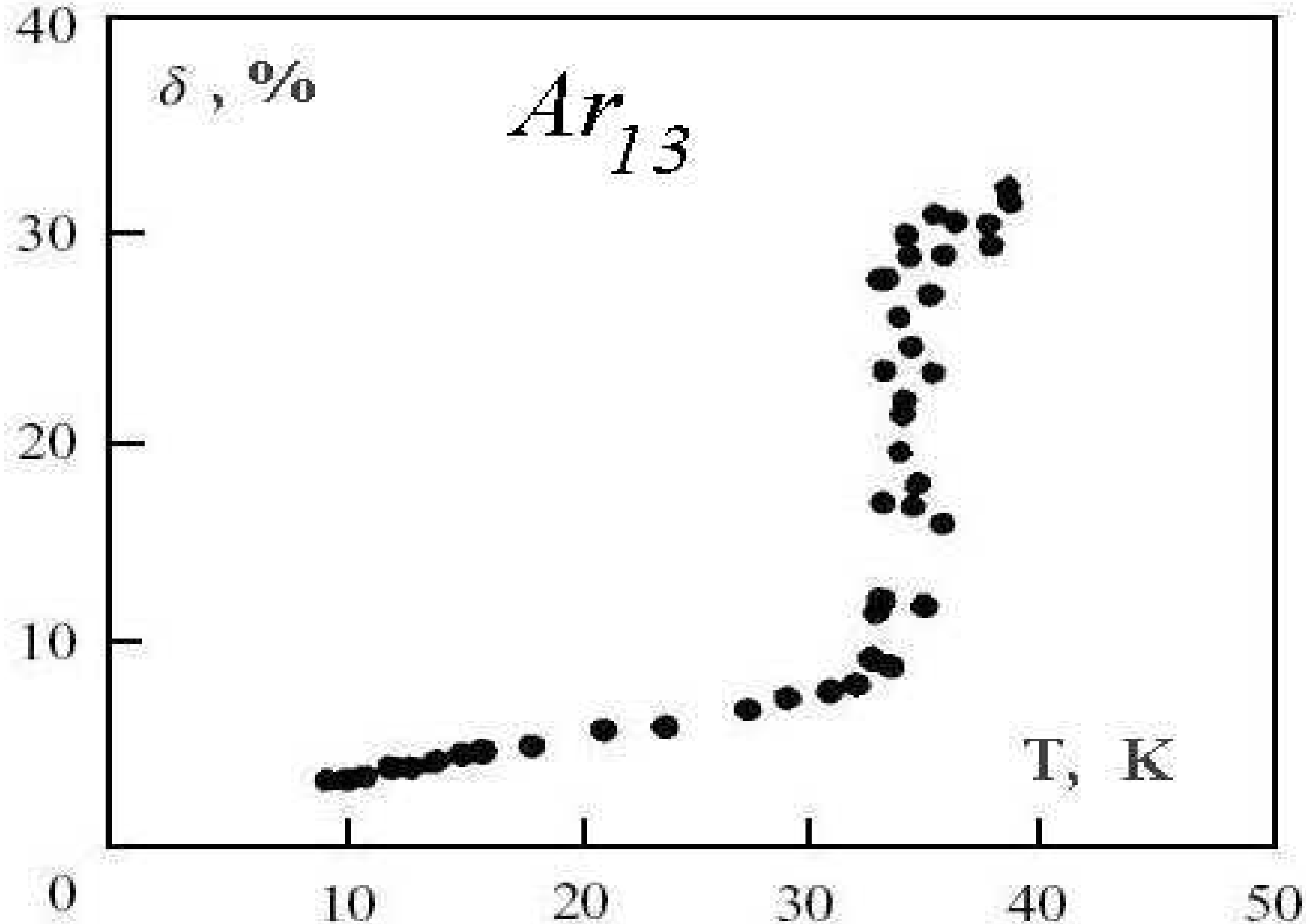
$$T_{liq}^{m} = \frac{2\eta (E_m - \Delta E)}{33} = (0.27 \pm 0.01)\, D$$

$$\Delta T = T_{sol}^{m} - T_{liq}^{m} = \frac{2\eta \Delta E}{33} = (0.057 \pm 0.001)\, D$$

The entropy jump reduced to isothermal conditions.

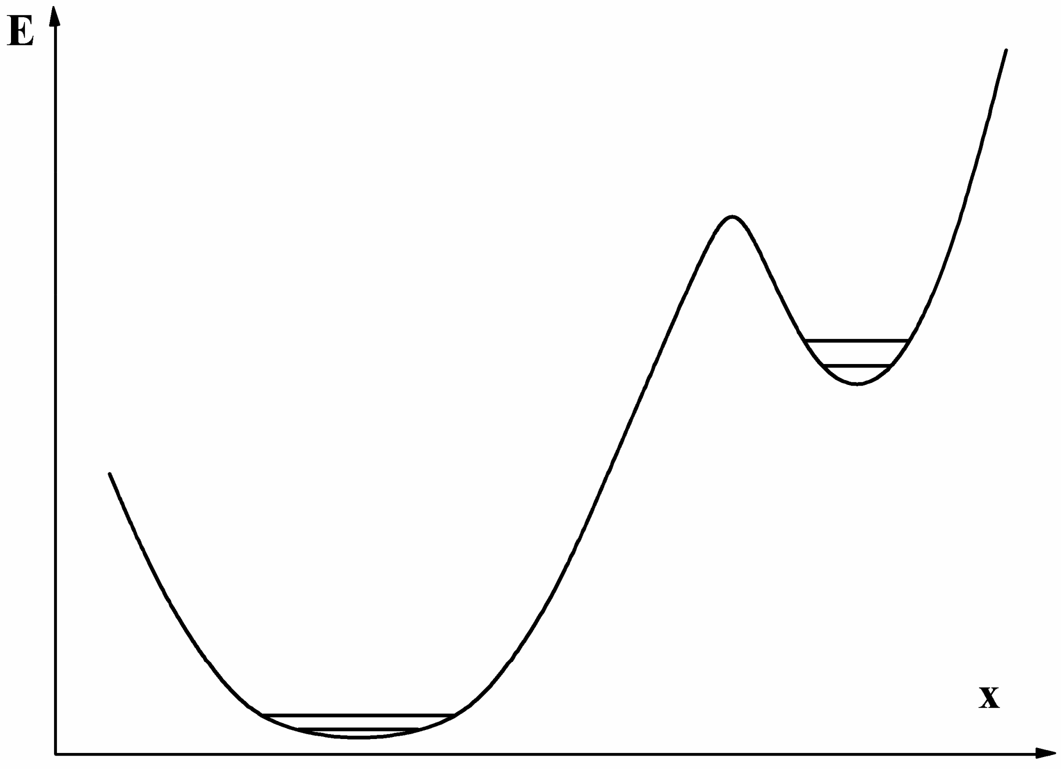


Melting criterion.

