# Complex Disordered Systems

## Colloids as Big Atoms

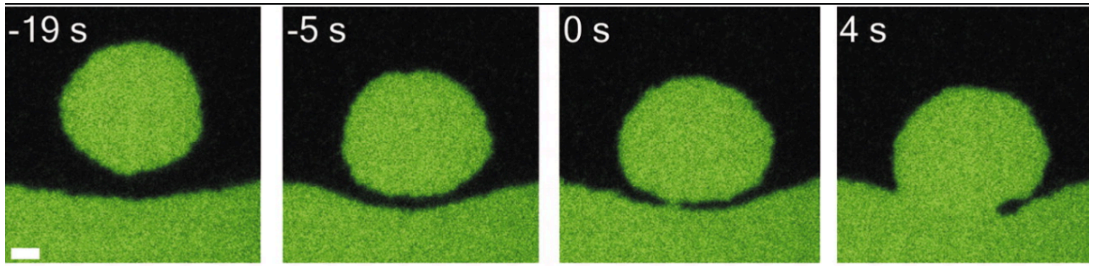
Francesco Turci

# Today

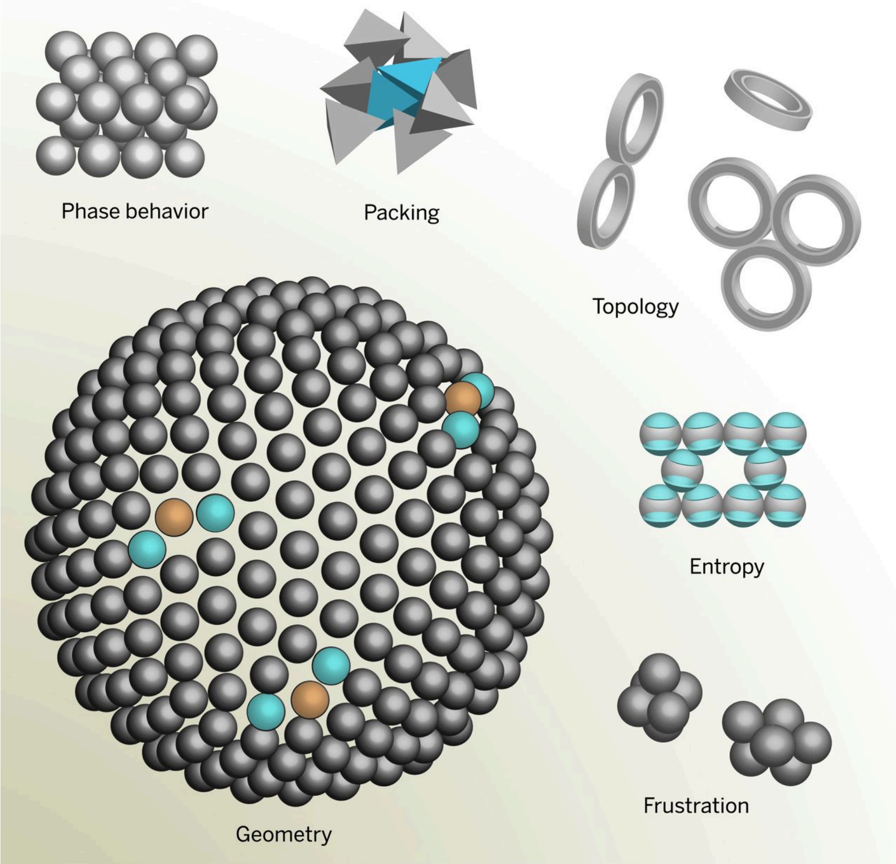
- **Colloids as big atoms**
    - Colloidal hard spheres
    - Phase diagram of hard spheres
    - Metastability
    - Phase diagrams of simple liquids

# 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



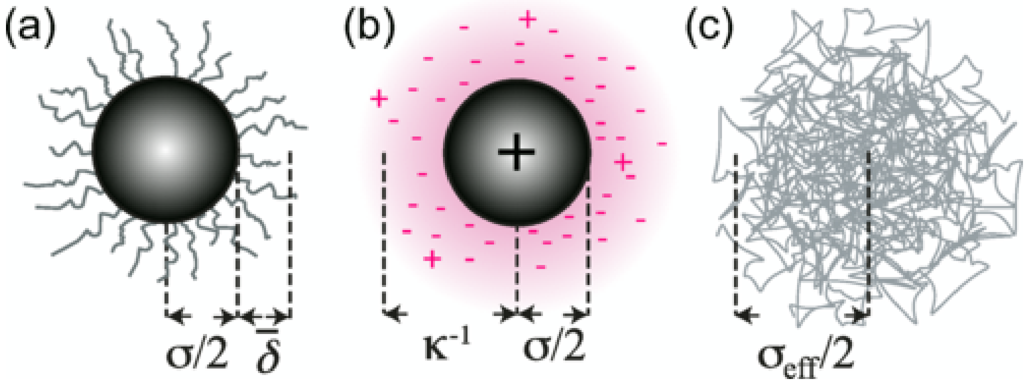
Coalescence of a colloidal liquid droplet, Aarts et al. *Science* (2004)



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.

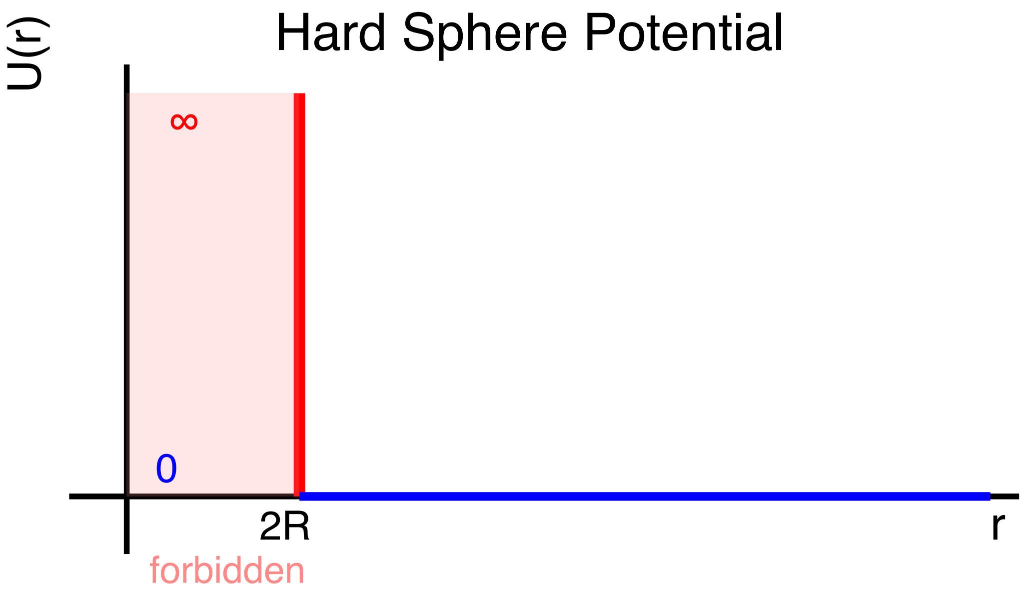


Schematic representation of various models for hard-sphere colloids. (a) A sterically stabilized particle has surface “hairs” (not to scale). (b) A charged colloid has an electrical double layer (shaded area) that gives rise to an effective diameter (c) A microgel particle is a heavily cross-linked polymer.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

# Hard spheres

Idealised hard spheres are impenetrable objects.

They are characterised by the simplest of potentials.



# Phase behaviour of hard spheres

For a sphere of diameter $\sigma$, 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, 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.

