

Hanson 1

Caloric curve by MD

Caloric curve: definition

- The caloric curve plots the average energy (e.g., total energy or potential energy per atom) or temperature of the cluster as a function of the total energy input or heat added.
- Typically, it's expressed as temperature (T) (or $k_B T/\epsilon$) versus total energy E/ϵ or potential energy per atom $\langle U \rangle/N\epsilon$, where k_B is the Boltzmann constant.
- The curve reveals thermodynamic properties, including phase-like transitions (e.g., solid-like to liquid-like) in finite systems, which differ from bulk phase transitions due to the absence of sharp discontinuities.

Physical meaning

- **Solid-Like to Liquid-Like Transition:** For small LJ clusters (e.g., $N = 13$), the caloric curve shows a characteristic “loop” or plateau, indicating a melting-like transition. This is due to the coexistence of solid-like (ordered, icosahedral) and liquid-like (disordered) states over a range of energies.
- **Liquid-Like to Gas-Like Transition:** For larger clusters or higher energies, evaporation or fragmentation may occur, though this is less common in small, isolated clusters.
- **Finite-Size Effects:** Unlike bulk systems, LJ clusters exhibit broadened transitions and size-dependent melting temperatures, with “magic number” clusters (e.g., $N = 13, 55$) showing distinct stability due to geometric packing (e.g., icosahedral structures).

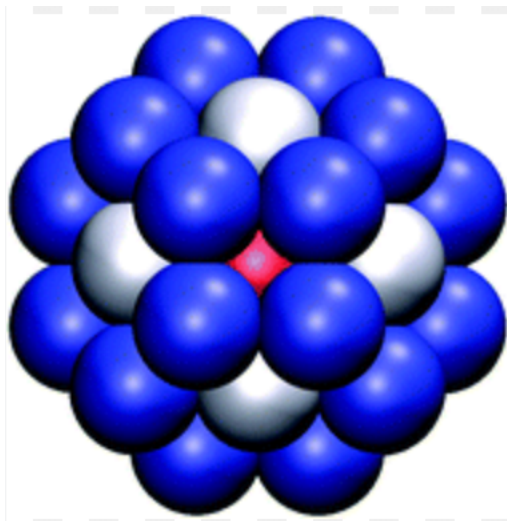
Application to LJ clusters

- The LJ potential models pairwise interactions between neutral atoms (e.g., noble gases like argon) and is given by:

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$$

where (r) is the distance between atoms, ϵ is the depth of the potential well (interaction strength), and σ is the distance at which the potential is zero (characteristic length scale).

- LJ clusters consist of (N) atoms interacting via this potential, forming finite systems (e.g., $N = 13, 55, 147$) that exhibit size-dependent properties.



How to calculate the curve

Choose cluster size

Common sizes: LJ₁₃, LJ₃₈, LJ₅₅, etc.

You'll want to simulate a fixed number of particles under **microcanonical (NVE)** or **canonical (NVT)** conditions.

Generate Initial configurations

- Place atoms in a minimum-energy geometry (use e.g. icosahedral structures for LJ₁₃, etc.)
- Add random velocities to atoms corresponding to different total energies or temperatures.

Run MD simulations

- Use either **NVE (constant energy)** or **NVT (with a thermostat)** MD.
- Simulate at various energy levels.
- For each energy level, compute the **temperature** using the equipartition theorem:

$$T = \frac{2}{3Nk_B} \langle K \rangle$$

Where K is the kinetic energy, and $\langle \cdot \rangle$ denotes time average.

Note: in reduced LJ units, $k_B = 1$.

Compute and plot the caloric curve

For each simulation point:

- Average total energy (or internal energy) E
- Corresponding temperature T

Plot:

E vs. T

This is your **caloric curve**.

You may observe:

- **Smooth regions** at low and high T (solid-like and gas-like phases)
- **Backbending or plateau** in the middle (melting-like transition in clusters)

To locate transitions, analyse specific heats

You can calculate the **heat capacity** as:

$$C = \frac{dE}{dT}$$

This can help identify transition-like features more clearly.

The MD code

for this hands-on lecture, a minimal MD code will be provided: “verlet.f”

the input is set modifying the file “verlet.in”, see below

```
5          read(5,*) natom
30000      read(5,*) nstep
000        read(5,*) neq
1          read(5,*) nene
1          read(5,*) ntraj      !# traiettorie per ogni energia
-1.4 -2.4,-0.8,-2.8,-2.7,-2.6,-2.5,-2.4,-2.3,-2.2,-2.1,-2.0,-1.9,-1.8,-1.7,-1.6,-1.5,-1.4,-1.3,-1.2,-1.1,-1.0,-0.9,-0.8,-0.7,-0.6,-0.5,-0.4
, -0.9,-0.8,-0.7,-0.6,-0.5,-0.4      read(5,*) (etot(i),i=1,nene)
1.0        read(5,*)  eps
1.0        read(5,*)  sigm
0.001      read(5,*)  dt
6.0        read(5,*)  dmax
2000       read(5,*)  nw          ! frequenza di scrittura della traiettoria, e dell'eq. check
10         read(5,*)  nwe        ! frequenza di scrittura delle energie
50         read(5,*)  nwa        ! frequenza di scrittura dell'animazione
```

Details of the initial condition generation

- 1) Normal modes of vibrations associated to the minimum energy configuration. Can be obtained as the eigenvectors of the mass weighted Hessian matrix

$$H_{ij} = \frac{1}{\sqrt{(m_i m_j)}} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0$$

the eigenvalues are related to “frequencies”, $3N$

$$\nu_i = \frac{\sqrt{(\lambda_i)}}{2\pi}$$

among these, 6 will be nearly zero (5 for a linear molecule), corresponding to overall translation and rotation of the system. $3N-6(5)$ will be the harmonic vibrational frequencies

A velocity component assigned to a direction in configuration space corresponding to a normal mode or to any combination of normal modes will have no rotational component (zero angular momentum).

If some angular momentum has to be assigned, this can be achieved adding to the Cartesian velocities some rotational velocity component different from zero indeed:

$$\vec{L} = I\vec{\Omega} \qquad I^{-1}\vec{L} = \vec{\Omega}$$

the rotational velocity component, consistent with angular momentum L , is for a given particle

$$\vec{v}_i^r = \vec{\Omega} \times \vec{r}_i$$