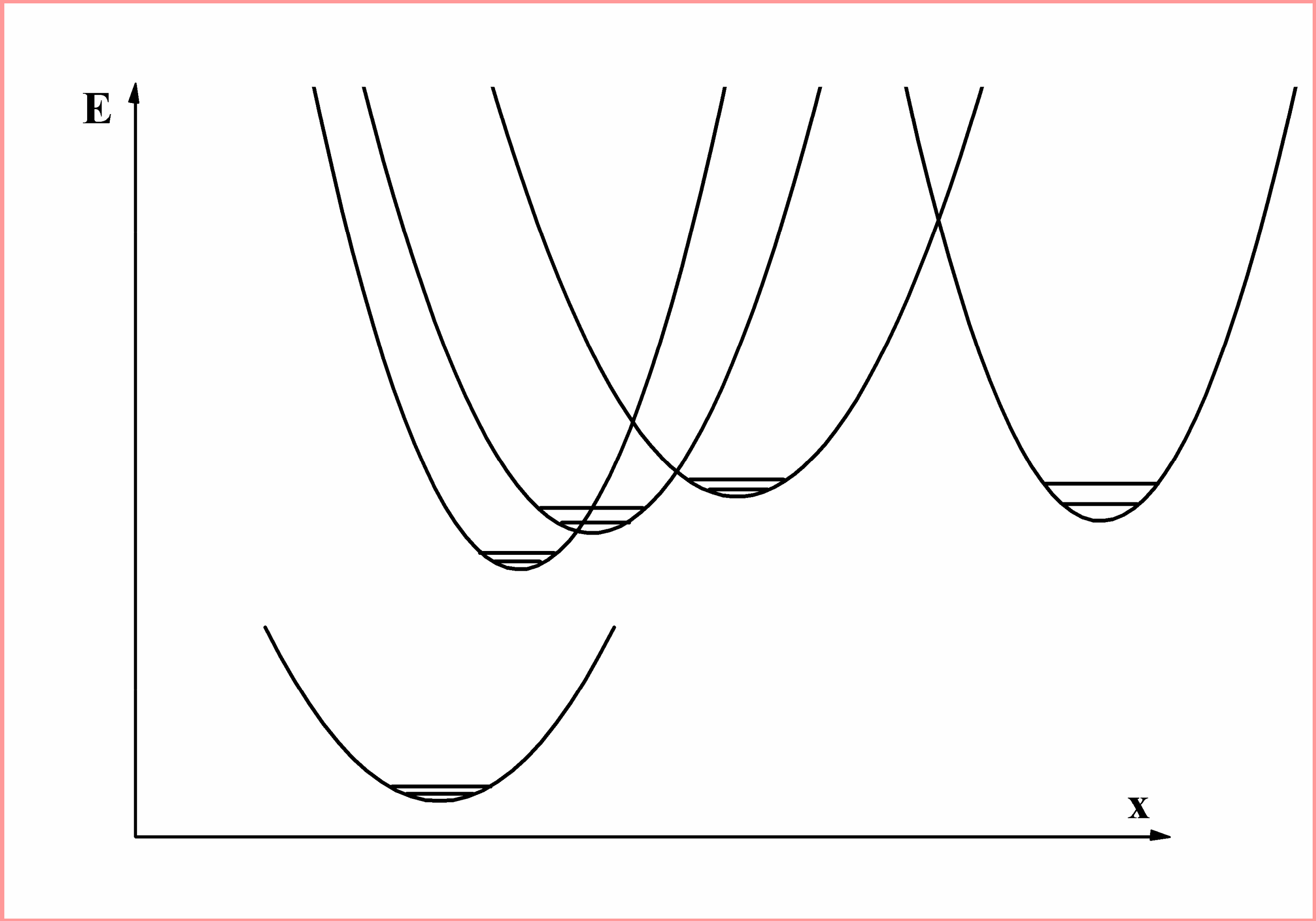


Jellinek, Beck, Berry, 1986

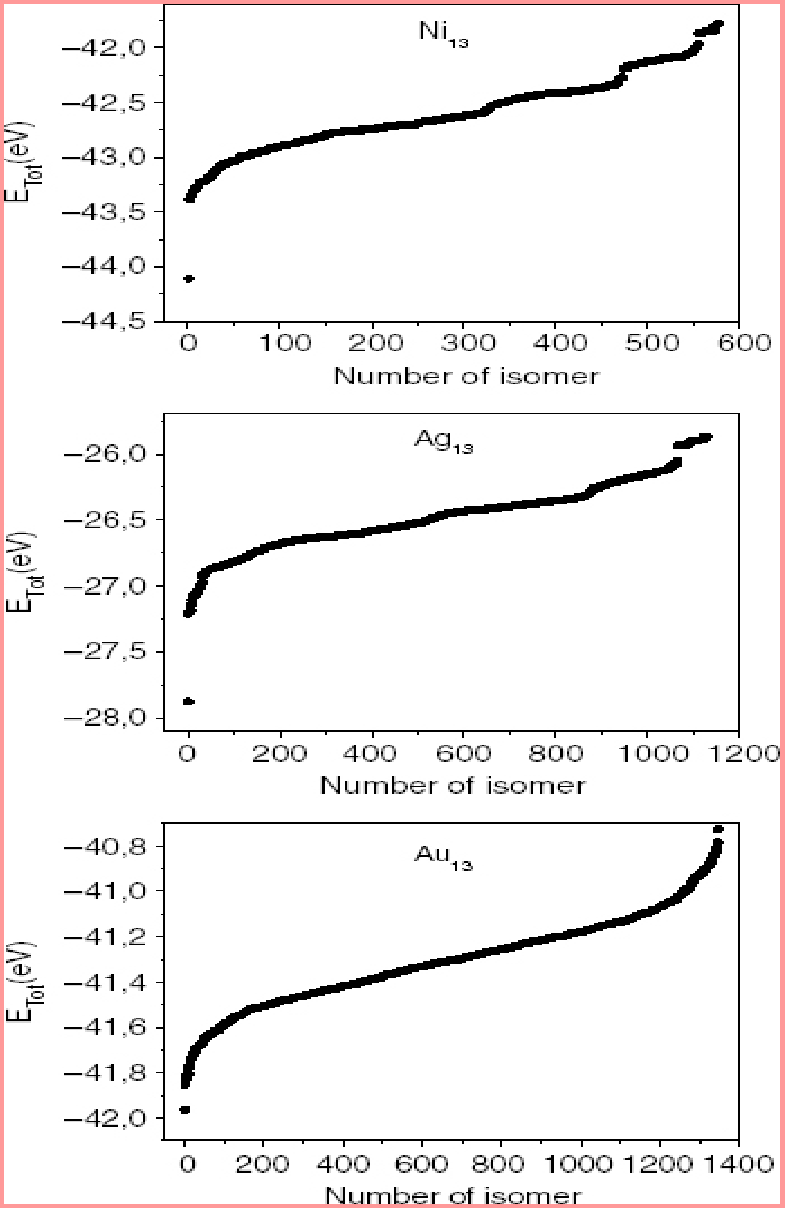
Cross section of the potential energy surface for a dielectric cluster.



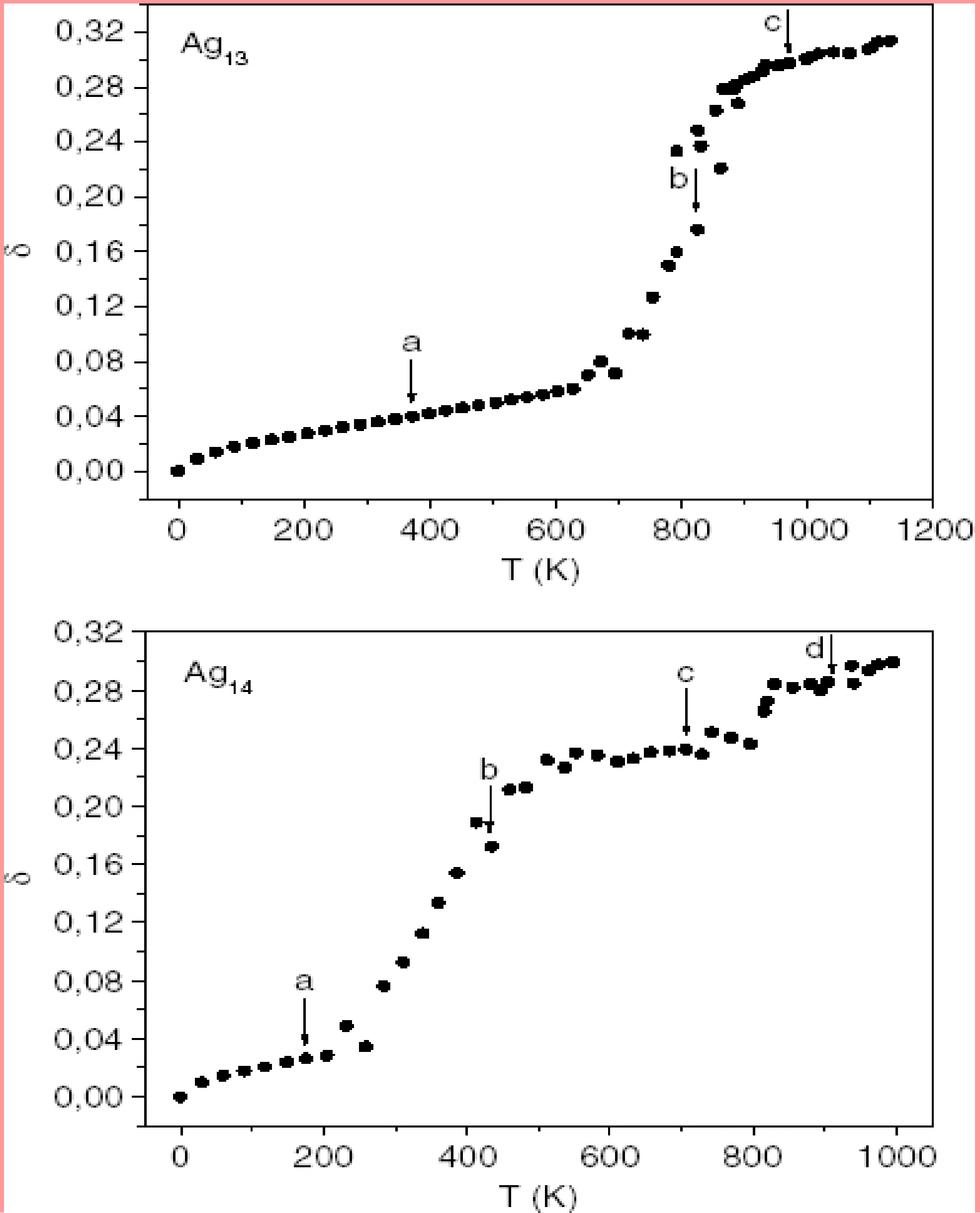
Cross section of the potential energy surface for a metal cluster.



