

1. THERMODYNAMICS OF RUBBER ELASTICITY

1a. Historical Background.—In 1805 John Gough,² a contemporary of John Dalton and a sharp critic of the latter's views on the nature of gases, reported a series of experiments on rubber which were offered in substantiation of the then prevailing calorific fluid theory of heat. These simple experiments, though qualitative only, embrace all of the important thermodynamic features of the elastic behavior of natural rubber.

Gough described his first experiment as follows:

Hold one end of the slip [of rubber] . . . between the thumb and forefinger of each hand; bring the middle of the piece into slight contact with the lips; . . . extend the slip suddenly; and you will immediately perceive a sensation of warmth in that part of the mouth which touches it. . . . For this resin evidently grows warmer the further it is extended; and the edges of the lips possess a high degree of sensibility, which enables them to discover these changes with greater facility than other parts of the body. The increase in temperature, which is perceived upon extending a piece of Caoutchouc, may be destroyed in an instant, by permitting the slip to contract again; which it will do quickly by virtue of its own spring, as oft as the stretching force ceases to act as soon as it has been fully exerted.

In the second experiment he observed:

If one end of a slip of Caoutchouc be fastened to a rod of metal or wood, and a weight be fixed at the other extremity . . . ; the thong will be found to become shorter with heat and longer with cold.

Finally reporting on the results of his third experiment, he concluded as follows:

If a thong of Caoutchouc be stretched, in water warmer than itself, it retains its elasticity unimpaired; on the contrary, if the experiment be made in water colder than itself, it loses part of its retractile power, being unable to recover its former figure; but let the thong be placed in hot water, while it remains extended for want of spring, and the heat will immediately make it contract briskly. . . . The object of the present letter is to demonstrate, that the faculty of this body to absorb the calorific principle, may be lessened, by forcibly diminishing the magnitude of its pores; and this essential point of the theory may be confirmed by experiment: for the specific gravity of a slip of Caoutchouc is increased, by keeping it extended, while it is weighed in water.

The full significance of these observations could not be appreciated in advance of the formulation of the second law of thermodynamics by Lord Kelvin and Clausius in the early 1850's. In a paper³ published in 1857 that was probably the first to treat the thermodynamics of elastic deformation, Kelvin showed that the quantity of heat Q absorbed during the (reversible) elastic deformation of any body is related

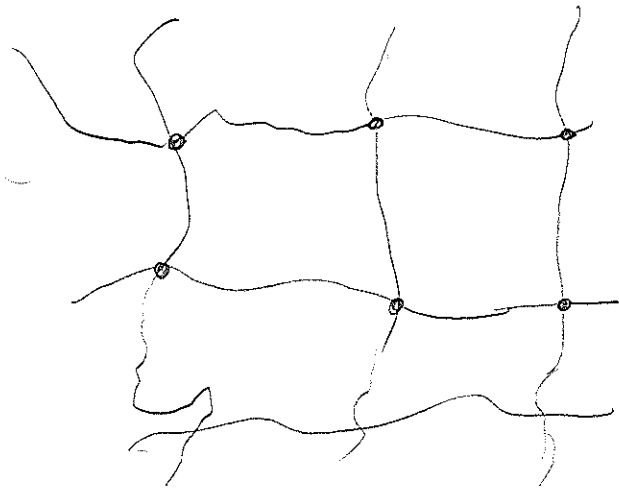
Free energy of an ideal chain

(2)

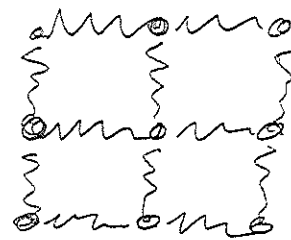
$$F(r) = \frac{3}{2} \frac{Tr^2}{R_0^2} \Rightarrow \langle r \rangle = \sqrt{\frac{R_0^2}{3T}}$$

with temperature increase spring constant is increasing and $\langle r \rangle$ is decreasing

Consider a polymer network



We can replace it by springs



If N is the average number of monomers between the crosslinks (or entanglement points), then each "spring" contains N monomers \Rightarrow

Total number of springs in the volume V is

$$N_s = \frac{V \cdot c}{N}$$

- monomer concentration

Thus change in energy under strain is

$$\frac{\Delta F}{V} = \frac{E}{2} \left(\frac{\delta L}{L} \right)^2 \quad \text{and} \quad E \sim \frac{N_s}{V} T \sim \frac{cT}{N} \quad (1)$$

