

Complex Disordered Systems

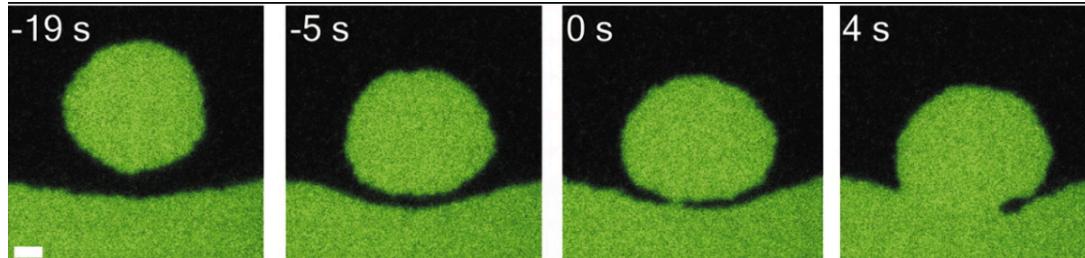
Francesco Turci

Today

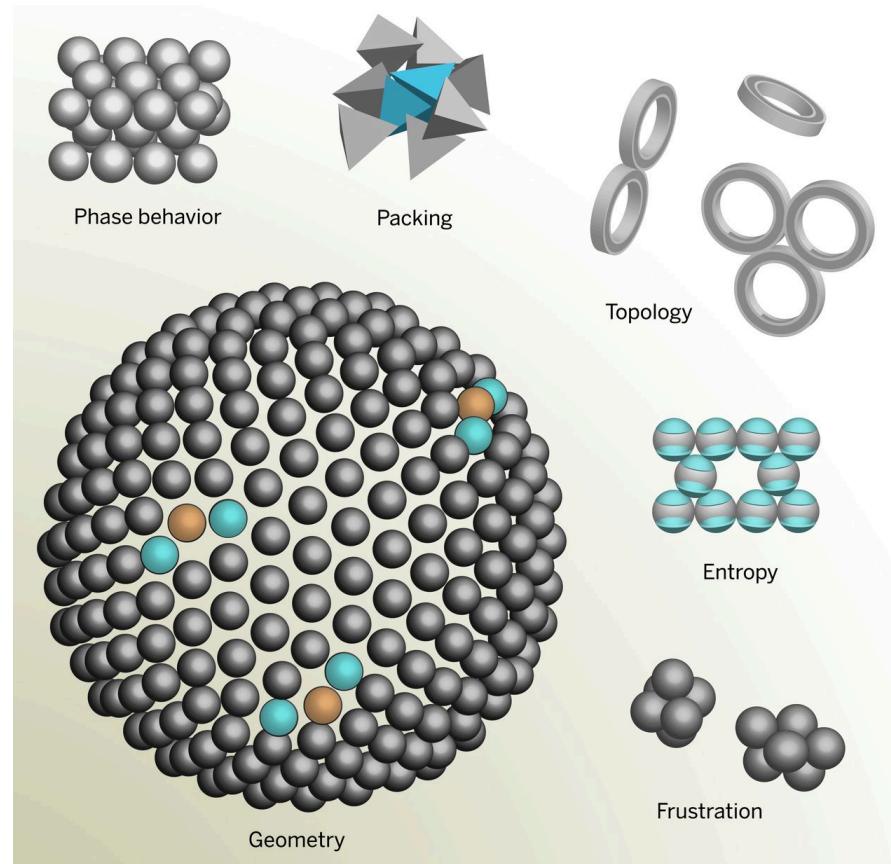
- **Colloids as big atoms**
 - Colloidal hard spheres
 - Phase diagram of hard spheres
 - Metastability
 - Phase diagrams of simple liquids

Colloids as big atoms

- Colloids can mimic atomic systems
- Serve as models for studying phase transitions, transformations, surface phenomena
- Examples:
 - Hard-sphere colloids
 - Charged-stabilized colloids



