University of Rhode Island

# DigitalCommons@URI

5-5-2017

# 06. Polymers III

Gerhard Müller
*University of Rhode Island*, gmuller@uri.edu

## Recommended Citation

# Contents of this Document [ptc6]

### 6. Polymers III

- Polymer viscoelasticity
  - creep compliance and stress relaxation [pln52]
  - linear response and superposition principle
  - zero shear viscosity
  - polymer creep compliance: linear response [pex35]
  - polymer stress relaxation: linear response [pex36]
  - relaxation modulus of polymer melt [pln53]
  - time regimes: glassy - rubbery - viscous
  - characteristic dependences on degree of polymerization [psl9]
- Polymer crystallinity
  - semi-crystalline state [pln54]
  - hierarchical structure (chain-folding, lamellae, spherulites) [psl10]
  - lateral versus linear lamellar growth [pln55]
  - criteria for lateral growth (minimum stem length, temperature window)
  - velocity of lateral growth
  - conditions for fastest lateral growth [pex37]
- Gelation [pln56]
  - chemical gels [psl11]
  - physical gels [psl12]
  - rubber elasticity [pln64]
  - elasticity of balloon during inflation [pex60]
  - polymer gel [pln65]
  - polymer gel free-energy density of mixing [pex14]
  - swelling equilibrium of polymer gel [pex13] [pex12]
  - polymer gel compressed uniaxially [pex11]
  - percolation threshold and gel fraction
  - percolation on Bethe lattice [pex38], [nex40]

# Polymer Viscoelasticity: Linear Response

**Creep compliance:** $J(t)$

- Constant stress applied abuptly: $\sigma(t) = \sigma_0 \theta(t)$.
- Linear time-dependent strain: $e(t) = J(t)\sigma_0$.
- Regimes of linear strain response (see graph):
    - (1) fast elastic response,
    - (2) creep response (crossover),
    - (3) long-time asymptotic viscous response.
- Phenomenological model: $J(t) = bt + c\sqrt{t}, \quad b, c \geq 0$.
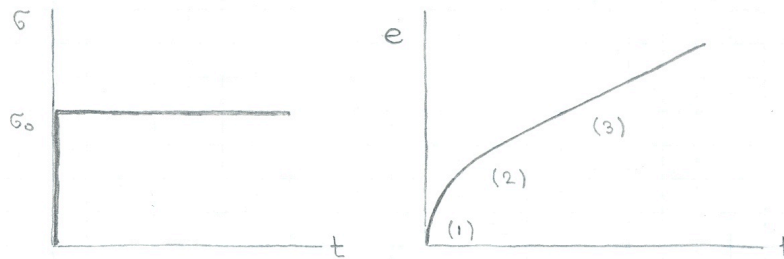


Time-dependent stress $\sigma(t)$ of arbitrary profile.

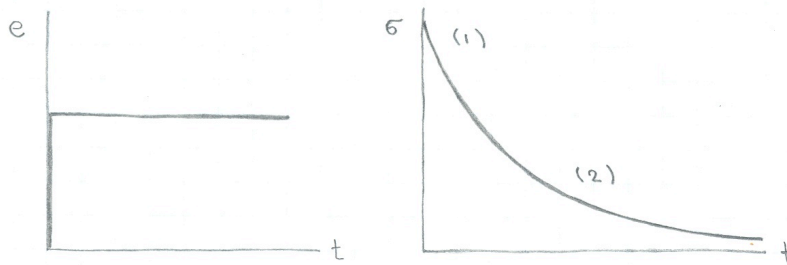Linear strain response constructed via superposition principle:

$$e(t) = \sum_i \Delta\sigma(\tau_i) J(t - \tau_i) \;\rightarrow\; \int_{\sigma(t_0)}^{\sigma(t)} d\sigma(\tau) J(t - \tau) = \int_{t_0}^{t} d\tau\, J(t - \tau)\frac{d\sigma}{d\tau}.$$
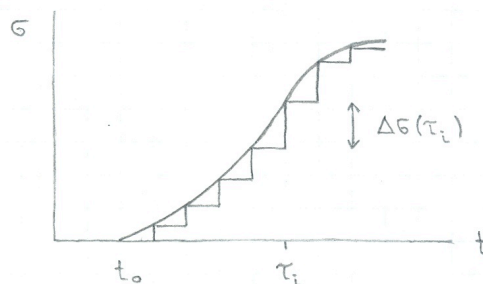


Strain response for linear and oscillatory stress profiles explored in [pex35].

**Stress relaxation modulus:** $G(t)$

- Constant strain applied abruptly: $e(t) = e_0 \theta(t)$.
- Linear time-dependent stress: $\sigma(t) = e_0 G(t)$.
- Regimes of linear stress response (see graph):
  - (1) instant elastic response,
  - (2) stress relaxation due to viscous flow.
- Phenomenological models of stress relaxation:
  - $\triangleright$ $G(t) = e^{-t}$ (fast),
  - $\triangleright$ $G(t) = (1+t)^{-1}$ (slow).



Time-dependent strain $e(t)$ of arbitrary profile.

Linear stress response constructed via superposition principle:

$$\sigma(t) = \sum_i \Delta e(\tau_i) G(t - \tau_i) \;\rightarrow\; \int_{e(t_0)}^{e(t)} de(\tau) G(t - \tau) = \int_{t_0}^{t} d\tau\, G(t - \tau) \frac{de}{d\tau}.$$
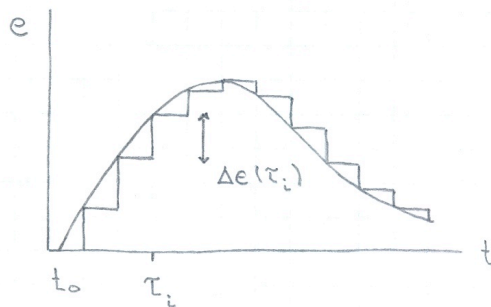


Stress response for model strain profiles explored in [pex36].

2

Oscillatory strain:   $e(t) = \sin(\omega t)$.

Steady-state stress response:   $\sigma(t) = G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)$.
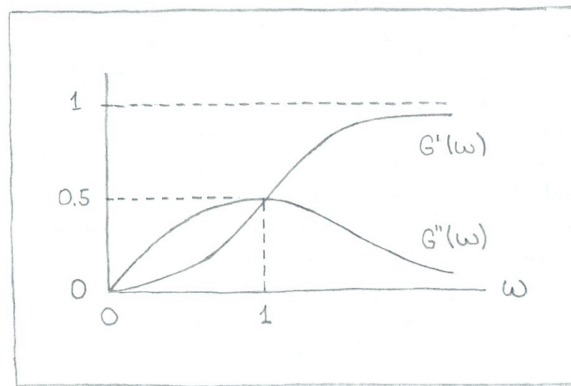
- $G'(\omega)$:   storage modulus describes elastic response,
- $G''(\omega)$:   loss modulus describes viscous response.

Example:   $G(t) = e^{-t}$.

$$\Rightarrow\ \sigma(t) = \frac{\omega}{1+\omega^2}\Big[e^{-t} + \omega\sin(\omega t) + \cos(\omega t)\Big],$$

where the first term represents a transient response and the two remaining terms the steady-state response with moduli

$$G'(\omega) = \frac{\omega^2}{1+\omega^2}, \quad G''(\omega) = \frac{\omega}{1+\omega^2}.$$



Zero-shear viscosity $\eta_0$ defined via $\sigma \doteq \eta_0\,(de/d\tau)$ for circumstances where it is justified to assume that a constant strain rate produces a constant steady-state stress.

$$\sigma = \eta_0\,\frac{de}{d\tau} = \int_{-\infty}^{t} d\tau\, G(t-\tau)\,\frac{de}{d\tau} = \int_{0}^{\infty} dt'\, G(t')\,\frac{de}{d\tau}$$

$$\Rightarrow\ \eta_0 = \int_{0}^{\infty} dt\, G(t).$$

[extracted in part from Jones 2002]

3

# [pex35] Polymer creep compliance: linear response

The basic model for creep compliance expresses the time-dependent strain $e(t)$ that results from a stress $\sigma_0$ turned on abruptly and held constant, $e(t) = J(t)\sigma_0$. For a viscoelastic material, the creep compliance $J(t)$ is a monotonically increasing function that rises very steeply from zero and then approaches a more moderate, linear increase at large $t$. For situations with time-dependent stress $\sigma(t)$, this linear response generalizes into the relation (Boltzmann superposition principle)

$$e(t) = \int_{-\infty}^{t} d\tau \, J(t - \tau) \frac{d\sigma(\tau)}{d\tau}.$$

Here we consider the following two-parameter creep compliance representing the viscoelastic behavior of some hypothetical polymer melt:

$$J(t) = bt + c\sqrt{t}, \quad b, c > 0,$$

(a) Calculate the time-dependent strain, $e(t)$, in (linear) response to a stress that increases from zero at constant rate: $\sigma(t) = at$. Plot both $J(t)$ and $e(t)$ versus $t$ for $a = 1, c = 1$, and $b = 0.1, 0.5, 1$. Interpret your results.

(b) Calculate the time-dependent strain, $e(t)$, in (linear) response to a harmonically oscillating stress: $\sigma(t) = a \sin(\omega t)$. Write the result in the form $e(t) = e_b(t) + e_c(t)$, where each term represents the linear response to one term of $J(t)$. Plot $e(t), e_b(t), e_c(t)$ versus $t$ for $a = 1, c = 1, b = 0.2$, and $\omega = 0.5, 1, 2$. Produce three graphs for different values of $\omega$, each with three curves. Use the range of $t$ such that $0 < \omega t < 10$ in each graph. Interpret your results.

Note that the term "linear" is used or implied to describe three different aspects: (i) the linear term in $J(t)$, (ii) the linear relation between strain $e(t)$ and stress rate $d\sigma/d\tau$, (iii) the linear stress increase in $\sigma(t) = at$.

**Solution:**

## [pex36] Polymer stress relaxation: linear response

The basic model for stress relaxation expresses the time-dependent stress $\sigma(t)$ that results from a strain $e_0$ forced abruptly and held constant, $\sigma(t) = G(t)e_0$. For a viscoelastic material, the relaxation modulus $G(t)$ is a monotonically decreasing function that approaches zero asymptotically as $t \to \infty$. For situations with time-dependent strain $e(t)$, this linear response generalizes into the relation (Boltzmann superposition principle)

$$\sigma(t) = \int_{-\infty}^{t} d\tau\, G(t-\tau)\frac{de(\tau)}{d\tau}.$$

Here we consider two alternative relaxation moduli: one decaying exponentially and the other as a power law, representing the viscoelastic behavior of different hypothetical polymer melts:

$$G_1(t) = e^{-t}, \qquad G_2(t) = \frac{1}{1+t}.$$

(a) Calculate the time-dependent stress, $\sigma_i(t)$, $i = 1, 2$, in (linear) response to a harmonically oscillating strain: $e(t) = \sin(\omega t)$ for the two model relaxation moduli. Plot $G_1(t)$ and $G_2(t)$ in the same graph for $0 < t < 5$ for comparison. Then plot $\sigma_1(t)$ and $\sigma_2(t)$ (two frames) for $0 < t < 10$ and $\omega = 0.5, 1, 2$ (three curves each). Interpret your results.
(b) Calculate the time-dependent stress, $\sigma_i(t)$, $i = 1, 2$, in (linear) response to a strain that rises from zero at a constant rate: $e(t) = t$. Plot $\sigma_1(t)$ and $\sigma_2(t)$ in the same frame for $0 < t < 5$ for comparison. Interpret your results.


**Solution:**

# Relaxation Modulus of Polymer Melt [pln53]

In a monodisperse polymer melt, the relaxation modulus $G(t)$ exhibits distinct behavior on three different time scales:

(1) The high initial value at short time reflects stiff *glassy* behavior.

(2) The plateau modulus $G_\mathrm{p}$ at intermediate times reflects *rubbery* elastic behavior. Entanglement produces contacts that act like temporary cross-links.

(3) At long times *viscous* behavior is in evidence with a strong dependence on $N$ (degree of polymerization). The terminal time $\tau(N)$ is related to the zero shear viscosity introduced in [pln52]:

$$\eta_0 = \int_0^\infty dt\, G(t) \simeq G_\mathrm{p}\tau(N).$$

Experimental evidence suggests that $\eta_0 \sim N^{3.4}$. [psl9]
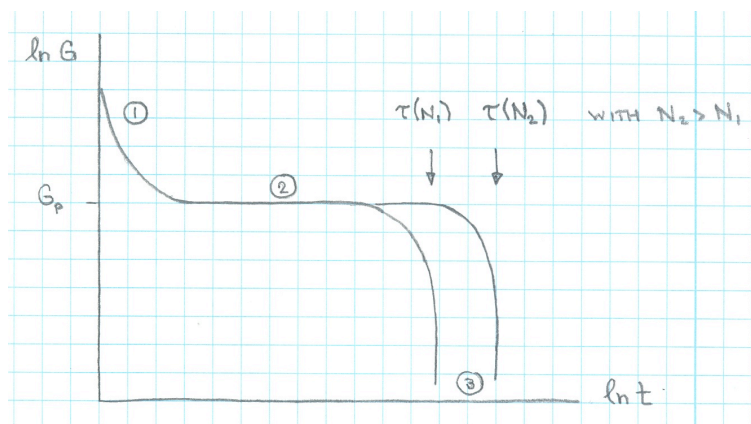


**Reptation:** diffusion of polymers along tubular space.

- mobility: $\mu_\mathrm{pol} = \mu_\mathrm{mon}/N$,
- diffusivity: $D_\mathrm{pol} = k_\mathrm{B}T\mu_\mathrm{pol} \sim N^{-1}$,
- effective random walk:[1]  $\langle L^2 \rangle = D_\mathrm{pol}\tau(n) \sim N^2$,
- terminal time:  $\Rightarrow \tau(N) \sim N^3$  (exp. evidence: $\sim N^{3.4}$ [psl9]),
- self diffusion: $D_\mathrm{s} \sim \dfrac{\langle x^2 \rangle}{\tau} \sim \dfrac{N}{N^3} \sim N^{-2}$  (exp. evid.: $\sim N^{-2.3}$ [psl9]).

[extracted in part from Jones 2002]

---

[1]using $L \propto N$.

# Dependences on Degree of Polymerization

## Zero shear viscosity



**Fig. 5.8** Zero shear viscosity of polybutadiene as a function of the relative molecular mass. At high relative molecular mass, the viscosity fits a power law $\eta_0 \sim N^{3.4}$. At lower relative molecular mass, if the data is corrected for the relative molecular mass dependence of the glass transition temperature (crosses) we find $\eta_0 \sim N$. Data from Colby *et al.* (1987).
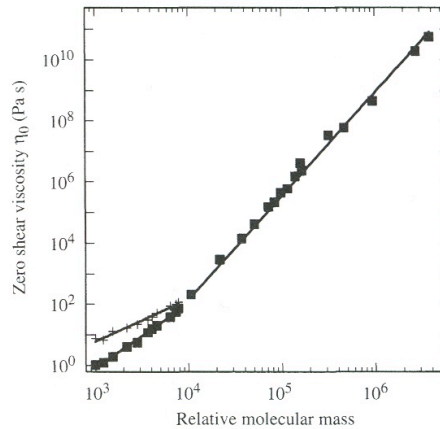
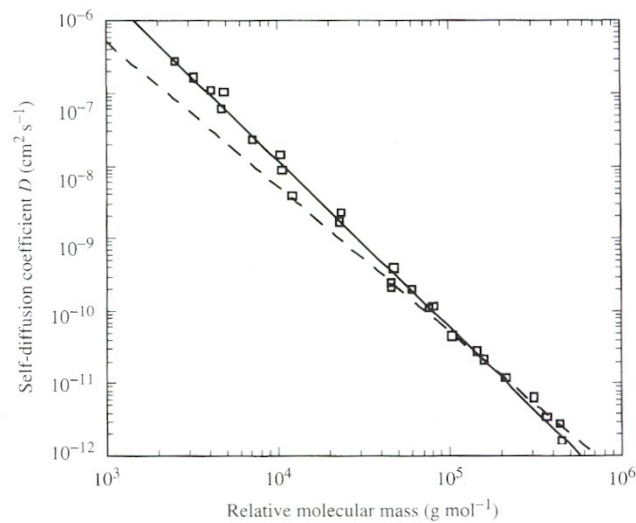## Self-diffusion coefficient



**Fig. 5.10** Self-diffusion coefficients of hydrogenated polybutadiene as a function of relative molecular mass. The dashed line is the prediction of the simple reptation theory that $D_{\text{self}} \sim N^{-2}$, while the solid line is the best-fit power law, $D_{\text{self}} \sim N^{-2.30}$. Data from a number of authors, cited in Lodge (1999).

[from Jones 2002]

# Crystallinity in Polymers [pln54]

Macroscopic crystallinity in polymers is rare. Polymer crystallinity tends to stay incomplete.

The most common form of polymer crystallinity is a *semi-crystalline state*: small crystals are embedded in an amorphous (glassy or rubbery) i.e. less ordered state of the same material.

Reasons for partial crystallinity:

- slow kinetics caused by entanglement;
- ordering obstructed by
  - random sequencing in copolymers,
  - stereochemical randomness,
  - polymer branching.

Common hierarchical structures of semi-crystalline polymers:

- Chain-folded lamellae:
  - typical width: $\sim$ 10nm,
  - lamellae separated by amorphous regions,
  - individual polymer may be part of more than one lamella.
- Spherulites:
  - typical size: $\sim \mu$m
  - formed by sheaves of lamellae,
  - grow as fibrils from central nucleus.

Illustrations of lamellae and spherulites in [psl10].

The texture of the hierarchical structure depends on whether the nucleation is faster, comparable, or slower than the lateral growth from the nucleus.

# Hierarchical Strucure of Crystalline Polymers [psl10]



spherulite

lamellar stack

crystalline layer

amorphous layer

section of an extended or folded polymer chain

[from Hamley 2007]

Fold surface
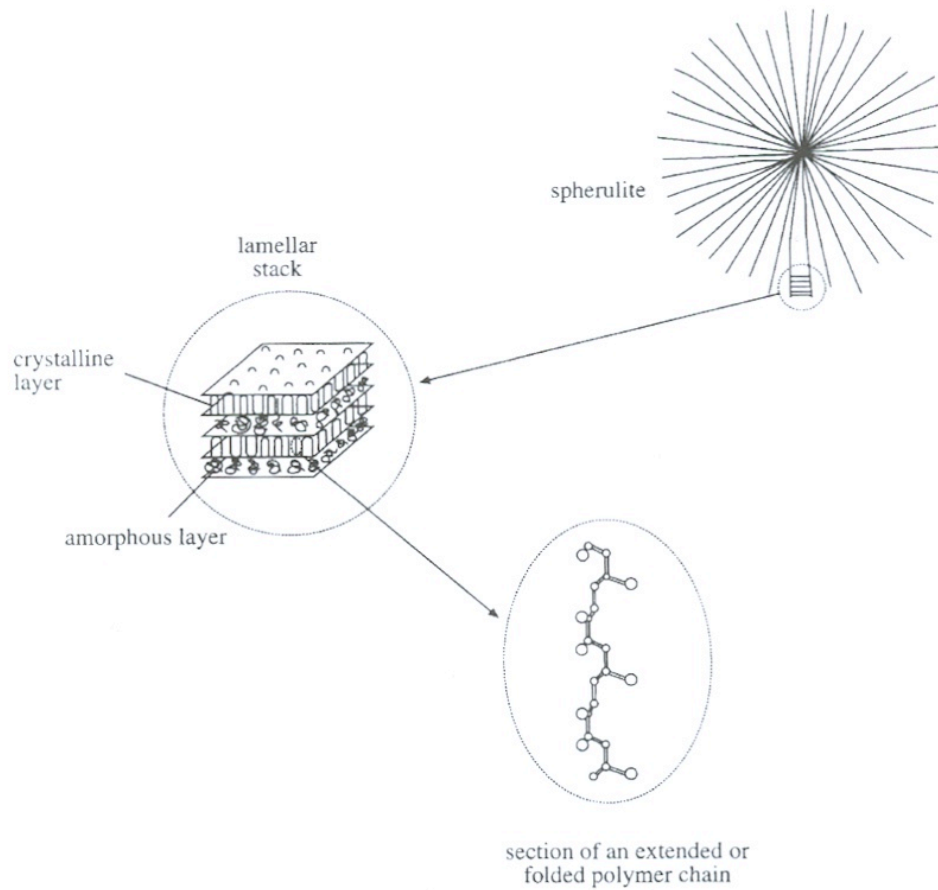
[from Jones 2002]

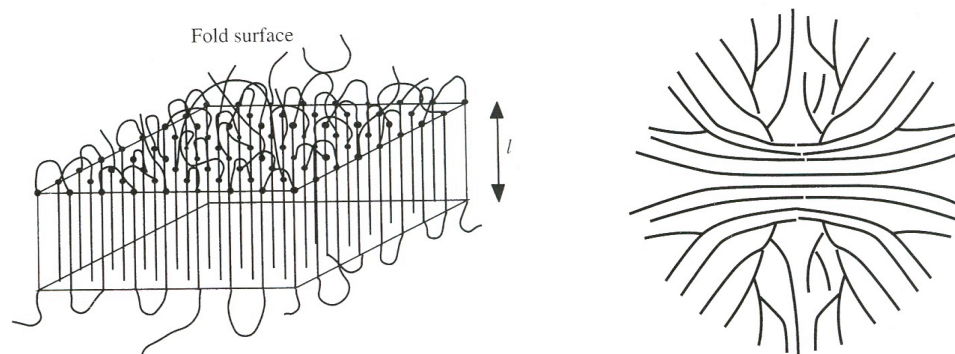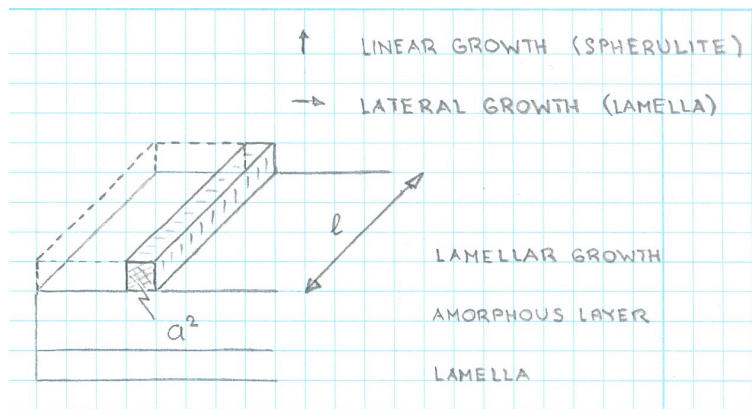# Lamellar Growth: Lateral vs Linear [pln55]

Chain-folded lamellae are not equilibrium structures.

Lamellae of width $l$ grow laterally at temperature $T < T_m(l) < T_m(\infty)$,

- $T_m(\infty)$: bulk melting temperature,
- $T_m(l)$: threshold temperature of lateral growth,
- $\lim_{l \to \infty} T_m(l) = T_m(\infty)$.



Change in free energy when one stem of volume $la^2$ is added to lamella:

$$\Delta g = -\frac{L_m}{T_m(\infty)}(la^2)\Delta T + 2a^2 \sigma_f, \tag{1}$$

- $L_m$: latent heat of melting per unit volume,
- $\Delta T = T_m(\infty) - T$: amount of undercooling,
- $\sigma_f$: interfacial energy per unit area,
- $L_m/T_m(\infty)$: entropy density of polymer stem in coil conformation.

Condition for lateral growth: $\Delta g < 0$ implying $l > l_c$ at given $\Delta T$.

Threshold width $l_c(\Delta T)$ or threshold temperature $T_m(l)$ inferred from criterion $\Delta g = 0$ [pex37]:

$$l_c(\Delta T) = \frac{2\sigma_f T_m(\infty)}{L_m \Delta T}, \quad T_m(l) = T_m(\infty)\left[1 - \frac{2\sigma_f}{L_m l_c}\right]. \tag{2}$$

Fastest lateral lamellar growth occurs at preferred width $l^*$ (to be determined). Criterion involves a free energy barrier:

- To join the lamella, a stem of width $l$ must straighten out; the uncoiling reduces the entropy, $\Delta S < 0$, thus raises the free energy, $T|\Delta S| > 0$.
- The joining of straightened out stem to lamella reduces the enthalpy, $\Delta H < 0$, thus lowers the free energy by the same amount.
- Net change of free energy: $\Delta g = T|\Delta S| - |\Delta H| < 0$.
- Entropy: $|\Delta S|/k_B = l/l_0$ (emprirical model).
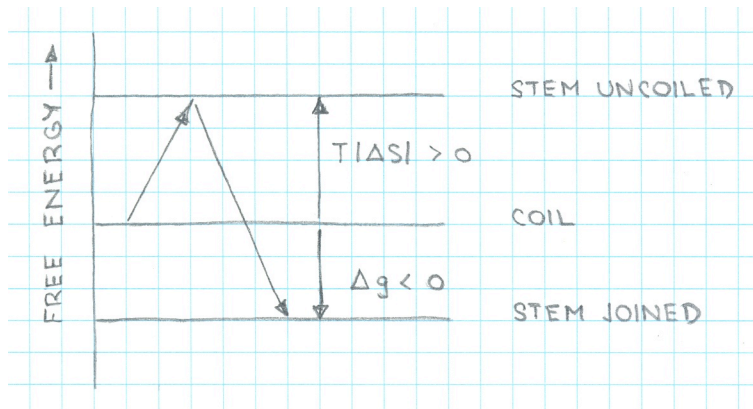


Transition rates:

- melt $\rightarrow$ crystal: $\quad u_{MC} = \dfrac{1}{\tau} \exp\left(-\dfrac{T|\Delta S|}{k_B T}\right),$

- crystal $\rightarrow$ melt: $\quad u_{CM} = \dfrac{1}{\tau} \exp\left(-\dfrac{T|\Delta S| - \Delta g}{k_B T}\right).$

Empirical model for reference time scale borrowed from [pln24]: Vogel-Fulcher relaxation time near glass transition:

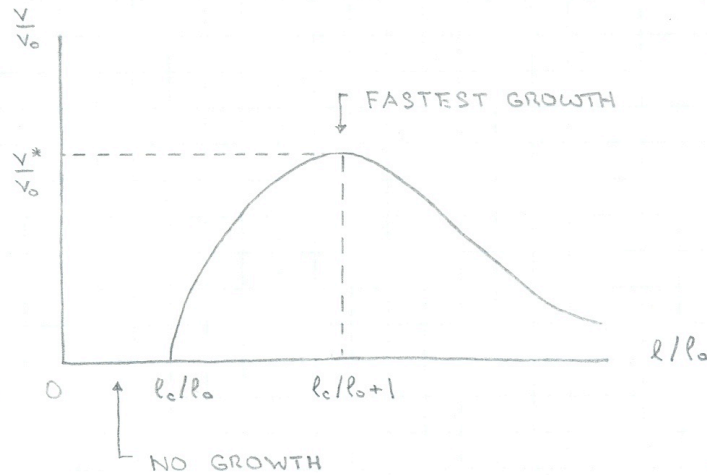$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right). \tag{3}$$

Rate of crystal growth:

$$u \doteq u_{MC} - u_{CM} = \frac{1}{\tau} \exp\left(-\frac{T|\Delta S|}{k_B T}\right)\left[1 - \exp\left(\frac{\Delta g}{k_B T}\right)\right]$$

$$\overset{|\Delta g| \ll k_B T}{\rightsquigarrow} -\frac{1}{\tau} \exp\left(-\frac{|\Delta S|}{k_B}\right)\frac{\Delta g}{k_B T}. \tag{4}$$

2

Velocity of crystal growth, $v \doteq ua$, at given $T$ using (1) and (4) [pex37]:

$$v(l) = v_0 e^{-l/l_0} \left[ \frac{l}{l_c} - 1 \right], \quad v_0 = \frac{2\sigma_f a^3}{\tau k_B T}. \tag{5}$$

Fastest growth from $(dv/dl)_{l^*} = 0$ [pex37]:

$$\Rightarrow \quad l^* = l_c + l_0, \quad \frac{v(l^*)}{v_0} = \frac{l_0}{l_c} e^{-1-l_c/l_0}. \tag{6}$$



With deeper quench, meaning larger undercooling $\Delta T$, the lamellar width $l^*$ of fastest growth becomes thinner.

Evaluate fastest-growth velocity (5) using (3) [pex37]:

$$v(l^*) = \frac{l_0 a^3 L_m e^{-1}}{k_B T \tau_0 T_m(\infty)} \underbrace{\exp\left( \frac{-B}{T - T_0} \right)}_{(i)} \underbrace{\left[ T_m(\infty) - T \right] \exp\left( -\frac{2\sigma_f T_m(\infty)}{l_0 L_m [T_m(\infty) - T]} \right)}_{(ii)}.$$

(i) factor controlling mobility of polymer in melt,

(ii) factor controlling thermodyanmic driving fore.

The final morphology is far from equilibrium. In practice, the morphology with the lowest free energy not really attainable.

# [pex37] Lateral growth of polymer lamellae

Consider a polymer chain modelled as a chain of cubes with side $a$ undergoing lateral lamellar growth at a temperature $T = T_m(\infty) - \Delta T$ below the bulk melting temperature $T_m(\infty)$.

(a) If $L_m$ is the latent heat of melting per unit volume and $\sigma_f$ the interfacial energy per unit area, reason that

$$\Delta g = -L_m l a^2 \frac{\Delta T}{T_m(\infty)} + 2a^2 \sigma_f \tag{1}$$

is the change in free energy when a stem of length $l$ is added to a preexisting lamella. Note that $L_m/T_m(\infty)$ can be interpreted as the configurational entropy per unit volume lost in the process. Then show that spontaneous growth at given $\Delta T$ only takes place if $l > l_c = 2\sigma_f T_m(\infty)/L_m \Delta T$ or $T < T_m(l) = T_m(\infty)[1 - 2\sigma_f/L_m l]$.

(b) If the melt $\to$ crystal and crystal $\to$ melt transition rates can be written in the form $u_{mc} = \tau^{-1} e^{-\epsilon_{mc}/k_B T}$ and $u_{cm} = \tau^{-1} e^{-\epsilon_{cm}/k_B T}$, respectively, where $\tau$ is a convenient reference time scale, and the energy barrierers are $\epsilon_{mc} = T|\Delta S|$ and $\epsilon_{cm} = T|\Delta S| - \Delta g$, respectively, and if we assume that the entropy change is simply proportional to the length of the stem, $|\Delta S|/k_B = l/l_0$, then we can write the velocity of lateral lamellar growth as $v(l) = (u_{mc} - u_{cm})a$. Show if we also assume that $|\Delta g|/k_B T \ll 1$ we obtain

$$v(l) = v_0 e^{-l/l_0} \left[ \frac{l}{l_c} - 1 \right], \quad v_0 = \frac{2\sigma_f a^3}{\tau k_B T}. \tag{2}$$

Plot $v/v_0$ versus $l/l_0$ for a scenario with $l_0/l_c = 2$. Identify the stem length $l^*$ for which lamellar growth is fastest and determine the maximum growth velocity $v^*/v_0$ for that scenario. Connect that point in the curve by a horizontal and a vertical dashed line to the axes.

(c) Use the Vogel-Fulcher relaxation time, $\tau = \tau_0 \exp(B/(T - T_0))$ from [pln14] to evaluate (2) at $l = l^*$ and bring it into the form shown in [pln55].

[adapted from Jones 2002]

**Solution:**

# Gelation of Polymers

Gelation taking place in colloidal aggregates of any type is known under the name *sol-gel transition*.

Gelation of polymers in solution involves the formation of a macroscopic network of cross links.

Characterizations of gels:

- structural disorder with randomness in the conformation of polymers and in the positions of cross links,
- rubber-like elasticity and potential for glass transition,
- potential for containing high volume fraction of liquid solvent,
- distinction between *rubbers* (dry gels) and gels proper that contain solvent,
- distinction between *chemical* gels and *physical* gels,
- chemical gels are mostly thermo-irreversible; cross links are formed e.g. by thermo-setting or vulcanisation [psl11],
- physical gels are mostly-thermo-reversible; cross links are formed e.g. by micro-crystallisation or microphase separation [psl12].

Percolation model of gelation:

Molecules are represented by points on a lattice. Nearest-neighbor bonds are added randomly with random clusters of growing size emerging. The *percolation threshold* is associated with the appearance of a cluster spanning the lattice.

Some relevant questions:

- What minimum fraction of bonds produces an infinite cluster?
- How does the average cluster size depend on the fraction of active bonds?
- What fraction of bonds belong to the infinite cluster?

# Chemical Gels [psl11]

Thermosetting gel consisting of short polymers with reactive endgroups and multifunctional hardener molecules
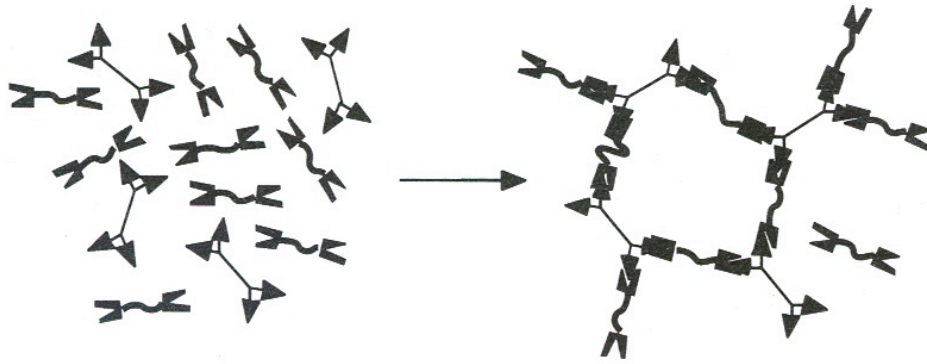


Vulcanisation of long, entangled polymers (e.g. polyisoprene) by chemical bonding (e.g. using sulphur) of adjacent chains.
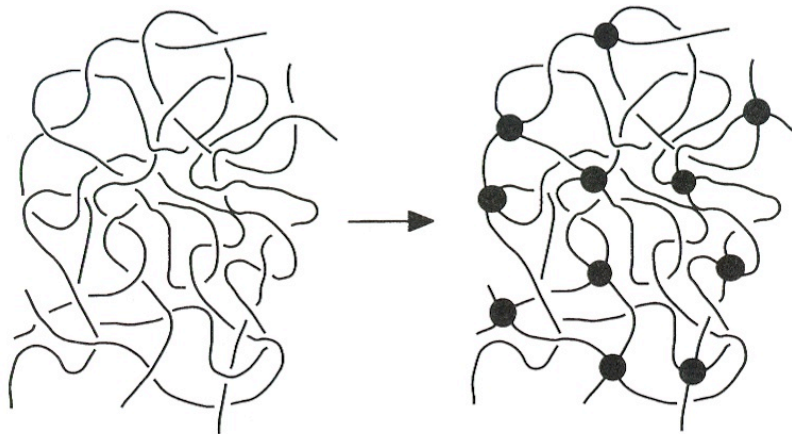


[from Jones 2002]

# Physical Gels [psl12]

Thermoreversible gelation via physical links between long polymers in the form of microcrystals.



Thermoreversible gelation of long triblock copolymers (with short and identical endblocks) via microphase separation.



[from Jones 2002]

# Rubber Elasticity

Consider a dry chemical gel of cross-linked polymers (see [psl11]).

Model of deformation free-energy density:

$$f(\mathbf{E}) = \frac{1}{2} n_\mathrm{c} k_\mathrm{B} T \left[ \sum_{\alpha\beta} E_{\alpha\beta}^2 - 3 \right].$$
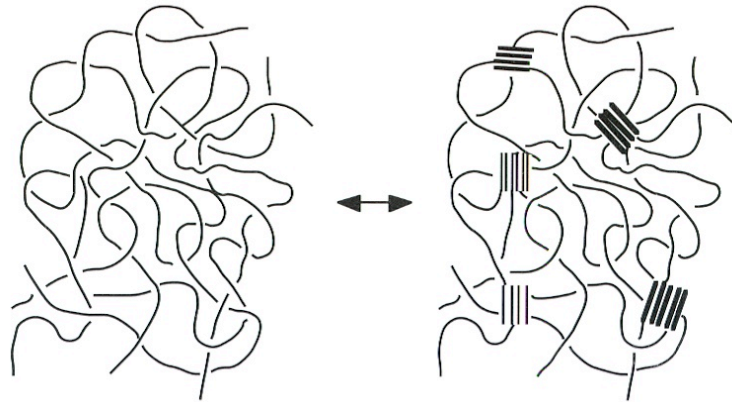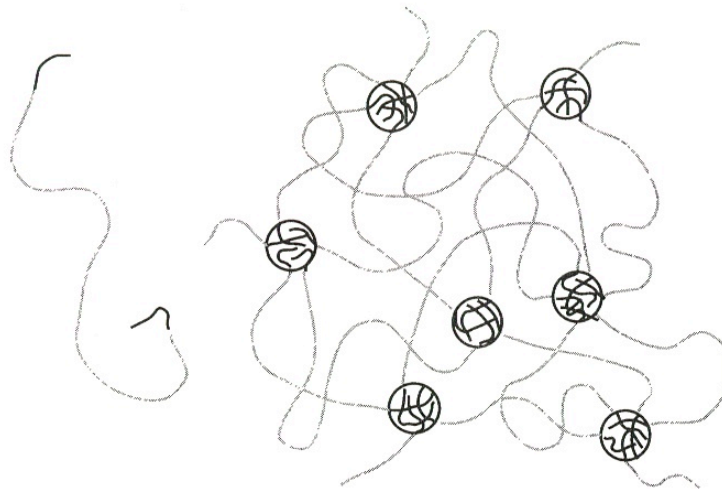
- $n_\mathrm{c}$: number of segments between cross links per unit volume,
- $\mathbf{E}$: deformation gradient tensor (see pln63]).

Consider two principal types of deformation:

1. **Shear deformation:**

$$\mathbf{E} = \begin{pmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \Rightarrow \quad f(\gamma) = \frac{1}{2} n_\mathrm{c} k_\mathrm{B} T \gamma^2,$$

   shear strain: $e = \gamma \ll 1$,

   shear stress: $\sigma \doteq G e = \dfrac{\partial f}{\partial \gamma} = n_\mathrm{c} k_\mathrm{B} T \gamma$,

   shear modulus: $G = n_\mathrm{c} k_\mathrm{B} T$.

2. **Tensile deformation** (with incompressibility constraint):

$$\mathbf{E} = \begin{pmatrix} \lambda^{-1/2} & 0 & 0 \\ 0 & \lambda^{-1/2} & 0 \\ 0 & 0 & \lambda \end{pmatrix} \quad \Rightarrow \quad f(\lambda) = \frac{1}{2} G \left( \lambda^2 + \frac{2}{\lambda} - 3 \right),$$

   tensile strain: $\epsilon \ll 1$ from $\lambda = 1 + \epsilon$,

   tensile stress:[1] $\sigma \doteq Y \epsilon = \lambda \dfrac{\partial f}{\partial \lambda} = G \left( \lambda^2 - \dfrac{1}{\lambda} \right) \quad \rightsquigarrow \quad 3 G \epsilon$,

   Young modulus: $Y = 3G = 3 n_\mathrm{c} k_\mathrm{B} T$.

[gleaned from Doi 2013]

---

[1] The factor $\lambda$ arises due to the shrinking of the cross section upon elongation.

## [pex60] Elasticity of balloon during inflation

Consider a rubber balloon in the shape of a sphere during inflation. At some instant during quasistatic inflation the balloon has radius $R$ and the material thickness is $h$. Upon further inflation the radius increases to $R' = \lambda R$. If we assume that the material is incompressible the thickness must decrease to $h' = \lambda^{-2}h$.

(a) Infer from this information the structure of the deformation gradient tensor $\mathbf{E}(\lambda)$ and the expression for the (tensile) deformation free-energy density $f(\lambda)$ (with guidance from [pln64]).

The total free energy then has two terms, one associated with the elasticity of the rubber material and the other associated with the elasticity of the gas inside the balloon:

$$F_{\text{tot}} = 4\pi R^2 h f(\lambda) - \frac{4\pi}{3}R^3(\Delta p)(\lambda^3 - 1),$$

where $\Delta p$ is the excess pressure inside the balloon. The opposite signs of the two terms are consistent with the fact that a change in volume converts one kind of elastic energy into the other kind.

(b) The equilibrium condition that balances the rubber elastic force and pressure is $\partial F_{\text{tot}}/\partial \lambda = 0$. Infer from this condition the dependence of excess pressure $\Delta p$ on the extent of inflation $\lambda = R'/R$.

(c) Plot the scaled excess pressure $R\Delta p/Gh$ versus $\lambda$ over the range $1 < \lambda < 3$ and draw your conclusions from the resulting curve.

[adapted from Doi 2013]

**Solution:**

# Polymer Gel

Mixture of polymer network and solvent. Swelling or shrinking of gel described quantitatively via deformation free-energy density.

## Deformation free energy

Volume increase: $V_{\mathrm{g}} \to V_{\mathrm{g}} \lambda_1 \lambda_2 \lambda_3, \quad \lambda_i > 1.$

Free-energy density:

$$f_{\mathrm{gel}}(\lambda_1, \lambda_2, \lambda_3) = f_{\mathrm{ela}}(\lambda_1, \lambda_2, \lambda_3) + f_{\mathrm{mix}}(\lambda_1, \lambda_2, \lambda_3). \tag{1}$$

- Elastic part is an application of [pln63] [pln64].

$$f_{\mathrm{ela}}(\lambda_1, \lambda_2, \lambda_3) = \frac{1}{2} G_0 \big( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \big). \tag{2}$$

- Mixing part is worked out in [pex14].

$$f_{\mathrm{mix}}(\lambda_1, \lambda_2, \lambda_3) = \frac{\phi_0}{\phi} f_{\mathrm{sol}}(\phi), \tag{3}$$

$$f_{\mathrm{sol}}(\phi) = \frac{k_{\mathrm{B}} T}{v_{\mathrm{c}}} \big[ (1 - \phi) \ln(1 - \phi) + \chi \phi (1 - \phi) \big], \quad \frac{\phi_0}{\phi} = \lambda_1 \lambda_2 \lambda_3,$$

  - $v_{\mathrm{c}}$: is the volume of solvent molecules,
  - $\chi > 0$: interaction constant controlling phase separation [pln32].

## Swelling equilibrium

Application to isotropically swelling gel: $\lambda_1 = \lambda_2 = \lambda_3 \doteq \lambda = (\phi_0/\phi)^{1/3}.$

$$f_{\mathrm{gel}}(\phi) = \frac{3}{2} G_0 \left[ \left( \frac{\phi_0}{\phi} \right)^{2/3} - 1 \right] + \frac{\phi_0}{\phi} f_{\mathrm{sol}}(\phi). \tag{4}$$

Equilibrium condition, $\partial f_{\mathrm{gel}}/\partial \phi = 0$, is worked out in [pex13]:[1]

$$G_0 \left( \frac{\phi}{\phi_0} \right)^{1/3} = \pi_{\mathrm{sol}}(\phi), \quad \pi_{\mathrm{sol}}(\phi) = \frac{k_{\mathrm{B}} T}{v_{\mathrm{c}}} \big[ -\ln(1 - \phi) - \phi - \chi \phi^2 \big]. \tag{5}$$

Balance of forces:

- osmotic pressure (right) represents expanding force,
- gel elasticity (left) represents restoring force.

---

[1] Note that swelling is associated with a decrease in polymer volume fraction $\phi$.

## [pex14] Polymer gel free-energy density of mixing

A dry gel of volume fraction $\phi_0$ and volume $V_{\mathrm{g}}$ swells, when immersed in a solvent, to volume $V_{\mathrm{g}}\lambda_1\lambda_2\lambda_3$. Hence its volume fraction decreases to the value $\phi = \phi_0/\lambda_1\lambda_2\lambda_3$. From [pln47] we pull the expression for the free-energy density of a polymers solution and set $N \to \infty$ in the first term on account of the cross-linking, yielding the expression

$$f_{\mathrm{sol}}(\phi) = \frac{k_{\mathrm{B}}T}{v_{\mathrm{c}}}\big[(1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)\big].$$

From these ingredients derive the following expression for the free-energy density of mixing:

$$f_{\mathrm{mix}}(\lambda_1, \lambda_2, \lambda_3) = \frac{\phi_0}{\phi}\big[f_{\mathrm{sol}}(\phi) - f_{\mathrm{sol}}(0)\big] - \big[f_{\mathrm{sol}}(\phi_0) - f_{\mathrm{sol}}(0)\big] \rightsquigarrow \frac{\phi_0}{\phi}f_{\mathrm{sol}}(\phi),$$

where the simplified expression to be used in [pln65] disregards terms that are not affected by swelling and uses $f_{\mathrm{sol}}(0)$ as a reference value.

[adapted from Doi 2013]

**Solution:**

# [pex13] Swelling equilibrium of polymer gel I

The swelling equilibrium of a polymer gel is a combination of thermal, chemical, and mechanical equilibrium. We take the expression for the free-energy density,

$$f_{\text{gel}}(\phi) = \frac{3}{2}G_0 \left[ \left( \frac{\phi_0}{\phi} \right)^{2/3} - 1 \right] + \frac{\phi_0}{\phi} f_{\text{sol}}(\phi), \quad f_{\text{sol}}(\phi) = \frac{k_{\text{B}}T}{v_{\text{c}}} \left[ (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi) \right],$$

from [pln65] and implement the equilibrium condition at constant temperature, $\partial f_{\text{gel}}/\partial\phi = 0$. Show that the result becomes

$$G_0 \left( \frac{\phi}{\phi_0} \right)^{1/3} = \pi_{\text{sol}}(\phi), \quad \pi_{\text{sol}}(\phi) = \frac{k_{\text{B}}T}{v_{\text{c}}} \left[ -\ln(1-\phi) - \phi - \chi\phi^2 \right],$$

where we use the expression for osmotic pressure derived in [pln28] in the slightly adapted rendition,

$$\pi_{\text{sol}}(\phi) \doteq \phi f'_{\text{sol}}(\phi) - f_{\text{sol}}(\phi).$$

[adapted from Doi 2013]

**Solution:**

## [pex12] Swelling equilibrium of polymer gel II

The swelling equilibrium as established in [pex13] depends on temperature directly, via the factor $k_B T/v_c$, and indirectly, via the interaction parameter $\chi$ in the expression for osmotic pressure. The lattice-gas origin of that expression (see [pln32]) predicts that $\chi \sim T^{-1}$. Use this information to rewrite the condition of swelling equilibrium in the form

$$\phi^{1/3} = \frac{T}{T_1}\left[-\ln(1-\phi) - \phi - \frac{T_2}{T}\phi^2\right], \tag{1}$$

where $T_1, T_2$ are independent reference temperatures, which allow us to explore the $T$-dependence of the swelling in a two-dimensional parameter space.
(a) Extract from Eq. (1) an explicit function $T(\phi)$.
(b) Invert that function into a function $\phi_{es}(T)$ for the special case of extreme swelling ($\phi \ll 1$).
(c) Plot a curve $\phi$ vs $T$ for the general case over the range $0 \leq T \leq 2$ and parameter values $T_1 = 0.001$, $T_2 = 0.5$. Interpret the curve in the light of the function $\phi_{es}(T)$, which is expected to be accurate only at low $\phi$.


**Solution:**

## [pex11] Polymer gel compressed uniaxially

Consider a rectangular slab of polymer gel with volume fraction $\phi_0$ when dry and $\phi_1 < \phi_0$ when immersed and swelled in solvent. Now this swelled slab is being compressed uniaxially (in $z$-direction), causing an elongation in $x$-direction and $y$-direction. We expect the volume of the slab to be reduced somewhat in the process and the volume fraction somewhat increased, implying that some amount of solvent will be squeezed out of the gel.

We construct the free-energy-density of the compressed polymer gel using the expression developed in [pln65] with $\lambda_1 = \lambda_2 = (\phi_0/\phi_1)^{1/3}\lambda_x$ and $\lambda_3 = (\phi_0/\phi_1)^{1/3}\lambda_z$ to account for the change in reference state from dry gel to immersed gel:

$$f_{\text{gel}} = \frac{1}{2}G_0 \left[ \left(\frac{\phi_0}{\phi_1}\right)^{2/3} \left(\lambda_z^2 + 2\lambda_x^2\right) - 3 \right] + \frac{\phi_0}{\phi} f_{\text{sol}}(\phi).$$

The uniaxial compression will be described by $\lambda_x > 1$ and $\lambda_z < 1$. In order to find the equilibrium polymeric volume fraction $\phi$ of the uniaxially compressed state as a function of length ratio $\lambda_z$ in the direction of the compression force we take two steps:

(i) Express $\lambda_x$ as a function of $\lambda_z$ and $\phi$ using conservation of polymeric volume.

(ii) Find a relation between $\phi$ andf $\lambda_z$ from the extremum condition $\partial f_{\text{gel}}/\partial\phi = 0$. Confirm that compression, $\lambda_z < 1$, leads to an increase in $\phi$, implying smaller volume of the slab of polymeric gel.

[adapted from Doi 2013]

**Solution:**

## [pex38] Percolation on Bethe lattice

The Bethe lattice with coordination number $z$ is a tree-like structure emanating from a central node out to infinity. Each node bonds with one node down the tree and $z-1$ nodes up the tree. The figure shows three generations of bonds for $z = 3$. The number of nodes or bonds in generation $k$ is $N_k = z(z-1)^{k-1}$. Now we connect nodes randomly with probability $f$, meaning that any bond is active with probability $f$ and inactive with probability $1 - f$. Note that the number of nodes out to any generation of is equal to the number of bonds.

(a) Show and reason that the threshold fraction of active bonds that produce an infinite cluster with non-vanishing probability is

$$f_c = \frac{1}{z-1}.$$

(b) If $P$ is the probability that a node is connected to infinity and $Q$ the probability that a node is not connected to infinity via a specific neighbor then show that the following relation holds:
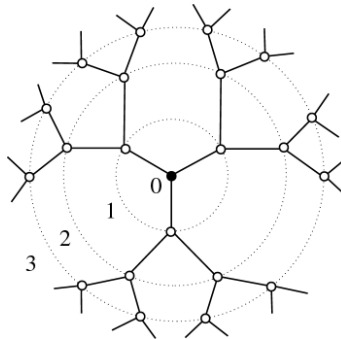
$$P = f - fQ^z$$

(c) Next show that $Q$ is the solution of the polynomial equation,

$$Q = 1 - f + fQ^{z-1}.$$

(d) The gel fraction is equal to the fraction of active bonds that are part of the infinite network. That fraction is $P/f$. Plot the gel fraction $P/f$ vs $f$ for $0 < f < 1$ and $z = 3, 4, 5$ as three curves in the same graph.

[adapted from Jones 2002]



[image from Wikipedia]

**Solution:**

## [nex40] Random walk in Las Vegas: chance and necessity

A gambler with \$1 in his pocket starts playing a game against a casino with infinite monetary resources. In each round of the game, the gambler wins \$1 (with probability $p$) or loses \$1 (with probability $1 - p$). The game ends when the gambler is bankrupt.

(a) Express the probability $P_C$ that the gambler goes bankrupt eventually as a function of $p$.

(b) Plot $P_C$ versus $p$ for $0 < p < 1$.

(c) For what value of $p$ is it a fair game in the sense that the gambler has a 50% chance of staying in the game forever?

**Solution:**