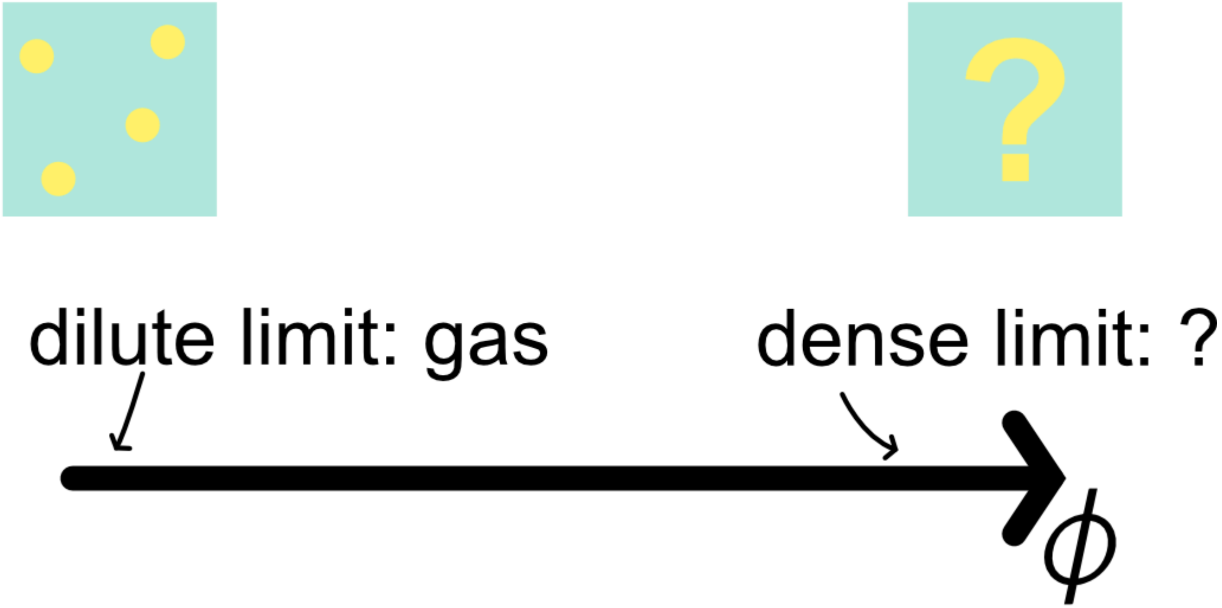
Changing temperature is immaterial to the free energy: it is a simple rescaling factor.

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.



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

## Low packing fractions

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

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

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

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

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

- 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

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

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

  Mass and temperature are factoring 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

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

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

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

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

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

- This can be rewritten as

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

# Low packing fraction: equation of state

The **equation of state** links the three relevant thermodynamic variables $P, T$ and $\phi$

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

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

$$Z_{\mathrm{comp}} = \frac{PV}{Nk_BT} = \frac{1}{1-4\phi} \quad (\phi \ll 1)$$

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

For small $\phi$ we have

$$Z_{\mathrm{comp}} = \frac{PV}{Nk_BT} = 1 + 4\phi + O(\phi^2)$$

**Note**

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

# Virial expansion

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

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

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

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

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

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

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

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

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 $P, T, \phi$
- The **compressibility factor** in terms of the packing fraction $\phi$ is the most condensed expression and is

$$Z_{\text{comp}} = \frac{PV}{Nk_BT} = 1 + 4\phi + O\left(\phi^2\right)$$

  highlighting the first non-trivial perturbation to the ideal gas

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

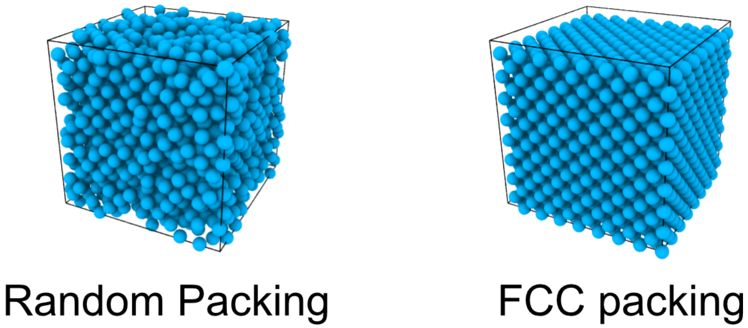
$$Z_{\text{comp}} = 1 + B_2\rho + B_3\rho^2 + \dots$$