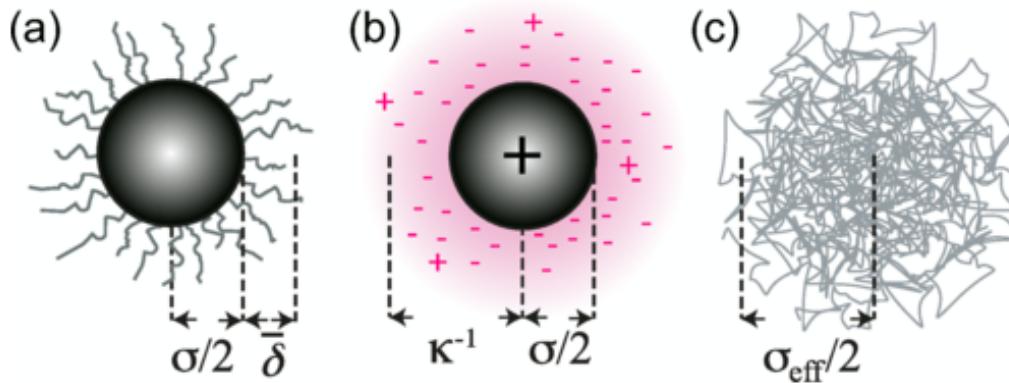
Coalescence of a colloidal liquid droplet, Aarts et al. *Science* (2004)



The self-assembly of colloids can be controlled by changing the shape, topology, or patchiness of the particles, by introducing attractions between particles, or by constraining them to a curved surface. From Manoharan *Science* (2015)

Colloidal hard spheres

True hard spheres do not exist. Colloidal hard spheres approximate the behaviour in many ways

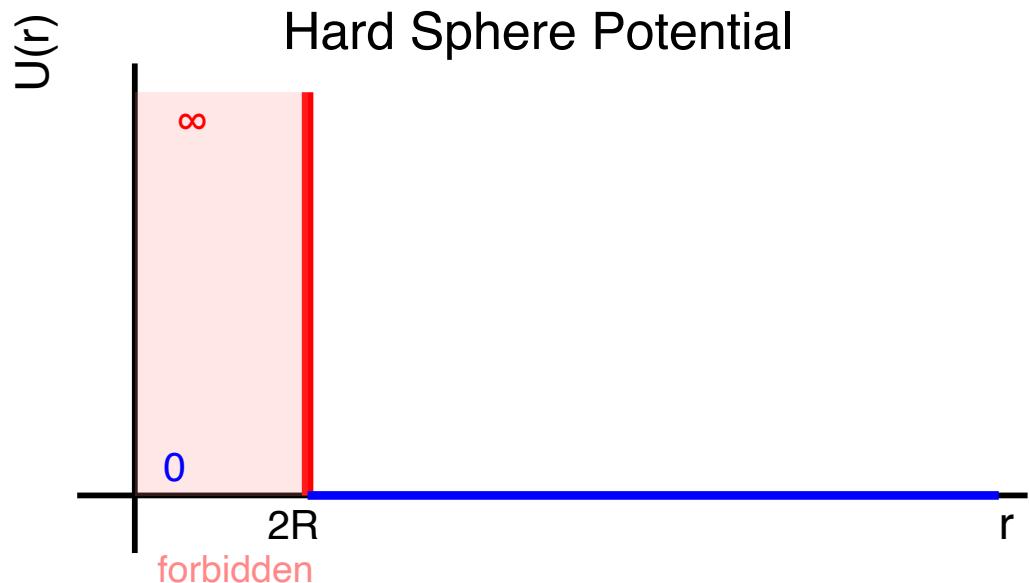


Schematic representation of various models for hard-sphere colloids. (a) A sterically stabilized particle has surface "hairs" (not to scale). (b) A charged colloid has an electrical double layer (shaded area) that gives rise to an effective diameter (c) A microgel particle is a heavily cross-linked polymer. From Royall et al Soft Matter (2013)

Hard spheres

Idealised hard spheres are impenetrable objects.

They are characterised by the simplest of the potentials.



Phase behaviour of hard spheres

For a sphere of diameter σ , enormous simplification of the Boltzmann factor:

$$e^{-\beta U(r)} = \begin{cases} 0 & \text{if } r < \sigma \\ 1 & \text{if } r \geq \sigma \end{cases}$$

This simplification arises because the potential ($U(r)$) is either infinite (forbidden region) or zero (allowed region).

For this reason, they hard spheres are **entropy driven**.

Constructing partition functions is then just counting **valid configurations**, linking geometry to thermodynamics.

- A good example: **Asakura-Oosawa** depletion, that we have already seen.

Phase diagram of hard spheres

Since we have a single control parameter, the phase diagram is one-dimensional.