Let us deform the sample by $\lambda_x, \lambda_y, \lambda_z$ along the x, y, z axes. Simplest assumption is that R_0 before the deformation will go to $R = (\lambda_x R_{0x}, \lambda_y R_{0y}, \lambda_z R_{0z})$. $R_i = \lambda_i R_{0i}$

Then $\Delta F(R) = F(R) - F(R_0) = \frac{3T}{2Na^2} \sum_i (R_i^2 - R_{0i}^2) =$
 $= \frac{3T}{2Na^2} \sum_i (\lambda_i^2 - 1) R_{0i}^2$

To get full change in energy we should average it over all springs \Rightarrow

$$\Delta F = \frac{3TN_s}{2Na^2} \sum_i (\lambda_i^2 - 1) \langle R_{0i}^2 \rangle$$

$$R_0^2 = \sum_i R_{0i}^2 = Na^2 \Rightarrow \langle R_{0i}^2 \rangle = \frac{Na^2}{3} \Rightarrow$$

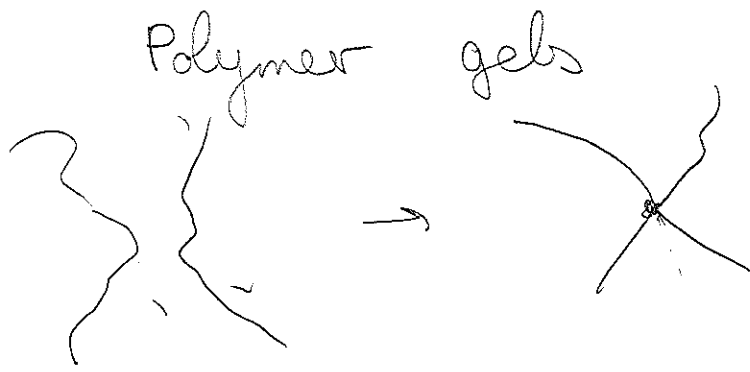
$$\Delta F = TN_s \sum_i (\lambda_i^2 - 1) = TN_s \frac{(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)}{2}$$

Consider uniaxial deformation. Usually volume of the network remains unchanged $\Rightarrow \lambda_x = \lambda, \lambda_y = \lambda_z = \lambda^{-1/2}$

and $\Delta F = \frac{TN_s}{2} \left(\lambda^2 + \frac{2}{\lambda} - 3 \right)$. Stress

$$e = \frac{1}{V} \frac{\partial \Delta F}{\partial \lambda} = \frac{TN_s}{V} \left(\lambda - \frac{1}{\lambda^2} \right)$$

For $\lambda \rightarrow 1$ we have linear elasticity for large λ not.



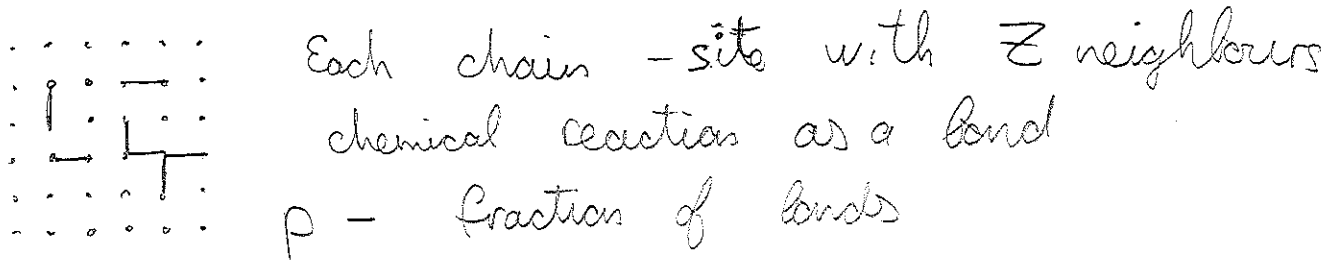
chemical reaction

If we change concentration or temperature we may have a sol-gel transition

- sol - solution of chains ~ liquid

- gel - finite fraction of chains belong to the network ~ elasticity ~ solid

Percolation model



- At some p_c - percolation transition

Below p_c : $p = p_c - \Delta p$ average polymerization

index diverges

$$N_w \sim \Delta p^{-\gamma}$$

$\gamma \sim 1.8$ in 3d

The average size of the clusters is

(5)

$$\xi(\Delta p) = a \Delta p^{-\nu} \quad \nu \sim 0.8 \text{ in } 3d$$

Above the threshold

gel fraction S_∞ - fraction of the monomers belonging to the infinite cluster

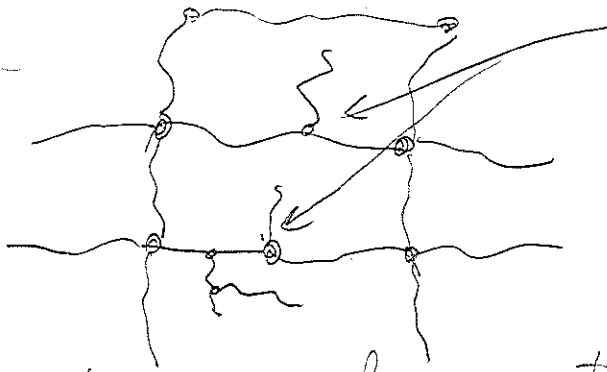
$$S_\infty \sim (\Delta p)^\beta \quad \beta \sim 0.39 \text{ in } 3d$$

However elastic moduli of the gel

E are not $\sim S_\infty$ but are much smaller

$$E \sim (\Delta p)^t \quad \text{with } t \sim 1.8 \text{ in } 3d$$

This is due to dangling chains



They contribute to S_∞ but not to the elasticity \Rightarrow

$$E \ll S_\infty$$

This was known to polymer physicists (Flory etc.)

For the conductivity problem later

the same was found by Last and Thouless (1971)

There is a mapping between gel elasticity⁽⁶⁾ and conductivity of random network. Then conductivity \Leftrightarrow elastic modulus (de Gennes 1976)

1. For elastic deformation

$$E_{el} = \frac{1}{2} \sum K_{ij} (x_i - x_j)^2, \quad K_{ij} - \text{spring constants} \quad (2)$$

for neighbouring bonds

- Minimizing E we obtain the force equation

$$\sum_j K_{ij} (x_j - x_i) = 0 \quad \text{for all } i \quad (3)$$

2. For electric network K_{ij} - local conductance and x_i - voltage on node i

Then Eq. (3) is just the Kirchhoff law

$$\sum_j j_i = 0$$

And Eq. (2) is the Joule dissipation in the network (principle of minimum dissipation)

On a macroscopic scale

$$J = -\partial \nabla X \quad \text{-el. field}$$

For elastic problem

$$\text{Stress} = -E \nabla X \Rightarrow E \text{ and } \partial$$

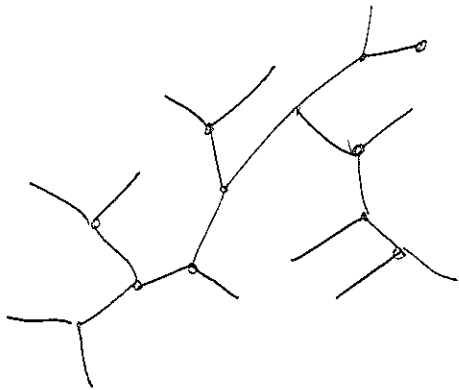
scale in the same way.

"Classical" theory of percolation

Tree approximation

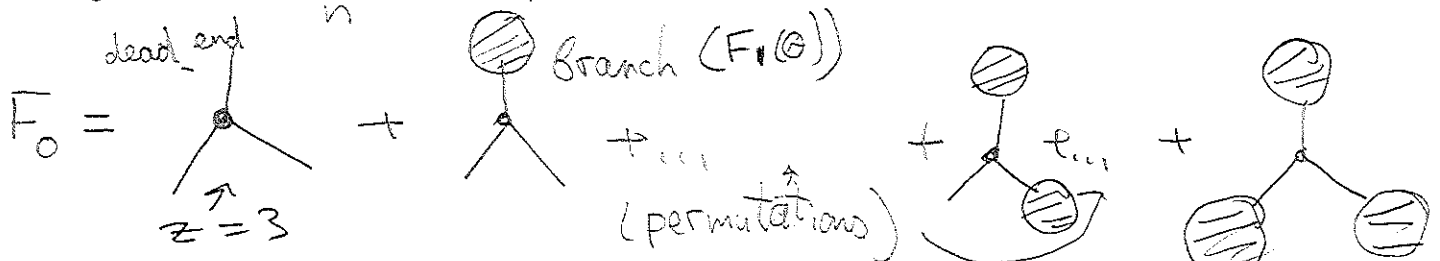
No loops

Each monomer can link to z others



$W_n(p)$ - probability to belong to a cluster of n monomers. Let us introduce a generating function $F_0(\theta)$:

$$F_0(\theta) = \sum_n W_n(p) \theta^n, \text{ where } \theta \text{ is some number}$$



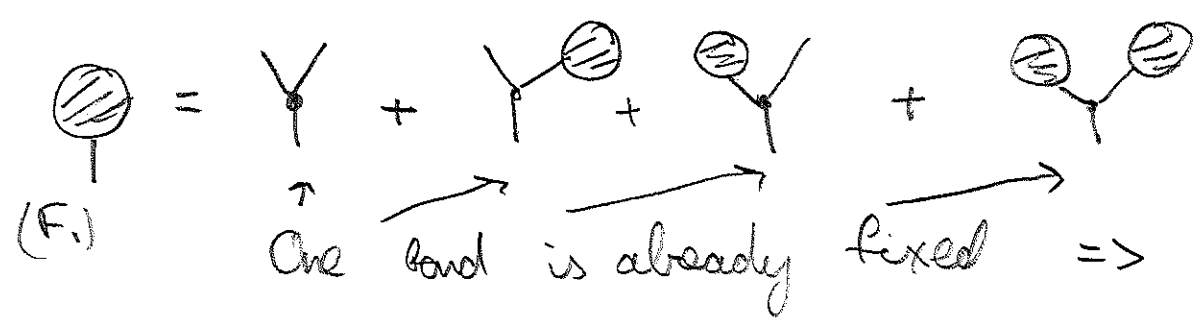
F_1 - generating function for lateral tree

$$F_0(\theta) = (1-p)^z + zp\theta F_1(1-p)^{z-1} + \frac{z(z-1)}{2}(p\theta F_1)^2(1-p)^{z-2} + \dots$$

$$\dots + (p\theta F_1)^z = (1-p + p\theta F_1)^z$$

The difference between F_0 and $F_1 \rightarrow$ one chemical function of monomer is reacted

For $F_1(\theta)$ we can write closed equations



$F_1 = (1 - p + \theta p F_1)^{z-1}$ we can solve it and

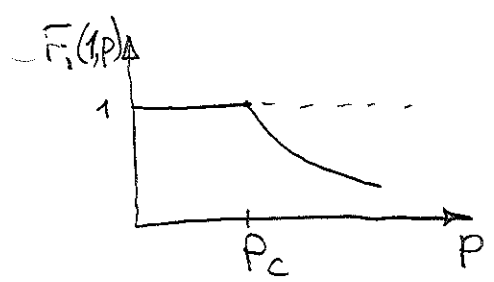
find F_0 for $\theta = 1$

$F_0(\theta = 1) = \sum_n w_n(p)$

Below the threshold this sum = 1 but above there is a probability to be in the infinite cluster \Rightarrow

$F_0(\theta = 1) = 1 - S_\infty(p)$

For $\theta = 1$ we find $p = \begin{cases} \frac{1 - F_1^{\frac{1}{z-1}}}{1 - F_1} \\ \text{indeterminate if } F_1 = 1 \end{cases}$



$p_c = \frac{1}{z-1}$

Close to p_c $F_1(p_c + \Delta p) = 1 - \text{const} \Delta p$

$F_0(p)$ looks similar $S_\infty = 1 - F_0 \propto \Delta p \Rightarrow$

$\beta = 1$, analogously

- $\gamma = 1$
- $\nu = 1/2$
- $t = 3$

Critical dimension

9

"Ginzburg" criteria

Correlation volume $V_c = \xi^d \sim \Delta p^{-d}$

Average number of sites in the infinite cluster in V_c

$$\bar{V}_{gel} \approx \sum_{\infty} (p) V_c \sim (\Delta p)^{\beta - d} \quad \text{finite cluster}$$

fluctuations in V_{gel} $V_{gel} + V_c = \text{const} \Rightarrow$

$$\delta V_{gel} = -\delta V_c$$

$$\delta V_c^2 \approx V_c N_w \quad (\text{each site is on the average}$$

connected to N_w other sites)

near threshold $\bar{V}_{gel} \rightarrow 0 \Rightarrow V_c \approx$ total number of sites \Rightarrow

$$\langle \delta V_g^2 \rangle = \langle \delta V_c^2 \rangle = \frac{V_c}{d^d} N_w \sim (\Delta p)^{-2d - \gamma}$$

Compare $\langle \delta V_g^2 \rangle$ with $\bar{V}_g^2 \Rightarrow$

$$\frac{\langle \delta V_g^2 \rangle}{\bar{V}_g^2} \approx (\Delta p)^{-\gamma - 2\beta + 2d} \sim \Delta p^{-3 + \frac{d}{2}} \quad (\gamma = \beta = 2\nu = 1)$$

\Rightarrow upper critical dimension $d_c = 6$

Tree approximation is good for dense system of linear chains $N \gg 1$. Large \approx limit $\approx \propto N$

This corresponds to the vulcanization of rubber

Mapping to the Potts model

110

The Potts model - generalization of the Ising, spin at each site may be in Q possible states (e.g. $1, 2, \dots, Q$)

Hamiltonian

$$H = - \sum_{ij} J_{ij} \delta_{s_i, s_j}, \quad J_{ij} > 0$$

For $Q = 2$, Potts model \Rightarrow Ising.

Consider nearest neighbours interactions.

Then $e^{J \delta_{s_i, s_j}} = 1 + x \delta_{s_i, s_j}$ with $x = e^J - 1$

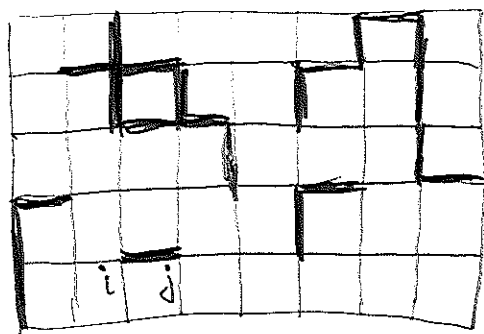
$$\Rightarrow Z(Q, x) = \prod_S \prod_{n.n} (1 + x \delta_{s_i, s_j})$$

We can expand in powers of x .

If there are N nearest neighbour bonds

then there are 2^N terms. Each may

be represented as a graph on the lattice



Each bond corresponds to $\prod_{i,j} \delta_{S_i, S_j}$.

Connected bonds form clusters

and within each cluster all the spins are the same

Thus, the trace over S will lead to a factor Q for each cluster, and the partition function is

$$Z(Q, x) = (1+x)^{-N} \sum_C Q^{N_c} x^{N_b} \quad (4)$$

Where N_c is the total number of clusters

(including isolated sites), N_b is the total number of bonds in the configuration. $(1+x)^{-N}$ is introduced

for convenience (it is analytic in $x \Rightarrow$ does not affect the critical behaviour). For a finite

lattice $Z(Q, x)$ is polynomial in Q and may be defined for non-integer values.

In the bond percolation ^{problem} bonds are present with probability p and absent with probability $(1-p)$. The weight for a given configuration is therefore $p^{N_b} (1-p)^{N-N_b}$

Two problems are then equivalent if we choose $x = \frac{p}{1-p}$ and $Q=1$.

However, exactly at $Q=1$, partition function is trivial, $Z=1$. (\sum probabilities = 1)

In order to obtain nontrivial information, we must consider limit $Q \rightarrow 1$

Then if $Q = 1 + \epsilon$ expanding $\epsilon \ll 1$ (4)

$$\left. \frac{\partial \ln Z}{\partial Q} \right|_{Q=1} = \frac{\sum N_c P(c)}{\sum P(c)} \approx \langle N_c \rangle$$

where $P_c = p^{N_c} (1-p)^{N-N_c}$ is the probability of given configuration of clusters

- Thus the mean number of clusters $\langle N_c \rangle$

- is given by the derivative of Free energy for the Potts model

$$\langle N_c \rangle = -\frac{1}{T} \left. \frac{\partial F}{\partial Q} \right|_{Q=1} \propto (p_c - p)^{2-d}$$

where d is specific heat exponent for the Potts model with $Q \rightarrow 1$