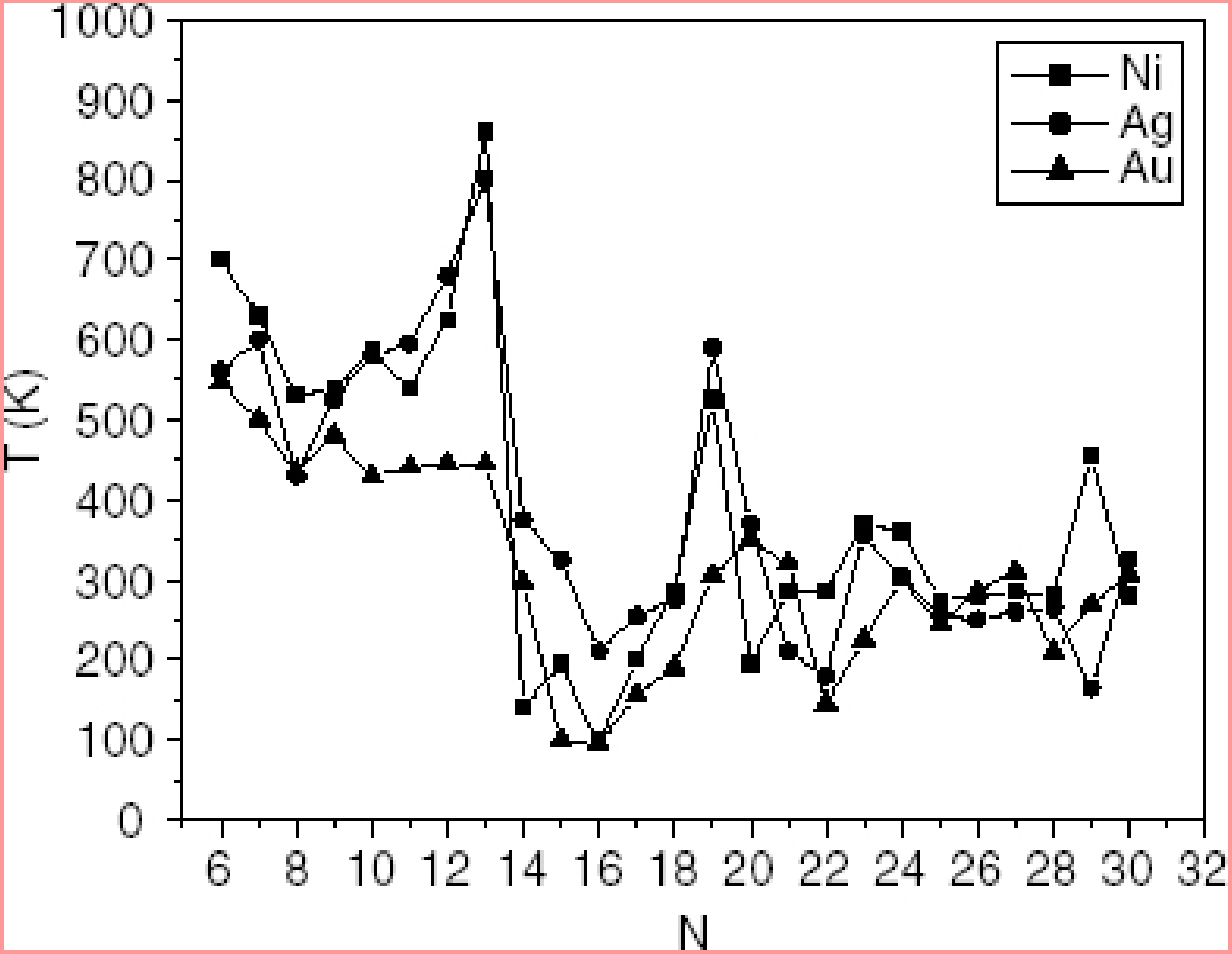
Isomers of metal clusters.



Correlation of cluster atoms at melting.



Melting point via cluster size.



Phase transition of 13-atom silver cluster.

The parameters of the phase transition :
the melting point T_m=820 K,
the kinetic energy of atoms E_{kin}=1.16eV,
the excitation energy at the melting point E_{ex}=2.89eV,
the average potential energy for the solid state U=1.73eV,
the anharmonicity parameter $\eta=E_{kin}/E_{ex}=0.4$,
the entropy jump at the melting point $\Delta S_m = \Delta E/T_m = 16.4$,
the entropy jump at zero temperature $\Delta S_o = \ln 1000 = 6.9$,
$\Delta S_o / \Delta S_m = 0.42$

Coexistence of cluster phases.

$p=w_{liq}/w_{sol}$, w_{liq}, w_{sol} -the probability of the liquid and solid aggregate states.

Define the coexistence range as $0.1 < p < 10$.