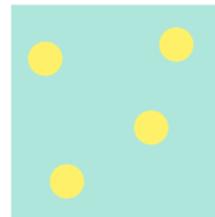
Changing temperature is immaterial to the free energy: it is a simple rescaling factor.

It is intuitive to guess the **low density limit** of hard spheres:

- few spheres in a box should behave similarly to an ideal gas

It is harder to guess the **high density limit**

We will gradually build our understanding from low to dense packing.



dilute limit: gas



dense limit: ?



ϕ

Hard spheres have a single control parameter, the packing fraction.

Low packing fractions

When treating the Asakura-Osawa depletion we introduced the **excluded volume**. It is also key for hard spheres.

- The distance of closest approach between two identical spheres is σ , which corresponds to the diameter of the spheres. The excluded volume of one particle is

$$v_{\text{ex}} = 4\pi\sigma^3/3$$

- At low densities, hard spheres are isolated and so no overlaps occur and the accessible volume for N spheres is

$$V_{\text{accessible}} = V - Nv_{\text{ex}}$$

- For phase behaviour, we need the thermodynamic potential. At constant volume and number of particles, the partition function is a measure of the accessible volume

$$\mathcal{Z} = \frac{1}{N!\Lambda^{3N}} \int_{V_{\text{accessible}}} d\mathbf{r}_1 \dots d\mathbf{r}_N$$

where Λ is the thermal de Broglie wavelength $\Lambda = h/\sqrt{2\pi mk_B T}$.

Mass and temperature are factorising out.

Low packing fractions: entropy

We integrate over valid (**non-overlapping**) configurations such that $|\mathbf{r}_i - \mathbf{r}_j| \geq \sigma$ for all $i \neq j$. This yields

$$\mathcal{Z} = \frac{(V - Nv_{\text{ex}}/2)^N}{N! \Lambda^{3N}},$$

with the $1/2$ factor coming from the fact that we avoid double counting the excluded volume of pairs.

- We immediately obtain the entropy as

$$S = k_B \ln \mathcal{Z} = k_B [N \ln(V - Nv_{\text{ex}}/2) - \ln N! - 3N \ln \Lambda]$$

- Via Stirling approximation $\ln N! = N \ln N - N$ we get

$$S = k_B [N \ln(V - Nv_{\text{ex}}/2) - (N \ln N - N) - 3N \ln \Lambda]$$

- This can be rewritten as

$$S = Nk_B \left[\ln \left(\frac{V - Nv_{\text{ex}}/2}{N\Lambda^3} \right) + 1 \right]$$

Low packing fraction: equation of state

The **equation of state** links the three relevant thermodynamics variables P, T and ϕ

$$P = - \left(\frac{\partial F}{\partial V} \right)_{N,T} = T \left(\frac{\partial S}{\partial V} \right)_{N,T} = \frac{k_B T}{v - v_{\text{ex}}/2}$$

This expression can be simplified (do it as an exercise) to obtain the equation of state

$$Z_{\text{comp}} = \frac{PV}{Nk_B T} = \frac{1}{1 - 4\phi} \quad (\phi \ll 1)$$

where Z_{comp} is **compressibility factor** (to not be confused with the partition function).

For small ϕ we have

$$Z_{\text{comp}} = \frac{PV}{Nk_B T} = 1 + 4\phi + O(\phi^2)$$

Note

Inspect this term and recognise that this illustrates that the dilute limit is an ideal gas + a correction.

Virial expansion

The expression $Z_{\text{comp}} = 1 + 4\phi + O(\phi^2)$ is just the simplest form of the more generic **virial expansion**, the perturbative series

$$Z_{\text{comp}} = 1 + B_2\rho + B_3\rho^2 + \dots$$

The B_2, B_3, \dots are known as **virial coefficients** and for non-hard-sphere systems they also depend on temperature, $B_2(T), B_3(T), \dots$

They encode **correlations** (pairs, triplets and so on). In a generic setting

$$Z_N = \frac{1}{N! \Lambda^{3N}} \int \cdots \int \exp \left[-\beta \sum_{i < j} U(r_{ij}) \right] d\mathbf{r}_1 \dots d\mathbf{r}_N$$

can be re-written using the **Mayer function** $f_{ij} = e^{-\beta u(r_{ij})} - 1$ and $e^{-\beta \sum_{i < j} U(r_{ij})} = \prod_{i < j} (1 + f_{ij})$ yielding

$$Z_N = \frac{1}{N! \Lambda^{3N}} \int \cdots \int \prod_{i < j} (1 + f_{ij}) d\mathbf{r}_1 \dots d\mathbf{r}_N$$

Cluster expansion and second virial

One can expand the product

$$\prod_{i < j} (1 + f_{ij}) = 1 + \sum_{i < j} f_{ij} + \sum_{\substack{\text{distinct} \\ i < j, k < l}} f_{ij} f_{kl} + \dots$$

The first term is the ideal gas, the second is clearly **pair correlations** (only pairwise distances).