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

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

# 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 $\phi_{\rm rcp} \approx 0.64$: this is not unique and depends on the **protocol of preparation**.
- Kepler's conjecture (1611, proved only in 2017):
- Densest packings are **Face Centred Cubic (FCC) or Hexagonally Close Packed (HCP)** $\phi_{\max} = \frac{\pi}{3\sqrt{2}} \approx 0.74$



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 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 $\sigma$.
- 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

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

- And the pressure

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

# Dense packing: cell model

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

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

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

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

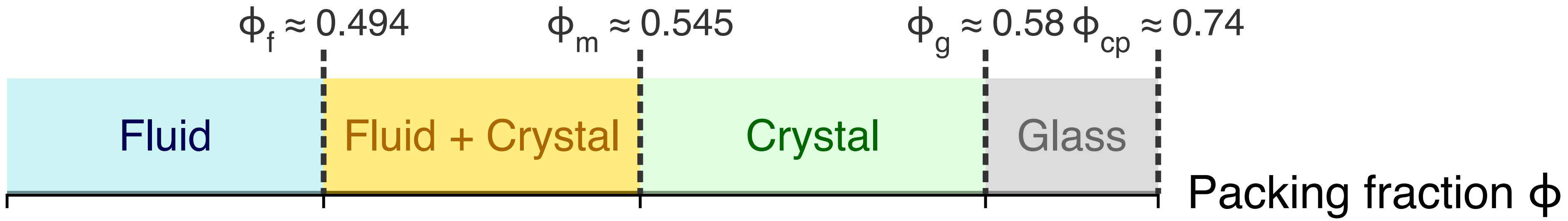
- The incompatibility signals **non-analyticity** and hence a **discontinuous phase transition**: **first order transition**.
- First order phase transitions are characterised by **interfaces** and **coexistence between phases**.
- We should therefore observe **phase coexistence** in simulations and 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 non-equilibrium: if a system has enough time to relax, it will eventually form a **crystal**.

