# *SIMPLE STATISTICAL MODELS OF THE NON-GAUSSIAN CHAIN AND ONE OF APPLICATIONS TO THE THEORY OF RUBBER ELASTICITY*

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Several convenient and simple models for the non-Gaussian chain are presented in this paper. The clear limit of the finite extensibility of the chain can be obtained by these models; namely, when the chain is extended, the end-to-end distance does not exceed the length of the chain. Moreover, the distributions derived from these models become the usual Gaussian, when the chain takes the full coil-shape. A series including such models is also introduced and the survey in this series is given.

As an application of these models, the tension-extension curve calculated by the models is compared with the experimental one in a rubber vulcanizate. Especially notable rising of the tension in the high extension region can be represented.

Also, these models are based on the conception of the element-space which is defined here as the movable spatial domain for an element connected with the chain under the Brownian motion. Therefore these models had a rough picture on the motional region of the single element in the chain.

## 1. INTRODUCTION

As well known the effect of the finite extensibility of the single chain within the high polymers plays an important part in the consideration of the phenomena, such as the large elastic deformation in the rubber-like substances, the moderate deformation in the swollen polymers or the highly cross-linked polymers or the drawn polymers, the strain-birefringence or the flow-birefringence in the polymer systems, and so on.

In such cases the Gaussian statistical treatment is no longer valid, since an appreciable proportion of the chains in the specimen becomes highly extended, and it is necessary to try the treatments of some non-Gaussian statistical analyses, which take account of the finite extensibility of the chains.

Although there are several studies with regard to the finite extensibility of the single chain, and hence of the network chains,[1)2)3)] these treatments are considerably complicate and unsuitable for rough estimation in many practical applications.

In response to these requests, the simple calculation models for the non-Gaussian chain are presented here. And these models have the two features that they have the finite extensibility of the chain and they have the ordinary Gaussian distribution when the chain is enough contracted.

Consider a perfectly flexible chain with $n$ elements of each length $a$ and the end-to-end distance $r$ between both fixed ends. Then the "degree of contraction", $\lambda$, of the chain is defined as $\lambda=r/(na)$. According to the usual way, when $w_n(r)4\pi r^2dr$ denotes the probability of the end-to-end distance $r$ lying between $r$ and $r+dr$, irrespective of direction, the two features of these models are represented by the following conditions:

(1°) **the finite extensibility of the chain :**

$$\left.\begin{aligned} w_n(r) &\neq 0, \quad (0\leq r<na, \ \text{or} \ \lambda<1) \\ &= 0, \quad (na=r \ \text{or} \ \lambda=1) \end{aligned}\right\} \qquad (1.1)$$

(2°) **the reducibility to the Gaussian distribution:**

$$w_n(r)=C_n e^{-\beta_n^2 r^2} \qquad \text{when} \quad \lambda\ll 1 \ , \qquad (1.2)$$

where the parameter $C_n$ is a normalized factor and the parameter $\beta_n$ represents sharpness in the distribution.

## 2. CHAIN ELLIPSOID AND ELEMENT-SPACE[3)5)]

It is clear that if the chain assumes a flexible yarn with the unalterable length $na$ and the both ends are fixed at the distance $r$, a spatial domain

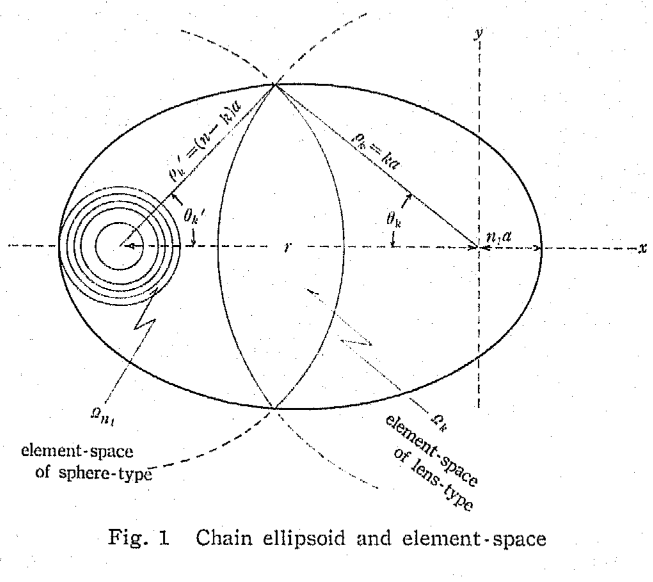


Fig. 1 Chain ellipsoid and element-space

constructed from all the spatial points that are occupied by at least one point on the chain becomes an ellipsoid of revolution with the major radius $na/2$, the minor radii $(na/2)\sqrt{1-\lambda^2}$ , the eccentricity $\lambda$, and the foci as both ends. The above assumption of substituting the flexible yarn for the chain is sufficiently appropriate if $1\ll n$. The ellipsoid of revolution is hereafter called the "chain ellipsoid".

Also let us define the $k$ th "element-space", $\Omega_k$, as the proper domain being occupied by at least one point belonging to $k$ th element counted from one end in the chain.

Let $n_1$, $n_2$ defined as

$$n_1=(n/2)(1-\lambda), \qquad n_2=(n/2)(1+\lambda) \tag{2. 1}$$

respectively. If $k \leq n_1$ or $n_2 \leq k$, $k$ th element-space becomes the spherical domain with radius $ka$, and if $n_1 < k < n_2$, it becomes a following lens-type domain, which is the common space cut off from the two spherical domains with radii $ka$ and $(n-k)a$ respectively, each center located at two foci of the ellipsoid. The volume of the element-space $\Omega_k$ for $k$ th element denotes $v_k$, and then $v_k$ is easily calculated as follows (Appendix, Eq. (A-3) cf.) :

$$v_k=v_{n-k}=(4\pi/3)a^3k^3, \quad (1 \leq k \leq n_1) \cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots \text{for the element-spaces of the sphere-type,} \tag{2. 2}$$

$$v_k=v_{n-k}=\pi n a^3 \frac{(1-\lambda)^2}{\lambda}\left\{\left(\frac{n}{2}\right)^2\frac{\lambda(2+\lambda)}{3}-\left(\frac{n}{2}-k\right)^2\right\}, \quad (n_1<k<n_2)$$

$$\cdots\cdots\cdots \text{for the element-spaces of the lens-type.} \tag{2. 3}$$

## 3. THE SATISTICAL MODEL OF RANDOM CHAIN BASED ON THE ELEMENT-SPACE

As well known the probability $w_n(r)$ in the previous section means the configuration number of the chain. The present purpose is to estimate the configuration number of the chain $w_n(r)$ in terms of the conception of the element-space. It is very difficult, however, to derive the accurate condition of connectivity in which an element is tied up to the chain.

From the definition, $k$ th element can move within the space $\Omega_k$ under the constrained condition in which $k$ th element is connected with the two neighbour, and each neighbour is connected with its successive neighbour respectively, and so on. Although the position of $k$ th element exists in its space $\Omega_k$, it is very difficult to obtain the coordinates of $k$ th element because of the condition of connectivity.

In the present paper, we assume a very loose condition of connectivity in which $k$ th element can occupy any position with equal probability in own space $\Omega_k$ independent of other elements in the chain. And more detailed examinations for the conditions of the connectivity in the chain will be passed to the later studies.

According to this rough assumption, the configuration number for such a model of the random chain can be expressed as

$$w_n(r)=v_1v_2\cdots\cdots\cdots\cdots\cdots\cdots v_n=\prod_{k=1}^{n} v_k \tag{3. 1}$$

At the calculation in Eq. (3. 1), we consider the following several cases:

**Model A**: All $v_k$ are, just so, calculated from Eqs. (2. 2) and (2. 3), i. e.,

$$w_n(r)=v_1v_2\cdots\cdots\cdots v_n=\{v_1v_2\cdots\cdots v_{n_1}\}^2\, v_{n_1+1}\cdots\cdots v_{n_2} \tag{3.2}$$

**Model B**: The volume $v_k$ of the element-spaces of the lens-type are replaced by some mean volume $\bar{v}$ such as $v_{n_1}\leq\bar{v}\leq v_{n/2}$, i. e.,

$$v_k=\bar{v},\quad (n_1<k\leq n_2). \tag{3.3}$$

Therefore

$$w_n(r)=\{v_1v_2\cdots\cdots\cdots v_{n_1}\}^2\,(\bar{v})^{n-2n_1}. \tag{3.4}$$

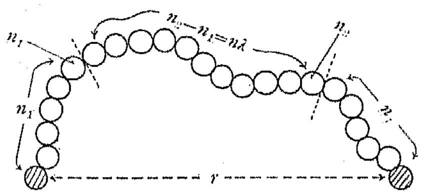

Fig. 2 Element number in peal-necklace model for a network chain.

But, still there are many cases in the model B, according to the selection of the mean volume $\bar{v}$, e.g., $\bar{v}=v_{n_1}$ or $\bar{v}=v_{n/2}$ or $\bar{v}=v_{n/4}$ etc. So we should examine the next main one of these models.

Model $B_1$ : $v_k=\bar{v}=v_{n_1}$, $(n_1<k<n_2)$. (3.5)

Model $B_2$ : $v_k=\bar{v}=v_{n/2}$, $(n_1<k\leq n_2)$., etc. (3.6)

The model $B_1$ is constructed from the element-spaces of the spherical type only, and the model $B_1$ is called the element-space model of the spherical type, hereafter.

For the calculation of $w_n(r)$ in Eq. (3.2) or (3.4), the calculation of $\{v_1v_2\cdots\cdots\cdots v_{n_1}\}^2$ is necessary and it is given by

$$\{v_1v_2\cdots\cdots v_{n_1}\}=\{(4\pi/3)a^3\}^{2n_1}\{1^3\cdot 2^3\cdot 3^3\cdot\cdots\cdots n_1^3\}^2 \tag{3.7}$$

$$=v_0^{2n_1}\{\Gamma(n_1+1)\}^6 \tag{3.7'}$$

$$\simeq v_0^{2n_1}e^{-6n_1}n_1^{6n_1},\quad (\text{if } 1\ll n_1), \tag{3.7''}$$

where $v_0=(4\pi/3)a^3$, and $\Gamma$ denotes the Gumma function. And although $n_1$ is not always integer, we substitute the nearest integer to $n_1$ for $n_1$. Such approximations are used over the paper without notice. Besides, the Stirling's formula

$$n!\simeq e^{-n}n^n \tag{3.8}$$

is used in Eq. (3.7''). Let us assume that the Stirling approximation (3.8) is always effective in this paper.

As a matter of course, the molecule-space $v_k$ of $k$ th molecule, the configuration number $w_n(V)$ in the perfect gas with $n$ molecules and the volume of a vessel $V$ at the absolute temperature $T$ and the pressure $P$, are respectively given as follows;

$$v_k=V,\quad (k=1,2,\cdots\cdots\cdots,n) \tag{3.9}$$

and

$$w_n(V) \propto v_1 v_2 \cdots\cdots v_n = V^n. \qquad (3.10)$$

The entropy of the system $s_n$ is given by the Boltzmann's relation as following

$$s_n = k \log w_n \qquad (3.11)$$
$$= nk \log V + s_0,$$

where $k$ is Boltzmann's constant and $s_0$ denotes the constant part in $s_n$. Using the equation (3.11), the pressure $P$ is easily obtained that

$$P = \frac{\partial (Ts_n)}{\partial V} = \frac{\partial (kT \log w_n)}{\partial V} = \frac{nkT}{V}. \qquad (3.12)$$

## 4. INDIVIDUAL MODEL OF RANDOM CHAIN

### 4.1 Model A

Substituting the next number $s$ for the number $k$ in Eq. (2.3)

$$s = k - n_1, \qquad (1 \leq s \leq n_2 - n_1 = n\lambda),$$

and the functions $\phi(\lambda)$, $g(\lambda)$ and $h(\lambda)$ define as

$$\phi(\lambda) = \sqrt{\lambda(2+\lambda)/3} \qquad (4.1)$$

and

$$\left.\begin{aligned} g(\lambda) &= (n/2)(\phi+\lambda), \\ h(\lambda) &= (n/2)(\phi-\lambda), \end{aligned}\right\} \qquad (4.2)$$

then Eq. (2.3) becomes

$$v_k = v_{n-k} = \pi n a^3 \{(1-\lambda)^2/\lambda\} (h+s)(g-s), \quad (1 \leq s \leq n\lambda). \qquad (4.3)$$

While the useful relation

$$\prod_{s=1}^{n\lambda}(h+s)(g-s) = (h+1)(h+2)\cdots\cdots\cdots\cdots(h+n\lambda)$$
$$\times (g-1)(g-2)\cdots\cdots\cdots\cdots(g-n\lambda)$$
$$= \frac{\Gamma(g)}{\Gamma(g-n\lambda)} \frac{(h+n\lambda)\Gamma(h+n\lambda)}{h\Gamma(h)}$$
$$= \frac{g}{h}\left\{\frac{\Gamma(g)}{\Gamma(h)}\right\}^2 = \frac{h}{g}\left\{\frac{\Gamma(g+1)}{\Gamma(h+1)}\right\}^2 \qquad (4.4)$$

is written down at once by using the relation

$$g(\lambda) = h(\lambda) + n\lambda. \qquad (4.5)$$

From the equations (4.4) and (4.3), we obtain

$$\left\{v_{n_1+1}\cdots\cdots\cdots v_{n_2}\right\} = \left\{\pi n a^3 \frac{(1-\lambda)^2}{\lambda}\right\}^{n\lambda} \frac{h}{g}\left\{\frac{\Gamma(g+1)}{\Gamma(h+1)}\right\}^2. \qquad (4.6)$$

