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On the temperature dependence of elasticity of thermo-reversible gels

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Résumé. — Pour expliquer la dépendance en température de l'élasticité des gels thermo-réversibles, nous proposons un modèle simple. Ce modèle suppose que le gel est formé de chaînes de Langevin dont les deux bouts sont fixés à des jonctions qui sont des régions cristallines. Les segments proches de chaque extrémité sont fortement liés. Lorsque la température augmente on suppose que les segments sont libérés de la jonction comme des molécules gazeuses qui s'évaporent ou se subliment à partir de la phase condensée. Quand tous les segments de l'une des deux extrémités sont libérés de la jonction, la chaîne ne contribue plus à l'élasticité. La mécanique statistique permet d'évaluer l'élasticité des gels numériquement. On montre que ce modèle reproduit bien le comportement caractéristique de la dépendance en température de l'élasticité des gels thermo-réversibles.

Abstract. — In order to explain the temperature dependence of elasticity of thermo-reversible gels, a simple model is proposed. It assumes that the gel consists of Langevin chains whose both ends are loosely fixed in crystalline junction regions in such a way that the segments near each end are bound densely in one of the junction region. The segments are assumed to be released from the junction with increasing temperature just as gas molecules evaporate or sublimate from the condensed phase. When all the segments in one of the both ends are liberated from the junction, the chain would cease to contribute to the elasticity. The elastic modulus of the gel is estimated numerically by means of statistical mechanics and the characteristic behaviour of the temperature dependence of thermo-reversible gels is shown to be well reproduced on the basis of this model.

1. Introduction.

There have been many investigations on the rheological properties of gels such as gelatin [1], agar-agar [2, 3], carrageenan [4, 5], pectin [6, 7] and so forth because of their importance in food industry [8] and biomedical application [9]. The gelling materials can control the food viscoelasticity by a small amount of their presence, and so they are called texture modifiers. Elasticity of these gels changes drastically at the gel-sol transition. The material is called *gel* when the lifetime of the cross-links in the network is longer than the experimental time scale, and is called *sol* when the lifetime is shorter. Therefore the term gel or sol depends on the time scale of the rheological measurement. However, even at the temperature range lower than the transition point, the elasticity remains often remarkably temperature dependent. Since this quality is very important in actual applications, many studies have been carried out on the temperature dependence of the elasticity of gels [10-12]. However, there have

been no investigations on the molecular mechanism for the temperature dependence of thermo-reversible gels. We propose here a simple model for explaining the temperature dependence of elastic modulus of weak gels.

2. A model for thermo-reversible gels.

Thermo-reversible gels are assumed to consist of two regions : somewhat crystalline region consisting of junction zones and the amorphous region consisting of long flexible chains. This picture is widely accepted for kappa-carrageenan gels and other polysaccharide gels [13] and for poly-vinyl alcohol gels [14, 15].

The nature of the binding in such junction zones is considered to be of secondary weak interactions as hydrogen bonding, van der Waals interactions or molecular entanglements. In some cases this region consists of close association of double helices.

The following model may, therefore, be plausible. The gel consists of Langevin chains having N segments

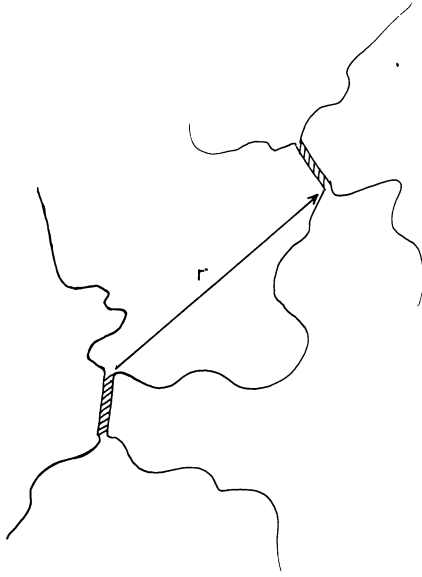


Fig. 1. — The schematic representation of network structure in weak gels. The shaded part stands for cross-linking junction. Cross-linking junctions are linked by a long chain whose end-to-end distance is r . This long chain is composed of n segments, each of which has length a .

of length a (Fig. 1). The Langevin model, which is more general than the Gaussian chain model, is adopted here so that the case of strong stretching of chains can be taken into account. The both ends of each chain are bound to two of the junction zones by the weak secondary interactions. The number of captured segments depends on temperature, i.e. the segments are released from the junction with increasing temperature and reeled in it with decreasing temperature. In other words, the junction region is considered to be a reservoir of the snaking chain. For simplicity, we will neglect the spatial extent of the junction zones.

Suppose n segments are released into the amorphous region between two junction zones distant from each other by ra . The thermodynamic weight of the snaking part of the chain is given by

$$w(r) = C \left(\frac{\sinh \beta}{\beta} \right)^n e^{-\beta r} \quad (1)$$

where β is related to r by

$$\frac{r}{n} = \mathcal{L}(\beta) = \coth \beta - \frac{1}{\beta}. \quad (2)$$

Here $\mathcal{L}(\beta)$ is the so-called Langevin function [16]. The work required to increase the end-to-end distance of a chain is given by the change in its Helmholtz free energy $A(r, T)$, thus the tensile force X along the direction of r is expressed as

$$X = \left(\frac{\partial A}{\partial r} \right)_T = \frac{\partial}{\partial r} (u - Ts) = -T \frac{\partial s}{\partial r},$$

because the energy u of the random-coil chain is independent of r . Since the entropy s of the chain is related to the above $w(r)$ as $s = k \log w(r)$, we easily get

$$X = -kT \frac{\partial}{\partial r} \log w(r) = \frac{kT}{a} \beta, \quad (3)$$

thence $\beta = aX/kT$. Then the partition function of a chain can be written as

$$Z = \sum_n f_n$$

$$f_n = \left(\frac{\sinh \beta}{\beta} \right)^n e^{-\beta r} e^{(N-n)\varepsilon/kT}, \quad (4)$$

where ε is the binding energy required for a segment to be liberated from the junction zone. Since β depends upon n , the sum (4) is not simple geometric series and we have to make some approximation to calculate it. Let n_0 be the number of released segments which maximizes the summand f_n of Z . Then

$$\frac{\sinh \beta_0}{\beta_0} = e^{\varepsilon/kT}, \quad (5)$$

where β_0 is the value of β corresponding to n_0 , i.e.

$$\beta_0 = \mathcal{L}^{-1} \left(\frac{r}{n_0} \right), \quad (6)$$

where \mathcal{L}^{-1} represents the inverse Langevin function.

Now, let us remember that the gel elasticity decreases drastically at the gel-sol transition. We restrict our consideration to the temperature range lower than the transition point. Then there must be an upper limit ν for the number of segments released from the junction zone because a chain will be liberated from the junction and ceases to contribute to the elasticity. We assume that this takes place when $n > \nu$. The value of this ν should be determined semi-empirically so as to get agreement with experiment. This point will be discussed later.

Replacing the summation approximately by integration, we can rewrite Z as

$$Z = e^{N\varepsilon/kT} e^{-\beta_0 r} \int_{-\infty}^{\nu - n_0} e^{-\alpha x^2/2} dx \quad (7)$$

where

$$\alpha = \frac{\kappa^2}{n_0^3} \frac{\beta_0^2 e^{2\varepsilon/kT}}{e^{2\varepsilon/kT} - 1}. \quad (8)$$

By the transformation of variable,

$$\eta = (\nu - n_0) \sqrt{\alpha} \quad (9)$$

and

$$\phi(\eta) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\eta} e^{-x^2/2} dx, \quad (10)$$

Z is represented as

$$Z = e^{N\varepsilon/kT} e^{-\beta_0 r} \sqrt{\frac{2\pi}{\alpha}} \phi(\eta). \quad (11)$$

Now, let us consider the relation between infinitesimal macroscopic strain and the relative change in r . Imagine an infinitesimal longitudinal deformation of a cylinder of length l_0 and radius R_0 (Fig. 2). Since gels can be regarded as incompressible, the relation

$$\gamma \equiv \frac{\Delta l}{l_0} = -2 \frac{\Delta R}{R_0} \quad (12)$$

holds for $\Delta l = l - l_0$ and $\Delta R = R - R_0$. Suppose the vector \mathbf{r} combining two junction zones in this cylinder is replaced by \mathbf{r}' after the deformation. Then we can easily show the following relations;

$$\begin{aligned} \frac{\Delta l}{l_0} &= (\tan \theta) \delta\theta + \frac{\delta r}{r}, \\ \frac{\Delta R}{R_0} &= -(\cot \theta) \delta\theta + \frac{\delta r}{r}, \end{aligned} \quad (13)$$

where $\delta r = r' - r$ and $\delta\theta = \theta - \theta'$. Substitution of equation (13) into equation (12) leads to

$$\frac{\delta r}{r} = \gamma \frac{3 \cos^2 \theta - 1}{2}. \quad (14)$$

The mean free energy for chains will be obtained by taking its average over directions, assumed to be random, as

$$F = \iiint \left\{ A(r) + \frac{\partial A}{\partial r} \delta r + \frac{1}{2} \frac{\partial^2 A}{\partial r^2} (\delta r)^2 + \dots \right\} \times r^2 f(r) dr \sin \theta d\theta d\phi \quad (15)$$

where $A = -kT \log Z$ is the free energy per single chain with fixed r , and $f(r)$ denotes the statistical