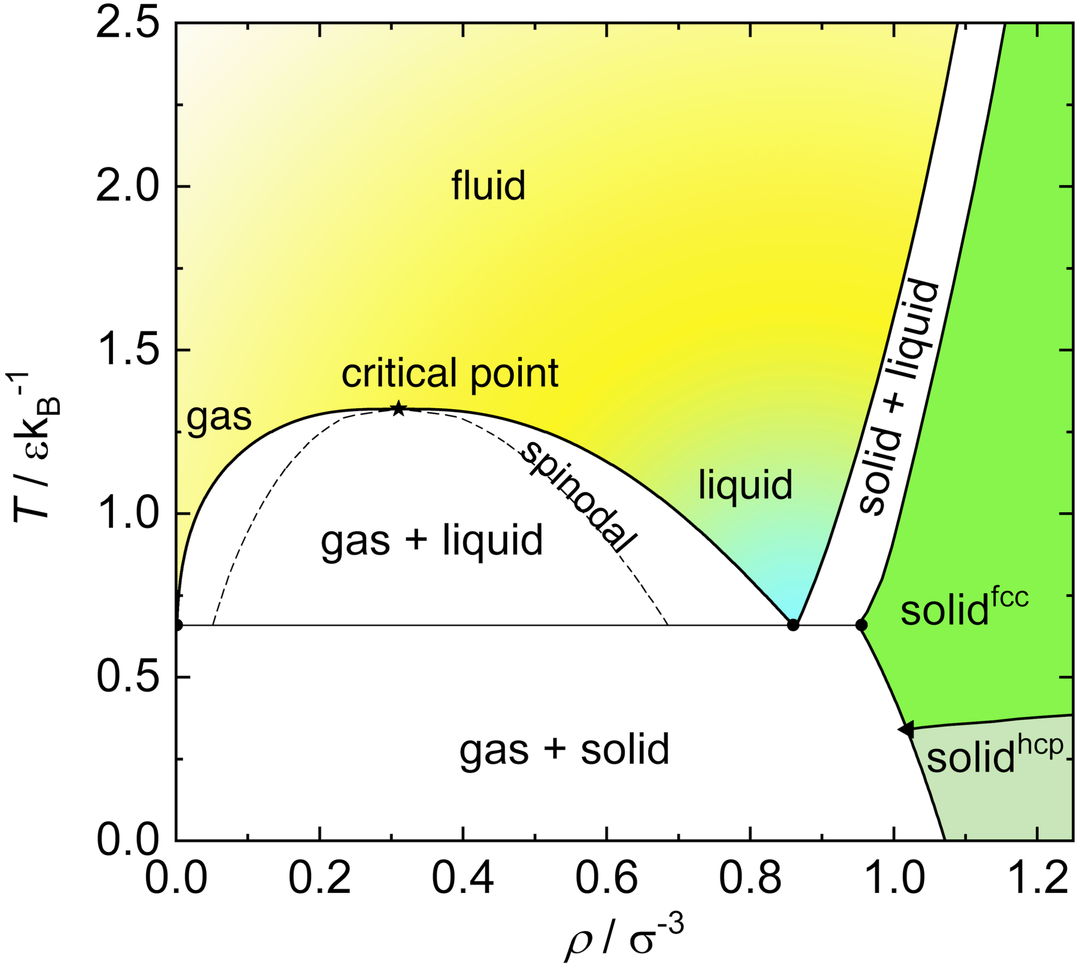
# Beyond hard spheres: simple liquids

- 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**

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

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

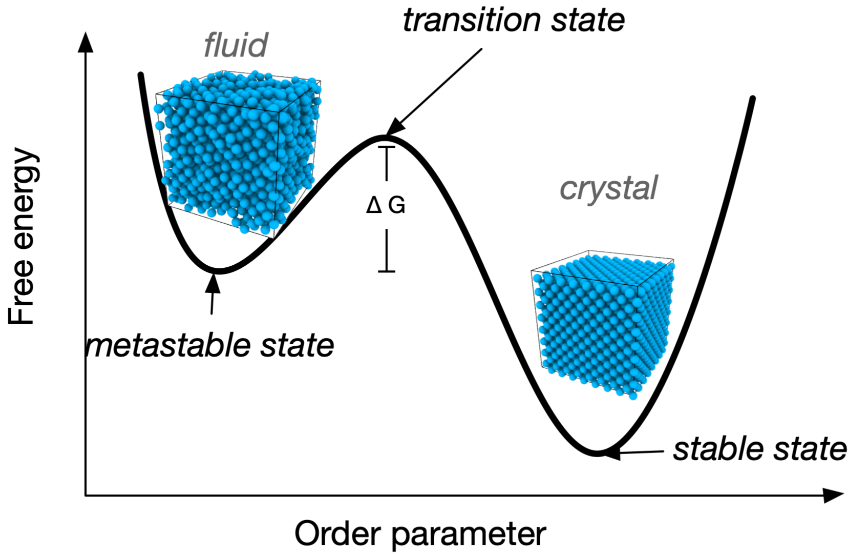
- The $r^{-12}$ term models steep repulsion, while $r^{-6}$ describes the attractive tail.
- The Lennard-Jones fluid exhibits rich phase behavior: gas, liquid, supercritical fluid and crystalline solid
- The LJ model is widely used to study atomic and molecular liquids, and serves as a reference for 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 fluids 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 $\tau$ is related to the free energy barrier $\Delta G^*$ 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**.