Now the configuration number of the random chain $w_n(r)$ in the model A can be calculated as following expression, when Eqs. (3.7') and (4.6) substituted in $w_n(r)$ in Eq. (3.1):

$$w_n(r) = v_0^{n(1-\lambda)}\left\{\Gamma(n_1+1)\right\}^6 \cdot \left\{\pi n a^3 \frac{(1-\lambda)^2}{\lambda}\right\}^{n\lambda} \frac{h}{g}\left\{\frac{\Gamma(g+1)}{\Gamma(h+1)}\right\}^2. \qquad (4.7)$$

This expression is written in the various types

$$w_n(r)=\left[\frac{4\pi}{3}\left(\frac{na}{2e}\right)^3(1-\lambda)^3\left\{\frac{\phi+\lambda}{\phi-\lambda}\right\}^{\phi}e^{\lambda}\right]^n$$

$$=V_0^n(1-\lambda)^3\exp\{\lambda+2\lambda\varphi(\xi)\}^n \tag{4.8}$$

$$=V_0^n\exp(n)[3\log(1-\lambda)+3\lambda+2\lambda\{\varphi(\xi)-1\}]$$

$$=V_0^n\exp(n)\left\{-3\sum_{m=2}^{\infty}\frac{\lambda^m}{m}+\sum_{m=1}^{\infty}\frac{2\lambda}{2m+1}\left(\frac{3\lambda}{2+\lambda}\right)^m\right\}, \tag{4.8'}$$

where $V_0$ stands for $(4\pi/3)(na/2e)^3$ and a function $\varphi(\xi)$ is defined as

$$\varphi(\xi)=\frac{1}{2\lambda}\phi\log\frac{\phi+\lambda}{\phi-\lambda}$$

$$=\sum_{m=1}^{\infty}\frac{\xi^m}{2m+1}, \qquad \text{here} \qquad \xi=\frac{\lambda}{2+\lambda}. \tag{4.8a}$$

When the degree of contraction of the chain $\lambda$ is very small, $w_n(r)$ becomes the next expression

$$w_n(r)=V_0^n e^{-\frac{r^2}{2na^2}}. \tag{4.9}$$

This is the case that $\beta_n^2=1/(2na^2)$ in the normal distribution Eq. (1.2)

### 4.2 Model B

The model B splites into the individual model $B_1$, $B_2$, and so on, if the number $k$ take special values such as $n_1$, $n/2$ etc., and such values of $k$ substituted in Eq. (2.3).

(1°) **Model $B_1$**: When the value of $k$ takes $n_1=(n/2)(1-\lambda)$ in Eq. (2.3), $\bar{v}$ in Eq. (3.5) becomes

$$v_k=\bar{v}=(4\pi/3)(na/2)^3(1-\lambda)^3. \tag{4.10}$$

Using this equation, the expression (3.4) becomes

$$w_n(r)=v_0^n\left(\frac{n}{2}\right)^{3n\lambda}(1-\lambda)^{2n\lambda}\left\{\Gamma\left(\frac{n}{2}(1-\lambda)+1\right)\right\}^6$$

$$=v_0^n(n/2)^{3n}(1-\lambda)^{3n}e^{-3n(1-\lambda)} \tag{4.11}$$

$$=V_0^n\exp(3n)\{\log(1-\lambda)+\lambda\}$$

$$=V_0^n\exp(-3n)\left\{\sum_{m=2}^{\infty}\frac{\lambda^m}{m}\right\}. \tag{4.11'}$$

If the chain takes full coil-shape, this expression reduces into the usual Gaussian distribution as

$$w_n(r)=V_0^n e^{-\frac{3r^2}{2na^2}}. \tag{4.12}$$

This is the case that $\beta_n^2=3/(2na^2)$ in the normal distribution Eq. (1.2), and the standard Gaussian which is always used in the kinetic theory of rubber-like elasticity.

(2°) **Model $B_2$**: In the similar way, taking $k=n/2$ in Eq. (2.3), $\bar{v}$ in Eq. (3.6) is

$$v_k=\bar{v}=v_0^n(n/2)^3(1-\lambda)^2(1+\lambda/2). \tag{4.13}$$

and then Eq. (3.4) becomes

$$w_n(r)=v_0^n\,(n/2)^{3n\lambda}\left\{\Gamma(n/2)(1-\lambda)+1\right\}^{n\lambda}\left\{(1-\lambda)^2(2+\lambda/2)\right\}^{n\lambda}$$

$$=V_0^n e^{3n\lambda}\,(1-\lambda)^{n(3-\lambda)}\,(1+\lambda/2)^{n\lambda} \tag{4. 14}$$

$$=V_0^n\exp(n)\{3\lambda+(3-\lambda)\log(1-\lambda)+\lambda\log(1+\lambda/2)\}$$

$$=V_0^n\exp(n)\left\{3\lambda-(3-\lambda)\sum_{m=1}^{\infty}\frac{\lambda^m}{m}+\lambda\sum_{m=0}^{\infty}\frac{(-1)^{m-1}\lambda^m}{2^m m}\right\}. \tag{4. 14'}$$

But this model does not reduce one of the normal distribution in Eq. (1. 2) even if $\lambda\ll 1$, because the coefficient $\beta_n^2$ becomes zero in the expansion formula of the power in Eq. (4. 14′). Therefore this model is unsuitable to our purpose in the region of $\lambda\ll 1$.

## 5. A SERIES OF MODELS BASED ON VARIABLE LENS

Let us consider the element-spaces of the lens-type given by the number

$$k=n_1+n\lambda/\nu, \qquad (1\leq\nu<\infty), \tag{5. 1}$$

where $\nu$ in a parameter. According to the values of $\nu$ changes from 1 to $\infty$, the element-space of the lens-type given by Eq. (2. 3) represents any lens in the middle of $\Omega_{n_1+1}$ to $\Omega_{n_2}$, and also it coincides the sphere $\Omega_{n_1}$, as $\nu\to\infty$.

From the definition of $k$ and Eq. (2. 3), the quantity

$$[(n/2)^2\{\lambda(2+\lambda)\}/3-(n/2-k)^2]$$

is

$$\left(\frac{n}{2}\right)^2\frac{\lambda(2+\lambda)}{3}-\left(\frac{n}{2}-k\right)^2=\left(\frac{n}{2}\right)^2\frac{2\lambda}{3}\left\{1-\frac{(\nu^2-6\nu+6)\lambda}{\nu^2}\right\}, \tag{5. 2}$$

and therefore $v_k$ in Eq. (2. 3) becomes

$$v_k=\frac{4\pi}{3}a^3\left(\frac{n}{2}\right)^3(1-\lambda)^2\left\{1-\frac{(\nu^2-6\nu+6)\lambda}{\nu^2}\right\}. \tag{5. 3}$$

So the configuration number $w_n(r)$ in this model can be obtained as

$$w_n(r)=v_0^n(n/2e)^{3n}(1-\lambda)^{n(3-\lambda)}\{1-(\nu^2-6\nu+6)\lambda/\nu^2\}^{n\lambda} \tag{5. 4}$$

$$=V_0^n\exp(n)[3\lambda+(3-\lambda)\log(1-\lambda)+\lambda\log\{1-(\nu^2-6\nu+6)\lambda/\nu^2\}]. \tag{5. 5}$$

In the similar way as previous section the normal distribution derived from Eq. (5. 5) is given by

$$w_n(r)=V_0^n\exp\left\{-\frac{3}{2}\left(1-\frac{2}{\nu}\right)^2\frac{r^2}{na^2}\right\}, \qquad (\lambda\ll 1), \tag{5. 6}$$

or

$$w_n(r)=V_0^n e^{-\beta_n^2 r^2}, \tag{5. 6'}$$

where

$$\beta_n^2=\frac{3}{2}\left(1-\frac{2}{\nu}\right)^2\frac{1}{na^2}. \tag{5. 6'a}$$

In this expression, if $\nu$ takes *1* or $\infty$, $w_n(r)$ becomes

$$w_n(r) = V_0^n e^{-3r^2/2(na)^2}. \tag{5.6''}$$

Of course this coincides the case of Eq. (4.12) in the model B.

When the lens represented by Eq. (5.3) moves between $\Omega_{n_1}$ and $\Omega_{n/2}$, the sharpness parameter $\beta_n^2$ of the normal distribution in Eq. (1.2) decreases from

Table 1
The change of sharpness parameter $\beta_n^2$ in normal distribution

| $\nu$ | $\beta_n^2$ | $b^2=\beta_n^2(na^2)$ | tape of model |
|---|---|---|---|
| $\infty$ or *1* | $3/(2na^2)$ | $3/2 \fallingdotseq 1.50$ | sphere |
| ......... | .................... | .................... | lens |
| *100* | $7203/(5000na^2)$ | $7203/5000 \fallingdotseq 1.44$ | 〃 |
| *10* | $24/(25na^2)$ | $24/25 \fallingdotseq 0.96$ | 〃 |
| *8* | $27/(32na^2)$ | $27/32 \fallingdotseq 0.85$ | 〃 |
| *6* | $2/(3na^2)$ | $2/3 \fallingdotseq 0.67$ | 〃 |
| *4* | $3/(8na^2)$ | $3/8 \fallingdotseq 0.27$ | 〃 |
| *3* | $1/(6na^2)$ | $1/6 \fallingdotseq 0.17$ | 〃 |
| *2* | *0* | *0* | 〃 |

*3/2* to *0* as shown in Table 1. It is the notable fact that $\beta_n^2$ is *0* for $\nu=2$ in Eq. (5.6′); namely, $k=n_1+n\lambda/2=n/2$. But it is a matter of course, because this case coincides with the case in the model $B_2$ based upon $\Omega_{n/2}$, and it is pointed out that this model does not reduce to the normal distribution.

It is clear that every one of the present models has the finite extensibility of the chain : namely, the condition

$$\left.\begin{aligned} w_n(\lambda) &\neq 0 \quad \text{for } 0<\lambda<1, \\ &= 0 \quad \text{for } \lambda=1 \end{aligned}\right\}$$

is satisfied in every expressions (4.8), (4.11), (4.14) and (5.4).

In addition to this condition, the tensile force in the single chain derived from these expressions becomes $\infty$, as $\lambda \to 1$.

## 6. THE LARGE EXTENSION IN RUBBER ELASTICITY

As an application, the expression for the tension-extension ratio derived from the present model is compared with a experimental curve in a simple elongation of a natural rubber vulcanizate.

Suppose a regular network structure with $N$ network chains of the same length $na$ per unit volume. The network chain are distributed in isotropic, namely, the end-to-end directions of $N/3$ by $N/3$ chains are arranged in the direction of $x$, $y$ and $z$ axis respectively in the same manner.

The entropy of a chain along $x$ axis, $s_n(x)$, can be calculated from the present models, for instance, model $B_2$ in Eq. (4. 11) such as

$$s_n(x)=k\log w_n(x), \qquad \text{(Eq. (3. 11) cf. )}$$
$$=3nk\{\lambda_1+\log(1-\lambda_1)\},$$

where $\lambda_1=x/(na)$. Then the entropy caused by $N/3$ network chains along $x$ direction $S(x)$ can be written as

$$S(x)=(N/3)(3nk)\{\lambda_1+\log(1-\lambda_1)\}.$$

Similarly

$$S(y)=(N/3)(3nk)\{\lambda_2+\log(1-\lambda_2)\},$$
$$S(z)=(N/3)(3nk)\{\lambda_3+\log(1-\lambda_2)\},$$

where $\lambda_2=y/(na)$ and $\lambda_3=z/(na)$. Therefore the entropy $S$ and the free energy $F$ in the system are given by

$$S=Nnk\{\lambda_1+\lambda_2+\lambda_3+\log(1-\lambda_1)+\log(1-\lambda_2)+\log(1-\lambda_3)\} \tag{6. 1}$$

and

$$F=U_0-NnkT\{(\lambda_1+\lambda_2+\lambda_3)+\log(1-\lambda_1)+\log(1-\lambda_2)+\log(1-\lambda_3)\}, \tag{6. 2}$$

respectivery, where $U_0$ denotes the internal energy caused by the liquid-like int eraction energy among the chain segments, and it is kept constant because of the assumption of the incompressibility for the rubber.

Let us also assume the requirement of proportionality in the usual theory of rubber elasticity

$$x=\alpha_1 x_0, \quad y=\alpha_2 y_0, \quad z=\alpha_3 z_0,$$

where $x_0$, $y_0$, $z_0$ and $x$, $y$, $z$ are the end-to-end distances of the chains in the natural state and the deformed state respectively, and $\alpha_1$, $\alpha_2$, $\alpha_3$ denote the extension ratio of the system. Because the network structure is isotropic

$$\frac{x_0}{na}=\frac{y_0}{na}=\frac{z_0}{na}\equiv\lambda_0$$

and then

$$\lambda_1=\frac{x_0}{na}\frac{x}{x_0}=\lambda_0\alpha_1, \quad \lambda_2=\frac{y_0}{na}\frac{y}{y_0}=\lambda_0\alpha_2, \quad \lambda_3=\frac{z_0}{na}\frac{z}{z_0}=\lambda_0\alpha_3. \tag{6. 3}$$

If $\lambda_1$, $\lambda_2$ and $\lambda_3$ in Eq. (6. 3) are substituted in Eq. (6. 2), we obtain

$$F=U_0-NnkT\{\lambda_0(\alpha_1+\alpha_2+\alpha_3)+\log(1-\lambda_0\alpha_1)+\log(1-\lambda_0\alpha_2)$$
$$+\log(1-\lambda_0\alpha_3)\}. \tag{6. 4}$$

Also the assumption of the incompressibility of rubber in the simple elongation is represented by

$$\alpha_1\alpha_2\alpha_3=1, \quad \alpha_2=\alpha_3, \qquad \text{or} \qquad \alpha_1=\alpha, \quad \alpha_2=\alpha_3=1/\sqrt{\alpha}.$$

Taking account of this, the free energy $F$ in Eq. (6. 4) is written as

$$F=U_0-NnkT\{\lambda_0(\alpha+2/\sqrt{\alpha})+\log(1-\lambda_0\alpha)+2\log(1-\lambda_0/\sqrt{\alpha})\}. \tag{6.5}$$

Now the tension $\sigma$ is obtained in the following formula

$$\sigma=\left(\frac{\partial F}{\partial\alpha}\right)_T=\lambda_0^2NnkT\left\{\frac{\lambda_0\alpha}{1-\lambda_0\alpha}-\frac{1}{\alpha^2}\frac{1}{1-\lambda_0/\sqrt{\alpha}}\right)\Big\} \tag{6.6}$$

$$=G\left\{\frac{\alpha-1/\alpha^2}{1-\lambda_0\alpha}+\frac{1}{\alpha^2}\left(\frac{1}{1-\lambda_0\alpha}-\frac{1}{1-\lambda_0/\sqrt{\alpha}}\right\},\right. \tag{6.6'}$$

where $G$ stands for $NkT$. But the second term in Eq. (6. 6′) is considerably smaller than the first term, so that the approximate formula of Eq. (6. 6′)

$$\sigma=G\frac{\alpha-1/\alpha^2}{1-\lambda_0\alpha} \tag{6.7}$$

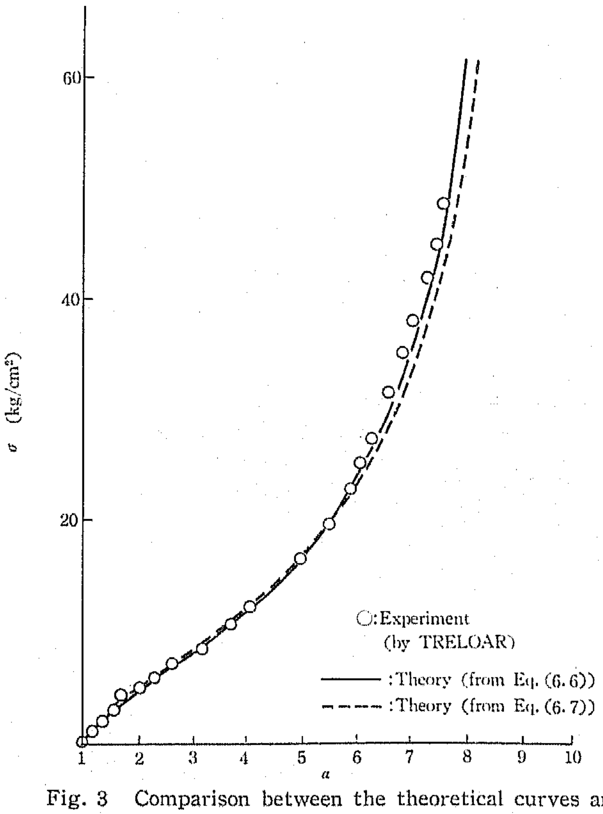


Fig. 3 Comparison between the theoretical curves and a experimental values in the stress-strain of a natural rubber vulcanizate.

is often convenience.

The comparison between the theoretical tension[3)5)] and the experimental one[4)] is shown in Fig. 3. The theoretical curves are calculated from Eq. (6. 6′)

taking values of the parameters $G=2.0\,\mathrm{kg/cm^2}$, $\lambda_0=1/11$, and from Eq. (6.7) taking $G=2.1\,\mathrm{kg/cm^2}$, $\lambda_0=1/10$ respectively. Of course, rapid rising of the tension as seen in the highly extended natural rubber vulcanizate is not only the effect of the finite extensibility of the chain, but also one of the crystallization.[5] But the only effect of the extensibility of the chain is compared with experiment in most of the studies. Since the two effects can not be separated into each other, now, such comparisons are not sufficient, but at any rate the effect of the finite extensibility which is the main purpose of this study can be represented in the present models.

## 7. CONCLUSION

The simple calculation models for the statistics of the random chain are presented here. All of them have the clear limit of the finite extensibility of the chain, and the reducebility to the normal distribution.

The analyses from these models are more simple than the previous one for the finite extensibility of the random chain, except the one from the model A. The treatment for the model A seems so considerably complicate that it is equivalent to the one given by the inverse Langevin function.

Already the rapid rising of the tension in the high extension region of a vulcanized rubber is analysed by author, considering the only effect of a rate processes in the crystallization also,[5] but it is not translated into English, yet.

The connectivity of an element with the chain must be consider in detail, but it is pass to the later studies.

