Complex Disordered Systems

Gelation

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Downloading package: ipython

Today

- Physical gels and percolation
- Colloid-polymer mixtures
- Structure and characterization
- Arrested spinodal decomposition

Pyodide environment setup

What is a Physical Gel?

Physical gel: Particles/polymers connected via **reversible**, non-covalent bonds forming a **percolating network**

Key features:

- Bonds break/reform dynamically
- Energy ~ $k_B T$
- Self-healing possible
- **Thermoreversible**

Examples:

- Gelatin
- Agarose
- Yoghurt
- Paint, inks

Cross-links form via dense local regions (microcrystalline/glassy)

Physical vs Chemical Gels

Physical Gels

- Reversible bonds
- Energy ~ $k_B T$
- Dynamic network
- Thermoreversible

Chemical Gels

- Irreversible covalent bonds
- High energy barriers
- Permanent network

Key transition:

- Fluid → Gel occurs when a **system-spanning cluster** forms (**percolation**)
- Dramatic viscosity increase + elastic response

Gels are a second example of disordered solids (after glasses)

Percolation Theory

Problem: Square grid $L \times L$ sites, randomly label N of them. When does a spanning cluster form?

- $p = N/L^2$ = occupation probability
- **Percolation threshold** p_c
- Below p_c: small clusters
- Above p_c: giant spanning cluster

2D square lattice:

$$p_c \approx 0.5927$$

Transition: Continuous (2nd order)

Percolation Simulation

Python Code ⟳ Start Over ▷ Run Code

```python
p, L = 0.5, 120
grid, mask = sample_percolation(L,p)
plt.figure(figsize=(6, 6))
plt.imshow(grid, cmap='gray', interpolation='none')
plt.imshow(np.ma.masked_where(~mask, mask), cmap='autumn', alpha=0.8, interpolation='none')
plt.axis('off');plt.title(f'Percolation in 2D (p={p})\nLargest cluster highlighted in red');plt.show()
```

Percolation Transition

Python Code ⟳ Start Over ▷ Run Code

```
1 plot_transition(npoints=50)
```

```
name 'sample_percolation' is not defined
```

Percolation Threshold: p_c Values

Non-universal: p_c depends on lattice type and dimension

Lattice	**Dim**	z	p_c^{site}	p_c^{bond}
Square	2	4	0.593	**0.5**
Triangular	2	6	**0.5**	0.347
Cubic	3	6	0.312	0.249
Hypercubic	4	8	0.197	0.160
Hypercubic	6	12	0.109	0.094

Higher dimensions $\rightarrow$ lower p_c (easier to percolate)

Critical Exponents: Universal

Universal: Critical exponents independent of lattice details

$$P_\infty(p) \propto (p - p_c)^\beta$$

Dimension d	β
2	5/36 ≈ 0.14
3	≈ 0.41
≥6	**1** (mean-field)

Gels require percolation for mechanical stability!

Colloidal Gel Formation

MD simulation of dilute colloidal gel formation (largest cluster in red)

Percolating cluster → mechanical rigidity

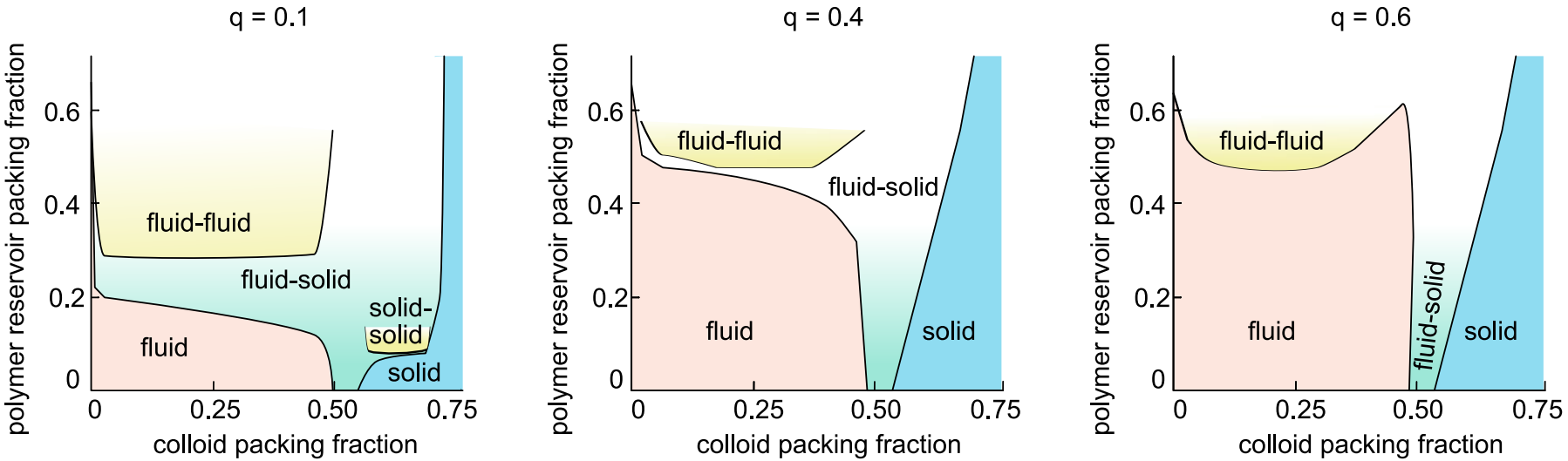
Colloid-Polymer Mixtures

Depletion interactions like the Asakura-Oosawa model produce a **very short ranged** potential with strong **attractive part**.

$$W_{\mathrm{AO}}(r) = -\frac{4\pi\rho_p k_B T}{3} R^3 (1+q)^3 \left[1 - \frac{3}{4}\frac{r}{R(1+q)} + \frac{1}{16}\left(\frac{r}{R(1+q)}\right)^3\right], \quad 2R < r < 2(R+R_p), \quad q = \frac{R_p}{R}$$

attractive + very short ranged → **sticky** interaction

- Colloids cluster into nonequilibrium branched phase
- Binodal becomes **metastable** to fluid-solid coexistence



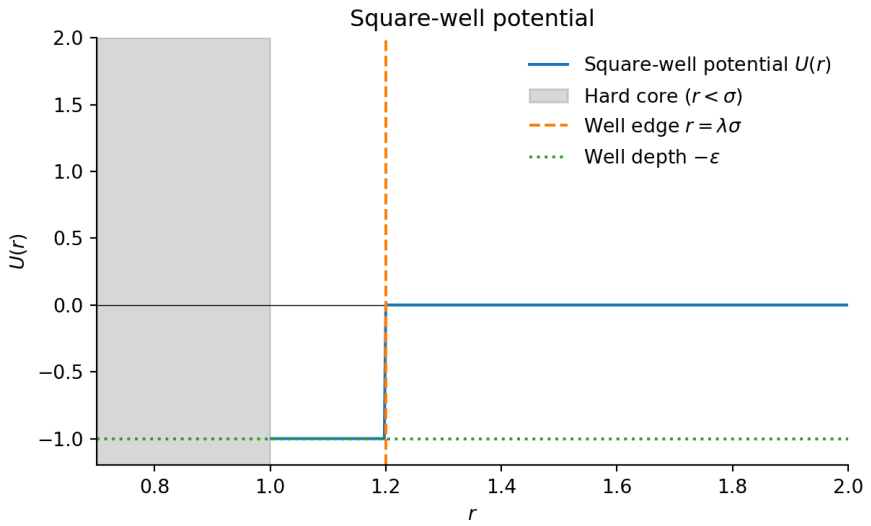
Phase diagram of colloid-polymer mixtures for varying polymer-colloid aspect ration q. Small

Simple Model Potentials

Square-well potential:

$$U(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma \leq r < \lambda\sigma \\ 0 & r \geq \lambda\sigma \end{cases}$$

- σ: particle diameter
- ϵ: well depth
- λ: range parameter

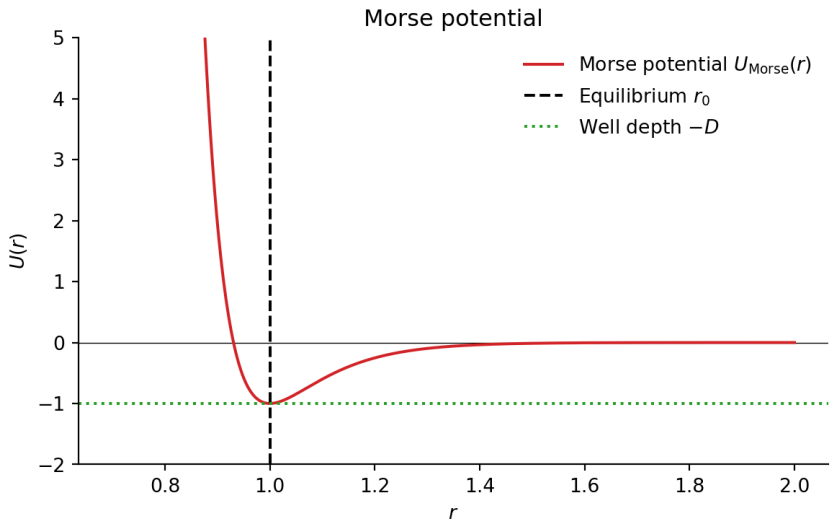


Morse Potential (MD Simulations)

Smooth short-range attractive potential:

$$U_{\text{Morse}}(r) = D\left[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}\right]$$

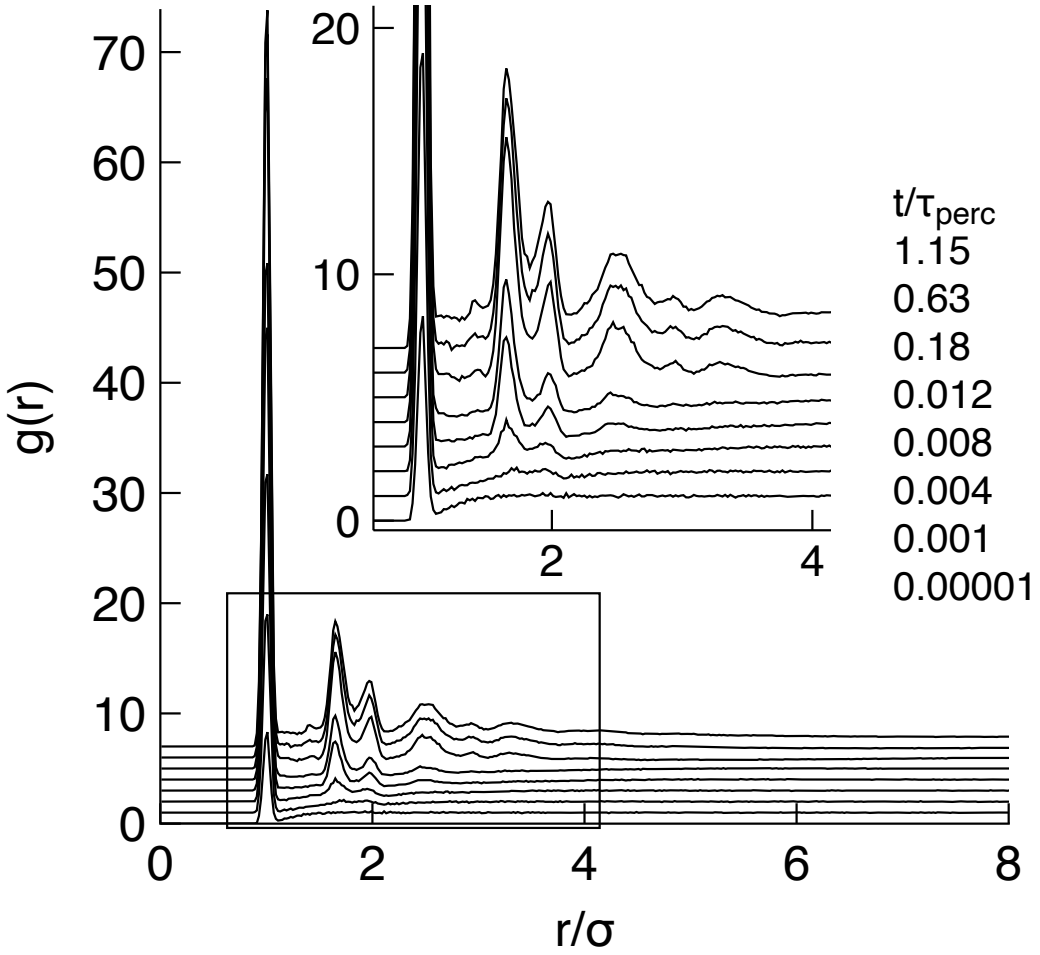
- D: well depth
- α: steepness (controls range)
- r_0: equilibrium distance



Pair Correlations: $g(r)$

Radial distribution function $g(r)$: best at short distances

- Captures cluster structure
- Sharp peaks at dilute concentrations
- Nearest/second-nearest neighbor shells



Time evolution of $g(r)$ ina dilute gel in units of the time to percolate τ_{perc}

Structure Factor: $S(q)$ and Fractals

Near percolation threshold, the loq-q trend from the trsucture factor links to the compressibility: **power-law behavior**: Clusters become **fractal objects** with self-similar structure at all length scales.

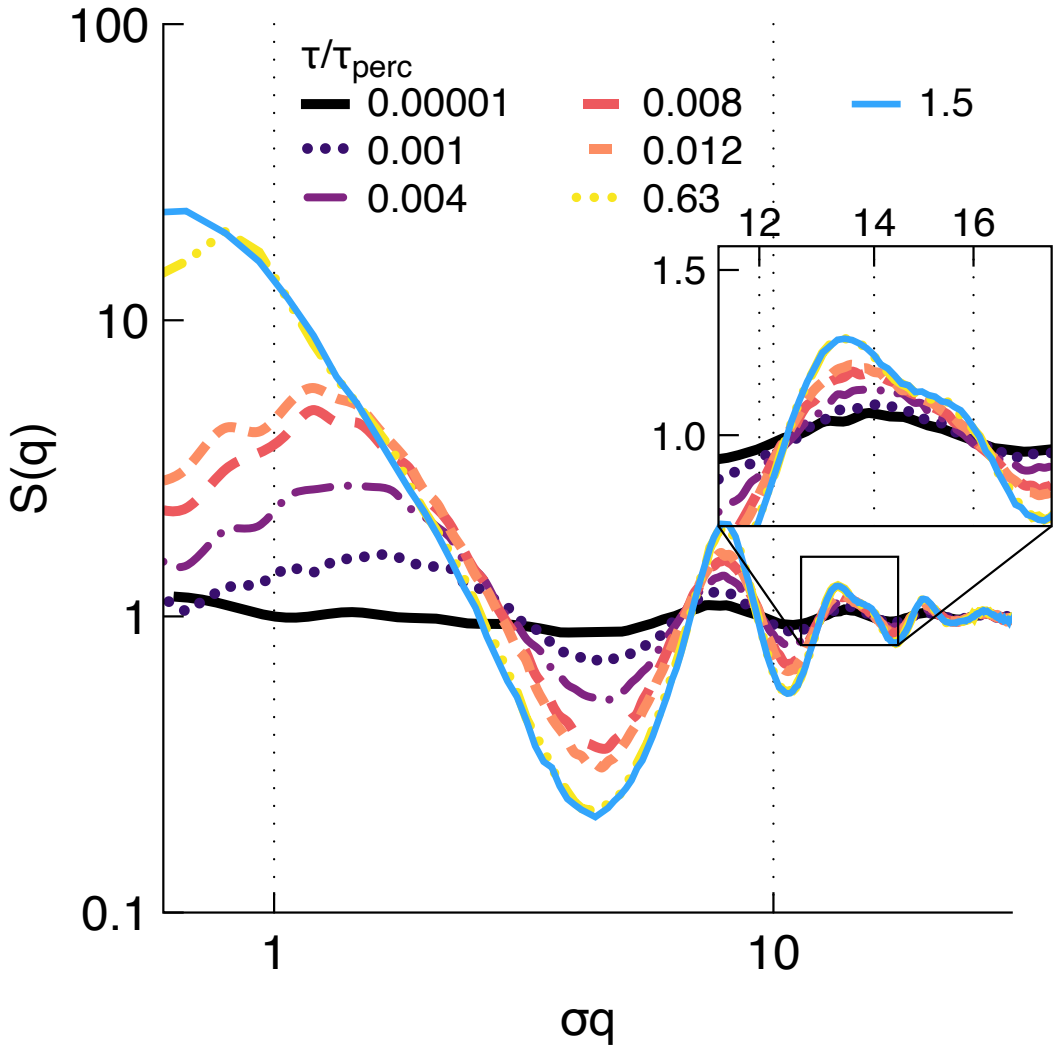
For a fractal object with dimension D_f:

- Mass scales as $M(R) \sim R^{D_f}$
- Density correlations decay as $\rho(r) \sim r^{-(d-D_f)}$

Fourier transform of power-law correlations gives:

$$S(q) \sim q^{-D_f}$$

- D_f: fractal dimension
- No characteristic length scale
- Typical 3D: $D_f \approx 2.5$



Arrested Spinodal Decomposition

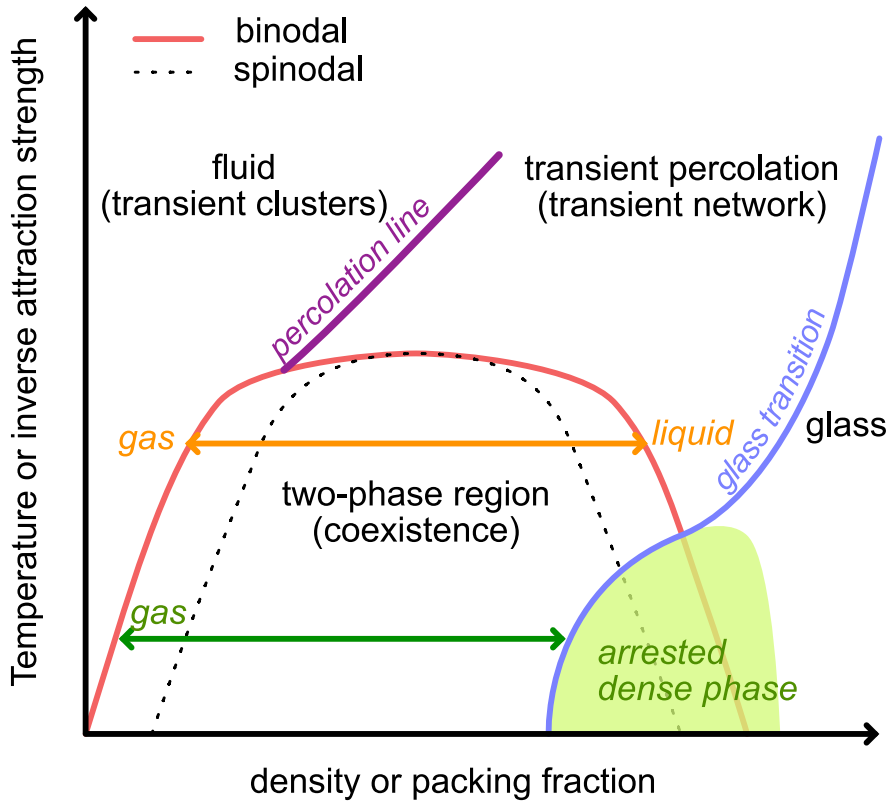
How do gels form?

Scenario:

1. Rapid quench into unstable region
2. Phase separation begins (spinodal)
3. Dense regions arrest (glass/jamming)
4. Bicontinuous frozen structure

The picture suggest the progressive **freezing of coarsening upon spinodal decomposition**.

Phase Diagram: Arrested Spinodal



Arrested spinodal scenario, see Zaccarelli et al 2007

Key lines:: - Binodal (red): liqiid-gase coexistence at equilibrium - Spinodal (dashed): limit of stability of the metastable phases. Instability (i.e. spinodal decomposition) starts **inside** - Percolation (purple): At some density, the clusters percolate (span the system) - Glass transition (blue): Dense phase becomes dynamically arrested (non-ergodic)

Gel path: Rapid cooling → arrested dense phase + vapor