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04. Polymers I

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Contents of this Document [ptc4]

4. Polymers I

- Introduction
    - variety – structure – architecture – conformations [pln45]
    - polydispersity index
    - biopolymers [pln41]
    - rheology of viscoelastic polymers [psl7]
    - extensional rheometry of polymers
    - effectiveness of centrifugation [pln46]
    - polymer solutions [pln47]
    - polymer blends [pln48]
    - phase separation in polymer solution [pex51]
    - phase separation in polymer blend [pex52]
    - interface width in phase-separated polymer blend [pex58]

Variety of Polymeric Materials [pln45]

Synthesis, architecture, and attributes:

- Polymers are macromolecules of covalently bonded repeat units (monomers).

- The repeat units may be assembled uniformly, periodically (alternatingly), or aperiodically. In stereochemistry such arrangments are named *isotactic*, *syndiotactic*, and *atactic*, respectively. Polymers with single (multiple) repeat unit are called *homopolymers* (*copolymers*).

- Synthetic polymers include glues, fibres, resins, and rubbers. They are assembled industrially via *polymerization* from monomers or via *polycondensation* from shorter polymers.

- Biopolymers include nucleic acids, proteins, ad sugars. They are assembled organically.

- Most synthetic polymers are carbon based.

- Aperiodic polymers may

    - manifest quenched disorder (in industrial synthesis),

    - carry information on structural/functional units (in DNA),

    - carry building blocks for structural/functional units to be self-assembled via folding (in proteins).

- Polymers may be linear or branched. Branching strongly affects rheology. Branching is another manifestation of quenched disorder.

- *Degree of polymerization*: numbers N of monomeric repeat units. Monodisperse polymers have the same N and polydisperse polymers a distribution of N.

- *Entanglement* of polymers produces viscoelasticity. Branching suppresses (viscous) flow and enhances elasticity.

- *Block copolymers* have repeat units with different chemical attributes arranged in blocks. They can be designed for self-assembly into nano-structures via micro-phase separation.

- Polymer macrostates:

    - *liquid*: melt, solution, very viscous or viscoelastic,

    - *glass*: amorphous, solid-like,

    - *semi-crystalline*: small crystals embedded in amorphous matrix,

    - *liquid crystalline*: liquid with (mostly) orientational order.

- Bonds too weak for a stable gas except at at low temperature under very low pressure. Dilute polymer solution is effectively a gas state.

- Polymer classification dominated by rheology (rich solution behavior).
- Distinguish between
    - *configurations:* electronic structure of monomers and bonds,
    - *conformations:* spatial arrangements and motion of monomers.

  Statistical physics of macromolecules is concerned with conformations.
- Long-range correlations:
    - high susceptibility to external forces and strong fluctuation effects are linked by fluctuation-dissipation relation,
    - bonds between monomers suppress entropy.
- Memory effects:
    - memory of formation conditions,
    - memory of previous motion,
    - topological memory (exclusion of crossings).
- Entropic nature of elasticity:
    - stretching constrains available conformations.
- Miscibility of polymers dominated by enthalpic term in free energy. Polymers have small entropy of mixing. Phase separation caused by very small repulsive force.
- Fibres:
    - Cell walls in plants contain the biopolymer *cellulose.*
    - Fibres harvested from diversity of plants: cotton, flax, hemp,...
    - Fabrics woven with polymer fibres.
    - Wool made from protein *keratin.*
    - Silk contains biopolymer *fibrion.*
    - Fibres from synthetic polymers: *polyamides*, *polyesters* (e.g. nylon), *polyacrylics.*
    - Useful fibres have high tensile strength, are pliable, and resist abrasion.
    - Fibres are spun in different ways, synthetic fibres mostly from solution or melt.
    - Polymer fibres can be stengthened by a process of drawing (stretching out).

Biopolymers [pln41]

Biopolymers are assembled by living organisms. *Synthetic polymers* are assembled in the lab or in an industrial production line.

Three major kinds of biopolymers:

- *Nucleic acids:* Polymeric nucleotides of linear structure. Examples are DNA [pln39] and RNA. Aperiodic sequence of bases carries genetic information, e.g. blueprint for composition of proteins.
- *Polypeptides:* Polymeric amino acid residues linearly joined by peptide bonds. Examples include (short) peptides and (longer) proteins. Aperiodic sequence of side chains provide shapes and interactions conducive to very diverse biological functions upon folding.
- *Polysaccharides:* Polymeric carbohydrates of structure ranging from linear to highly branched. Biological functions include energy storage (e.g. starch) and structural support (e.g. cellulose).

DNA vs Proteins: commonalities and differences.

Non-random aperiodicity:

- Aperiodic structure of DNA (sequence of base pairs) encodes genetic information on biological functions. Two distinct base pairs are realized: AT and CG. Nucleotide triplets form codons.
- In aperiodic structure of proteins (amino acid residues with side chains) that information is translated into building materials. 20 distinct residues are realized.

Hierarchical structure: primary, secondary, tertiary, quaternary

- DNA: (i) Nucleotide sequence, (ii) double helix, (iii) nucleosome, chromosome.
- Proteins: (i) amino acid sequence, (ii) α-helix and β-sheet, (iii) and (iv) folding into functional units.

Helicity:

- DNA: Double helix has aperiodic features on the inside. Genetic information needs protection.
- Proteins: α-helix (and β-sheets) have aperiodic parts on the outside. Building blocks with specific shapes and interactions need exposure.
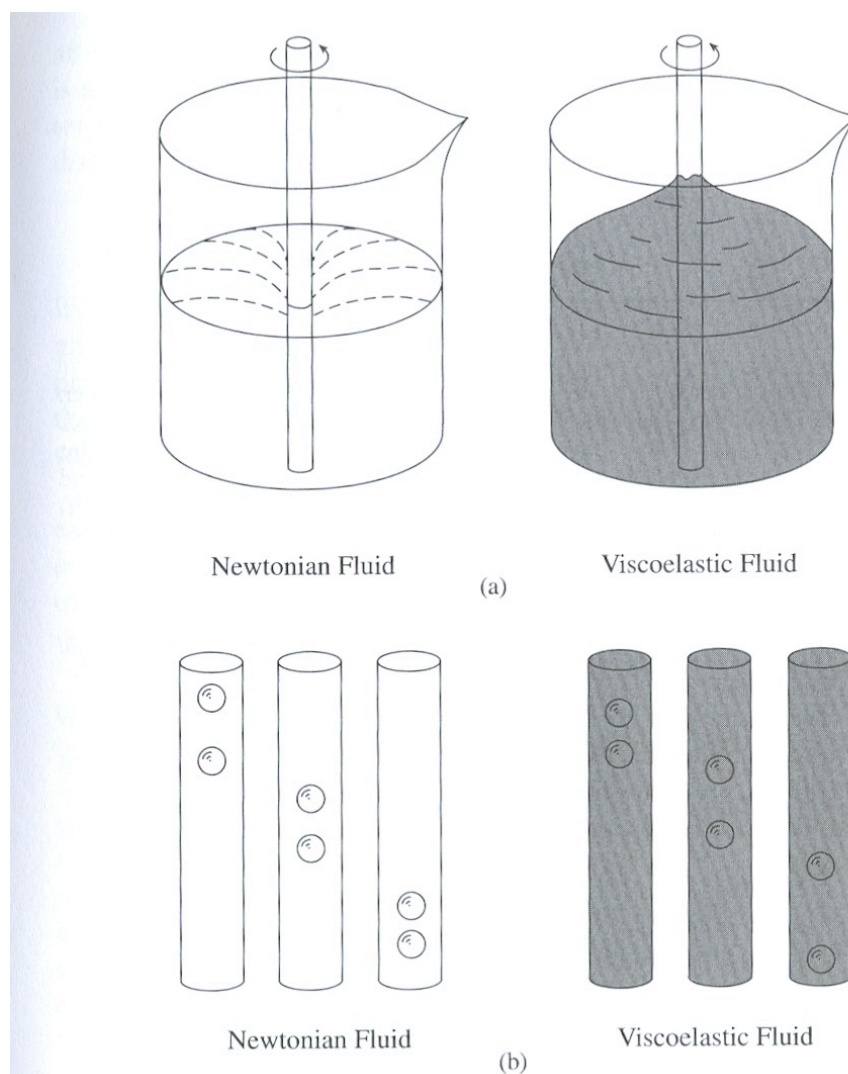
Rheology of viscoelastic polymers

Figure 2.11 Illustrating the viscoelasticity of polymers. (a) A polymer melt or solution will climb up a rotating rod, whereas in an ordinary viscous liquid the liquid is 'sucked in' near the rod. (b) Spheres falling through a Newtonian fluid will tend to get closer, whereas in a viscoelastic fluid they separate as they drop
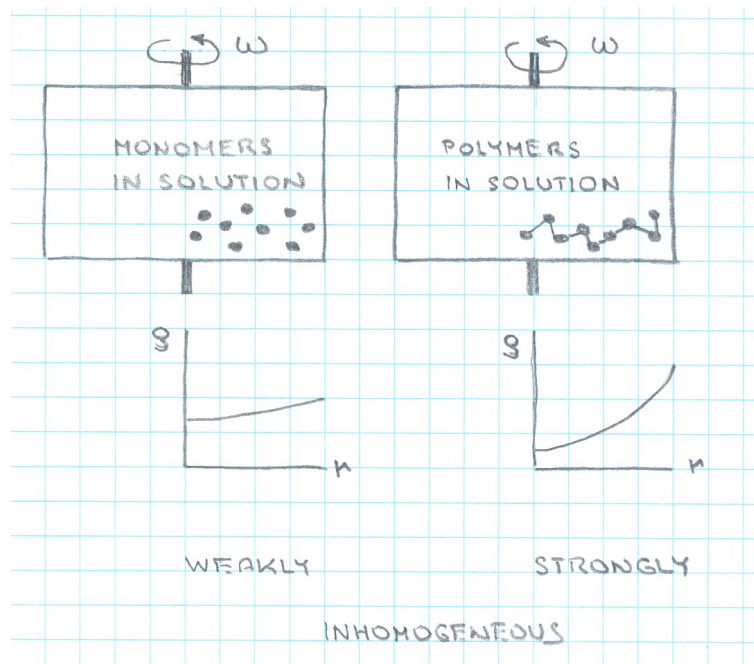
[copied from Hamley 2007]

Effectiveness of Centrifugation [pln46]

Consider centrifuge vessels containing

   (i) *monomers* of mass $m = m_0$ in solution,

  (ii) *polymers* of mass $m = Nm_0$ in solution.

Centrifugal potential: $U(r) = -\dfrac{1}{2}m\omega^2 r^2.$

Density profile: $\rho(r) \propto \exp\left(-\dfrac{U(r)}{k_B T}\right).$

[extracted from Doi 2013]

Polymer Solutions [pln47]

Starting point: lattice model of two-component fluid [pln32].

Adaptation assumes that monomers and solvent particles are of equal size v_c and that (monodisperse) polymers contain N monomers.

Modified expression for free-energy density:

$$f(T, \phi, N) = \frac{k_B T}{v_c}\left[\frac{1}{N}\phi \ln \phi + (1-\phi)\ln(1-\phi) + \chi \phi(1-\phi)\right], \quad \chi = -\frac{z\Delta\epsilon}{2k_B T} > 0.$$

The entropy of the solute is suppressed by a factor N when N monomers are bound together to form one polymer. The conformational entropy of polymers is neglected here. It will be analyzed later as manifestation of self-avoiding random walk.

The prescription worked out in [pex48] then yields the following expression for the osmotic pressure [pex51]:

$$\pi(T, \phi, N) = \frac{k_B T}{v_c}\left[-\phi\left(1-N^{-1}\right) - \ln(1-\phi) - \chi\phi^2\right] \overset{\phi \ll 1}{\rightsquigarrow} \frac{k_B T}{v_c}\left[\frac{\phi}{N} + \left(\tfrac{1}{2} - \chi\right)\phi^2\right].$$

The critical point for phase separation has the following coordinates in the phase diagram [pex51]:

$$\phi_c(N) = \frac{1}{\sqrt{N}+1}, \quad \chi_c(N) = \frac{1}{2}\left(1 + \frac{1}{\sqrt{N}}\right)^2.$$

This point moves from $(0.5, 2.0)$ for $N = 1$ as shown in [psl4] to $(0.09, 0.61)$ for $N = 100$.

The spinodal line in the phase diagram can then be inferred from the locations of the inflection point in the ϕ-dependence of the function $f(T, \phi, N)$ [pex51]:

$$\chi_{sp}(\phi, N) = \frac{1}{2}\left[\frac{1}{1-\phi} + \frac{1}{N\phi}\right].$$

The determination of the coexistence curve from the geometric conditions stated in [pln31],

$$f'(\phi_a) = f'(\phi_b), \quad f(\phi_a) + f'(\phi_a)[\phi_b - \phi_a] = f(\phi_b),$$

is a bit more involved [pex51].

[extracted from Doi 2013]

Polymer Blends [pln48]

Both solute and solvent are polymers.

Adaptation of lattice model for two-component fluid from [pln32] assumes that both kinds of polymers are monodisperse.

Degrees of polymerization:

- solute: N_A (with volume fraction ϕ),
- solvent: N_B (with volume fraction $1 - \phi$).

Modified expression for free-energy density:

$$f(T, \phi, N_A, N_B) = \frac{k_B T}{v_c} \left[\frac{1}{N_A} \phi \ln \phi + \frac{1}{N_B}(1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right],$$

where $\chi = -z\Delta\epsilon/2k_B T$. For specificity we assume $N_A > N_B$.

The coordinates in the phase diagram of the critical point are [pex52]

$$\phi_c(N) = \frac{1}{\sqrt{N_A/N_B} + 1}, \quad \chi_c(N) = \frac{\left(\sqrt{N_A} + \sqrt{N_B}\right)^2}{2N_A N_B}.$$

Spinodal line [pex52]:

$$\chi_{sp}(\phi, N_A, N_B) = \frac{1}{2} \left[\frac{1}{N_A \phi} + \frac{1}{N_B(1 - \phi)} \right].$$

Special case: $N_A = N_B \doteq N$ [pex52]:

- critical point: $\phi_c = \frac{1}{2}, \quad \chi_c = 2/N$,
- spinodal line: $\chi_{sp}(\phi, N, N) = \frac{1}{2N} \frac{1}{\phi(1 - \phi)}$,
- coexistence line: $\chi_{co}(\phi, N, N) = \frac{1}{2N} \frac{\text{Artanh}(1 - 2\phi)}{1 - 2\phi}$.

For large N_A, N_B the spinodal line touches down to a value close to zero, implying that polymer blends have a strong tendency to phase separate. Interfaces tend to be weak, which makes plastic recycling problematic. The entropy of mixing is small compared to that of small molecules. Polymer blends that mix experience a strong mutual attraction.

[extracted from Doi 2013]

[pex51] Phase separation in polymer solution

Consider a monodisperse polymer composed of N monomers in solution. Under the assumption that the volume of monomers and and solvent particles are of very similar size we can adapt the mean-field lattice model used in [pex47] to this case. The free-energy density then reads

$$f(T, \phi, N) = \frac{k_B T}{v_c} \left[\frac{1}{N} \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi (1 - \phi) \right], \quad \chi = -\frac{z \Delta \epsilon}{2 k_B T} > 0,$$

where ϕ is the volume fraction of the polymer, v_c is the specific volume of monomer and solvent particles, z is the coordination number, and $\Delta \epsilon$ is a measure of the (attractive) interaction between solute particles and between solvent particles.
(a) Plot the function $f(T, \phi, N)$ vs ϕ across the range $0 \leq \phi \leq 1$ for $N = 100$ with appropriately scaled curves for $\chi = 0.5, 0.75, 1.0, 1.25$. Describe the physical meaning of the main features identified in these curves.
(b) Use the general expression for the osmotic pressure derived in part (a) of [pex48] to produce a specific expression $\pi(T, \phi, N)$ for the case of a polymer solution. Then plot this result for $N = 100$ as a function of ϕ using vertical and horizontal scales that highlight the features of interest. Describe those features.
(c) Identify the critical point by determining its coordinates $\phi_c(N)$ and $\chi_c(N)$ in the phase diagram. Show that your result is consistent with the result obtained in [pex47] for $N = 1$.
(d) Show that the spinodal line in the phase diagram, the locations of inflection points in the free-energy-density, has the following dependence on ϕ for any given N:

$$\chi_{sp}(\phi, N) = \frac{1}{2} \left[\frac{1}{1 - \phi} + \frac{1}{N \phi} \right].$$

Verify that this result is consistent with the result for $N = 1$ derived in [pex47]. Plot $\chi_{sp}(\phi, 100)$ with the vertial scale ranging from 0.5 to 1.0 and the horizontal scale ranging from zero to 0.5.
(e) Identify the coexistence line from the following construction. For a given value of $\chi > \chi_c$ the curve of $f(T, \phi, N)$ touches a tangent at two point with volume fractions $\phi_a < \phi_b$. These values are the solutions of the two equations $f'(\phi_a) = f'(\phi_b)$, $f(\phi_a) + f'(\phi_a)[\phi_b - \phi_a] = f(\phi_b)$. Produce some data for the coexistence line and include them into the phase diagram of part (d).

Solution:

[pex52] Phase separation in polymer blend

Consider a polymer blend composed of two kinds of monodisperse polymers with degrees of polymerization N_A and N_B, respectively. Under the assumption that the volume of monomers of either kind are of very similar size we can adapt the mean-field lattice model used in [pex47] to this case. The free-energy density then reads

$$f(T, \phi, N_A, N_B) = \frac{k_B T}{v_c}\left[\frac{1}{N_A}\phi\ln\phi + \frac{1}{N_B}(1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)\right], \quad \chi = -\frac{z\Delta\epsilon}{2k_B T} > 0,$$

where ϕ is the volume fraction of the type-A polymer and $1 - \phi$ the volume fraction of the type-B polymer. All monomers have volume v_c, the coordination number of the model lattice is z, and $\Delta\epsilon$ is a measure of the (attractive) interaction between type-A and type-B polymers.

(a) Derive the critical-point coordinates in the phase diagram: $\phi_c(N_A, N_B)$, $\chi_c(N_A, N_B)$ from the function $f(T, \phi, N_A, N_B)$.

(b) Show that the spinodal line in the phase diagram, the locations of inflection points in the free-energy-density, has the following dependence on ϕ for any given N_A, N_B:

$$\chi_{sp}(\phi, N_A, N_B) = \frac{1}{2}\left[\frac{1}{N_A\phi} + \frac{1}{N_B(1-\phi)}\right].$$

Plot $\chi_{sp}(\phi, 50, 20)$ with the vertical scale ranging from zero to 0.3 and the horizontal scale ranging from zero to one. Identify the location of the critical point on that line.

(c) Derive the coexistence line $\chi_{co}(\phi, N_A, N_B)$ for the special case $N_A = N_B \doteq N$. Plot $\chi_{sp}(\phi, 50, 50)$ and $\chi_{co}(\phi, 50, 50)$ versus ϕ in the same diagram with the vertical scale ranging from zero to 0.3 and the horizontal scale ranging from zero to one.

Solution:

[pex58] Interface width in phase-separated polymer blend

Consider a blend of two homopolymers with large and roughly equal degrees of polymerization N and roughly equal monomeric length a. The phase separation is driven by an unfavorable (meaning more repulsive or less attractive) interaction energy between unlike polymers, characterized by a dimensionlss interaction constant χ (see [pln48]). A sharp interface would minimize that interaction energy, producing an enthalpic gain ($\Delta H < 0$) but at too high an entropic cost ($\Delta S < 0$). A compromise minimizes the free energy $G = H - TS$. An interface of width w has loops of contour length $N_{\mathrm{L}}a$ from one species of polymer protruding into the space occupied by polymers from the other species. If the conformation can be assumed to take on the shape of a random walk we have

$$\frac{w}{a} \sim \sqrt{N_{\mathrm{L}}}. \tag{1}$$

It is reasonable to assume that at thermal equilibrium the (positive) interaction energy of a protruding loop is of the order of $k_{\mathrm{B}}T$.

(a) Show that the estimated width w of the interface then depends on the interaction constant χ as follows:

$$\frac{w}{a} \sim \frac{1}{\chi}. \tag{2}$$

(b) The interfacial energy density γ (interfacial energy per unit area) of the phase boundary can now be estimated from these ingredients. An additional assumption is that monomers are compact, implying that their cross section has area a^2. Show that the estimate is

$$\gamma \sim \frac{k_{\mathrm{B}}T}{a^2}\sqrt{\chi}. \tag{3}$$

[adaptd from Jones 2002]

Solution: