Phase transitions in metal clusters.

Contents.
1. Peculiarities of phase transitions in dielectric clusters.
2. Phase transition in metal clusters.
3. Phase coexistence in clusters.
4. Hysteresis effect in melting of large metal clusters and glassy transition.
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.

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

\[ E_{\text{ex}} = U_{\text{sol}} + K_{\text{sol}} = \Delta E + U_{\text{liq}} + K_{\text{liq}} \]

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

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

For 13-atom Lennard-Jones cluster

\[ \Delta E = \left( 2.47 \pm 0.03 \right)D \]
The anharmonicity parameter.

\[ \eta = \frac{K}{K + U} \]
Parameters of the phase transition in the adiabatic case for 13-atom Lennard-Jones cluster.

\[ T_{\text{sol}}^m = \frac{2\eta E_m}{33} = (0.33 \pm 0.01) D \]

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

\[ \Delta T = T_{\text{sol}}^m - T_{\text{liq}}^m = \frac{2\eta \Delta E}{33} = (0.057 \pm 0.001) D \]
The entropy jump reduced to isothermal conditions.
Melting criterion.
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.

- $\text{Ni}_{13}$
- $\text{Ag}_{13}$
- $\text{Au}_{13}$
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 $E_{\text{kin}} = 1.16 \text{eV}$,
the excitation energy at the melting point $E_{\text{ex}} = 2.89 \text{eV}$,
the average potential energy for the solid state $U = 1.73 \text{eV}$,
the anharmonicity parameter $\eta = E_{\text{kin}} / E_{\text{ex}} = 0.4$,
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.

$p = \frac{w_{\text{liq}}}{w_{\text{sol}}}, w_{\text{liq}}, w_{\text{sol}}$ - 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

$$\delta T \approx \frac{5}{\Delta S}$$

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.

![Diagram showing phase transitions in large metal clusters.](image)
Phase diagram of large gold clusters.
Phase transition of 561-atom gold cluster.
Phase transition icosahedron – decahedron.
Free energy of bulk argon

![Graph showing specific free energy against reduced specific volume for different temperatures. The temperatures are labeled as $T=T_m$ and $T=T_r$. The graph illustrates the relationship between specific free energy and the reduced volume at various temperatures.](image-url)
Caloric curves for bulk argon
Decay of an argon glassy state.

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>Theory</th>
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<tbody>
<tr>
<td>$T_g$, K</td>
<td>20±1</td>
<td>21</td>
</tr>
<tr>
<td>$T_{crys}$, K</td>
<td>24±1</td>
<td>23</td>
</tr>
<tr>
<td>$\varepsilon(v)$, K</td>
<td>730 ±90</td>
<td>790</td>
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<tr>
<td>$E_a$, K</td>
<td>330 ±20</td>
<td>350</td>
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Thank you!