The virial expansion can also be represented diagrammatically. For the compressibility factor ($Z_{\{\}}$), we have:

This motivates one to define

$$B_2(T) = -\frac{1}{2} \int f(r) d\mathbf{r} = -2\pi \int_0^\infty [e^{-\beta U(r)} - 1] r^2 dr$$

For hard spheres this results in

$$B_2 = \frac{2\pi}{3} \sigma^3$$

So $Z = 1 + \frac{2\pi}{3} \sigma^3 \rho = 1 + 4 \left(\frac{\pi}{6} \sigma^3 \rho \right) = 1 + 4\phi$ as we calculated earlier.

Low density limit: key points

Important

- We can simply focus on the **accessible volume** and ignore overlap between **exclusion volumes**
- We can focus on the **configurational entropy** and extract the equation of state relating P, T, ϕ
- The **compressibility factor** in terms of the packing fraction ϕ is the most condensed expression and is

$$Z_{\text{comp}} = \frac{PV}{Nk_B T} = 1 + 4\phi + O(\phi^2)$$

highlighting the first non-trivial perturbation to the ideal gass

- We can see this as an instance of the more general **virial** and **cluster expansion** formalism. which can used for any fluid.

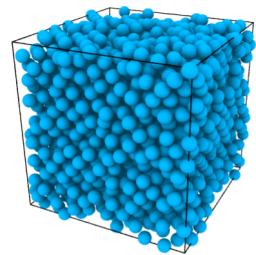
$$Z_{\text{comp}} = 1 + B_2\rho + B_3\rho^2 + \dots$$

- The first nontrivial correction is the **second virial coefficient**

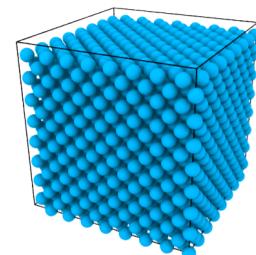
$$B_2(T) = -2\pi \int_0^\infty [e^{-\beta U(r)} - 1] r^2 dr$$

Dense packing

- As we increase the packing fraction, the accessible (free) volume reduces rapidly and thermal motion is hindered.
- Tight disordered (random) packing of spheres are described as **jammed**: link with glasses (in future lectures).
- Densest packing reaches a maximum packing of around $\phi_{rcp} \approx 0.64$: this is not unique and depends on the **protocol of preparation**.
- Kepler's conjecture (1611, proved only in 2017):
- Densest packings are **Face Centerd Cubic (FCC)** or **Hexagonally Cosed Packed (HCP)** $\phi_{\max} = \frac{\pi}{3\sqrt{2}} \approx 0.74$



Random Packing



FCC packing

Packings

Dense packing

Q: Can purely repulsive spheres assemble spontaneously into an FCC crystal?

YES

- Entropy in AO interactions causes an effective interaction that has a minimum
- Disordered packings are **less efficient** than ordered ones

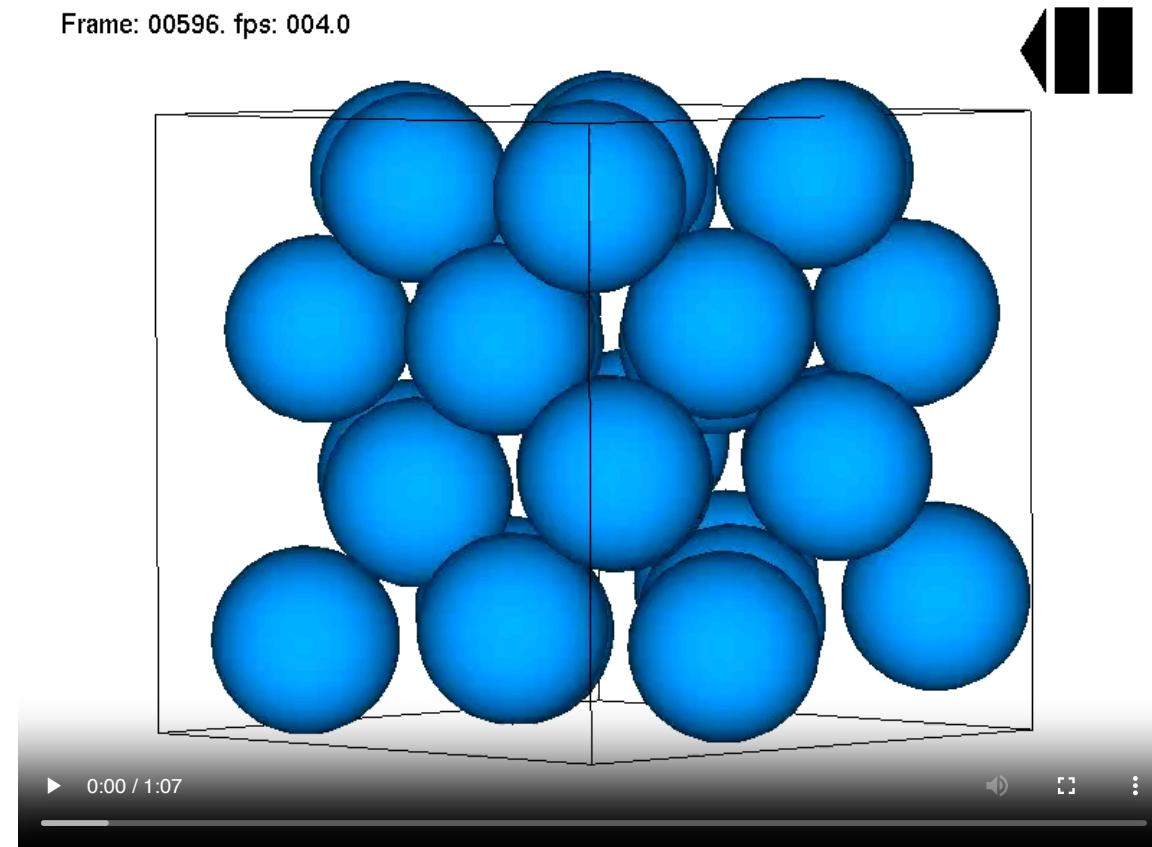
NO

- Hard sphere potential only prevents overlaps
- There is no minimum in the interaction potential to favour a crystal lattice and localisation
- Entropy is just *disorder*

- The matter was hotly debated in conferences in the 1950s and got to evenly split votes multiple times

Dense packing and crystallisation

Early **computer simulations** (molecular dynamics, Alder and Wainwright 1957, Monte Carlo, Wood and Jacobson (1957)) proved that that crystallisation is possible.



The video shows a Monte-Carlo simulation at packing $\phi = 0.49$ for a small system of 32 particles. Small systems have enhanced fluctuations, leading to spontaneous freezing and unfreezing.

Dense packing: cell model

- In an FCC cell, particles can move very little beyond their own diameter σ .
- Assume that the volume per particle is v and the (geometrically constrained) close packed volume is v_{cp} .
- The maximum displacement is

$$\delta = \frac{\sigma}{\sqrt{2}} \left(\left(\frac{v}{v_{cp}} \right)^{1/3} - 1 \right)$$

- The corresponding free volume is then $v_f = \frac{4\pi}{3} \delta^3$ from which we can calculate the entropy

$$S = -Nk_B T \ln(v_f/\Lambda^3)$$

- And the pressure

$$P = T \left(\frac{\partial S}{\partial V} \right)_{N,T} = \frac{Nk_B T}{v_{cp}} \frac{(v/v_{cp})^{-2/3}}{(v/v_{cp})^{1/3} - 1}$$

Dense packing: cell model

Rearranging and expressing everything in terms of packing fraction $\phi = \frac{\pi\sigma^3}{6v}$ yields

$$Z_{\text{comp}} = \frac{1}{1 - (\phi/\phi_{cp})^{1/3}}$$

- This expression is **completely different from the low density regime**

$$Z_{\text{comp}}^{\text{low}} = 1 + B_2\rho + B_3\rho^2 + \dots$$

- The incompatibility signal **non-analiticity** and hence a **discontinuous phase transition: first order transition**.
- First order phase transition are characterised by **interfaces** and **coexistence between phases**.
- We should therefore observe **phase coexistence** in simulations and experiments of hard spheres.

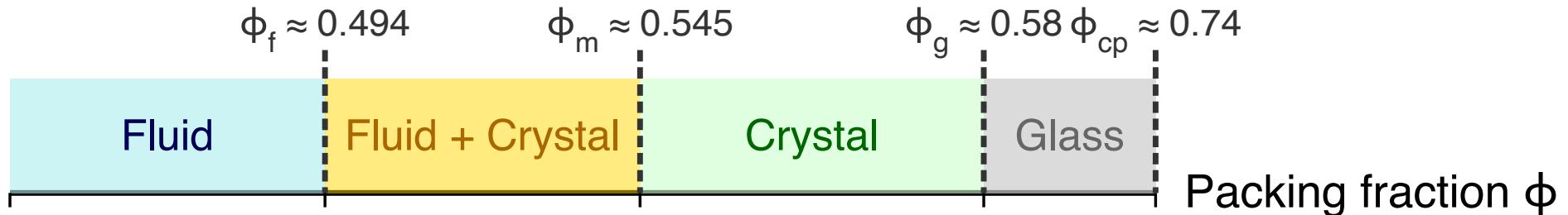
Colloidal hard spheres: phase behaviour



Vials of colloidal hard spheres under the effect of sedimentation: the gravitational field imposes a density gradient. At low packing fraction this maintains the dispersed fluid, but when the packing fraction is sufficiently high, it spontaneously forms a crystalline phase (speckled areas) after some time, in coexistence with a fluid. Notice that at very high packing the interfaces disappear and one has a disordered phase again: it is the glass, see Pusey et al, *Philosophical Transactions of the Royal Society A* (2009).

Colloidal hard spheres: phase behaviour

In conclusion, the one dimensional phase diagram of hard spheres is the following



Hard spheres phase diagram

Notice that the **glass phase** is purely nonequilibrium: if a system has enough time to relax, it will eventually form a **crystal**.