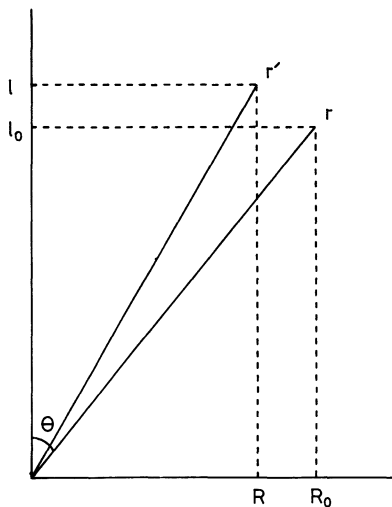


Fig. 2. — The uniaxial deformation of a cylindrical gel whose initial diameter and height are R_0 and l_0 respectively.

distribution function of the distances r . This F can be rewritten as [17]

$$F = F_0 + E\gamma^2, \quad (16)$$

where

$$\begin{aligned} F_0 &= \iiint A(r) r^2 f(r) dr \sin \theta d\theta d\phi, \\ E &= \frac{4\pi}{5} \int_0^\infty \frac{\partial^2 A}{\partial r^2} r^4 f(r) dr. \end{aligned} \quad (17)$$

Let \mathcal{N} be the number of chains in a unit volume, then

$$\begin{aligned} \mathcal{N} &= \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\phi f(r) r^2 \sin \theta \\ &= 4\pi \int_0^\infty f(r) r^2 dr. \end{aligned} \quad (18)$$

Comparing this with the second expression of equation (17), we obtain

$$E = \frac{\mathcal{N}}{5} \left\langle \frac{\partial^2 A}{\partial r^2} r^2 \right\rangle_r \quad (19)$$

where $\langle \dots \rangle_r = 4\pi \int_0^\infty \dots f(r) r^2 dr / \mathcal{N}$ represents the average over the distance r .

Since, however, all the chains do not contribute to the elasticity, the number \mathcal{N} must be replaced by the number of active chains. We may assume that the active chains are those having $n < v$ as stated before;

$$\mathcal{N}_A = \mathcal{N} \phi(\eta) / \phi(\infty) = \mathcal{N} \phi(\eta). \quad (20)$$

The elastic modulus E is, therefore, given by

$$E = \frac{\mathcal{N}}{5} \left\langle \phi(\eta) \frac{\partial^2 A}{\partial r^2} r^2 \right\rangle_r.$$

The calculation of $\partial^2 A / \partial r^2$ from

$$A = -kT \log Z = -kT \left[\frac{N\varepsilon}{kT} - \beta_0 r + \frac{1}{2} \log \frac{2\pi}{\alpha} + \log \phi(\eta) \right]$$

is a little tedious but straightforward. The final result is

$$\begin{aligned} E &= \frac{\mathcal{N}kT}{10} \left\langle \phi(\eta) \left[1 + \frac{MPr^2}{2\sqrt{2\pi}} \times \right. \right. \\ &\quad \left. \left. \times \left(\frac{1}{r} + \eta\sqrt{\alpha}M + \frac{MP}{\sqrt{2\pi}} \right) \right] \right\rangle_r \end{aligned} \quad (21)$$

where

$$\begin{aligned} M &= \frac{v}{r} - \frac{1}{\Gamma(\beta_0)}, \\ P &= \sqrt{\alpha} e^{-\eta^2/2} / \phi(\eta). \end{aligned} \quad (22)$$

3. Comparison with experiments and discussion.

The open circles in figure 3 show the temperature dependence of the dynamic Young's modulus of an 8 % w/w poly (vinyl alcohol) (PVA) gel observed at 2 Hz [18]. The degree of polymerization of PVA was 2 400. The number of molecular chains \mathcal{N} in 1 cm³ is about 10¹⁸. The curves in figure 3 are those obtained by numerical calculation of equation (21) for various values of $\mu = v/r_m$. Since we know very little about the distribution function $f(r)$, we replace it by a delta function having the peak at certain average value r_m of the end-to-end distance r . The energy ε and the assumed mean end-to-end distance r_m are chosen as 100 k and 400, respectively. The characteristic feature of the experimental Young's modulus is well reproduced by the calculated curves.

Figures 4-7 show the calculated values for the elastic modulus for different values of μ . The number \mathcal{N} is

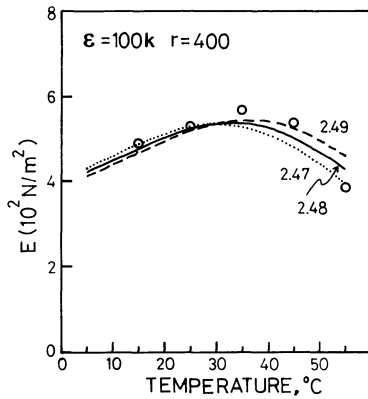


Fig. 3. — The comparison of observed Young's modulus for a PVA gel (O) with calculated values obtained from equation (21). The figures besides the curves represent the value of μ .

