



Note that in every atom condensation step, the binding energy is transferred to the cluster, thereby heating it up. The released energy is for small clusters sufficient to heat it over the melting point. Thus small clusters are formed in their equilibrium shape. Clusters formed this way are usually hot when they leave the cluster formation area. Either special care is exercised to thermalize clusters or one has to take into account atom evaporation from clusters. See Fig 5.5

5.3. Cluster temperature, evaporation and magic clusters

Although in classical thermodynamics temperature is defined only in the limit of large particle numbers, one may generalize the concept of temperature to finite size objects.

$$\frac{KT}{2} = \frac{\langle E_{\text{kin}} \rangle}{3N-6} = \frac{1}{3N-6} \sum_{\text{atoms } i} \frac{1}{2} m \langle v_i^2 \rangle$$

Here $3N-6$ = # degrees of freedom of the cluster and $\langle \rangle$ denotes a time average over a suitable period τ . Note that on a short time scale temperature defined in this way fluctuates considerably due to

variations in the distribution of energy in potential and kinetic. Due to heating by the heat of condensation clusters are usually very hot at the end of their growth phase. They lose energy and thereby temperature through evaporation

$$X_N(E_N) \rightarrow X_{N-1}(E_{N-1}) + X$$

with
$$E_{N-1} = E_N - D_N - \epsilon_{\text{kin}}$$

where D_N is the dissociation energy for an atom of cluster size N and ϵ_{kin} is the (usually small) kinetic energy transported away by the dissociated atom. Due to dissociation the cluster cools.

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See Fig 5.6. The rate of cluster dissociation events can be shown to be

$$k_N(E) = \nu \cdot g e^{-\frac{D_N}{kT}}$$

with $\nu = 10^{12} - 10^{13}$ Hz, a typical value for vibration frequencies

g = degree of degeneracy $\sim N_s$ = # surface atoms

T = cluster temperature

Mass spectra usually display a convolution of the cluster growth distribution with the cluster evaporation rates. The cluster distributions are therefore also termed "evaporative ensemble".

If the dissociation energy D_N for a given cluster size is especially large, then evaporation from this cluster size will be especially difficult. Strongly structured mass spectra therefore are usually a consequence of evaporation processes from hot clusters. Large abundances are observed for especially stable cluster sizes.

Fig 5.7 displays two mass spectra of Na and Ar.

Na displays "electronic magic numbers" 8, 20, 40 which we will consider below, they are not related to structure.

Ar displays "structural magic numbers", especially the large abundance of cluster size 55 is visible, indicative for the icosahedral structure.

Fig 5.8 displays two more examples for structural magic numbers.

5.4. Cluster electronic structure

It is evident that if we go from the atoms to the bulk solid the discrete atomic and molecular levels spread to bands as we discussed in solid state physics course. This is especially obvious in the tight binding model. Let us view the behavior of free-electron-like metals from a different viewpoint: If we confine the free electron gas of the valence band to a cluster geometry, quantization effects will take place.

We may consider a small metal cluster to first approximation as small

spherical droplet. If we apply the jellium model (the nuclear charge forms a uniform positive background) we may consider the electrons to move in a radially symmetric potential formed by the positive background and the average electron density of the other electrons. As we know from atomic physics every radially symmetric potential gives rise to wave function solutions which separate into radial and angular solutions. The angular solutions given by the Y_{lm} have a degeneracy of $2(2l+1)$ for each l . That the states l to a given radial quantum number n are degenerate is a special property of the Coulomb potential and is generally not true. Fig. 5.9 displays electronic energy levels for different radially-symmetric potentials schematically. Cluster energy spectra are similar to those of nuclei and follow their nomenclature. Fig. 5.10 displays a beautiful confirmation of the jellium model. In the theoretical curve the energy differences $\Delta(N+1) - \Delta(N)$ are plotted with $\Delta(N) = E(N) - E(N-1)$. Even fine details in the mass spectra become understandable, if one allows also for distortions of the cluster shapes. Fig. 5.11 displays photoelectron spectra of negatively charged ions [for negatively charged ions there is no Coulomb energy needed to remove a photoelectron]. These spectra directly confirm the existence of atom like spectra of the electron gas in clusters.

Another nice example for unique effects in cluster electronic structure is displayed in Fig. 5.12. The electronic structure of Hg is $[Xe] 4f^{14} 5d^{10} 6s^2$. Hg is metallic due to the overlap of the 6s and 6p bands within a bulk solid. For a cluster the discrete 6s and 6p levels split into a bunch of levels (indicated in the middle panel of Fig. 5.12 as narrow bands) which are separated by a large band gap, which closes only for $N > 400$ atoms.

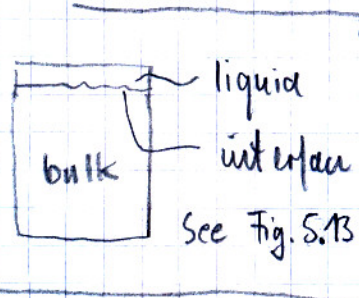
5.5 Surface melting

Let us consider first an extended solid. A solid melts as due to increasing temperature the vibration amplitudes of the bulk atoms exceed a critical value given by the Lindemann criterion:

$$\frac{\langle u^2 \rangle}{a}^{\frac{1}{2}} > 0.1 - 0.15, \quad a = \text{nn-distance}$$

In the interior of the bulk the atoms are properly coordinated, but at the surface their coordination is lower. Already at about $0.9 T_m$ the Lindemann criterion is full filled for surface atoms. Thus the

first few atom layers melt already below T_m and an interface between the molten layers and the bulk is formed. Upon approaching



T_m the liquid layer thickens and diverges at T_m .

Note that interface energy γ is associated with the formation of the interface between the liquid layer and the solid. The existence of the liquid surface

layer below T_m explains also why it is impossible to superheat a solid. The energy to form the interface between the new phase (the

liquid) and the old phase (the solid) is already paid below T_m - no nucleation barrier exists. To the contrary, it is well possible to undercool liquids as the new crystalline phase has to be formed with an interface to the liquid. The nucleation barrier may be lowered by impurities, limiting the possible undercooling.

Surface melting has important consequences. The low friction of snow relies on the liquid surface layer. It is not due to pressure induced melting as frequently stated. Below -40°C the liquid

surface layer on snow is frozen out. When Robert F. Scott was approaching the South Pole in 1912 he experienced record low temperatures. He wrote in his diary that his skis move like on

gravel. Probably the freeze out of the liquid layer contributed to the exhaust of his expedition and the death of the group. For clusters the Lindemann criterion can be rewritten

$$\frac{2}{N(N-1)} \sum_{i < j} \frac{\langle \Delta r_{ij}^2 \rangle^{\frac{1}{2}}}{\langle r_{ij} \rangle} \approx 0.03 - 0.05$$

We replaced the nn-distance by $\langle r_{ij} \rangle$ and the amplitude Δ by the variance of the nn-distance. Clusters melt at lower temperatures than solids, as there is an additional driving force to move the interface into the solid: Upon shrinking inwards interface energy is gained.

However this effect alone is not sufficient to explain melting temperatures up to 30% lower than for the bulk. Also the great fraction of surface atoms itself is important for destabilization.

For large clusters

$$T_m(N) = T_m(\infty) \cdot \left(1 - \frac{C}{N^{\frac{1}{3}}}\right)$$

For small cluster melting temperature depends significantly on structural details. Magic number cluster (closed icosahedral shell) are of enhanced stability. Detailed measurements for Na are shown in Fig 5.14

5.6 Cluster magnetism

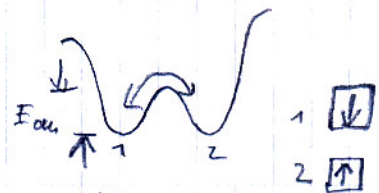
Clusters have different structures and different nearest neighbour distances compared to the corresponding bulk material. Therefore it is not surprising that the exchange interaction may induce ferromagnetism for materials which are in their bulk form not ferromagnetic. A famous example are small Rh-clusters for which the atomic spins couple to a total magnetic moment.

Clusters, which are from their nature ferromagnetic display a unique behaviour at sufficiently small sizes or large temperatures, which is termed superparamagnetic. Remember that ferromagnetic materials

have their magnetic moments coupled and oriented in specific directions with respect to the crystal lattice. As the charge distributions of atoms in a crystal are usually not radially symmetric but related to the crystal lattice. Due to spin-orbit coupling the preferred spin directions are coupled to the orbital moment. Rotating the spin moment out of the preferred directions costs thus energy, exchange energy and electrostatic interaction energy (comp. Fig. 5.15). Bulk ferromagnets are usually multidomain materials to minimize stray fields. Upon decreasing size the particles display single domains. When the size decreases further, the total anisotropy energy E_{an} becomes comparable with kT .

Then through thermal fluctuations the direction of magnetisation may fluctuate with a frequency

$$\gamma = \gamma_0 e^{-E_{an}/kT}$$



with γ_0 = attempt frequency of the order of 10^{10} Hz.

The temperature at which flipping of magnetisation disappears on the experimental time scale is called blocking temperature. The existence of the superparamagnetic limit is of profound importance for the miniaturization limits of magnetic data storage.

5.7 Supported clusters

Although cluster properties can be studied for free cluster beams in the vacuum, if one wants to apply clusters to something useful, one has to support or embed clusters on or to solid or liquid phases.

Applications of supported or embedded clusters are

- catalysis
- magnetic data storage
- plasmonics (for optics and biology)