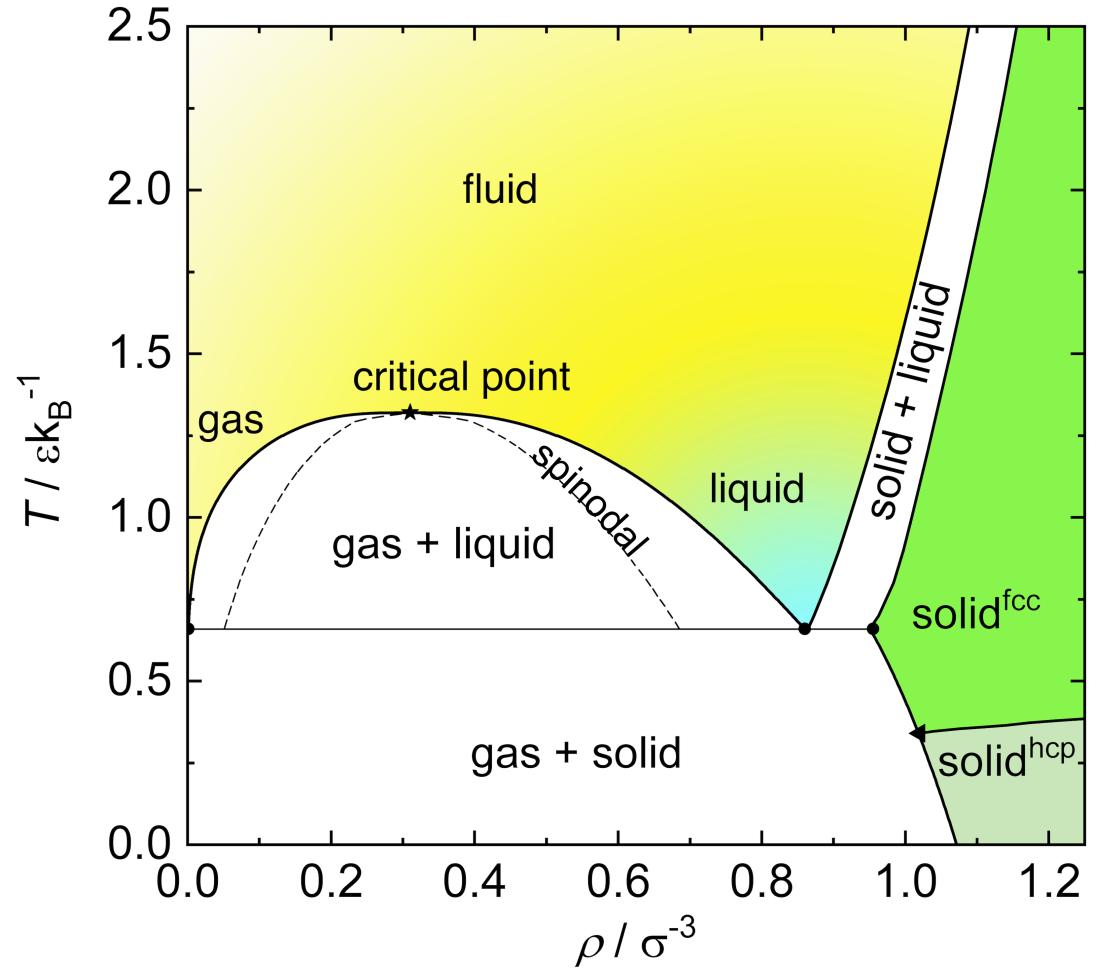
Beyond hard spheres: simple liquids

- A **simple liquid** is a system of particles interacting via short-range, spherically symmetric (isotropic) pair potentials.
- A very common model is the **Lennard-Jones (LJ) potential**

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

where ϵ sets the depth of the potential well (interaction strength) and σ is the particle diameter (distance at which $U = 0$).

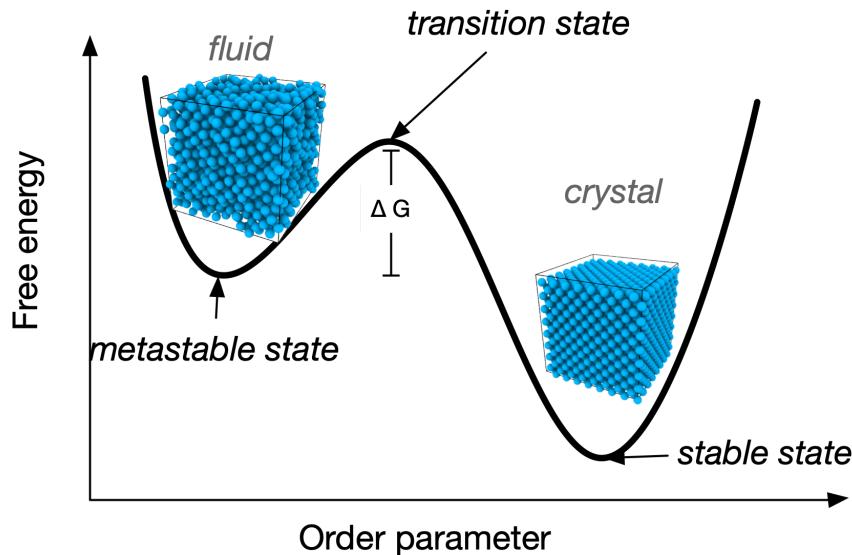
- The r^{-12} term models steep repulsion, while r^{-6} describes the attractive tail.
- The Lennard-Jones fluid exhibits rich phase behavior: gas, liquid, supercritical fluid and crystalline solid
- The LJ model is widely used to study atomic and molecular liquids, and serves as a reference for understanding real fluids and their phase transitions.



Phase diagram of the Lennard-Jones Fluid, adapted from Wikimedia.

Coexistence: Metastability and Instability

- Lennard Jones and hard sphere fluid present **coexistence regions**.
- The **binodal** line determines phase coexistence. It is the locus where the free energy satisfies the condition of equal chemical potential and pressure between coexisting phases. When crossing the binodal, one enters a regime of **metastability**.



Schematic free energy for hard spheres compressed at high pressures: the fluid branch becomes metastable and the free energy minimum is located in the crystal phase

Coexistence: Metastability and Instability

- The **spinodal** line marks the boundary of metastability. It is the **limit of stability**

$$\frac{\partial^2 G}{\partial \phi^2} = 0$$

- Between the binodal and spinodal lines, the system is metastable, meaning it can persist in a non-equilibrium state for a finite time.
- The nucleation time τ is related to the free energy barrier ΔG^* by an activated (also called Arrhenius) law

$$\tau \propto \exp\left(\frac{\Delta G^*}{k_B T}\right)$$

- Inside the spinodal there is no nucleation: **coarsening** occurs

You have seen some of this physics when discussing the **Ising model**.