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01. Fundamentals I

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Interdisciplinary Field of Research [pln1]

Traditional academic disciplines

- physics
- chemistry
- biology
- engineering

Modern specializations and combinations

- biological physics
- medical physics
- biochemistry
- biomedical engineering
- materials science
- nanoscience
- *soft matter physics*

Characteristics of soft matter

- attributes of solids mixed with attributes of liquids
- materials from everyday life strongly represented
- mutable and polymorphic materials, quenched randomness
- hierarchic structures on microscopic and mesoscopic length scales
- conditions favorable for self-assembly of structures
- materials highly responsive to surroundings
- ubiquity of nonlinear effects
- response strongly dependent on time scale of perturbation
- strong fluctuations and fragile ordering
- weak stimuli with strong impact
- additives with strong impact
- relaxation times directly accessible to human senses

Major topics

- polymers
- colloids
- surfactants (amphiphiles)
- liquid crystals
- surfaces and interfaces
- elasticity, viscosity, viscoelasticity
- diffusion, permeation
- microfluidity, nanofluidity
- ionic soft matter
- biological matter
- self-assembly

Theoretical methodologies

- equilibrium statistical mechanics
  e.g. http : //digitalcommons.uri.edu/equilibrium_statistical_physics/
- nonequilibrium statistical mechanics
  e.g. http : //digitalcommons.uri.edu/nonequilibrium_statistical_physics/
- transport theory
- physical kinetics
- stochastic processes
- fluid mechanics including microfluidics and nanofluidics
- simulations: molecular dynamics, Monte Carlo
- self-consistent field theory
- density functional theory
- statistically interacting particles with shapes

Experimental Techniques

Microscopy

- Optical microscopy for colloidal particles and aggregates of polymers.
- Polarized optical microscopy for identifying birefringent structures in liquid crystals.
- Differential interference contrast (DIC) microscopy for large colloidal particles.
- Electron microscopy for structures with sub-nanometer resolution. High vacuum restricts applications to dry materials.
- Scanning electron microscopy (SEM) probes surfaces. Transmission electron microscopy (TEM) probes structure of nanoscale slices. Soft matter provides marginal electron density contrast.
- Atomic force microscopy (AFM) measures forces on piconewton scale.

Scattering

- Small-angle light scattering (SALS) probes objects much larger than the wavelength (Rayleigh regime) and objects of comparable sizes (Mie regime). Dynamic light scattering (DLS) probes temporal fluctuations in scattered light.
- Main advantage of X-ray and neutron scattering: shorter wavelengths. X-rays probe electron density distributions. Neutrons are scattered from atomic nuclei and from electron magnetic moments.

Spectroscopy

- Nuclear magnetic resonance (NMR) probes local microstructures. Molecular motion broadens NMR lines.
- Infrared (IR) spectroscopy and Raman spectroscopy probe vibrational and rotational motions of molecules. IR dichroism measurements extract information on bond orientations.
- Dielectric spectroscopy probes response to time-dependent electric field. Complex dielectric function measured over wide range of frequencies.
- Fluorescent spectroscopy probes location of specific molecules or specific parts of macromolecules in heterogeneous environment (e.g. biological tissue).
- Circular dichroism (CD) spectroscopy detects presence of chiral ordering (e.g. α-helix). Oriented circular dichroism (OCD)also detects spatial orientation of helical structures.

Rheology

- Mechanical response to dynamic stress or strain.
- Variety of responses to shear stress (for example):
  - *solid matter*: shear stress causes deformation, described by shear strain.
    Phenomenon: elasticity.
    Material property: shear modulus.
  - *liquid matter*: shear stress causes flow, described by shear rate.
    Phenomenon: viscous flow.
    Material property: viscosity.
  - *soft matter*: shear stress causes (reversible) deformation on short time scale and (irreversible) flow on longer time scale.
    Phenomenon: viscoelasticity.
    Material property: relaxation modulus.

Calorimetry

- Heat transfer at constant pressure measures change in enthalpy. Differential scanning calorimetry (DSC) locates phase transitions in soft matter.

[extracted in part from Hamley 2007]

Intermolecular Forces [pln18]

Pair interactions between molecules typically consist of a short-range repulsive part and a longer-range attractive part. The two parts produce a minimum interaction potential at some distance (e.g. Lennard-Jones potential). This minimum is interpreted as a bond and the depth as the binding energy.

The short-range repulsion is dominated by electronic Coulomb interaction as described quantum mechanically, involving symmetries and the Pauli principle. The longer-range attractive forces are more diverse in nature, strength, and range. They are commonly described as physical bonds of specific types.

Van der Waals bond: Quantum mechanical charge fluctuations intrinsic to electron wave functions of atoms or molecules produce random electric dipole moments. The fluctuating electric dipoles of adjacent molecules cause (on average) an attractive force. The range of the interaction potential depends on whether the molecules have fixed relative orientation ($\sim r^{-3}$) or are free to rotate ($\sim r^{-6}$). The van der Waals bond is only weakly directional if at all and its strength is comparable to $k_\mathrm{B}T$ at room temperature.

Ionic bond: Electronic charge transfer between adjacent atoms produces oppositely charged ions. The resulting Coulomb interaction potential is non-directional, much larger than $k_\mathrm{B}T$ at room temperature, and long-ranged ($\sim r^{-1}$). In solution ionic bonds become weaker and shorter-ranged due to screening effects.

Covalent bond: Electrons shared by adjacent atoms produce covalent bonds. Most covalent bonds have strengths similar to ionic bonds, some are weaker but still too strong to be broken by energies of $\mathrm{O}(k_\mathrm{B}T)$ at room temperature. Covalent bonds are short-ranged and highly directional.