## APPENDIX

**The volume of the lens**: Consider two caps of the spheres with the radii $\rho_k=ka$ and $\rho_k'=(n-k)a$ and the centers located at the focuses respectively about Fig. 4. The following equations are clear

$$\left.\begin{aligned}&\rho_k\sin\theta_k=\rho_k'\sin\theta_k',\\&\rho_k\cos\theta_k+\rho_k'\cos\theta_k'=r.\end{aligned}\right\}\qquad\text{(A-1)}$$

(The volume of a cap of sphere specified by $\rho$ and $\theta$)

$$=\int_\rho^{x_0}\pi y^2dx=\pi\int_\rho^{x_0}(\rho^2-x^2)dx,\quad(\text{where } x_0=\rho\cos\theta)$$

$$=-\pi\left(\frac{2}{3}\rho^3-\rho^2x_0+\frac{x_0^3}{3}\right)$$

$$=-(\pi/3)\rho^3(2-2\cos\theta-\cos\theta\sin^2\theta).\qquad\text{(A-2)}$$

Using Eq. (A-2), the volume $v_k$ of the lens $\Omega_k$, $(n_1<k\leq n_2)$ is given by

$$v=(\pi/3)\{2(\rho^3+\rho'^3)-2(\rho^3\cos\theta+\rho'^3\cos\theta')$$
$$+(\rho^3\cos\theta\sin^2\theta+\rho'^3\cos\theta'\sin^2\theta')\}.\qquad\text{(A-3)}$$

From Eq. (A-3) and the law of cosihes: $\rho\cos\theta=\{r^2+(\rho^2-\rho'^2)\}/2r)$, the next formula can be derived by elimination of $\theta$ and $\theta'$

$$\rho^3\cos\theta+\rho'^3\cos\theta'=\rho^3\cos\theta+\rho'^2(r-\rho\cos\theta)$$
$$=\rho'^2r+(\rho^2-\rho'^2)\{r^2+(\rho^2-\rho'^2)\}/(2r)$$
$$=(na/2)\{\lambda(\rho^2+\rho'^2)+(\rho-\rho')^2/\lambda\},$$

therefore

$$\rho^3+\rho'^3-(\rho\cos\theta+\rho'^3\cos\theta')$$
$$=\{na/(2\lambda)\}\{(\rho^2+\rho'^2)\lambda(2-\lambda)-2\lambda\rho\rho'-(\rho-\rho')^2\}$$
$$=\{na(1-\lambda)/(2\lambda)\}\{2\rho\rho'(2-\lambda)-(1-\lambda)(\rho+\rho')^2\}. \qquad \text{(A-4)}$$

Also the next formula is obtained in the same way as in Eq(A-4)

$$\rho^3\cos\theta\sin^2\theta\rho'^3\cos\theta'\sin^2\theta'$$
$$=\{na(1-\lambda^2)/\lambda\}\{\rho\rho'-(\rho+\rho')^2(1-\lambda^2)/4\}. \qquad \text{(A-5)}$$

The equation (A-3) becomes Eq. (2. 3) in section 2 by use of Eqs. (A-4), (A-5) and $\rho=ka$, $\rho=(n-k)a$ as follows:

$$v=\{\pi na(1-\lambda)/(3\lambda)\}[2\rho\rho'(2-\lambda)-(1-\lambda)(\rho+\rho')^2$$
$$-(1+\lambda)\rho\rho'+(1+\lambda)(1-\lambda^2)(\rho+\rho')^2/4]$$
$$=\pi na^3\{(1-\lambda)^2/\lambda\}\{k(n-k)+(n^2/12)(2\lambda+\lambda^2-3)\}$$
$$=\pi na^3\{(1-\lambda)^2/\lambda\}\{(n/2)^2\lambda(2+\lambda)/3-(n/2-k)^2\}. \qquad \text{(2. 3)}$$

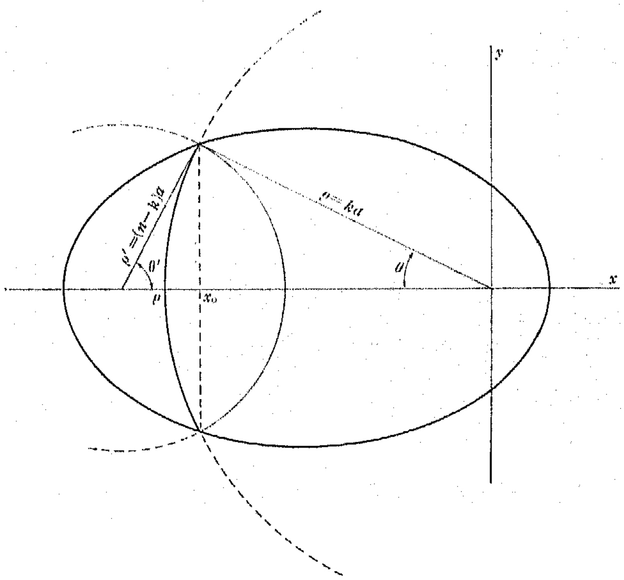


Fig. 4 Calculation of the volume of a cap of a sphere.

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