The Theory of the Rubber-like Elasticity in Monolayers.[1]

By Keizō SUZUKI.

Introduction. When a monolayer is made from high-molecular compound with rubber-like elasticity, what are its properties?

We succeeded in making a monolayer by dropping the benzene solution of the addition polymer of butadiene with acrylonitrile onto the water surface, and measured the surface pressure changing the surface area and temperature[2] (Fig. 1). The monolayer takes the most extended form under no external force. On the contrary the three-dimensional rubber block set free assumes the most contracted form as well known. A thin rubber layer on water which has a similar nature to the three-dimensional one was studied by Trapeznikov,[3] but it is too thick to be called a monolayer.

Fig. 1.

Fig. 1. The surface pressure and the surface area of the monolayer of addition polymer from butadiene 5 and acrylonitrile 2.

This difference between the two states of the substances seems, at first sight, to be a serious hindrance for us to find common properties in them. But we find the expression of the rubber-like elasticity in the two
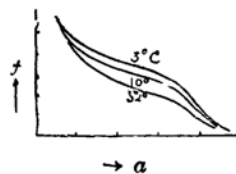
(1) Short abstract of the mathematical part is already reported in Japanese. K. Suzuki and Y. Suzuki, *Kagaku*, **17** (1947), 238.

(2) K. Suzuki, *J. Chem. Soc. Japan*, **63** (1942). 1058.

(3) A. A. Trapeznikov, *Compt. rend. U. R. S. S.*, **95** (1941), 138.

properties of the monolayer: extraordinarily large and reversible compressibility over a wide range of the area, and the decrease of the surface area and surface pressure with increasing temperature.

The Structure of the Monolayer. Can all the substances with rubber-like elasticity spread to monolayers? No; for example, natural cauchouc can never spread to the monolayer on water, for it has no "hydrophilic groups". The monolayer on water, generally speaking, can be formed only by the partially hydrophobic and partially hydrophilic molecules.[4] High polymeric molecules with hydrophobic backbones must have hydrophilic radicals to spread to monolayers; our sample has the nitrile groups. Another sample with phenyl radicals instead of nitriles failed to spread.

The hydrophilic radicals, which take the states of lower energy by attaching to water, tend to spread the molecule broader and thinner on the water surface, and on the other hand the thermal motion of the molecular chains tends to contract to the more coiled and gathered forms, the more probable state, like the three-dimensional case. The balance of the two forces appears to us as the properties of the monolayer above shown. The elevation of temperature increases the thermal motion and contracts the area of the film.

As long as we call the spontaneous contraction of the long chain molecule by thermal motion as the rubber-like elasticity,[5] we must regard the nature of this monolayer as an expression of the same sort of elasticity. The statistical treatment on the elasticity has had successful results. We shall now try a statistical evaluation of the mechanical and thermodynamical properties of the monolayer.

Fig. 2.

Fig. 2. The schema compression.

We must set up a model which fits this monolayer. The observed nature does not permit the simple translation of the finely constructed three-dimensinoal theory to the two-dimensional one. Our model must be able to bear under the reversible compression to the fairly thick layer which may irreversibly destroy the monolayers of low molecular compounds. By this compression some parts our molecule are pushed up from the water surface but they are ready to return to the water surface by the release from the compression (Fig. 2). This is the reason why the two-dimensional model cannot be adopted for our monolayer, although it was recently applied for some polymeric monolayer of the expanded type by Singer.[6]

Probability for Configurations of the Chain. We consider a long chain molecule with n hydrophilic groups in equal intervals. Let the intervals be m-membered chains, then the molecule is mn-membered

(4) N. K. Adam, " The Physics and Chemistry of Surfaces, " (Oxford 1941), Chapt. II.
(5) W. Kuhn, *Kolloid-Z.*, **86** (1936), 258; H. Dostal, *Mh. Chem.*, **71** (1938), 144; F. Horst Müller. *Kolloid-Z.*, **95** (1941), 133; R. Kubo, *Proc. Phys. Soc. Japan*, **2** (1947), 51.
(6) S. J. Singer, *J. Chem. Phys.*, **16** (1948), 842.

$(n \gg 1)$ (Fig. 3).

We shall estimate the probability W_{an} that an hydrophilic groups are in contact with water surface and $(1-a)$ n groups are not. For a while we put the energy difference due to the hydration out of consideration. Let u_i be the probability that when a certain group is on water the i-th group from it is on water and the intervening i-1 groups are not.
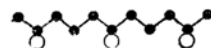

Fig. 3.

Fig. 3. The linear molecule.

Then the probability that the chain takes the configuration in Fig. 4 is $u_3 u_2 u_1 u_1$. Generally it becomes the product of $a\,nu_is$, where the sum of is becomes n. The number of selection of an groups is $_nC_{an}$, then the probability W_{an} is the sum of $_nC_{an}$ products similar to the product above shown:

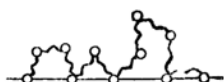Fig. 4.

Fig. 4. A schematic configuration.

$$W_{an} = \sum^{_nC_{an}} \overset{an}{II} u_i. \qquad (1)$$

This is obtained as the factor of x^n of $(\sum_i u_i x^i)^{an}$:

$$\sum_n W_{an} x^n = (\sum_i u_i x^i)^{an}. \qquad (2)$$

Next we rewrite u_i in the calculable form. Let p_i be the probability that when a certain group is on water the i-th group from it is on water too. p_i contains, contrary to u_i the cases that some of the i-1 intervening groups are on water. p_0 is the probability that when a group is on water the same group is on water, therefore

$$p_0 = 1.$$

p_1 is the probability that the next group is on water. In this case there is no intervening group, therefore

$$p_1 = u_1.$$

p_2 is the probability that the second group is on water, and is the sum of two cases: the case where the intervening group is on water and the case that it is not. The probabilities are

$$u_1 u_1 \text{ or } u_1 p_1, \ u_2 \text{ or } u_2 p_0$$

respectively. ·And then we have

$$p_2 = u_1 p_1 + u_2 p_0.$$

Similarly p_3 is separated into three cases and

$$p_3 = u_1 p_2 + u_2 p_1 + u_3 p_0$$

is obtained. Generally p_j is separated into j terms: the first group is on

water $= u_1 p_{j-1}$, the second group is on water $= u_2 p_{j-2}$, and the i-th group is on water $= u_i p_{i-j}$.   Then

$$p_j = \sum_{i=1}^{j} u_i p_{j-i} . \tag{3}$$

These lead to the equation:

$$p_1 x + p_2 x^2 + \ldots = (p_0 + p_1 x + \ldots)(u_1 x + u_2 x^2 + \ldots),$$

which gives the mother function of u_i by a transformation:

$$\sum_{i=1}^{\infty} u_i x^i = \sum_{i=1}^{\infty} p_i x^i \Big/ \sum_{i=0}^{\infty} p_i x^i . \tag{4}$$

Putting this in (2), we have

$$\sum_n W_{an} x^n = \left(\sum_{i=1}^{\infty} p_i x^i \Big/ \sum_{i=0}^{\infty} p_i x^i \right)^{an} \tag{5}$$

We shall now consider how p_is be expressed. p_i is the probability that when an end of the im-membered chain is on water another end is also on water.

The Brownian movement gives a good analogy.   Let us estimate the probability that a particle which started from a planar wall at time 0 comes back to and collides with the wall at time im.   Let the wall be the plane $z=0$.   We compare two sorts of traces of the particle which was on $z=0$ at $t=0$: one where the wall is perfectly elastic and the other where there is no wall.   The traces of the former are obtained from those of the latter by folding the one half on the side of the negative z on to the other half (Fig. 5).
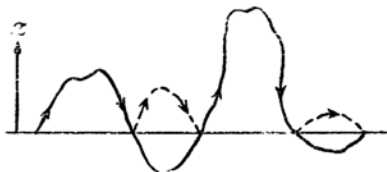

Fig. 5.

Fig. 5. A trace of a Brownian particle about an elastic wall.

Therefore the probability that the particle of the first kind passes through the plane $z=0$ in the time interval $t \sim t+dt$ equals the probability that the particle of the second collides in the same time.

Similarly p_i is otained as the probability that when an end of the im-membered chain is on the plane $z=0$ another end is also on the plane.

Here the plane is not a wall nor a water surface but an imagined geometrical surface.

Thus p_i can be known from the degree of flexibility of the chain. The more flexible the chain, the larger becomes p_i.

The estimation of p_i is perfectly mathematical on the simple chain, each unit of which has equal probability, $1/2$, to take $+1$ or -1 as the z-component of its length:

$$p_0 = 1, \; p_1 = {}_mC_{m/2}\, 2^{-m}, \; p_2 = {}_{2m}C_m 2^{-2m},$$

$$p_i = {}_{im}C_{im/2}\, 2^{-im} \simeq (\pi m/2)^{-0.5}\, i^{-0.5}\,.$$

If im is not so small, p_i is generally approximated as

$$p_0 = 1, \; p_i = Bi^{-0.5} \text{ for } i > 1, \tag{6}$$

where B is a constant proportional to the reciprocal square root of m, for the distribution of the relative position of the two ends of a chain is well approximated by the Gaussian distribution.[1],[7]

Putting $i=1$ in (6), we have $B=p_1$. B is the probability that when one end of m-membered chain is on water the other is also on it. This probability must be proportional to the square root of m, and the proportional constant can be known from the nature of the chain, from the pseudosegment[8] expressing the flexibility and the width of the potential valley at the surface of water for the hydrophilic group. A further estimation is deferred to another paper and here only the qualitative conclusion is stated: the more flexible chains with hydrophilic radicals in shorter intervals have larger values of B.

Surface Pressure. Statistical thermodynamics tells us the equation

$$fnda = -kTd \log Z_{an}, \tag{7}$$

where f is the surface pressure, a is the surface area per radical, and Z_{an} is the partition function. $fnda$ is the work done by the molecule with the increase of area nda, so it is equal to the decrease of the free energy $-kTd \log Z_{an}$.

We have neglected the energy due to the hydration of hydrophilic groups in the calculation of W_{an}. Therefore the partition function is substituted by W_{an} multiplied by $\exp(-\varepsilon an/kT)$, in which ε is the hydration energy of a group k is the Boltzmann's constant, and T is absolute temperature. Then the equation (7) gives

$$f = \left(\varepsilon + \frac{kT}{n}\frac{d}{da} \log W_{an}\right)\frac{da}{da}\,. \tag{8}$$

The differential calculus in the bracket is carried by the use of the mother function of W_{an} (5):

$$W_{an} = \frac{1}{2\pi\lambda}\oint \frac{dx}{x^{n+1}}\left(\sum_{i=1}^{\infty} p_i x^i \Big/ \sum_{i=0}^{\infty} p_i x^i\right)^{an},$$

where λ is $\sqrt{-1}$, i in the ordinary notation. Approximation at the saddle point leads to

---

(7) S. Chandrasekhar, *Rev. Mod. Phys.*, **15** (1943), 3 ∼ 16.

(8) K. Suzaki, this Bulletin, **20** (1947), 19.

$$W_{an} = x^{-n}\left(\sum_{i=1}^{\infty} p_i x^i \Big/ \sum_{i=0}^{\infty} p_i x^i\right)^{an} \cdots,$$

$$\frac{d}{da} \log W_{an} = n \log\left(\sum_{i=1}^{\infty} p_i x^i \Big/ \sum_{i=0}^{\infty} p_i x^i\right), \tag{9}$$

in which x is the value corresponding to the extreme value of the integrand in the course of the integration. x is given by the equation

$$a = \sum_{i=1}^{\infty} p_i x^i \sum_{i=0}^{\infty} p_i x^i \Big/ \sum_{i=1}^{\infty} i p_i x^i, \tag{10}$$

which is obtained by equating the differential coefficient of the logarithm of the integrand to zero. Inserting (9) in (8) one obtains

$$f = \left\{\varepsilon + kT \log\left(\sum_{i=1}^{\infty} p_i x^i \Big/ \sum_{i=0}^{\infty} p_i x^i\right)\right\} da/da, \tag{11}$$

in which x is given by (10). The use of (6) for p_i in (10) and (11) yields

$$f = \left[\varepsilon - kT \log\left\{\left(B \sum_{i=1}^{\infty} i^{-0.5} x^i\right)^{-1} + 1\right\}\right] da/da, \tag{12}{[9]}$$

$$a = \sum_{i=1}^{\infty} i^{-0.5} x^i\left(1 + B \sum_{i=1}^{\infty} i^{-0.5} x^i\right) \Big/ \sum_{i=1}^{\infty} i^{0.5} x^i. \tag{13}{[9]}$$

Surface pressure is independent of molecular weight or polymerization degree n, but depends only on the hydrophilicity ε of the groups and
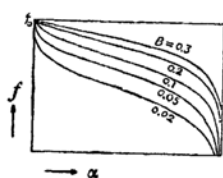
Fig. 6.

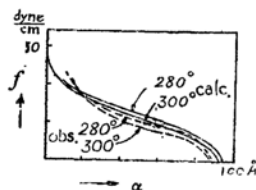Fig. 7.

Fig. 8.

Fig. 6. Calculated Relations of f with a.

Fig. 7. Comparison of theory and observation. Calc.: $B = 0.02$, $da/da = 100$ Å², $\varepsilon = 3.10^{-13}$ erg. Obs.: polymer from butadiene 5 and acrylonitrile 1.
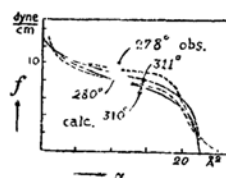
Fig. 8. Comparison of theory and observation. Calc.: $B = 0.1$, $da/da = 23$ Å², $\varepsilon = 1.3 \cdot 10^{-13}$ erg. Obs.: polymethylsiloxane.

the flexibility B of the m-membered chain.

The Numerical Results. Calculated relations of f with a are

(9) The numerical summations of the series in (12) and (13) are carried by the equations:

$$\sum i^{0.5} x^i = \frac{\sqrt{\pi}}{2}\{(1-x)^{-1.5} - x\} + \sum\left(i^{0.5} - \frac{\sqrt{\pi}}{2} \cdot \frac{3}{2} \cdot \frac{5}{4} \cdots \frac{2i-1}{2i-2}\right) x^i,$$

$$\sum i^{-0.5} x^i = \sqrt{\pi}\{(1-x)^{-0.5} - 1\} + \sum\left(i^{-0.5} - \frac{\sqrt{\pi}}{2} \cdot \frac{3}{4} \cdot \frac{5}{6} \cdots \frac{2i-1}{2i}\right) x^i.$$

plotted in Fig. 6 assuming the constant ε, T, and da/da. If the energy s becomes large f_0 becomes large and the curves move upwards conserving the forms. If the temperature becomes high, f_0-f becomes large proportionally to T. ($f_0=\varepsilon da/da$).

Experimental curves are compared with the theoretical ones in Fig. 7. The monolayer of polymethylsiloxane in Fig. 8 studied by Fox, Taylor, and Zisman[10] fits the larger B, for the molecule has more consecutive hydrophilic parts. They assume a particular structure, the helic form of the chain, but such a somewhat regular structure may not explain the temperature effect. It is necessary that the compression increases the entropy. The constant surface potential over the wide range of compression observed by Fox *et.al.* shows the validity of the assumption of constant da/da; because the constant da/da means the constant number of oriented radicals per area, and only the oriented ones are effective to surface potential, for the moments of the others take random directions and cancel each other.

Conclusion. It is a destined difficulty in the problem of the rubber elasticity what kind of macroscopic variable is combined with the microscopic thermal motion, since Kuhn assumed that the relative movement of the two ends of the chain is proportional to the macroscopic transformation.

In this theory the surface area is reasonably combined with the number of hydrated hydrophilic groups.

The second difficulty is the interaction of molecules, which is usually neglected and in this theory too. But we may expect the effect of the negligence to be smaller in the monolayer, because the chains are set more free from each other in it than in the three-dimensionally filled cases.

Thus the theory of the statistical elasticity seems to find the first step for its quantitative explanation.

Summary.

A discussion is made on the structure of the monolayer of the rubber-like highpolymer, and the equation of state is derived from the statistical theory. The extraordinarily large compressibility and the inverse temperature effect observed in the experiment are explained to be the expressions of the rubber-like elasticity. The theory is not a simple translation of the 3-dimensional theory to the 2-dimensional one.

Masaoka-cho, Toyokawa, Aichi pref.,
  Japan.

(10) H. W. Fox, P. W. Taylor, and W. A. Zisman, *Ind. Eng. Chem.*, **39** (1947), 1401.
   They also found the gradual metamorphosis of the rubber monolayer into the expanded film, which we reported in (2).