Metallic bond: Electrons are being shared between many atoms in metallic bonds. These electrons become effectively delocalized. Covalent bonds and metallic bonds are related from a quantum mechanical point of view. Metallic sharing produces electrical conductors and covalent sharing electrical insulators.

Hydrogen bond: Hydrogen atoms as constituents of molecules tend to be electropositive. They have a significant unshielded positive charge. They are attracted to electronegative parts of adjacent molecules. Typical strengths vary between $5k_\mathrm{B}T$ and $12k_\mathrm{B}T$ at room temperature. In biological macromolecules, hydrogen bonds produce structural stability but are readily counteracted by molecular agents or environmental changes.

Hydrophobicity [pln19]

H_2O molecules are *polar*, meaning that each hydrogen is electropositive and the oxygen is electronegative. Liquid water is a polar medium. It forms a dynamic network of hydrogen bonds between adjacent H_2O molecules.

Different kinds of polar molecules may participate in this dynamic network as both donor or receptor ends of hydrogen bonds. They are called *hydrophilic*. *Non-polar* molecules are electroneutral. They do not participate in the formation of hydrogen bonds and are called *hydrophobic*. Surfactant molecules consist of hydrophilic parts and hydrophobic parts (e.g. polar headgroups and non-polar tails of lipids) and are called *amphiphilic*.

When molecules in low concentration (*solute*) are added to liquid water (*solvent*) they behave such as to minimize the free energy. The change in Gibbs free energy,

$$\Delta G = \Delta H - T\Delta S,$$

has *enthalpic* and *entropic* contributions. A favorable enthalpic contribution, $\Delta H < 0$, results when repulsive interactions are avoided and/or attractive interactions facilitated. A favorable entropic contribution, $\Delta S > 0$, results when disorder (number of available microstates) increases overall.

Hydrophilic solute molecules lower the enthalpy by participating in the formation of hydrogen bonds with water and increase the entropy by spreading across the volume in solution.

Hydrophobic solute molecules and H_2O solvent molecules form interfaces with unsatisfied hydrogen bonds. Agglomeration of solute molecules lowers the interface area and thus lowers the enthalpy but it also lowers the entropy. The minimum free energy is a compromise, characterized by low solubility and significant agglomerations.

Amphiphilic solute molecules tend to self-assemble into structures (micelles, liposomes, bilayers, ...) that shield their hydrophobic parts from exposure to water while their hydrophilic parts participate in the dynamic network of hydrogen bonds of the solvent. This arrangement lowers the enthalpy considerably albeit at some cost in entropy.

Divertissement: Switzerland shares three of its four official languages (German, French, Italian) and a great deal of cultural affinity with powerful, sometimes overbearing neighbors. Its survival as a nation through the centuries (since 1291) is attributable, at least in part, to a hydrophobic effect in the realms of politics and ideology.

Elastic Constants [pln20]

Consider an ideal elastic material (Hookean solid).

Isotropic elastic materials are characterized by three elastic constants:

- shear modulus: $G \doteq \dfrac{\sigma}{e}, \quad e \doteq \dfrac{\Delta x}{y}, \quad \sigma \doteq \dfrac{F}{A}.$
  - $\triangleright$ σ: shear stress,
  - $\triangleright$ e: shear strain.

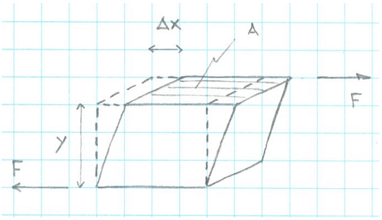
- bulk modulus: $K \doteq -\dfrac{\Delta p}{\Delta V/V} = \dfrac{1}{\kappa}.$
  - $\triangleright$ $\kappa \doteq -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_{[\,]}$: isothermal $[T]$ or adiabatic $[S]$ compressibility.

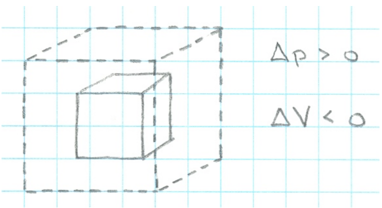
- Young modulus: $Y \doteq \dfrac{\sigma}{\epsilon}, \quad \sigma \doteq \dfrac{F}{A_0}, \quad \epsilon \doteq \dfrac{\Delta L}{L_0}.$
  - $\triangleright$ σ: tensile stress,
  - $\triangleright$ ϵ: tensile strain.

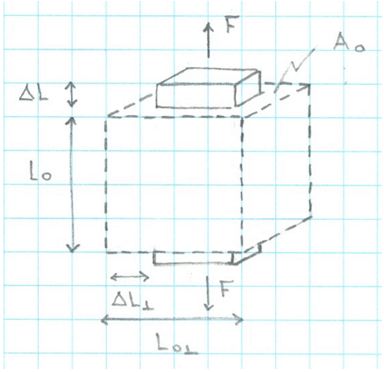
Relation between elastic constants from continuum mechanics:

$$Y = \frac{9KG}{3K+G} \quad \xrightarrow{K \gg G} \quad 3G \qquad (K \gg G: \text{ incompress. mat.})$$

Poisson ratio: $\nu \doteq -\dfrac{\epsilon_\perp}{\epsilon} = \dfrac{3K-2G}{2(3K+G)} \quad \xrightarrow{K \gg G} \quad \dfrac{1}{2}, \qquad \epsilon_\perp \doteq \dfrac{\Delta L_\perp}{L_{0\perp}}.$







Elastic Energy of Deformation [pln63]

Within a continuum description of elastic material calculate

- the deformation free-energy density $f(\mathbf{r})$,
- the deformation free energy $F = \int d^3r f(\mathbf{r})$.

We consider three successive stages of generality.

1. **Orthogonal deformation**
   Pure extension or compression in three orthogonal directions, expressed locally as follows:

$$r'_x = \lambda_1 r_x, \quad r'_y = \lambda_2 r_y, \quad r'_z = \lambda_3 r_z.$$

$$\Rightarrow \; f = f(\lambda_1, \lambda_2, \lambda_3), \quad \text{independent of position } \mathbf{r}.$$

2. **Uniform deformation**
   Linear transformation, expressed locally by deformation gradient tensor $\mathbf{E}$ as follows:

$$\mathbf{r}' = \mathbf{E}\cdot\mathbf{r} \quad \text{or} \quad r'_\alpha = \sum_\beta E_{\alpha\beta} r_\beta, \quad \text{where} \quad E_{\alpha\beta} = \frac{\partial r'_\alpha}{\partial r_\beta}.$$

   Convenient representation:[1] $\mathbf{E} = \mathbf{Q}\cdot\mathbf{L}$, where

   - $\sum_\gamma Q_{\alpha\gamma} Q_{\beta\gamma} = \delta_{\alpha\beta}$ (orthogonal tensor),
   - $L_{\alpha\beta} = \lambda_\alpha \delta_{\alpha\beta}$ (diagonal tensor),
   - $\det(\mathbf{E}) = \lambda_1\lambda_2\lambda_3$ (determinant of $\mathbf{E}$),
   - $\sum_{\alpha\beta} E^2_{\alpha\beta} = \sum_\alpha B_{\alpha\alpha} = \sum_\alpha \lambda^2_\alpha$ (trace of $\mathbf{E}\cdot\mathbf{E}^t$).

$$\Rightarrow \; f = f(\lambda_1, \lambda_2, \lambda_3), \quad \text{still independent of position } \mathbf{r}.$$

3. **General deformation**
   Local deformation assumed to be uniform.

$$\Rightarrow \; F = \int d^3r f\big(\mathbf{E}(\mathbf{r})\big).$$

   Equilibrium deformation from minimization of F for given boundary conditions.

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[1] Symmetric tensor $\mathbf{B} \doteq \mathbf{E}\cdot\mathbf{E}^t$ is diagonalized by orthogonal tensor $\mathbf{Q}$: $\mathbf{Q}^t\cdot\mathbf{B}\cdot\mathbf{Q} = \mathbf{L}^2$. It follows that $\mathbf{E}\cdot\mathbf{E}^t = \mathbf{B} = (\mathbf{Q}\cdot\mathbf{L})\cdot(\mathbf{L}\cdot\mathbf{Q}^t)$.

General expression for deformation energy density:

$$f(\mathbf{E}) \propto \mathrm{Tr}\big(\mathbf{E}\cdot\mathbf{E}^t - 3\big).$$

Consider two principal types of deformation:

- shear deformation:

$$\mathbf{E} = \begin{pmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \gamma > 0.$$

- uniform swelling:[2]

$$\mathbf{E} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}, \quad \lambda_i > 1.$$

- tensile deformation:

$$\mathbf{E} = \begin{pmatrix} \lambda_\perp^{-1/2} & 0 & 0 \\ 0 & \lambda_\perp^{-1/2} & 0 \\ 0 & 0 & \lambda_\parallel \end{pmatrix},$$

  where $\lambda_\perp = \lambda_\parallel$ means incompressibility.

[in part from Doi 2013]

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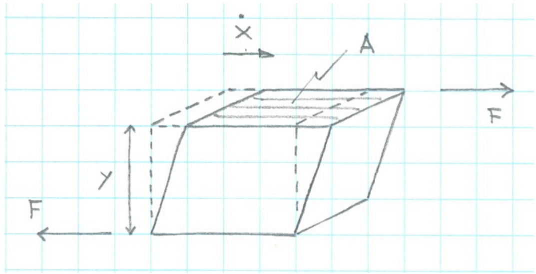
[2] For later applications to gels.

Viscous and Elastic Responses [pln21]

Ideal viscous material: Newtonian fluid.

- shear viscosity: $\eta \doteq \dfrac{\sigma}{\dot{e}}, \quad \dot{e} \doteq \dfrac{\dot{x}}{y}, \quad \sigma \doteq \dfrac{F}{A}.$
  - ▷ σ: shear stress
  - ▷ $\dot{e}$: shear strain rate

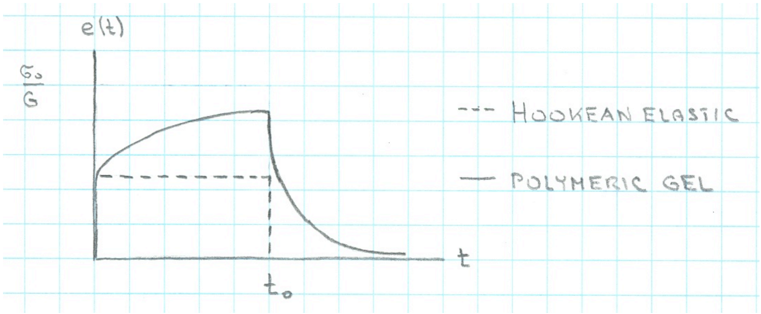


Elasticity and viscosity with transients.

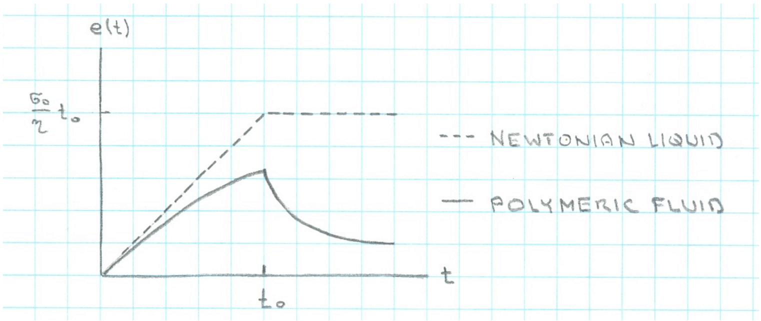
Shear stress turned on at $t = 0$ and turned off at $t = t_0$:

$$\sigma(t) = \sigma_0 \theta(t) \theta(t_0 - t).$$

Predominantly elastic response:



Predominantly viscous response:

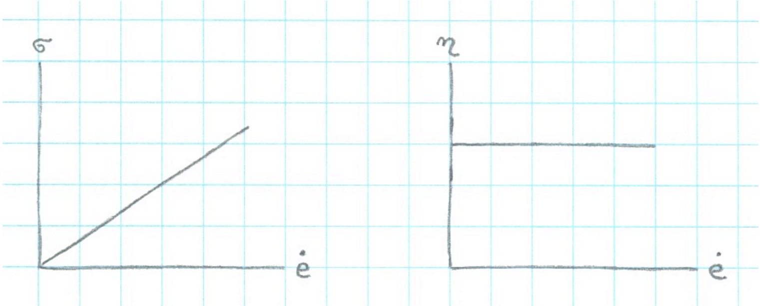


Nonlinear Viscous Behavior [pln22]

Nonlinear effects of all types as observed in dispersions can be interpreted as a consequence of particle rearrangements in response to flow (see section on colloids).

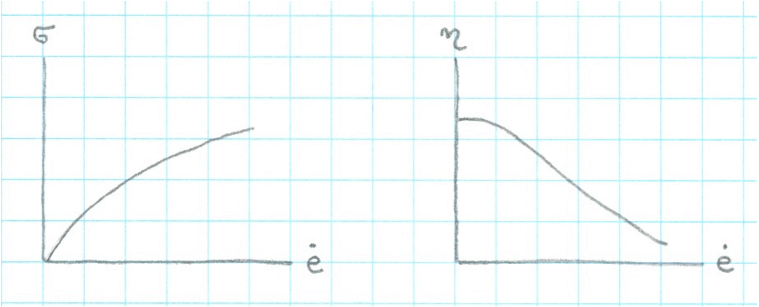
Shear stress versus strain rate: $\sigma(\dot{e}) = \eta(\dot{e})\dot{e}$.

(i) Newtonian liquid: reference system with $\eta = \text{const.}$

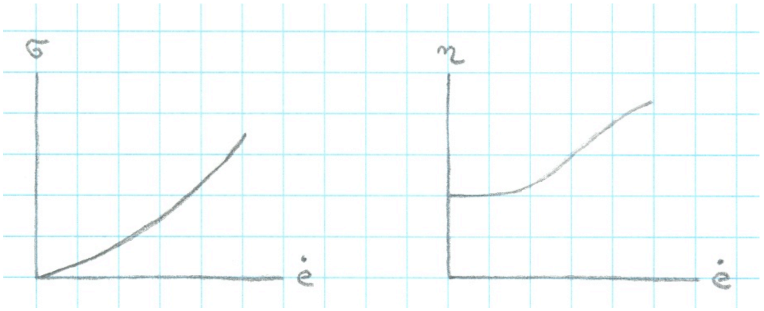


(ii) Shear thinning: paints, yoghurt.

- ▷ Model for polymeric fluids: $\eta(\dot{e}) = \dfrac{\eta_0}{1 + (\dot{e}/\dot{e}_c)^n}$,
- ▷ material parameters: $\eta_0, \dot{e}_c, n$,
- ▷ stress relaxation time: $\tau = 1/\dot{e}_c$,
- ▷ fast strain rates, $\dot{e} \simeq \dot{e}_c$, prevent polymers from relaxing to equilibrium.

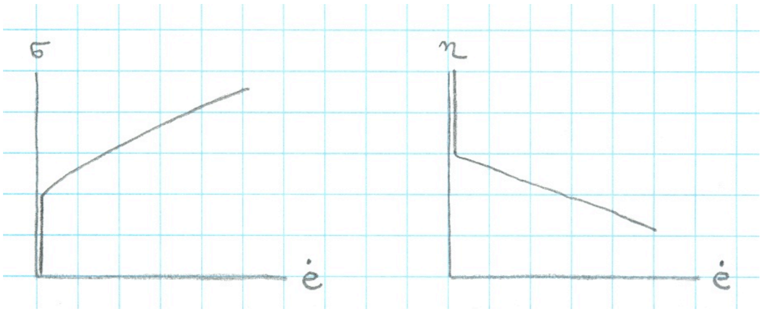


(iii) Shear thickening: pastes, whipped cream.



(iv) Bingham fluid: concentrated colloid suspensions.

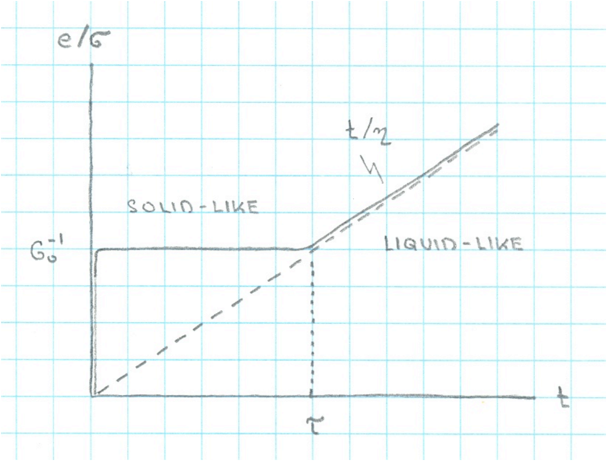
▷ Onset of flow requires threshold shear stress.



Simple model of viscoelasticity [pln23]

Characteristic stress relaxation time τ delimits regimes:

- $t \ll \tau$: solid-like (elastic) response, $\sigma = G_0 e \quad \Rightarrow \quad \dfrac{e}{\sigma} = G_0^{-1}$,
- $t \gg \tau$: liquid-like (viscous) response, $\sigma = \eta \dot{e} \quad \Rightarrow \quad \dfrac{e}{\sigma} = \eta^{-1} t$,
- $t \simeq \tau$: crossover behavior



Relation between shear modulus G_0 and viscosity η from graph e/σ vs t:

$$\frac{G_0^{-1}}{\tau} = \eta^{-1} \quad \Rightarrow \quad \eta = G_0 \tau.$$

Relaxation is due to thermally activated hopping: $\tau^{-1} = \nu \exp\left(-\dfrac{\epsilon}{k_B T}\right)$

- ▷ ϵ: energy barrier for hopping,[1]
- ▷ ν: optical phonon frequency.

Arrhenius law: $\eta = \dfrac{G_0}{\nu} \exp\left(\dfrac{\epsilon}{k_B T}\right) \quad \Rightarrow \quad \ln \eta \propto \dfrac{1}{k_B T}$.

Arrhenius law experimentally verified at not too low T.

In a more realistic scenario the viscoeleastic response is described by multiple relaxation times.

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[1] as derived, for example, from the latent heat of vaporization per molecule.

[pex16] Measuring viscosity and shear modulus

Consider two coaxial cylinders of length $l = 10\text{cm}$. The inner surface of the outer cylinder has radius $r_1 = 10\text{cm}$ and the outer surface of the inner cylinder has radius $r_2 = 9.5\text{cm}$. What torque is measured on the outer cylinder if
(a) the gap is filled with oil (viscosity $\eta = 10\text{P}$) and the inner cylinder rotates with angular velocity $\omega = 5\text{rad/s}$,
(b) the gap is filled with rubber (shear modulus $G = 5 \times 10^5\text{Pa}$) and the inner cylinder is turned an angle $\theta = 0.01\text{rad}$?
(c) What if the torque is measured on the inner cylinder and the outer cylinder is turned?
Note: Pascal (Pa) is an SI unit but poise (P) is not.

[adapted from Jones 2002]

Solution:

[pex15] Young modulus for generalized Lennard-Jones potential

Consider a crystal with simple cubic structure and an interatomic potential of the form

$$U(r) = 4\epsilon_0 \left[\left(\frac{r_0}{r} \right)^{2m} - \left(\frac{r_0}{r} \right)^{m} \right]$$

with $m > 0$ and positive constants ϵ_0, r_0. This potential has a unique minimum at $r = a$, where a is now taken to be the lattice spacing. For $m = 6$ it is the familiar Lennard-Jones potential.
(a) Find a/r_0 as a function of m and the value $U(a)$ of the potential minimum.
The Young modulus is defined as the ratio, $Y = \sigma/e$, of tensile stress, $\sigma = F/A_0$, and tensile strain, $e = \Delta L/L_0$. In the situation at hand, we can set $F = k(r - a)$ with $k = (d^2U/dr^2)_a$, $A_0 = a^2$, $\Delta L = r - a$, $L_0 = a$.
(b) Show that for the potential $U(r)$ we thus obtain $Y = k/a$. Then evaluate k in terms of ϵ_0, a, m.

[adapted from Jones 2002]

Solution:

[pex17] Arrhenius behavior of viscosity of water

The viscosity η of a fluid has been described to depend on temperature T according to the relation,

$$\eta = \frac{G_0}{\nu}\, e^{\epsilon/k_BT},$$

where ν is a characteristic frequency of vibration, ϵ is a characteristic energy barrier for hopping processes, and G_0 is the shear modulus for the elastic response at high frequencies. Investigate the usefulness of this relation in the face of the following empirical data:

- Eleven data points (temperature in units of °C, viscosity in units of 10^{-4}Pa s): (0,17.93), (10,13.07), (20,10.02), (30,7.98), (40,6.53), (50,5.47), (60,4.67), (70,4.04), (80,3.54), (90,3.15), (100,2.82).
- Shear modulus $G_0 \simeq 4 \times 10^9$Pa, the value of ice at 0°C.

(a) Plot $\ln\eta$ versus $1/k_BT$ along with a linear-model fit. Comment on the quality of the fit.
(b) Extract from the slope and the intercept estimates for ν and ϵ.
(c) Does the value for ν make any sense? If not, what adjustments are necessary?
(d) Compare the value of ϵ with the latent heat of vaporization per H_2O molecule. Comment on your finding.

[adapted from Jones 2002]

Solution:

Ordering in Soft Matter [pln25]

Soft matter exhibits a rich variety of ordering on a large span of length scales.

Orientational versus translational ordering: Different combinations of orientational and translational ordering are best known from realizations in liquid crystals [tsl51].

Hierarchical ordering: Ordering of molecules on a microscopic scale and ordering of molecular aggregates on a mesoscopic scale. The degree of ordering may be different one way or the other on the two scales. Hierarchical orderings are best known from realizations with surfactant molecules [tsl50].

Thermotropic versus lyotropic phase transitions: *Thermotropic* phase transitions are driven by changes in temperature and *lyotropic* phase transitions by changes in concentration.

Entropy driven ordering: Entropy is a measure of disorder overall. This notion is compatible with the possibility that a transition which establishes some kind of ordering increases the entropy.

Steric interactions: Macromolecules or aggregates of smaller molecules may be treated as constituent particles with shapes in the statistical mechanics of soft matter. Their dominant interactions may no longer by the molecular forces discussed in [pln18] but some hardcore repulsion (*steric interaction*) that can be accounted for as a *statistical interaction.*

Polydispersity: Constituent particles with a distribution of sizes such as in colloids are a common occurrence in soft matter.

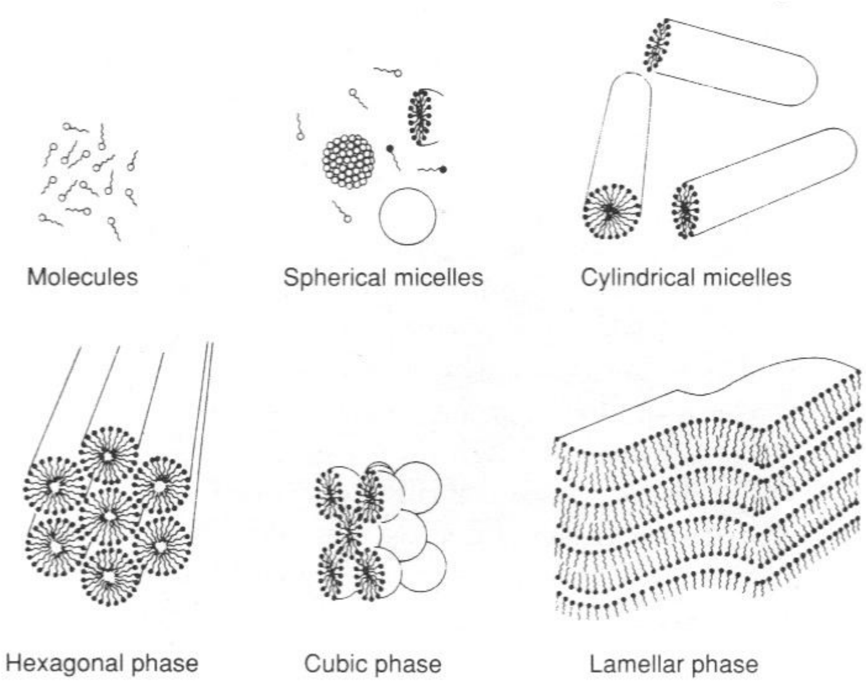
Polymorphism: Constituent particles of soft matter may further aggregate in configurations with different ordering tendencies.

Ordering of surfactant molecules [tsl50]

Surfactant molecules have highly soluble polar heads and barely soluble hydrocarbon tails. Increasing the surfactant concentration produces a succession of structures.

Cylindrical micelles have translational short-range order along the axis.
Amphiphilic bilayers have translational short-range order in the plane.

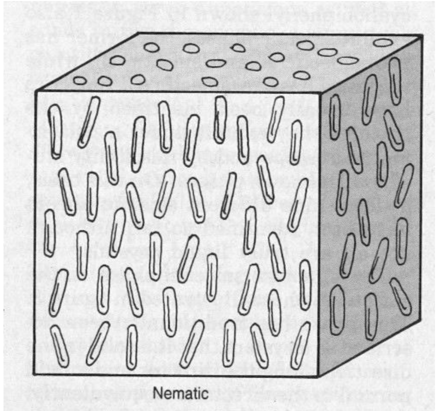
Hexagonal phase has 1D short-range order and 2D long-range order.
Lamellar phase has 2D short-range order and 1D long-range order.
Cubic phase has 3D long-range order on mesoscopic scale.

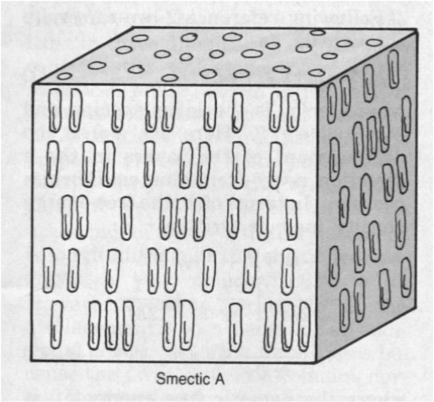


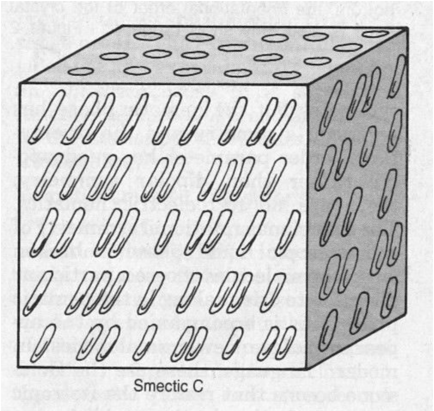
[from Yeomans 1992]

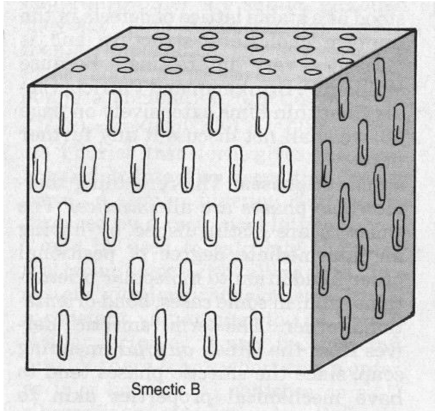
Common Liquid Crystal Phases [tsl51]

- **Nematic**: Molecular orientational ordering. Continuous rotational symmetry about *director*.
- **Smectic A**: Nematic ordering plus density wave along symmetry axis (director).
- **Smectic C**: Smectic A ordering with broken rotational symmetry. Density wave not perpendicular to director.
- **Smectic B**: Smectic A ordering plus density wave perpendicular to director.









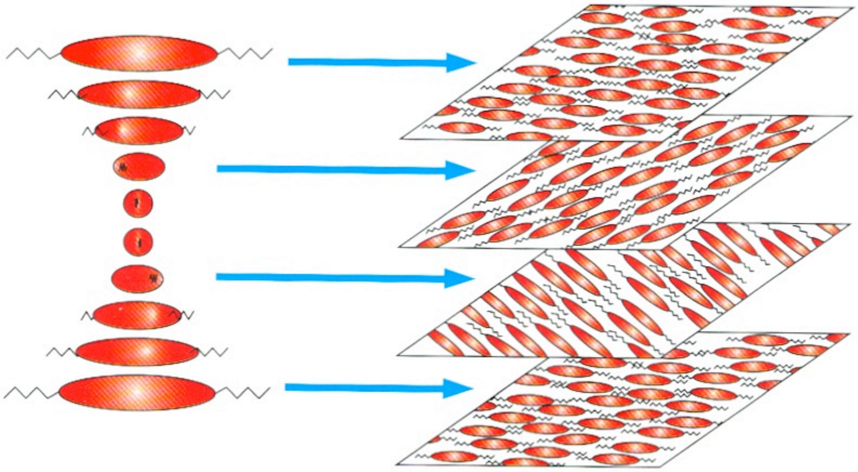
[images from Physics Today, May 1982]

Thermotropic transitions between smectic C and A are continuous. The tilt angle has a cusp singularity, $\theta(T) \sim (T_c - T)^\gamma$.

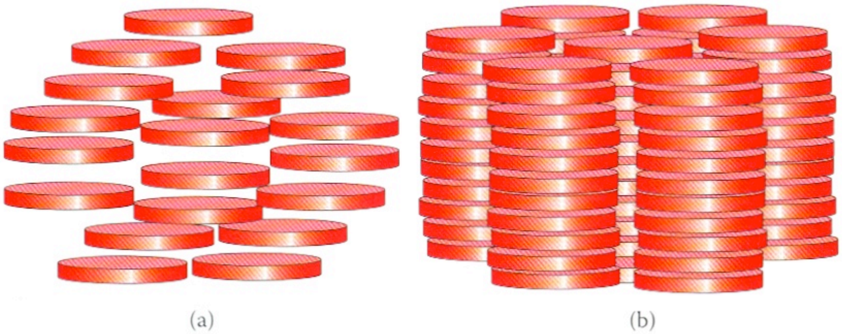
The layering in smectic phases is weak, characterized by a low-amplitude density modulation. True 1D LRO is suppressed by logarithmically diverging thermal fluctuations (Landau-Peierls instability).

- **Cholesteric**: Chiral nematic order with director rotating systematically about axis of fixed direction.

  The cholesteric phase (also named chiral nematic) has a T-dependent pitch P. The director $\mathbf{n}$ rotates 360° over this repeat distance. With T increasing, the pitch diverges at the cholesteric-nematic transition point. The T-dependent pitch is used for the design of thermochromatic devices (thermometers, sensors).



- **Discotic**: Liquid crystal order of disk-shaped molecules.
  (a) nematic (orientational),
  (b) hexagonal columnar (orientational and positional).



[images from Hirst 2013]

Glass transition [pln24]

Characteristic attributes of glassy materials:

- solid-like behavior mechanically,
- liquid-like behavior structurally,
- infinite viscosity and finite shear modulus,
- no translational or orientational long-range order,
- amorphous state,
- optical transparency (sometimes).

Importance of time scales:

Viscosity η and stress relaxation time τ exhibit anomalous dependence on temperature (deviation from Arrhenius law).

Recall the relation, $\eta = G_0\tau$, from [pln23].

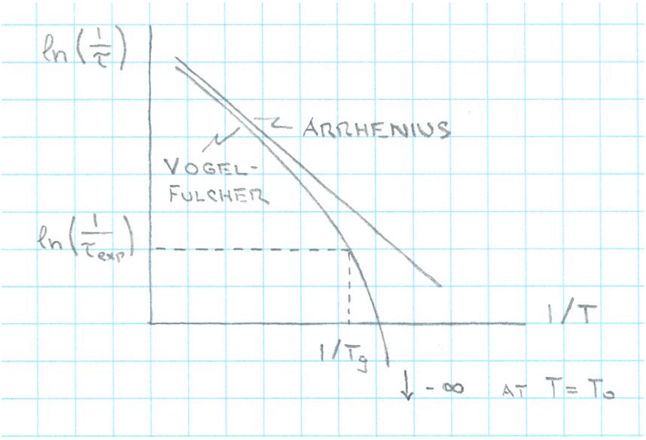
- Arrhenius law:

$$\eta = \eta_0 \exp\left(\frac{B}{T}\right) \quad \Rightarrow \quad \ln\frac{1}{\tau} \sim -\frac{B}{T}.$$

- Vogel-Fulcher model:

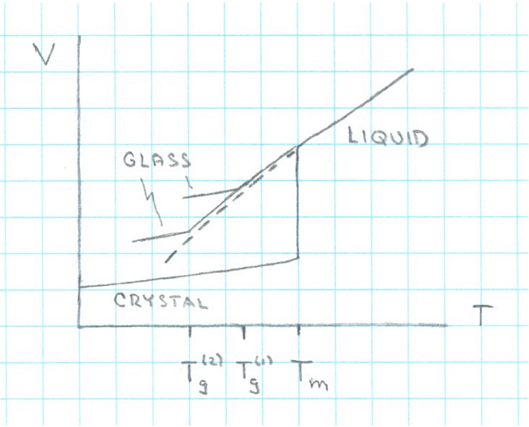
$$\eta = \eta_0 \exp\left(\frac{B}{T-T_0}\right) \quad \Rightarrow \quad \ln\frac{1}{\tau} \sim -\frac{B}{T}\left[\frac{1}{1-T_0/T}\right].$$

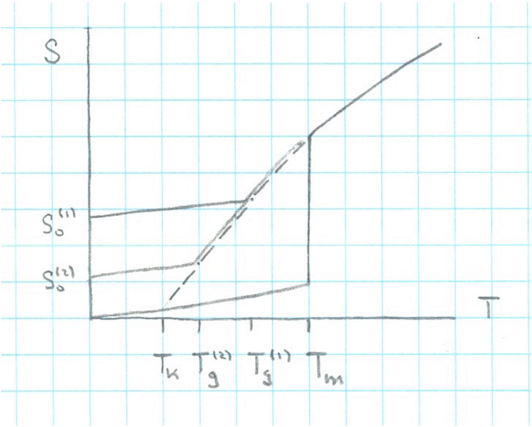
  - ▷ T_0: Vogel-Fulcher temperature,
  - ▷ T_g: glass transition temperature,
  - ▷ $\tau_{\rm exp}$: time scale of experiment.