The temperature range of phase coexistence is

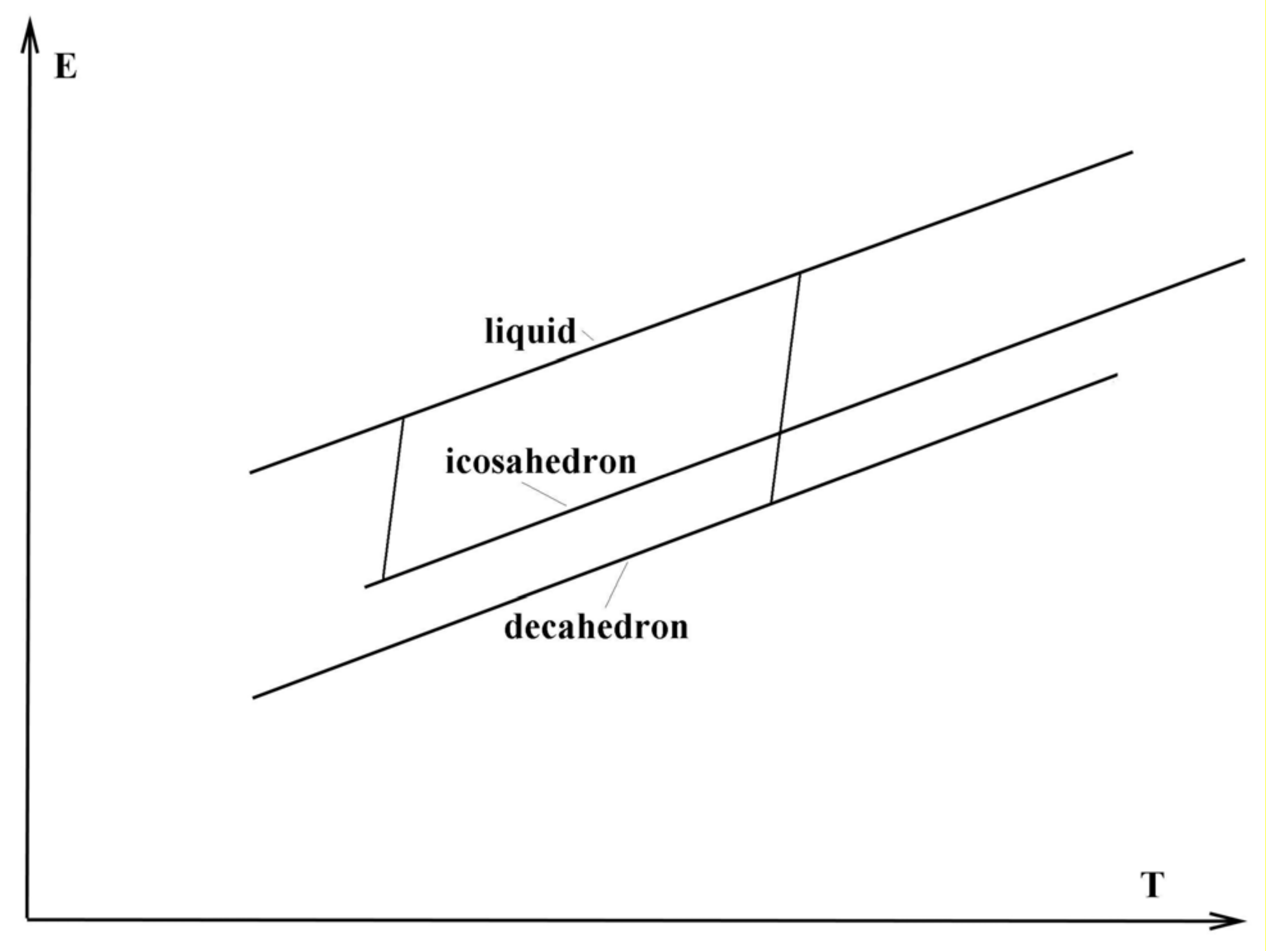
$$\delta T \approx 5/\Delta S$$

The coexistence range for the 13-atom Lennard-Jones cluster with argon parameters is 28-46 K,

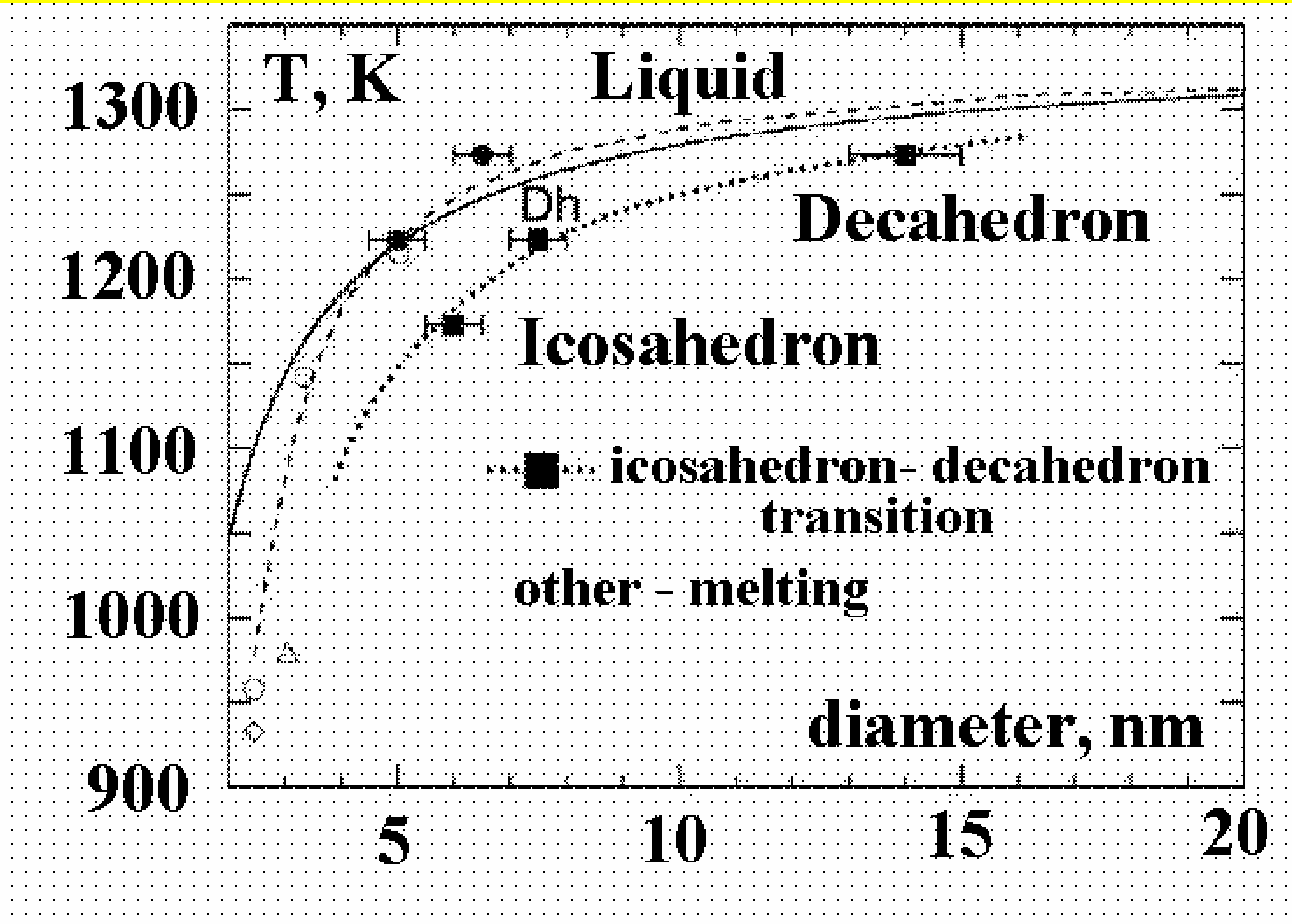
for the 13-atom nickel cluster is 740 - 980 K,

for the 55-atom Lennard-Jones cluster with argon parameters is 40 - 48 K.

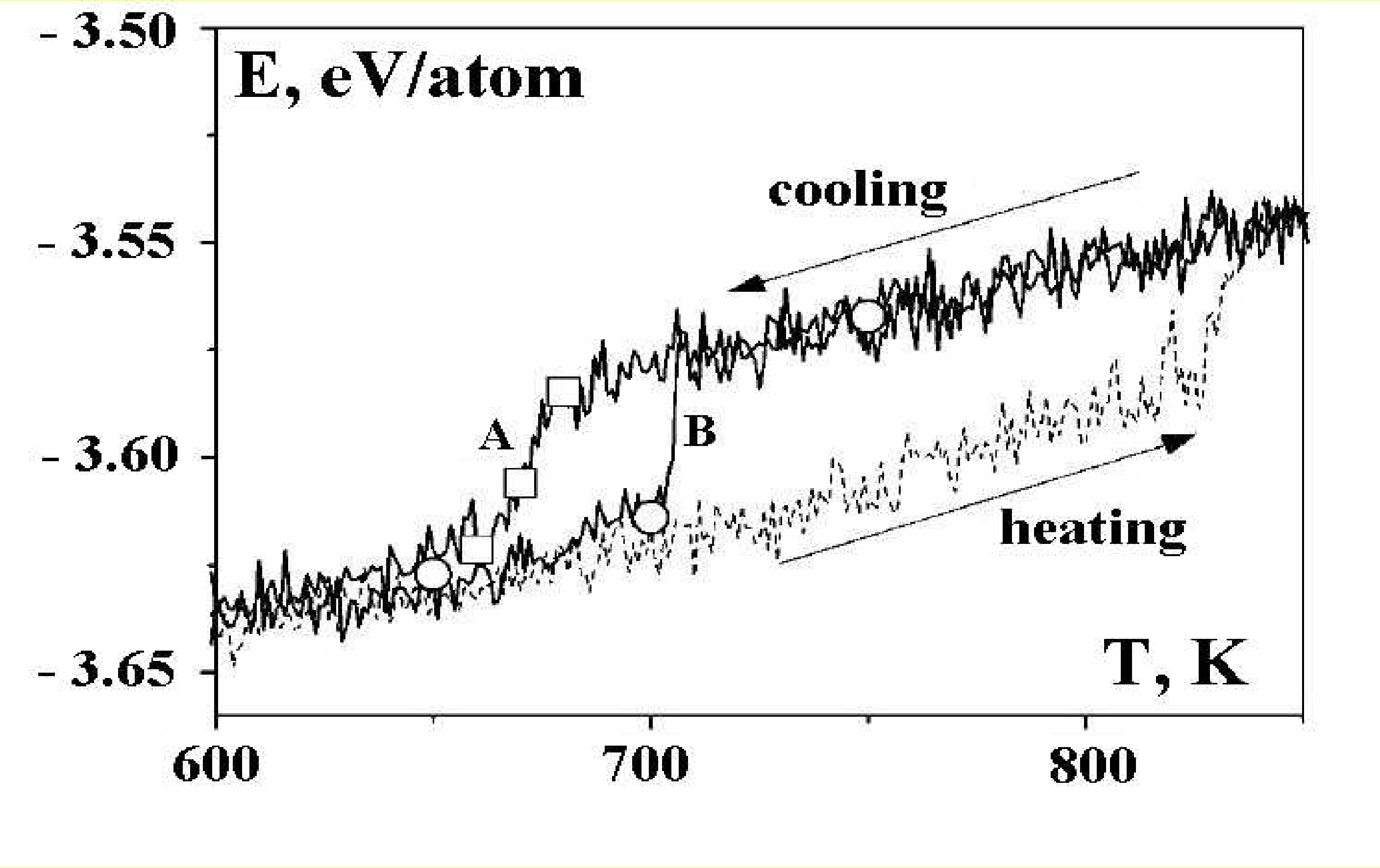
Phase transitions in large metal clusters.



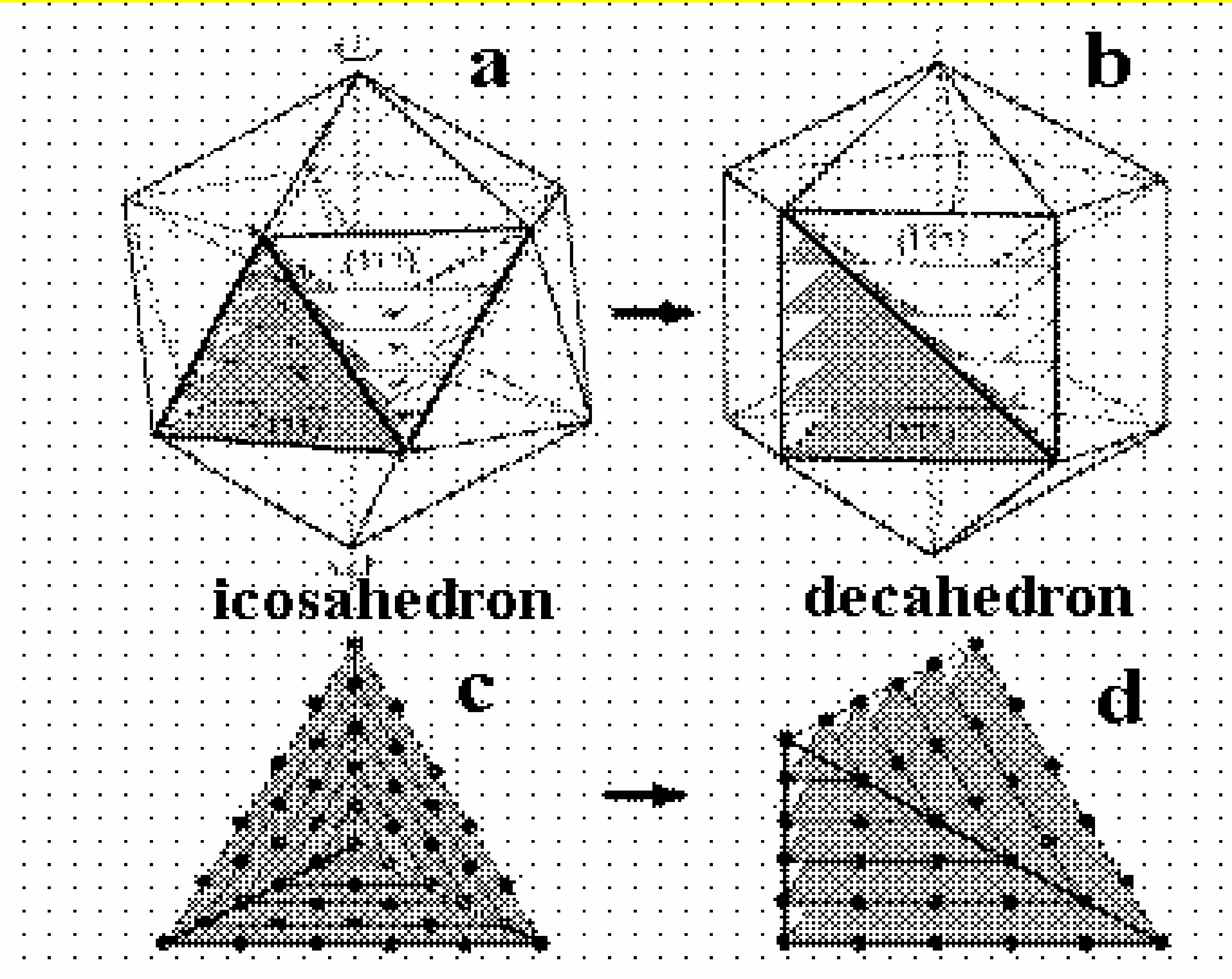
Phase diagram of large gold clusters.



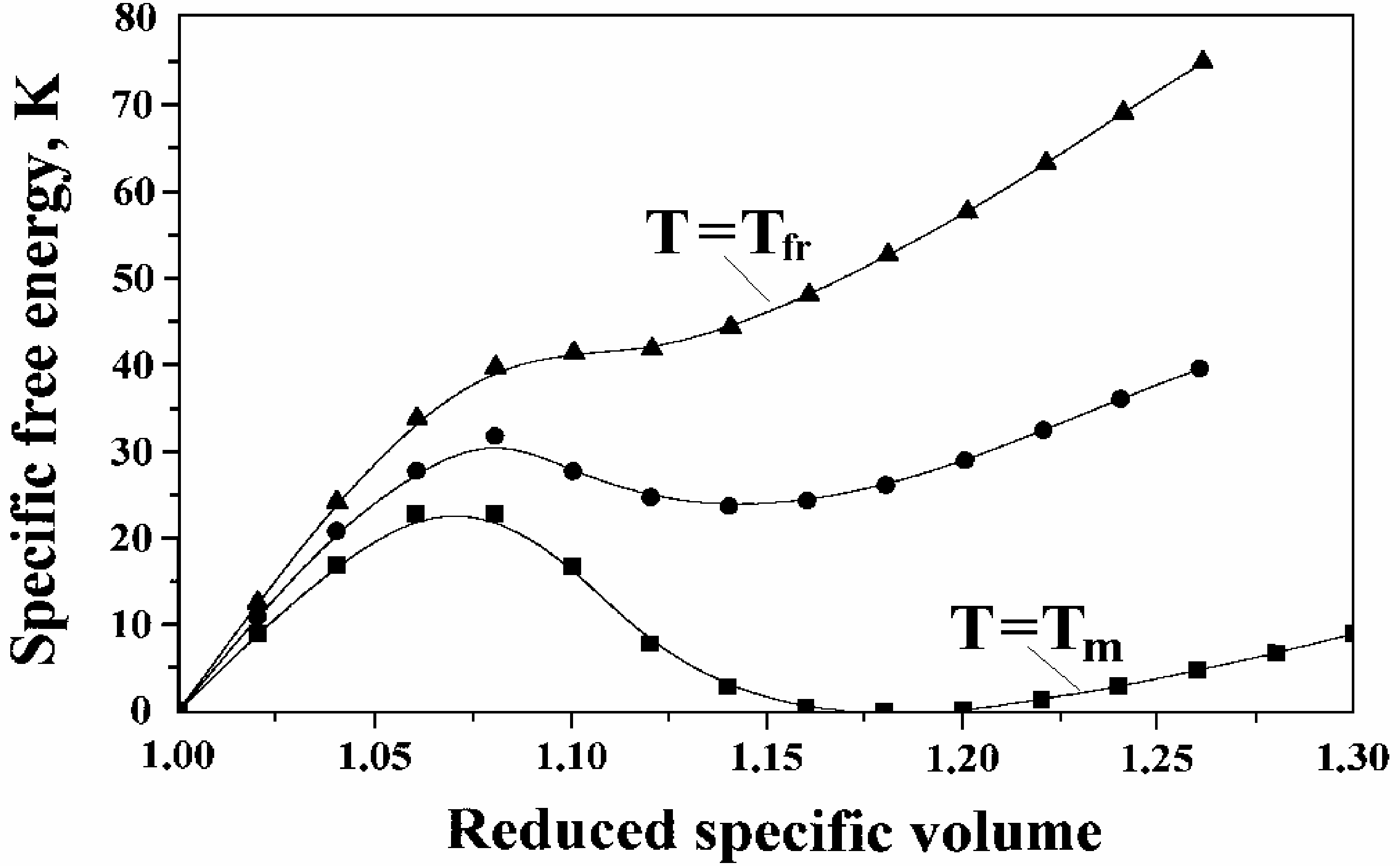
Phase transition of 561-atom gold cluster.



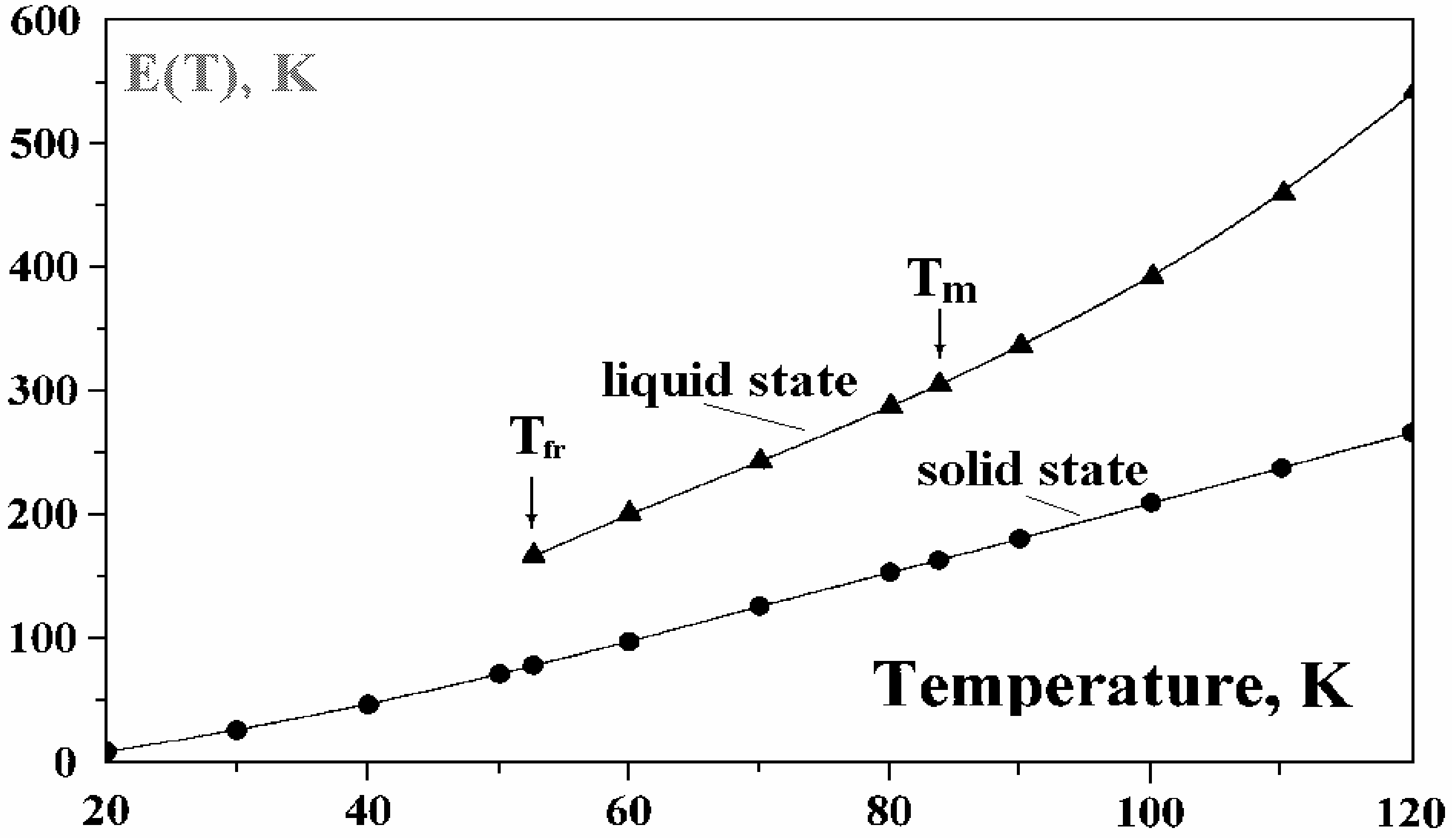
Phase transition icosahedron – decahedron.



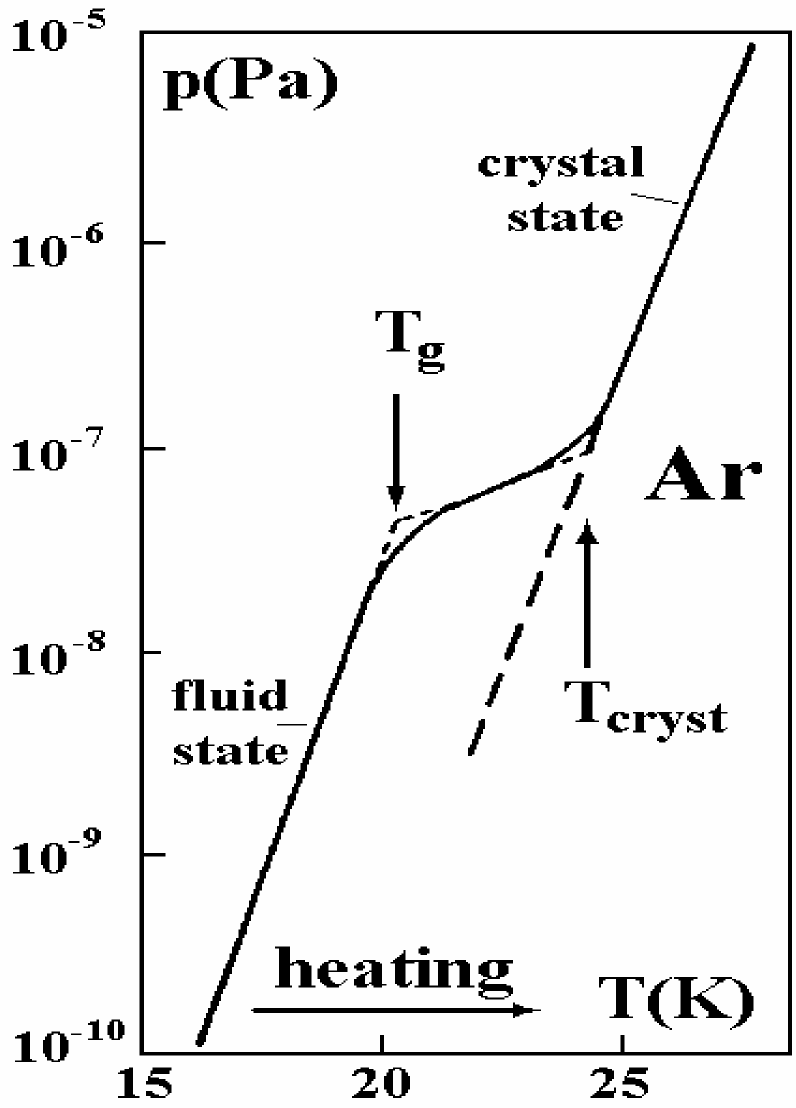
Free energy of bulk argon



Caloric curves for bulk argon



Decay of an argon glassy state.



	Experiment	Theory
T_g ,K	20±1	21
T_{crys} ,K	24±1	23
ε(v), K	730 ±90	790
E_a , K	330 ±20	350

Thank you !