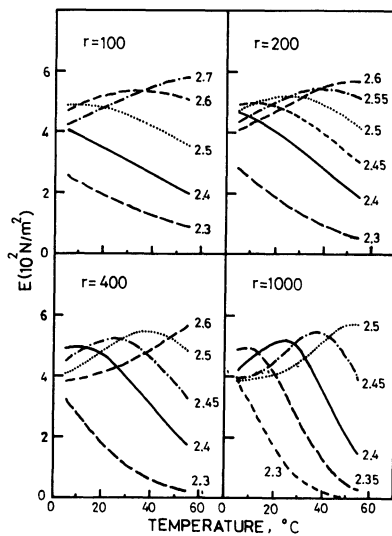


Fig. 4. — The calculated curves of elastic modulus obtained from equation (21). The figures besides the curves represent the values of μ . The bonding energy ε is fixed as 100 k .

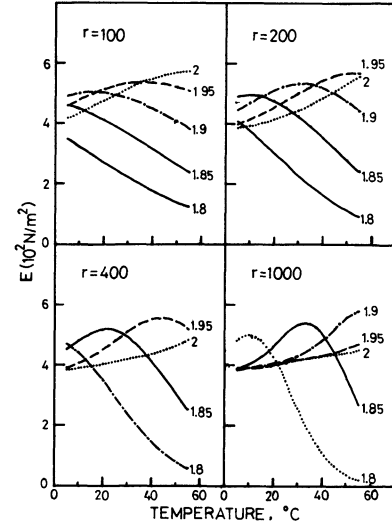


Fig. 5. — The calculated curves of elastic modulus obtained from equation (21). The figures besides the curves represent the values of μ . The bonding energy ε is fixed as 200 k .

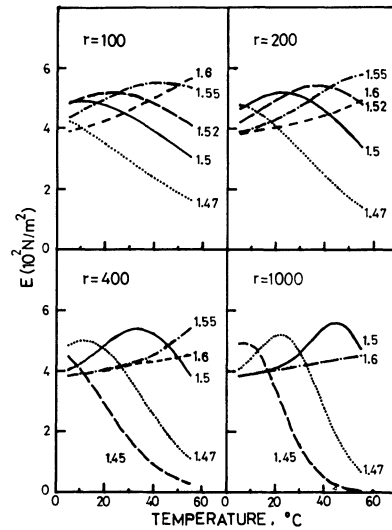


Fig. 6. — The calculated curves of elastic modulus obtained from equation (21). The figures besides the curves represent the values of μ . The bonding energy ε is fixed as 400 k .

always fixed to 10¹⁸ as in figure 3. As is seen from these curves, the increasing or decreasing tendency of the modulus depends quite sensitively upon the values of the parameter μ . Beyond some critical value of μ , the elastic modulus increases monotonously, while it decreases monotonously below it. For large values of the parameter μ , equation (21) tends to

$$E = \frac{1}{10} \mathcal{N}kT$$

which is the familiar expression for permanently cross-linked rubber like materials [16].

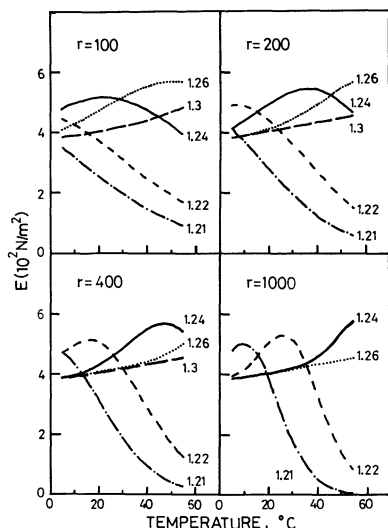


Fig. 7. — The calculated curves of elastic modulus obtained from equation (21). The figures besides the curves represent the values of μ . The bonding energy ε is fixed as 1 000 k .

Since we have assumed that the binding energy of the cross-linking junction is always the same for each dissociation, the total number N of the segments in a chain does not appear explicitly in equation (21). It is implicitly involved in ν (hence in η) because ν must be a certain number slightly smaller than N . More important simplification is that the interaction between chains has not been taken into account. So the concentration dependence of the elastic modulus of the gel cannot be explained by the present treatment. There are already many experimental results that the elastic modulus of the gel is roughly proportional to the second power of the concentration. The scaling treatment has accounted for this behaviour [19]. The aim of the present model is the explanation of the temperature dependence of the elastic modulus for weak gels based on widely accepted molecular picture of the gels.

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