Nature of transition:

- liquid → crystal: first-order transition (discontinuous),
- liquid → glass: more akin to second-order (continuous).
  - ▷ $T_{\mathrm{g}}^{(n)}$: glass transition temperature for given cooling rate,
  - ▷ T_{m}: melting temperature,
  - ▷ T_{K}: Kauzmann temperature,
  - ▷ $S_0^{(n)}$: residual entropy of glass for given cooling rate,
  - ▷ $--$: undercooled liquid.





Entropy:

The volume V can be measured directly whereas the entropy S must be determined from the heat capacity via integration:

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \quad \Rightarrow \quad S(T) = S(T_0) + \int_{T_0}^{T} dT' \frac{C_p(T')}{T'}.$$

[in part from Jones 2002]

Comments:

- Undercooled liquid is in metastable state. Nonequilibrium glass state with quenched randomness falls out of undercooled liquid.
- At constant $T \lesssim T_\mathrm{g}$ glass state undergoes slow ageing associated with densification toward density of undercooled liquid state. Ageing proceeds by spatial rearrangement of groups of molecules. As groups that need rearrangement grow larger, energy barriers grow higher and times scales longer.
- High density glasses are more durable due to more efficient packing of molecules. High-density assembly is achievable via vapor deposition. Molecules near surface have high mobility and thus produce efficient packing.
- Melting process of glass upon reheating depends on quality of packing:
  - loosely packed glass tends to gradually soften,
  - efficiently packed (high-density) glass tends to exhibit narrow moving front between soft and hard material.
- Quality of packing also leaves characteristic signature in heat capacity:
  - LDG: $C_p \sim T$ (typical for excitations of amorphous matter),
  - HDG: $C_p \sim T^3$ (typical for phonons in crystalline matter).
- Tempered glass is produced in a process that uses differential cooling rates for surface and interior parts, putting surface under compression and interior under tension. Cracks grow into explosive fragmentation. Small fragments are less dangerous than large shards.
- Deformation of glass produces irreversible rearrangements of molecules in spatially localized shear transformation zones. STZs have been interpreted as a defect structure that becomes manifest only under stress. With increasing stress, STZ have been observed to organize into bands that then mark the locations of initial failure.

[in part from Physics Today, 01/16]

[pex18] Glass transition in polystyrene

Polystyrene is a petrochemical polymer that is used, for example, for the manufacture of plastic food containers. The (visco-elastic) relaxation time of liquid polystyrene is known to satisfy the Vogel-Fulcher law,

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right),$$

with $T_0 = 50°\text{C}$, $B = 710°\text{C}$, and τ_0 to be determined.
(a) In an experiment performed on an effective time scale, $\tau_{exp}^{(1)} = 1000\text{s}$ (a good quarter of an hour), a glass transition is observed at $T_g^{(1)} = 101.4°\text{C}$. Find τ_0.
(b) What glass transition temperature $T_g^{(2)}$ is to be expected if an experiment on the much longer time scale of $\tau_{exp}^{(2)} = 10^5\text{s}$ (roughly one day) is carried out?
(c) Plot $\ln(\tau_0/\tau)$ versus $1/T$ as a solid curve. Mark the two experimental relaxation times as horizontal dashed lines and the two glass transition temperatures as vertical dashed lines.
(d) Show that in order to observe a glass transition as low as $T_g^{(3)} = 75°\text{C}$, the experimental time scale would have to be of the order of a human life time.

[adapted from Jones 2002]

Solution:

[pex19] Entropy from heat capacity of glass

Consider a glass-forming substance. The melting temperature is $T_m = 237\text{K}$ with latent heat $L_m = 24.2\text{kJ/mol}$. The glass transition temperature observed in an experiment carried out on a particular time scale is $T_g^{(1)} = 160\text{K}$. The molar heat capacity is measured to jump by $\Delta C_p^{(1)} = 180\text{JK}^{-1}\text{mol}^{-1}$ between the glass and the melt in this experiment. Experiments carried out on different time scales show that the jump in heat capacity is inversely proportional to the glass transition temperature: $\Delta C_p \propto 1/T$. The heat capacity is assumed to be the same, namely $C_p^0 = 90\text{JK}^{-1}\text{mol}^{-1} = \text{const}$, in the glass ($g$) state and in the crystalline (c) phase.
(a) Construct analytic expressions for $C_p^g(T)$ and $C_p^c(T)$ under the assumption that the glass transition takes place at $T_g^{(min)} < T_g < T_m$ with $T_g^{(min)}$ to be determined later.
(b) Infer analytic expressions for the entropies $S_c(T)$ and $S_g(T)$ with $S_c(T_m^+) = S_g(T_m)$ satisfied.
(c) Plot the functions $S_c(T) - S_c(T_0)$ and $S_g(T) - S_c(T_0)$ versus T for $T_0 = 100\text{K} < T < 250\text{K}$ and three values of T_g: 140K, 160K, and 200K. Here T_0 is a convenient reference temperature to be used already in part (a).
(d) The entropy difference $S_g(T) - S_c(T)$ between the glass state and the crystalline state depends on T_g. At the Kauzmann temperature, $T_K = T_g^{(min)}$, that difference is zero. Find T_K for the case at hand.

[adapted from Jones 2002]

Solution: