We have seen how polymers, in their simplest description (ignoring polymer-solvent and polymer-polymer interactions), are objects fully controlled by entropy. Their free-energy is entropic. The important role of entropy on the configuration of the single chain carries on also to polymer gels. In this section we discuss how to estimate the elastic constant of a network of ideal polymers. As expected, we will discover that, due to entropy, the network contracts on heating and expand on cooling.

1 Thermodynamics of rubbers

The first law of thermodynamics states that the change in internal energy of a system, such as a polymeric network, is the sum of all the energy changes: heat added to the system TdS, work done to change the network volume $-pdV$ and work done upon network deformation fdL:

$$dU = TdS - pdV + fdL$$

The differential dU represents the change in internal energy that arises if there is an entropy change dS, a volume change dV, or sample length change dL. The internal energy U is a thermodynamic state function of variables S, V, and L. The Helmholtz free energy F is defined as internal energy minus the product of temperature and entropy:

$$F = U - TS$$

The change in the Helmholtz free energy is written in differential form:

$$dF = dU - d(TS) = dU - TdS - SdT = -SdT - pdV + fdL.$$

The Helmholtz free energy is a thermodynamic state function of variables T, V, and L. The change in the Helmholtz free energy with the temperature is

$$\left(\frac{\partial F}{\partial T}\right)_{L,V} = -S$$

while the change with L can be written as a

$$\left(\frac{\partial F}{\partial L}\right)_{T,V} = f$$

The force f, applied to deform a network, consists of two contributions:

$$f = \left(\frac{\partial F}{\partial L}\right)_{T,V} = \left[\frac{\partial(U - TS)}{\partial L}\right]_{T,V} = \left(\frac{\partial U}{\partial L}\right)_{T,V} - T\left(\frac{\partial S}{\partial L}\right)_{T,V} = f_E + f_S$$

The two contributions to the force are an energetic term that is the change of internal energy with sample length

$$f_E = \left(\frac{\partial U}{\partial L}\right)_{T,V}$$

and an entropic term that is the product of temperature and the change of entropy with sample length:

$$f_S = -T \left(\frac{\partial S}{\partial L} \right)_{T,V}$$

Since the second derivative of the Helmholtz free energy does not depend on the order of differentiation:

$$\frac{\partial^2 F}{\partial L \partial T} = \frac{\partial^2 F}{\partial T \partial L}$$

the entropic force can be rewritten (as one of the Maxwell relations) as

$$f_S = -T \left(\frac{\partial S}{\partial L} \right)_{T,V} = T \left(\frac{\partial f}{\partial T} \right)_{V,L}$$

In a graph of the force vs T the slope indicates $\frac{\partial f}{\partial T}$. The tangent line with slope $\frac{\partial f}{\partial T}$, will intercept the y axis in a point indicating the energetic part of the force. The remaining part is the entropic one. This construction is called Flory construction.

In typical crystalline solids, such as metals, the energetic contribution dominates the force because the internal energy increases when the crystalline lattice spacings are distorted from their equilibrium positions. In rubbers, the entropic contribution to the force is more important than the energetic one. In 'ideal networks' there is no energetic contribution to elasticity, so $f_E = 0$. The dominance of the entropic part bestows a peculiar temperature dependence to the force at constant extension. While crystalline solids have the force decrease weakly with increasing temperature, rubbers show the opposite behaviour. The network strands lose conformational entropy when stretched making $dS/dL < 0$ and the, force increases with increasing temperature.

2 Un-entangled gel elasticity

2.1 affine stretching model

Let's try to describe the elastic properties of an ideal entropic gel, in which the energy of the gel does not depend on volume or shape. Suppose we make a deformation which leads

$$L_x = \lambda_x L_{x0} \qquad L_y = \lambda_y L_{y0} \qquad L_z = \lambda_z L_{z0}$$

In the hypothesis of an affine transformation, the chain ends will all change of the same factor $\lambda_x = \lambda_y = \lambda_z = \lambda$.

Writing the entropy of a polymeric chain composed of N Kuhn segments, each of length b, as

$$S(N, \mathbf{R}) = -\frac{3}{2} k_B \frac{<R^2>}{Nb^2} + S(N, 0)$$

we can write the variation of entropy induced by deformation on a single chain like

$$\Delta S = -\frac{3}{2}k_B \left(\frac{(\lambda_x^2 - 1) < R_x^2 > + (\lambda_y^2 - 1) < R_y^2 > + (\lambda_z^2 - 1) < R_z^2 >)}{Nb^2} \right)$$

In the undeformed state, $< R_x^2 > = < R_y^2 > = < R_z^2 > = \frac{Nb^2}{3}$. If we sum over all n chains composing the system

$$\Delta S_{tot} = -\frac{3}{2}k_B \frac{n}{3}(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) = -\frac{n}{2}k_B(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

and the free energy changes

$$\Delta F_{tot} = -T\Delta S_{tot} = \frac{n}{2}k_B T(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

Most gels are incompressible, and hence $\lambda_x \lambda_y \lambda_z = 1$.

2.2 Uniaxial Deformation

In a uniaxial expansion in which we deform the system of λ along x but at constant volume we have

$$\lambda_x = \lambda \qquad \lambda_y = \lambda_z = \frac{1}{\sqrt{\lambda}}$$

such that

$$\Delta F_{tot} = -T\Delta S_{tot} = \frac{n}{2}k_B T \left(\lambda^2 + \frac{2}{\lambda} - 3 \right)$$

The corresponding force, for an uni-axial deformation along z is

$$f_x = \frac{\partial \Delta F_{tot}}{\partial L_x} = \frac{1}{L_{x0}} \frac{\partial \Delta F_{tot}}{\partial \lambda} = \frac{nk_B T}{2L_x} \left(2\lambda - \frac{2}{\lambda^2} \right) = \frac{nk_B T}{L_{x0}} \left(\lambda - \frac{1}{\lambda^2} \right)$$

The stress component xx is calculated by dividing the force by the surface, in this case $L_y L_z$. From here

$$\sigma_{xx} = \frac{f_x}{L_y L_z} = \frac{nk_B T}{L_{x0} L_y L_z} \left(\lambda - \frac{1}{\lambda^2} \right) = \frac{nk_B T}{V} \lambda \left(\lambda - \frac{1}{\lambda^2} \right) = \frac{nk_B T}{V} \left(\lambda^2 - \frac{1}{\lambda} \right)$$

Finally, a Shear G module is defined as the relationship between stress and deformation. Is it so

$$G = \frac{nk_B T}{V}$$

hence each chain contributes $k_B T$ to the shear modulus.

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3 A micro-network approach to polymer-gel elasticity

3.1 Micro-networks

In real networks, the ends of network strands are attached to other strands at crosslinks. These crosslinks are not fixed in space — they can fluctuate around their average positions. These fluctuations lead to a net lowering of the free energy of the system by reducing the cumulative stretching of the network strands. The simplest model that incorporates these fluctuations is called the phantom network model. To understand the physics of the phantom network, we first study the elastic properties of micro-networks, networks on a Caley tree which can be solved analytically. In this model, the boundary sites are stretched affinely, while the interior sites are free to fluctuate.

The following derivation expands over the original calculation by W. W. Graessley, Statistical Mechanics of Random Coil Networks, Macromolecules, **8**, 186 (1975).
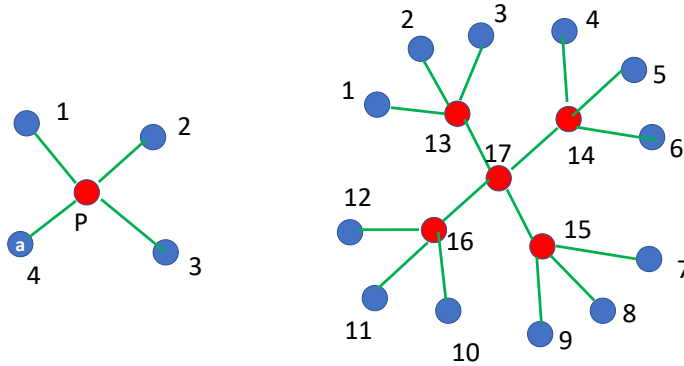

Figure 1: First two generation of a micro-network. The blue sites are pinned (boundary sites), the red sites (inner sites) are free to fluctuate.

We solve the first two iteration of the Caley tree and then we generalize the results to arbitrary iteration. We assume that a polymer is a spring K. We define $\alpha^2 \equiv K/2k_BT$, such that the energy of a polymer connecting sites i and j can be written as

$$U = \frac{1}{2}K|\vec{r}_i - \vec{r}_j|^2 = k_BT\alpha^2|\vec{r}_i - \vec{r}_j|^2$$

and the associated Boltzmann factor as $\exp(-\alpha^2|\vec{r}_i - \vec{r}_j|^2)$

3.2 Inner and boundary sites in a Caley tree

To evaluate the number of boundary sites in iteration j, P^j we can consider that the number of boundary sites in iteration j is the same as the number of boundary sites of the previous iteration times the new number of bonds departing from them $(f - 1)$

$$P_j = P_{j-1}(f - 1) \quad \text{with} \quad P_1 = f$$

and hence

$$P_j = f(f - 1)^{j-1}$$

The total number of strands at iteration j, $N_{j,strands}$ can be obtained by summing over all perimeter sites of all previous iterations. The new strands are indeed the one that connect to the new boundary sites. Then

$$N_{j,strands} = \sum_{k=1}^{j} P_k = \sum_{k=1}^{j} f(f - 1)^{k-1} = f \frac{(f - 1)^j - 1}{f - 2}$$

3.2.1 First iteration

In the first iteration the Caley tree is composed by a central site with f strands attached to it and f boundary sites. We call $\vec{r}_1, ..., \vec{r}_f$ the position of the boundary sites and $\vec{r}_p$ the central junction position. The position of the vertex sites and of the central site is controlled by statistical mechanics. Hence we will need to evaluate the partition function of the system. For each specific position of the vertex sites (each of them with its own probability to exist) the vertex sites act as an external field for the interior sites. We start by evaluating the free energy of the system for a fixed position of the vertex sites.

The partition function of the free sites of this $j = 1$ micro-network is then simply

$$Z = \int d\vec{r}_p e^{-\beta H}$$

and

$$\beta H = \alpha^2 \sum_{i=1}^{f} |\vec{r}_i - \vec{r}_p|^2$$

where $|\vec{r}_i - \vec{r}_p|^2 = (x_i - x_p)^2 + (y_i - y_p)^2 + (z_i - z_p)^2$. Expanding all the squares

$$\beta H = \alpha^2 \left(\sum_{i=1}^{f} x_i^2 - 2x_p \sum_{i=1}^{f} x_i + f x_p^2 + \ldots\ldots\text{same for } y \text{ and } z \right)$$

If we integrate over $\vec{r}_p$, direction by direction we have to calculate

$$\int dx_p \exp \left\{ -\alpha^2 \left(\sum_{i=1}^{f} x_i^2 - 2x_p \sum_{i=1}^{f} x_i + f x_p^2 \right) \right\}$$

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We can re-write the argument of the exponential function as

$$f(x_p - A)^2 + B = fx_p^2 - 2Afx_p + fA^2 + B$$

with the identification of

$$A = \frac{1}{f}\sum_{i=1}^{f} x_i \qquad\qquad\qquad B = \sum_{i=1}^{f} x_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} x_i\right)^2$$

such that

$$\int dx_p \exp(-\alpha^2[f(x_p - A)^2 + B]) = \sqrt{2\pi\sigma^2}\exp(-\alpha^2 B) = \sqrt{\frac{2\pi}{2\alpha^2 f}}\exp(-\alpha^2 B) =$$

$$\sqrt{\frac{\pi}{\alpha^2 f}}\, e^{-\alpha^2\left[\sum_{i=1}^{f} x_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} x_i\right)^2\right]}$$

Then

$$Z(\vec{r}_1,....\vec{r}_f) = \left(\frac{\pi}{\alpha^2 f}\right)^{3/2} e^{-\alpha^2\left[\sum_{i=1}^{f} x_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} x_i\right)^2\right]} e^{-\alpha^2\left[\sum_{i=1}^{f} y_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} y_i\right)^2\right]} e^{-\alpha^2\left[\sum_{i=1}^{f} z_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} z_i\right)^2\right]}$$

and the free energy is

$$\beta F(\vec{r}_1,....\vec{r}_f) = -\frac{3}{2}\log\left(\frac{\pi}{\alpha^2 f}\right) + \alpha^2\left(\left[\sum_{i=1}^{f} x_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} x_i\right)^2\right] + \left[\sum_{i=1}^{f} y_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} y_i\right)^2\right] + \left[\sum_{i=1}^{f} z_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} z_i\right)\right.\right.$$

The change in free energy upon stretching this specific configuration of boundary sites is then

$$\beta F(\vec{\lambda}\vec{r}_1,....\vec{\lambda}\vec{r}_f) - \beta F(\vec{r}_1,....\vec{r}_f) =$$

$$\alpha^2\left((\lambda_x^2 - 1)\left[\sum_{i=1}^{f} x_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} x_i\right)^2\right] + (\lambda_y^2 - 1)\left[\sum_{i=1}^{f} y_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} y_i\right)^2\right] + (\lambda_z^2 - 1)\left[\sum_{i=1}^{f} z_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} z_i\right)^2\right]\right.$$

We now have to average this free energy over all possible configurations of boundary sites. We need to calculate for each direction

$$<\left[\sum_{i=1}^{f} x_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} x_i\right)^2\right]>=< X^2 >$$

where we have defined implicitly X^2 and the average is now over $x_1,....x_f$. Thus we need to evaluate

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$$< X^2 >= \frac{\int dx_1...dx_f X^2 Z(\vec{x}_1,....\vec{x}_f)}{\int d\vec{x}_1...d\vec{x}_f Z(\vec{x}_1,....\vec{x}_f)}$$

where

$$Z(x_1,....x_f) = \sqrt{\frac{\pi}{\alpha^2 f}} e^{-\alpha^2 X^2}$$

Expanding X^2 one can write with a linear transformation

$$X^2 = \sum_i \sum_j b_{ij} \zeta_i \zeta_j = \sum_{i=1}^{f} \omega_i^2 v_i^2$$

where among the f eigenvalues one is zero due to the translational invariance of the system (the one that we would have eliminated by going from $x_1...x_f$ to $x_1, x_2 - x_1, ..x_f - x_1$). Hence we can change variable and write (eliminating the $\sqrt{\frac{\pi}{\alpha^2 f}}$ term from both numerator and denominator)

$$< X^2 >= \frac{V \int v_1...v_{f-1} \sum_{i=1}^{f-1} \omega_i^2 v_i^2 e^{-\alpha^2 \sum_{i=1}^{f-1} \omega_i^2 v_i^2}}{V \int dv_1...dv_{f-1} e^{-\alpha^2 \sum_{i=1}^{f-1} \omega_i^2 v_i^2}}$$

which separates in $f - 1$ factors, each of them equal to

$$\frac{\int dv_i \omega_i^2 v_i^2 e^{-\alpha^2 \omega_i^2 v_i^2}}{\int v_i e^{-\alpha^2 \omega_i^2 v_i^2}} = \omega_i^2 \sigma^2 = \omega_i^2 \frac{1}{2\alpha^2 f \omega_i^2} = \frac{1}{2\alpha^2}$$

Then, summing up each of the $f - 1$ terms

$$< X^2 >= (f-1) \frac{1}{2\alpha^2}$$

and

$$\beta \Delta F = \alpha^2 \left((\lambda_x^2 - 1) \frac{(f-1)}{2\alpha^2} + (\lambda_y^2 - 1) \frac{(f-1)}{2\alpha^2} + (\lambda_z^2 - 1) \frac{(f-1)}{2\alpha^2} \right)$$

$$\beta \Delta F = \frac{(f-1)}{2} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right)$$

Note that $f - 1 = P_1 - 1$. If we assume that our system is composed by N_0 of these micro-networks (or equivalently by $f N_0$ strands ($N_{strands} = f \ N_0$), we can multiply $\beta \Delta F$ by N_0 and, per unit volume

$$\frac{\beta \Delta F^*}{V} = \frac{N_0}{V} \frac{(f-1)}{2} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right) = \nu \frac{(f-1)}{2f} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right)$$

where we have defined $\nu = N_{strands}/V$.

3.2.2 Second iteration

Let's consider the case of a second iteration network, in a similar way. For simplicity let's assume $f = 4$ so that there are 12 boundary sites (numbered from 1 to 12) and five inner sites (numbered 13 to 17)

The hamiltonian is (only the x component for simplicity)

$$\beta H = \alpha^2 \left[(x_{13} - x_1)^2 + (x_{13} - x_2)^2 + (x_{13} - x_3)^2 + (x_{13} - x_{17})^2 + ...\right]$$

and by evaluating the squares

$$\beta H = \alpha^2 \left[x_{13}^2 + x_1^2 - 2x_{13}x_1 + x_{13}^2 + x_2^2 - 2x_{13}x_2 + x_{13}^2 + x_3^2 - 2x_{13}x_3 + x_{13}^2 + x_{17}^2 - 2x_{17}x_3 + ...\right]$$

$$\beta H = \alpha^2 \left[fx_{13}^2 + (x_1^2 + x_2^2 + x_3^2 + x_{17}^2) - 2x_{13}(x_1 + x_2 + x_3 + x_{17}) + ...\right]$$

$$\beta H = \alpha^2 [f \sum_{i=13}^{16} x_j^2 + \sum_{i=1}^{12} x_i^2 + fx_{17}^2 - 2x_{17} \sum_{i=13}^{16} x_i$$

$$-2x_{13}(x_1 + x_2 + x_3) - 2x_{14}(x_4 + x_5 + x_6) - 2x_{15}(x_7 + x_8 + x_9) - 2x_{16}(x_{10} + x_{11} + x_{12})]$$

and we need to integrate over $dx_{13}....dx_{17}$ to evaluate the free energy for fixed boundary sites.

Let's consider the integration over x_{13}.

$$\int dx_{13} e^{-\alpha^2 \left[fx_{13}^2 - 2x_{17}x_{13} - 2x_{13}(x_1 + x_2 + x_3)\right]}$$

The polynomial

$$\left[fx_{13}^2 - 2x_{17}x_{13} - 2x_{13}(x_1 + x_2 + x_3)\right] = f\left[x_{13}^2 - 2x_{13}(x_1 + x_2 + x_3 + x_{17})/f \right] =$$

$$f\left[\left(x_{13} - \frac{(x_1 + x_2 + x_3 + x_{17})}{f} \right)^2 - \frac{(x_1 + x_2 + x_3 + x_{17})^2}{f^2} \right]$$

which gives

$$\int dx_{13} e^{-\alpha^2 f\left[\left(x_{13} - \frac{(x_1 + x_2 + x_3 + x_{17})}{f} \right)^2 - \frac{(x_1 + x_2 + x_3 + x_{17})^2}{f^2} \right]} = e^{\alpha^2 f \frac{(x_1 + x_2 + x_3 + x_{17})^2}{f^2}} \sqrt{\frac{2\pi}{2\alpha^2 f}}$$

and after integrating over $dx_{14}....dx_{16}$

$$\left(\sqrt{\frac{\pi}{\alpha^2 f}} \right)^4 e^{\alpha^2 f \frac{(x_1 + x_2 + x_3 + x_{17})^2}{f^2}} e^{\alpha^2 f \frac{(x_4 + x_5 + x_6 + x_{17})^2}{f^2}} e^{\alpha^2 f \frac{(x_7 + x_8 + x_9 + x_{17})^2}{f^2}} e^{\alpha^2 f \frac{(x_{10} + x_{11} + x_{12} + x_{17})^2}{f^2}}$$

We can now integrate over x_{17}, after adding the term fx_{17}^2 which is in the Hamiltonian,

$$e^{-\alpha^2 fx_{17}^2} e^{\alpha^2 f \frac{(x_1 + x_2 + x_3 + x_{17})^2}{f^2}} e^{\alpha^2 f \frac{(x_4 + x_5 + x_6 + x_{17})^2}{f^2}} e^{\alpha^2 f \frac{(x_7 + x_8 + x_9 + x_{17})^2}{f^2}} e^{\alpha^2 f \frac{(x_{10} + x_{11} + x_{12} + x_{17})^2}{f^2}} =$$

$$e^{-\alpha^2 f x_{17}^2} e^{\alpha^2 f f \frac{x_{17}^2}{f^2}} e^{\alpha^2 f \frac{(x_1+x_2+x_3)^2+(x_4+x_5+x_6)^2+(x_7+x_8+x_9)^2+(x_{10}+x_{11}+x_{12})^2}{f^2}} e^{\alpha^2 f \frac{2x_{17}\sum_{i=1}^{12} x_i}{f^2}}$$

which gives

$$e^{\alpha^2 \frac{(x_1+x_2+x_3)^2+(x_4+x_5+x_6)^2+(x_7+x_8+x_9)^2+(x_{10}+x_{11}+x_{12})^2}{f}} \int dx_{17} e^{-\alpha^2 [(f-1)x_{17}^2 - \frac{2x_{17}\sum_{i=1}^{12} x_i}{f}]}$$

and similarly as previously done, completing the square

$$= e^{\alpha^2 \frac{(x_1+x_2+x_3)^2+(x_4+x_5+x_6)^2+(x_7+x_8+x_9)^2+(x_{10}+x_{11}+x_{12})^2}{f}} \int dx_{17} e^{-\alpha^2 (f-1)[x_{17} - \frac{\sum_{i=1}^{12} x_i}{f(f-1)}]^2} e^{\alpha^2 [\frac{\sum_{i=1}^{12} x_i}{f(f-1)}]^2}$$

such that the entire integration over the boundary sites is

$$\left(\sqrt{\frac{\pi}{\alpha^2 f}}\right)^4 \sqrt{\frac{\pi}{(f-1)\alpha^2}} e^{\alpha^2 \frac{(x_1+x_2+x_3)^2+(x_4+x_5+x_6)^2+(x_7+x_8+x_9)^2+(x_{10}+x_{11}+x_{12})^2}{f}} e^{\alpha^2 [\frac{\sum_{i=1}^{12} x_i}{f(f-1)}]^2}$$

To this term one need to add also the contribution

$$e^{-\alpha^2 \sum_{i=1}^{12} x_i^2}$$

which was already included in the Hamiltonian. Then defining

$$X^2 = \sum_{i=1}^{12} x_i^2 - \frac{(x_1+x_2+x_3)^2 + (x_4+x_5+x_6)^2 + (x_7+x_8+x_9)^2 + (x_{10}+x_{11}+x_{12})^2}{f} - [\frac{\sum_{i=1}^{12} x_i}{f(f-1)}]^2$$

the final result is obtained

$$= \left(\sqrt{\frac{\pi}{\alpha^2 f}}\right)^4 \sqrt{\frac{\pi}{(f-1)\alpha^2}} e^{-\alpha^2 X^2}$$

Repeating the same arguments already developed for the iteration one case, one can now evaluate $< X^2 >$ finding as result for the single micro-network (calling P_2 the number of boundary sites at the second iteration)

$$\beta \Delta F = \frac{(P_2 - 1)}{2} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right)$$

and for a collection of N_0 of them

$$\frac{\beta \Delta F^*}{V} = N_0 \frac{(P_2 - 1)}{2} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right) = \nu \frac{P_2 - 1}{2N_{2,strands}} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right)$$

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3.2.3 Infinite iteration

The previous expression can be generalized at infinite iteration $j \to \infty$ defining a quantity R_j (commonly named front factor) as

$$R_j = \frac{P_j - 1}{N_{j,strands}}$$

and evaluating its limiting value

$$lim_{j \to \infty} R_j = lim_{j \to \infty} \frac{f(f-1)^{j-1} - 1}{f \frac{(f-1)^j - 1}{f-2}} = \text{ neglecting the -1 in both expressions } = \frac{f-2}{f-1}$$

3.2.4 Inner and surface contributions

To separate the contribution to the elastic energy arising from the boundary sites and from the internal sites one can express R as a sum over the two contributions in the following way. We define F the fraction of boundary strands

$$F = \frac{P}{N_{strands}}$$

and similarly $1 - F$ the fraction of inner strands. Since

$$R = \frac{P-1}{N_{strands}}$$

$$R = F - \frac{1}{N_{strands}}$$

Next we want to express R as a function of F and $1-F$ only, so that we can discriminate between the contribution of the inner sites from the contribution of the boundary sites. From the expression of $N_{strands}$ and P,

$$N_{strands} = \frac{f}{f-2}[(f-1)^j - 1] \quad P = \frac{f}{f-1}(f-1)^j$$

we have

$$N_{strands} = \frac{f}{f-2}\left[\frac{f-1}{f}P - 1\right]$$

thus, dividing both sides by $N_{strands}$

$$1 = \frac{f}{f-2}\left(\frac{f-1}{f}F - \frac{1}{N_{strands}}\right)$$

or

$$-\frac{1}{N_{strands}} = \frac{f-2}{f} - \frac{f-1}{f}F$$

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such that

$$R = F + \frac{f-2}{f} - \frac{f-1}{f}F = F + \frac{f-2}{f}(1 - F + F) - \frac{f-1}{f}F$$

$$R = \frac{f-2}{f}(1 - F) + (1 + \frac{f-2}{f} - \frac{f-1}{f})F = \frac{f-2}{f}(1 - F) + \frac{f-1}{f}F$$

which tells us that $\frac{f-2}{f}$ comes from the internal strands and $\frac{f-1}{f}$ comes from the boundary strands.

Thus, for a real system, made essentially of internal strands, instead of R_∞ one need to use $\frac{f-2}{f}$. The final expression for the free-energy change upon stretching for a realistic network is thus

$$\frac{\beta \Delta F^*}{V} = \nu \frac{f-2}{f} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right)$$

3.3   Phantom Network Model

The main assumption of the affine network model is that the ends of network strands (the crosslink junctions) are fixed in space and are displaced affinely with the whole network, as if they were permanently attached to some elastic background. In real networks, the ends of network strands are attached to other strands at crosslinks. These crosslinks are not fixed in space — they can fluctuate around their average positions. These fluctuations lead to a net lowering of the free energy of the system by reducing the cumulative stretching of the network strands. The simplest model that incorporates these fluctuations is called the phantom network model. In a phantom network, the strands are ideal chains with ends joined at crosslinks. The ends of the strands at the surface of the network are attached to the elastic non-fluctuating boundary of the network. This attachment fixes the volume of the phantom network and prevents its collapse that would have been inevitable because such simple models ignore excluded volume interactions between monomers.

To evaluate the elastic modulus of the phantom network, we will progressively convert the cross-linked network into a polymer melt of suitable length polymers.

We have seen that an ideal polymer of length N can be considered as an entropic spring of elastic constant $K_p = 3k_B T / N b^2$. The network can be considered as composed by nodes of functionality f connected by springs of strength K_p.

The phantom network model assumes that the distance between two cross-links connected by a "spring" has a deterministic part (the time average) and a fluctuating part, and that there is no correlation between the two. In one dimension, calling x_0 the equilibrium distance and Δx the instantaneous displacement

$$< x^2 > = < (x_0 + \Delta x)^2 > = < x_0^2 > + < \Delta x^2 >$$

The phantom network model assumes that, upon stretching, x_0 is affinely deformed, while $< \Delta x^2 >$ remains identical.

Then

$$< x_\lambda^2 >=< (\lambda x_0 + \Delta x)^2 >= \lambda^2 < x_0^2 > + < \Delta x^2 >$$

The difference in elastic energy before and after stretching is thus

$$\Delta E = \frac{1}{2}K_p(< x_\lambda^2 > - < x^2 >) = \frac{1}{2}K_p < x_0^2 > (\lambda^2 - 1)$$

The phantom network model assumes also (see next subsection) that

$$< \Delta x^2 >= \frac{2}{f} < x^2 >$$

which implies, since $< x_0^2 >=< x^2 > - < \Delta x^2 >$

$$< x_0^2 >=< x^2 > \left(1 - \frac{2}{f}\right)$$

Then

$$\Delta E = \frac{1}{2}K_p(\lambda^2 - 1) < x^2 > \left(1 - \frac{2}{f}\right)$$

Here comes the delicate point. If we assume that we create the cross-links instantaneously, then the distribution of x^2 will be identical to the one just before cross-linking. But before cross-linking

$$\frac{1}{2}K_p < x^2 >= \frac{1}{2}k_B T$$

and than we can write that the change of energy per strand is

$$\Delta E = \frac{1}{2}k_B T(\lambda^2 - 1)\left(1 - \frac{2}{f}\right)$$

which coincides with the micro-network expression in the limit of infinite iteration and for internal bonds.

Note that, from an energetic point of view, assuming $\frac{1}{2}K_p < x^2 >= \frac{1}{2}k_B T$ means that *before* cross-linking the energy in the system was

$$\frac{1}{2}k_B T N_{strands}$$

and it was essentially all in $< \Delta x^2 >$, since in the absence of cross-links, $x_0 = 0$ and $< x^2 >=< \Delta x^2 >$. After cross-linking, this energy is splitted in two parts, a reference energy (the one associated to the average positions) which is in $\frac{1}{2}K_P < x_0^2 >$ and an additional energy which is associated to the fluctuations $\frac{1}{2}K_P < \Delta x^2 >$. This energy, summed over all strands, must be equal to $\frac{1}{2}k_B T$ time the number of sites, being after cross-linking nothing more than the energy of the N_{sites} phonon modes (in1 d, see next subsection).

3.4 How to explain $< \Delta x^2 >= \frac{2}{f} < x^2 >$

The phantom network model assumes that

$$< \Delta x^2 >= \frac{2}{f} < x^2 >$$

Consider that the network has N sites. We expand the potential energy around the average positions, such that the energy is a sum of a constant piece (the energy when there are no fluctuations) E_0 and a vibrational contribution. Being an harmonic system, the potential energy of this vibrational contribution is (3d).

$$U = \frac{3}{2} k_B T N$$

Then the energy per strand (associated to the vibration) is, since we have $N_{strands} = Nf/2$,

$$\frac{U}{N_{strand}} = \frac{3}{2} k_B T \frac{2}{f}$$

Then

$$\frac{1}{2} K_p < \Delta x^2 >= \frac{1}{2} k_B T \frac{2}{f}$$

or

$$< \Delta x^2 >= \frac{1}{K_p} k_B T \frac{2}{f}.$$

We have discussed previously that assuming cross-linking does not modify the equilibrium properties,

$$\frac{1}{2} K_p < x^2 >= \frac{1}{2} k_B T$$

such that

$$\frac{1}{K_p} k_B T =< x^2 > \quad \rightarrow \quad < \Delta x^2 >= \frac{2}{f} < x^2 >$$

4 Balloon inflation (Doi)

As an example of the nonlinear analysis of the deformation of rubbers, we consider the inflation of a rubber balloon. We assume that the balloon is a thin membrane arranged as a spherical shell (see Fig. 2). Let h be the thickness of the membrane and let R be the radius of the sphere in the force free state. Suppose that we inflate the balloon and make the pressure inside the balloon higher than that outside by ΔP . We will calculate the balloon radius R' as a function of ΔP.

If the radius is changed by a factor $\lambda = R'/R$, the rubber membrane is stretched by a factor λ in each orthogonal direction in the plane, and compressed by a factor λ^{-2} along
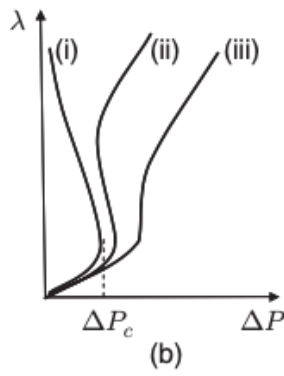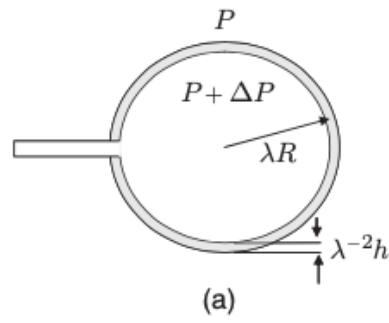
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Fig. 3.7 (a) Inflating a rubber balloon. (b) The relation between the expansion of the balloon λ and the applied pressure ΔP.

Figure 2:

the direction normal to the plane due to the incompressible condition. Therefore the free energy of deformation per unit volume is $(G/2)(2\lambda^2 + \lambda^{-4} - 3)$, and the total free energy of the system is given by

$$F_{tot}(\lambda) = 4\pi R^2 hG(2\lambda^2 + \lambda^{-4} - 3) - \frac{4\pi}{3}R^3\Delta P(\lambda^3 - 1)$$

The second term represents the work needed to change the air volume in the balloon (recall that ΔP is the difference of pressure between inside and outside). The equilibrium value of λ is given by the condition $\partial F_{tot}/\partial \lambda = 0$. This gives

$$4\pi R^2 hG(4\lambda - 4\lambda^{-5}) - \frac{4\pi}{3}R^3\Delta P 3\lambda^2 = 0$$

Figure 2(b) shows the relation between λ and ΔP. The curve denoted by (i) in the figure indicates the previous equation. According to this equation, ΔP takes a maximum ΔP_c at $\lambda_c = 7^{1/6} \approx 1.38$. If ΔP is less than ΔP_c, λ increases with the increase of ΔP. However if ΔP exceeds ΔP_c, there is no solution. If a pressure higher than ΔP_c is applied, the balloon will expand indefinitely and will rupture. In real rubbers, this does not happen due to the finite extensibility of the chain. If the effect of finite extensibility is taken into account, the relation between λ and ΔP becomes as shown by curves (ii) or (iii) in Fig. 2(b). In the case of (ii), the balloon radius changes discontinuously at a certain pressure. In the case of (iii), there is no discontinuity, but the balloon radius changes drastically at a certain pressure. Such phenomena are indeed seen in real balloons.

5   Swelling a gel (Doi)

A polymer gel is a mixture of a polymer network and a solvent. Such a gel is elastic like a rubber, but unlike rubber, gel can change its volume by taking in (or expelling) solvent. For example, when a dried gel is placed in a solvent, the gel swells by absorbing the solvent from the surroundings. This phenomenon is called swelling. Conversely, if the gel is placed in air, the solvent evaporates, and the gel shrinks. The volume change of a gel can also be caused by external forces. If a weight is placed on top of a gel, solvent is squeezed out from the gel, and the gel shrinks. To discuss the equilibrium state, we define the deformation free energy $f_{gel}(\lambda_i)$ for a gel. This is defined as follows.

We consider a gel which has a cubic shape of volume V_{g0} in the reference state. Suppose that this gel is immersed in a pure solvent of volume V_{s0} (same solvent as the one in which the gel was made for simplicity), and is stretched along three orthogonal directions by factors λ_1, λ_2, and λ_3. The volume of the gel is now $\lambda_1\lambda_2\lambda_3 V_{g0}$, and the total volume of the system is $V_{g0} + V_{s0}$. The deformation free energy density $f_{gel}(\lambda_i)$ is defined as the difference in the free energy between the final and initial state divided by V_{g0} . As in the case of rubber, the equilibrium state of the gel under external forces can be calculated if $f_{gel}(\lambda_i)$ is known. Let us consider the actual form of $f_{gel}(\lambda_i)$. The deformation free

energy of a gel consists of two parts. One is the elastic energy $f_{ela}(\lambda_i)$, the energy needed to deform the polymer network, and the other is the mixing energy $f_{mix}(\lambda_i)$, the energy needed to mix the polymer and solvent: $f_{gel}(\lambda_i) = f_{ela}(\lambda_i) + f_{mix}(\lambda_i)$. The elastic energy $f_{ela}(\lambda_i)$ has the same origin as that of rubber and can be written as

$$f_{ela}(\lambda_i) = \frac{G_0}{2}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)$$

where G_0 is the shear modulus of the gel in the reference state. The mixing energy $f_{mix}(\lambda_i)$ has the same origin as that of polymer solutions, and may be written in the same form. If the volume fraction of polymer in the reference state is ϕ_0, the volume fraction in the swollen state is

$$\phi = \frac{\phi_0}{\lambda_1 \lambda_2 \lambda_3}$$

When the volume fraction changes from ϕ_0 to ϕ, a polymer solution of concentration ϕ_0 and volume V_{g0} is mixed with pure solvent of volume ($\lambda_1\lambda_2\lambda_3 - 1)V_{g0}$, and becomes a solution of concentration ϕ and volume $\lambda_1\lambda_2\lambda_3 V_{g0}$.

Calling $f_{sol}(\phi)$ the free energy density of the polymer solution of concentration ϕ, the change in the free energy of the gel

$$\Delta F_{gel} = \lambda_1\lambda_2\lambda_3 V_{g0} f_{sol}(\phi) - V_{g0} f_{sol}(\phi_0)$$

to which we have to add the loss of free energy of the pure solvent which has entered in the gel (and it is now included in $f_{sol}(\phi)$)

$$\Delta F_{sol} = -[\lambda_1\lambda_2\lambda_3 - 1]V_{g0} f_{sol}(0)$$

Then,

$$\Delta F_{gel} + \Delta F_{sol} = V_{g0} f_{mix}(\lambda_i) = \lambda_1\lambda_2\lambda_3 V_{g0} f_{sol}(\phi) - V_{g0} f_{sol}(\phi_0) - (\lambda_1\lambda_2\lambda_3 - 1)V_{g0} f_{sol}(0)$$

Then

$$f_{mix}(\lambda_i) = \frac{\phi_0}{\phi}[f_{sol}(\phi) - f_{sol}(0)] - [f_{sol}(\phi_0) - f_{sol}(0)]$$

The last term does not depend on λ_i, and will be dropped in the subsequent calculation.

The free energy of the polymer solution $f_{sol}(\phi)$ is given by the Flory-Hugging free energy. Since the number of polymer segments, N, in the polymer network can be regarded as infinite, $f_{sol}(\phi)$ can be written as

$$f_{sol}(\phi) = \frac{k_B T}{v_c}[(1 - \phi)ln(1 - \phi) + \chi\phi(1 - \phi)]$$

We note that $f_{sol}(0) = 0$. Therefore, the free energy density of the gel is given by

$$f_{gel}(\lambda_i) = \frac{G_0}{2}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + \frac{\phi_0}{\phi}f_{sol}(\phi)$$

We shall now study the equilibrium state of the gel using this expression.

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5.1 Swelling equilibrium

Consider the equilibrium state of the gel. If there is no force acting on the gel, the gel expands isotropically, so we may set $\lambda_1 = \lambda_2 = \lambda_3 = \lambda$. Now λ can be expressed by ϕ and ϕ_0 as $\lambda = (\phi_0/\phi)^{1/3}$. Therefore,

$$f_{gel}(\phi) = \frac{3G_0}{2}\left(\left(\frac{\phi_0}{\phi}\right)^{2/3} - 1\right) + \frac{\phi_0}{\phi}f_{sol}(\phi)$$

The equilibrium state of the gel is obtained by minimizing this expression with respect to ϕ. The condition $\partial f_{gel}/\partial \phi = 0$ gives

$$\frac{\partial f_{gel}}{\partial \phi} = \frac{3G_0}{2}\left(-\frac{2}{3}\right)\phi_0^{2/3}\phi^{-5/3} - \frac{\phi_0}{\phi^2}f_{sol}(\phi) + \frac{\phi_0}{\phi}\frac{df_{sol}(\phi)}{d\phi} = 0$$

and multiplying by ϕ^2/ϕ_0,

$$G_0\left(\frac{\phi_0}{\phi}\right)^{1/3} = \phi\frac{df_{sol}(\phi)}{d\phi} - f_{sol}(\phi)$$

which, by defining $\Pi_{sol}(\phi)$ as the right site can be written

$$\Pi_{sol}(\phi) = G_0\left(\frac{\phi_0}{\phi}\right)^{1/3}$$

We note on passing that $\Pi_{sol}(\phi)$ is exactly the (osmotic) pressure. Indeed

$$F = Vf(\phi) \quad P = -\frac{\partial F}{\partial V} = -f(\phi) - V\frac{\partial f}{\partial V} = -f(\phi) + \phi\frac{\partial f}{\partial \phi}$$

Then, the left-hand side of the equation represents the force that drives polymers to expand and mix with the solvent, while the right-hand side represents the elastic restoring force of the polymer network which resists the expansion. The equilibrium volume of the gel is determined by the balance of these two forces. If the mixing free energy f_{sol} is given by the Flory Huggins free-energy, $\Pi_{sol}(\phi)$ is given by

$$\Pi_{sol}(\phi) = \frac{k_BT}{v_c}[-ln(1-\phi) - \phi - \chi\phi^2]$$

The parameter χ on the right-hand side is a function of temperature T. Therefore in the following, we shall discuss the volume change of the gel when χ is changed.

Figure 3(a) illustrates the graphical solution of the previous equation. The figure shows the right-hand side and the left-hand side of the equation as a function of ϕ for various values of χ. The solution is given by the intersection of the two curves. Figure 3(b) shows
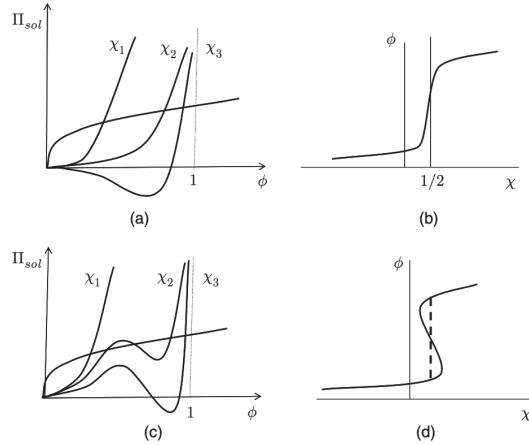
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Fig. 3.9 (a) Graphical solution of eq. (3.75), where $\chi_1 < \chi_2 < \chi_3$. (b) The solution of eq. (3.75) for ϕ is plotted against χ. In this case, the equilibrium volume of the gel changes continuously as a function of χ. Similar graphs are shown in (c) and (d) for the situation that $\Pi_{sol}(\phi)$ has a local maximum and minimum. In this case, the equilibrium volume of the gel changes discontinuously at a certain value of χ.

Figure 3:

the solution ϕ as a function of χ. As χ increases, i.e., as the affinity between the polymer and solvent decreases, the polymer concentration ϕ increases, and the gel shrinks.

An analytical solution can be obtained in the case of $\phi << 1$. In this case, $\Pi_{sol}(\phi)$ may be approximated as

$$\Pi_{sol}(\phi) = \frac{k_B T}{v_c} \left(\frac{1}{2} - \chi \right) \phi^2$$

such that ϕ

$$\phi = \phi_0 \left[\frac{G_0 v_c}{k_B T \phi_0^2} \frac{1}{(1/2 - \chi))} \right]^{3/5}$$

If $1/2 - \chi$ is large, ϕ is small, i.e., the gel is swollen. The gel starts to shrink quickly as χ approaches 1/2. Notice that the critical χ value $\chi_c = 1/2$ is equal to the critical χ value in polymer solutions. In the case of polymer solutions, if the affinity between polymer and solvent gets worse, phase separation takes place. In the case of gels, rapid shrinking of the gel takes place.

5.2   Volume transition

When phase separation takes place in solutions, $\Pi_{sol}(\phi)$ has a local maximum and local minimum as shown in Figure 3(c). If $\Pi_{sol}(\phi)$ has such a form, the equilibrium volume of the gel can change discontinuously as shown in Fig. 3(d). This phenomenon is called a volume transition. The volume transition of a gel is a phenomenon similar to the gas-liquid transition of a simple liquid: the volume of a liquid changes discontinuously at the boiling temperature. However, there is an essential difference between the two phenomena. The

difference comes from the fact that the usual gas-liquid transition is a phenomenon taking place in a fluid, while the volume transition of a gel is a phenomenon taking place in an elastic material. The difference can be seen in the transient states occurring during the phase transition. When a material changes from a liquid phase to a gas phase, there is an intermediate state where the two phases coexist. At this state, there is a cost of free energy for the coexistence of the two phases. In the case of a fluid, this cost is the interfacial energy (the energy which is proportional to the interfacial area, which is negligibly small compared with the bulk free energy. On the other hand, in the case of a gel, the cost of the coexistence is the elastic energy of the material. For example, consider the situation that a swollen phase of a gel coexists with a shrunken phase. Since the gel is a continuum, the phases cannot coexist keeping their shapes in the force free state; both phases must be deformed from the force free state (see Fig. 4). This cost is the elastic energy of deformation and is proportional to the volume of the material. Therefore the cost of coexistence cannot be ignored in the case of elastic materials. This affects the phase transition behaviour. For example, even if the bulk free energy of the swollen gel is equal to that of the shrunken gel at a certain temperature, the phase transition cannot take place at this temperature since for the transition to take place, a large free energy cost is needed. As a result, the temperature at which the shrunken phase turns into the swollen phase is different from the temperature at which the swollen phase turns into the shrunken phase. Therefore the volume transition of gels shows strong hysteresis.
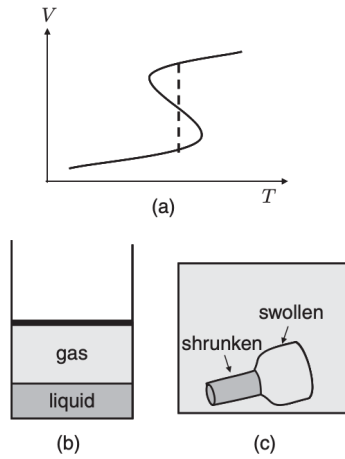
Fig. 3.10 (a) The equilibrium volume of a material showing a volume transition is plotted against temperature. (b) The coexistence state in a fluid. A gas phase and a liquid phase can coexist with negligible cost of free energy. (c) The coexistence state in a gel of cylindrical shape. When part of the shrunken gel turns into the swollen phase, both the swollen phase and the shrunken phase are deformed. As a result, there is a large cost of free energy for coexistence.

Figure 4:

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