Complex Disordered Systems

Polymers and solvents

Francesco Turci

Today

- Good, poor and theta solvents
- Concentrated polymer solutions

Polymers in solvents

- Polymers typically are dispersed in a medium (**solvent**).
- Solvent-polymer attractions (the **affinity**) influences the polymer conformations:
  - **good solvents** $\longrightarrow$ high affinity $\longrightarrow$ the polymer swells (expands)
  - **poor solvents** $\longrightarrow$ low affinity $\longrightarrow$ the polymer shrinks

The affinity depends on the details of the molecular interactions but can be *coarse-grained*.

We can construct a simple model with **effective interaction energies**

- ε_{ss} for the solvent-solvent
- $\varepsilon_{\mathrm{pp}}$ for monomer-monomer
- ε_{sp} for solvent-monomer interactions.

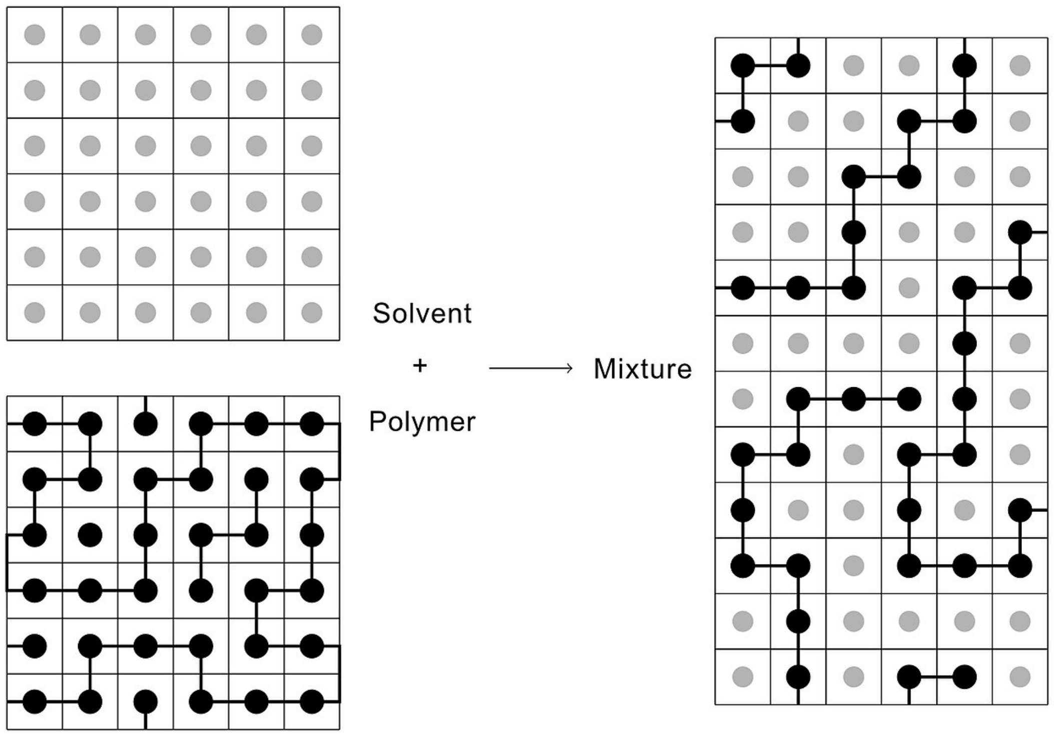
Energy of mixing

On-lattice model:

- each site has z nearest neighbours
- N_s solvent molecules
- N_p monomers
- N_{sp} solvent-monomer contacts.

Effective interactions:

- ε_{ss} for the solvent-solvent
- $\varepsilon_{\mathrm{pp}}$ for monomer-monomer
- ε_{sp} for solvent-monomer interactions.



Then the energy of mixing ΔU_{mix} is obtained as the difference between the total energy U of the mixed system and the sum of the energies of the **pure solvent** and **pure polymer**, $U_S + U_p$.

$$\Delta U_{\mathrm{mix}} = U - (U_S + U_p)$$

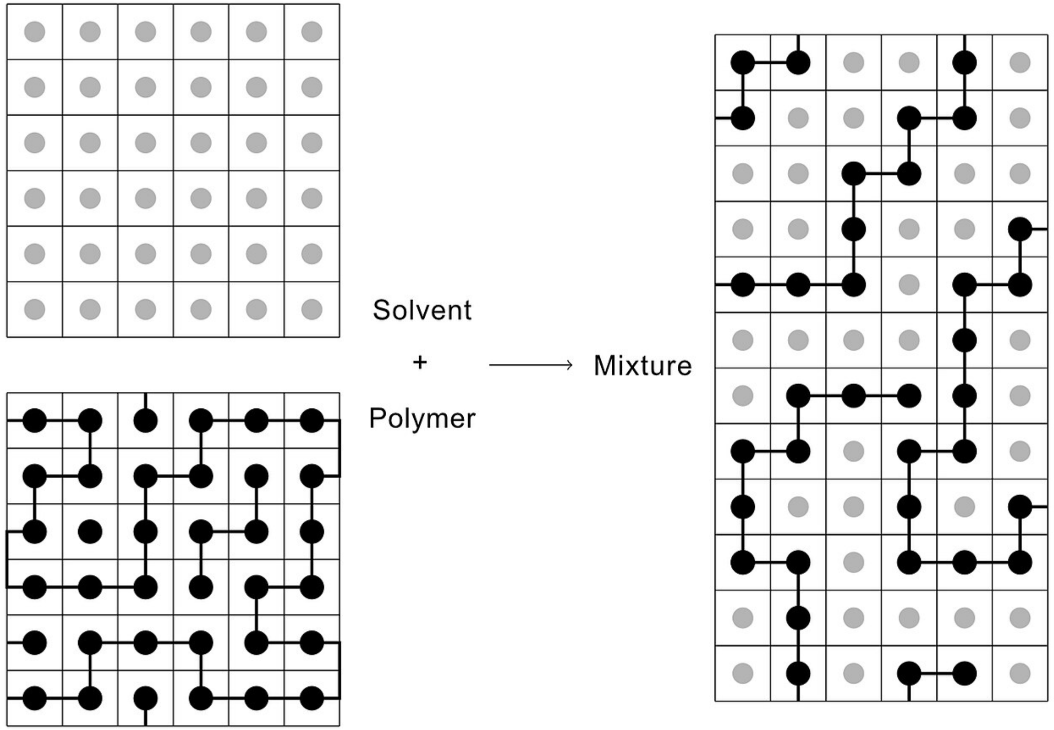
Energy of mixing

- Energy of pure solvent

$$U_s = \frac{zN_s\varepsilon_{ss}}{2}$$

- Energy of pure polymer

$$U_p = \frac{zN_p\varepsilon_{pp}}{2}$$



Energy of solution $U = N_{sp}\varepsilon_{sp} + \frac{(zN_s - N_{sp})\,\varepsilon_{ss}}{2} + \frac{(zN_p - N_{sp})\,\varepsilon_{pp}}{2}$

We obtain that the **energy of mixing** $\Delta U_{\text{mix}} = N_{sp}\left[\varepsilon_{sp} - \frac{1}{2}\left(\varepsilon_{ss} + \varepsilon_{pp}\right)\right]$

which can **change sign** depending on our choices for the effective interaction energies.

Good solvents, poor solvents and theta solvents

- **Good solvent**: $\varepsilon_{sp} < \frac{1}{2}\left(\varepsilon_{ss} + \varepsilon_{pp}\right) \quad \therefore \Delta \mathrm{U}_{\mathrm{mix}} < 0$

This is the case of a ‘good solvent’, because the monomers prefer to be near the solvent molecules. Excluded volume effects then expand the chain.

- **Poor solvent**: $\varepsilon_{sp} > \frac{1}{2}\left(\varepsilon_{ss} + \varepsilon_{pp}\right) \quad \therefore \Delta \mathrm{U}_{\mathrm{mix}} > 0$

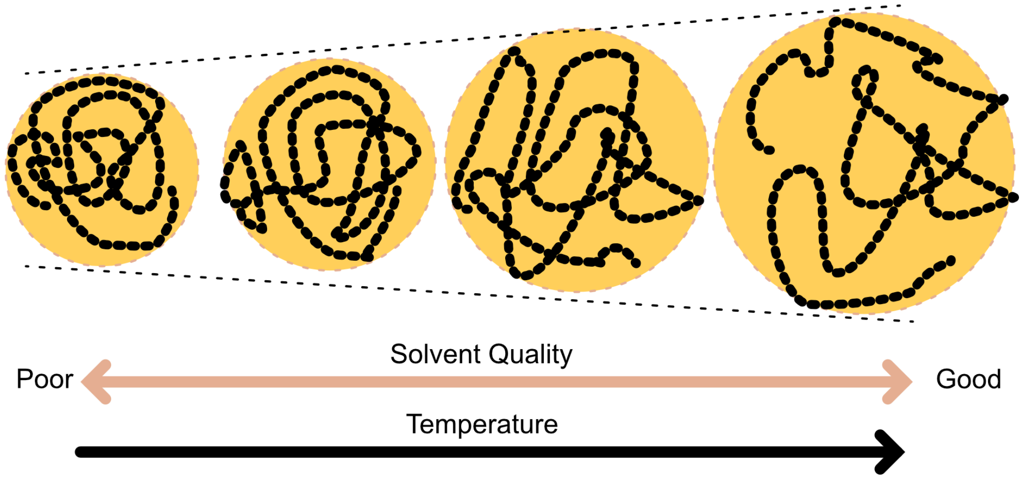
The attraction between the different monomers offset the excluded volume effect making the polymer collapse.

- Tuning solvent properties (e.g. the temperature) leads to **conformational changes**

Temperature dependence and theta (Θ) solvents

The various affinities have temperature dependencies. Typically:

- At high T, the coil expand and the solvent is *good*
- At low T the coil collapses and phase separation is observed (polymer-rich from polymer-poor phase)
- There is an intermediate temperature where the excluded volume and attractive interaction compensate each other and allow for the polymer to behave like an ideal chain (freely jointed chain).
    - The temperature is conventionally named Θ temperature (or *Flory* temperature, after physicist Paul Flory)
    - The Θ temperature increases wth the solvent-polymer attractions (we need higher temperature to reach ideal behaviour)



Swelling behaviour of polymers in solvent.

Examples

- Example: Food polymer — gelatine (from collagen) in water
  - Good solvent (hot water): gelatin chains hydrate and swell; the protein dissolves and the solution is fluid.
  - Θ / marginal: intermediate temperature where hydration and chain self-attraction roughly balance; solution is viscous but not set.
  - Poor solvent (cold): effective attractions dominate; chains associate into a network, causing gelation (collapsed/aggregated network).

We will see gelation in a few sessions.

Concentrated polymer solutions

- We mostly dealt with **single polymers** and their propertie up to now.
- Many polymers together make a **polymer solution**

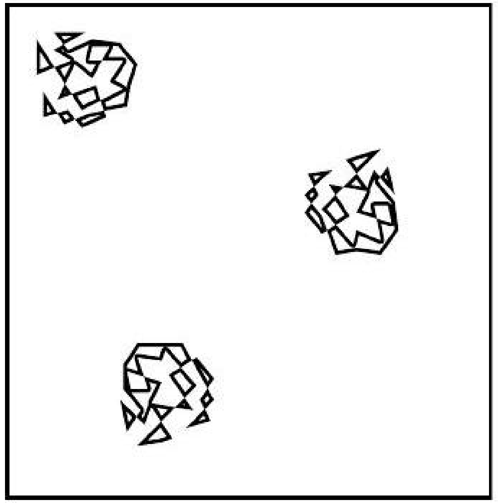
As we vary the **concentration** the behavior qualitatively changes.

We will increase the concentration in steps to reach **bulk polymers**

Dilute regime

- The polymer coils are well-separated on average.
- The system is dilute if the polymer concentration c is such that

$$\underbrace{\underbrace{\overset{\substack{\text{concentration in}\\ \text{mass per volume}\\ \downarrow}}{\frac{c}{M}}N_A}_{\substack{\text{number per}\\ \text{volume}}} \times \underbrace{\frac{4\pi}{3}R_g^3}_{\substack{\text{volume of}\\ \text{one coil}}}}_{\text{volume fraction of coils}} \ll 1$$



where N_A is Avogadro's number, M is the molar mass of a single chain and R_g is the radius of gyration of the chain.

Essentially, the polymers **do not overlap**.

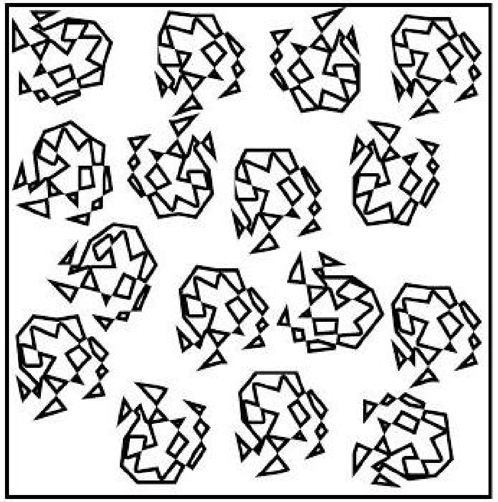
Overlap concentration $c*$

Overlap occurs when the volume fraction of coils reaches unity and thus

$$\frac{c^*}{M} N_A \frac{4\pi}{3} R_g^3 \sim 1 \qquad \therefore c^* = \frac{3M}{4\pi N_A R_g^3}$$

Phenomenologically one has $Rg = \langle R_g^2 \rangle^{1/2} = BM^\nu$ with an empirical exponent called the **Flory scaling exponent**. Hence

$$c^* = \frac{3}{4\pi N_A B^3} M^{1-3v}$$



Overlap concentration $c*$

$$c^* = \frac{3}{4\pi N_A B^3} M^{1-3v}$$

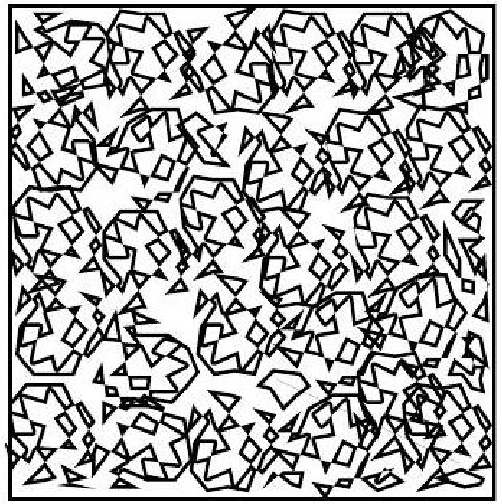
Example of polystyrene in a good solvent:

Parameter	**Value**	**Unit**
Molar mass (M)	10^6	g mol^{-1}
Flory exponent (v)	0.6	
Kuhn length (B)	0.028	nm (g mol^{-1})$^{-0.6}$
Overlap concentration (c*)	0.29	kg m^{-3} (or 0.29 mg/ml)
Polystyrene density (ρ)	1050	kg m^{-3}
Volume fraction of monomers	0.28×10^{-3}	

For large polymers, c^* can be very small.

Semi-dilute

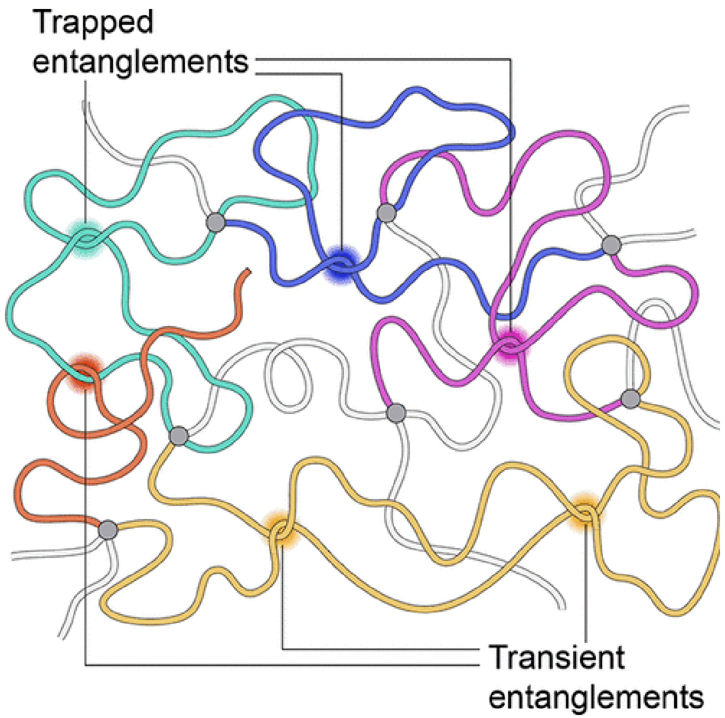
- The concentration is larger than the overlap concentration c^*, but still much smaller than the bulk density.
- The coils interpenetrate and **entanglement** begins
- Change in the dynamics (slowing down)
- Yet, the solution is still mostly solvent.



Start of the formation of a **polymer network** with transient **crowded regions** *within* the solvent.

Polymer entanglement

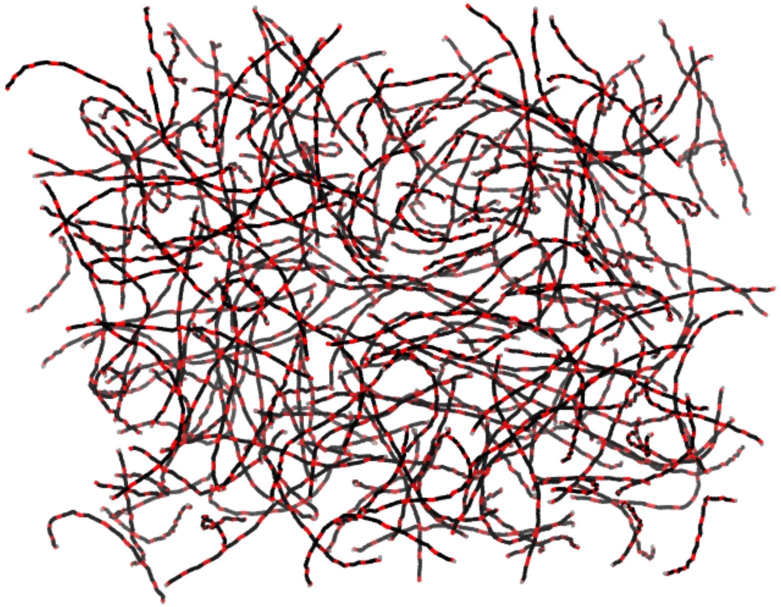
- Polymer entanglement occurs when overlapping polymer chains become topologically **intertwined**, creating temporary **physical knots** that restrict chain motion and significantly affect the material's mechanical and rheological properties.
- Introduces **topological constraints** (transient/permanent)



Concentrated: bulk polymers

- Polymer concentration approaches **bulk density**
- Monomers occupy significant fraction of total volume
- **Highly interpenetrated coils** form **continuous network**
- **Polymer-polymer** interactions dominate over polymer-solvent interactions
- Chain entanglements restrict segment motion
- Transition from solution-like to **solid-like** behavior
- Increased mechanical strength and viscosity
- Complex dynamics due to crowding effects

These are the feature of density-driven glassy behaviour.

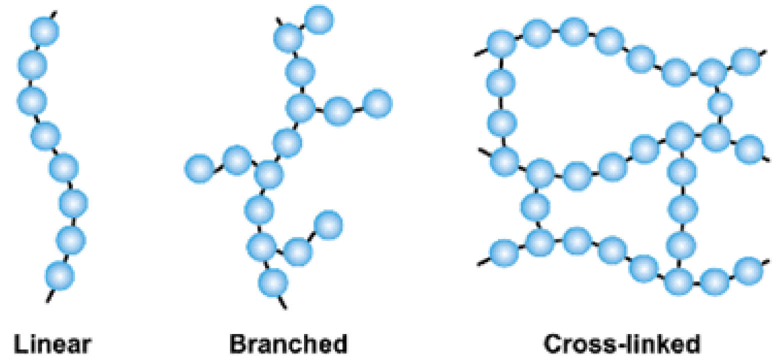


Polyethylene Glycol polymer melt (from Martini project)

Cross-linking

Cross-linking is the process of forming **covalent bonds between separate polymer chains**, creating a **three-dimensional network structure**. These bonds:

- **Connect different chains** at specific points
- **Restrict chain movement** and deformation
- **Increase mechanical strength and rigidity**
- Can be **temporary (reversible) or permanent (irreversible)**
- **Determine material properties**: low cross-linking allows flexibility, high cross-linking creates brittleness



Cross linking bonds (reversibly or irreversibly) different chains.

Bulk polymer classes

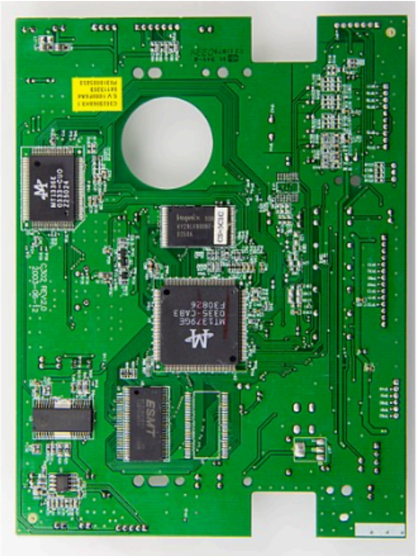
Two main classes of bulk polymers, characterised by whether they are cross-linked or not.

- **Elastomers** (rubbers): **low cross-linking** → flexible and elastic (stretch and return to original shape)
- **Thermosets**: **high cross-linking** → rigid, hard, brittle network
- **Thermoplastics**: **no cross-linking** → most everyday plastics; behavior upon cooling shows similarities to colloids

Polymer bulks are often referred to as **resins**.

Examples of bulk polymer classes

Class	Examples	Properties	Applications
Elastomers	Natural rubber, silicone rubber, neoprene	Flexible, elastic, low cross-linking	Tires, seals, gaskets, flexible tubing
Thermosets	Epoxy resins, phenolic resins, polyurethane foam	Rigid, hard, high cross-linking, irreversible	Circuit boards, adhesives, insulation, structural composites
Thermoplastics	Polyethylene (PE), polypropylene (PP), PET, polystyrene (PS), PVC	Recyclable, moldable upon heating, no cross-linking	Packaging, bottles, pipes, automotive parts, consumer products


Natural rubber, epoxy substrate for circuits, PET used in plastic bottles

Thermoplastics behaviour upon cooling

- At high temperature the free energy is dominated by **entropy**.
  - random assembly of intertwined flexible coils
- Upon cooling, potential energy dominates and chain rotation becomes restricted, favoring more extended configurations.
- Below melting temperature T_m, **crystals form** (lowest free energy state), but require slow cooling and significant molecular ordering.
- Rapid cooling below glass transition temperature T_g ($< T_m$) **prevents crystallization**, forming an **amorphous glassy state** instead—a metastable, long-lived solid.
- Solid thermoplastics typically contain a **mixture of crystalline and amorphous regions**.