On the Configuration of Chain Molecules. I.
Normal Paraffine.

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1. Introduction. The problem of configurations of chain molecules is the fundamental groundwork of the physics of chain molecules.

Quite concrete answers are given by studies through X-ray diffraction etc. in the cases when the molecule has only one regular configuration as in crystals. But in the cases of many configurations the problem becomes complicated.

The first quantitative treatment was developed by W. Kuhn, who took up the long chain molecule of n-paraffine type and calulated the relative position of the both ends of the chain.⁽¹⁾ Assuming the constant length a of the elements of the chain, the C–C bonds, the constant angle α of any two concecutive bonds, and the completely free rotation round the axis of any bond, he found the distance r of the both ends of the chain:

$$\langle r^2\rangle = a^2\{n(1+c)/(1-c) - 2c(1-c^n)/(1-c)^2\}, \qquad (1)$$

where n is the number of elements, c is $\langle\cos\alpha\rangle$, and $\langle\,\rangle$ means average.

His third assumption, the free rotation, is not satisfied by the real molecule, For the recent physico-chemical studies told us that the real molecule has no free rotation but the more or less hindered rotation at the ordinary temperature.

The stretched forms of the n-paraffine molecule are more stabile than the contracted and curled forms. So $\langle r^2\rangle$ must be larger than Kuhn's value, which is true only in the limiting case of high temperature.

We shall give a solution for the case of hindered rotation.

2. The molecule of normal paraffine. The series of n vectors, $a_0, a_1, a_2, \ldots, \ldots, a_i, \ldots, a_{n-1}$, represents one of the many configurations of a_n n-membered chain molecule, $C_{n+1}H_{2n+3}$, where a_i represents the ith element of the chain (Fig. 1). The four valencies of the carbon atom of paraffine have the tetrahedral symmetry:

$$\widehat{a_{i-1}a_i} = \alpha_i = \text{const.} = \cos^{-1}(1/3) \cong 71^\circ.$$

a_{i+1} rotate round a_i holding the angle α constant. And let the rotation angle φ_i be π when $a_{i+1} // a_{i-1}$ (Fig. 2).

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(1) W. Kuhn, *Kolloid Z.*, **68** (1934), 2.

Kuhn assumed the uniform distribution probability for the whole range of φ_i: $\langle \cos\varphi_i \rangle = 0$, $\langle \sin\varphi_i \rangle = 0$. We take up the none-uniform case. In paraffine the distribution is dominant in the 'trans' configuration $(\varphi = \pi)$, therefore $\langle \cos\varphi_i \rangle < 0$. But the probability is symmetrical as regard to the positive φ_i and negative φ_i, therefore $\langle \sin\varphi_i \rangle = 0$.

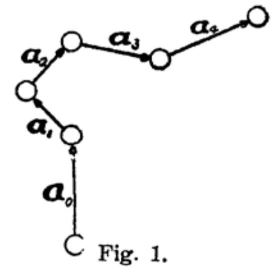

Fig. 1.
Vector representation of a molecule.

If the mean values of $\cos \widehat{a_j a_k}$ are known for all the sets of j and k, they can describe several mean properties of the chain.

Let ρ_i be $\widehat{a_0 a_i}$, and let us calculate $\langle \cos\rho_i \rangle$.

3. The problem of correlated random paths on the spherical surface. For a while put the magnitude of a_i out of consideration, and consider the direction only. And a_i is represented as a point A_i on the sphere of unit radius (Fig. 3). The tracing of a congiguration of the molecule from one end to other end is converted as follows.

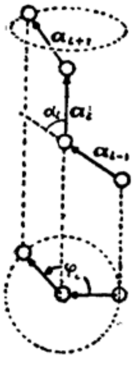

Fig. 2.
Bond angle α_i and rotation angle φ_i.

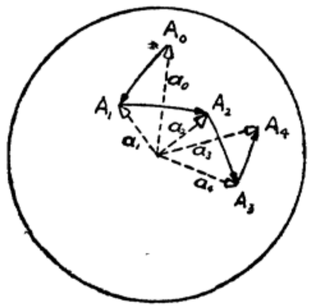

Fig. 3.
Spherical random paths.
(Formation)

A moving point on the unit sphere initially situated at the point A_0 travels step by step through the series of points, A_1, A_2, ..., A_i, ... a_i is the width of the ith path $\widehat{A_{i-1} A_i}$, φ_i is the angle between the ith path and the $i+1$th path, and ρ_i is the distance $\widehat{A_0 A_i}$ (Fig. 4).

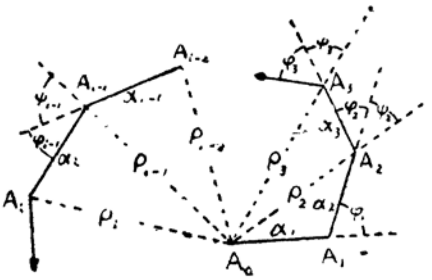

Fig. 4.
Spherical random paths.
(Analysis)

We solve the problem under three assumptions : (2)

1. the width of the paths is constant. $\cos\alpha_i = c$,
2. the direction of the ith path is correlated only with the $i-1$th path,
3. $\langle \sin\varphi_i \rangle = 0$, $\langle \cos\varphi_i \rangle = b$.

The first corresponds the constant bond angle, the second means that a_i has direct correlation with a_{i-2} but without a_{i-3}, a_{i-4} etc., and the third describes the correlation of a_i with a_{i-2}.

Calculation of $\langle \cos\rho_i \rangle$ is as follows :

$$\cos\rho_1 = \cos\alpha_1 ,$$

at the spherical triangle $A_0 A_1 A_2$

$$\cos\rho_2 = \cos\alpha_1\cos\alpha_2 - \sin\alpha_1\sin\alpha_2\cos\varphi_1\,,$$

and generally at the triangle $A_0 A_{i-1} A_i$

$$\cos\rho_i = \cos\rho_{i-1}\cos\alpha_i - \sin\rho_{i-1}\sin\alpha_i\cos(\varphi_{i-1}+\psi_{i-1})$$

where ψ_i is the angle between $\overrightarrow{\rho_i}$ and $\overrightarrow{\alpha_i}$. We can rewrite the last factor

$$\cos(\varphi_{i-1}+\psi_{i-1}) = \cos\varphi_{i-1}\cos\psi_{i-1} - \sin\varphi_{i-1}\sin\psi_{i-1}\,.$$

And at the triangle $A_0 A_{i-1} A_{i-2}$

$$\cos\rho_{i-2} = \cos\alpha_{i-1}\cos\rho_{i-1} + \sin\alpha_{i-1}\sin\rho_{i-1}\cos\psi_{i-1}\,.$$

Then from those three equations

$$\cos\rho_i = \cos\rho_{i-1}\cos\alpha_i - \sin\rho_{i-1}\sin\alpha_i\{\cos\varphi_{i-1}(\cos\rho_{i-2} - \cos\alpha_{i-1}\cos\rho_{i-1})/$$
$$\sin\alpha_{i-1}\sin\rho_{i-1} - \sin\varphi_{i-1}\sin\psi_{i-1}\}\,.$$

Taking average under the three assumptions (2) we get the recurrence formula,

$$\langle\cos\rho_i\rangle = c(1+b)\langle\cos\rho_{i-1}\rangle - b\langle\cos\rho_{i-2}\rangle\,, \qquad (3)$$

with the initial conditions,

$$\langle\cos\rho_1\rangle = c,$$
$$\langle\cos\rho_2\rangle = c^2-(1-c^2)b\,.$$

Solution of the formula (3) is

$$\langle\cos\rho_i\rangle = C_3 s_3^i + C_4 s_4^i\,, \qquad (4)$$

where s_3, s_4 are the two roots of the equation

$$s^2 - c(1+b)s + b = 0\,, \qquad (4\,\mathrm{a})$$

and C_3, C_4 are determined by the initial conditions:

$$C_3 = (c-s_4)\,/\,(s_3-s_4)\,,\quad C_4 = (c-s_3)\,/\,(s_4-s_3)\,. \qquad (4\,\mathrm{b})$$

An analogous derivation can be executed starting from A_j instead of A_0, giving

$$\langle\cos\rho_{jk}\rangle = \langle\cos\rho_{k-j}\rangle\,,$$

in which ρ_{jk} is $\widehat{A_j A_k}$.

4. The dipole momont of paraffine substituted at the both ends. The molecul $X(CH_2)_n Y$ is now under consideration. X and Y are substitutes groups with dipole moments μ_0 and μ_n in equal directions to a_0 and a_n respectively (Fig. 5.). The apparent dipolement μ must be

$$\mu^2 = (\overrightarrow{\mu_0}+\overrightarrow{\mu_n})^2 = \mu_0^2+\mu_n^2+2\mu_0\mu_n\cos\rho_n$$

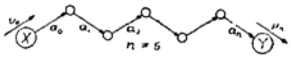

Fig. 5.
The molcule $X(CH_2)_n Y$

for each configuration. The mean value over all the configurations is observable and given theoretically as

$$\langle\mu^2\rangle = \mu_0^2+\mu_n^2+2\mu_0\mu_n(C_3 s_3^n + C_4 s_4^n)\,. \qquad (6)$$

If X = Y, $\mu_0 = -\mu_n$. So we have

$$\langle \mu^2 \rangle = 2\mu_0^2 (1 - C_3' s_3^n - C_4' s_4^n) . \qquad (7)$$

The value of the equation are plotted on Fig. 6 and compared with the observed value of $Br(CH_2)_nBr$.⁽²⁾ The indented theoretical values express quite well the tendency of the observed values. The old theoretical values of the free rotation model can give only a very poor coincidence (shown in the figure as $b = 0$). The repulsive interaction of two dipoles diminishes the observed μ for molecules of the shorter chains. The numerical value of b seems to be about $-1/2$ at the ordinary temperature.

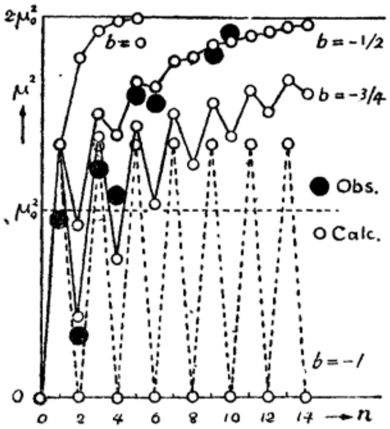

Fig. 6.
Dipole moment μ of $X(CH_2)_nX$

5. The distance of the both ends. The distance of the both ends of the molecule with n bonds, r, is obtained as follows: for any configuration,

$$r = \left|\sum_{i=0}^{n-1} a_i\right| , \quad |a_i| = a ,$$

$$r^2 = (\sum a_i \sum a_i) = \sum_{i=0}^{n-1} (a_i a_i) + \sum_{k=1}^{n-1} \sum_{j=0}^{k-1} (a_j a_k) ,$$

where ( ) is the scalar product of vectors:

$$(a_i a_i) = a^2 ,$$

$$(a_j a_k) = a^2 \cos \rho_{jk} .$$

Then we average r^2 over all the configurations, knowing that $\langle \cos \rho_{jk} \rangle$ is the function of $k-j$ only as seen in (6):

$$\langle r^2 \rangle = a^2 n + 2a^2 \sum_{i=1}^{n-1} (n-i) \langle \cos \rho_i \rangle^x . \qquad (8)$$

Putting (5) in (8) we finally

$$\langle r^2 \rangle = a^2 \{ n(1+c)(1-b)/(1-c)(1+b) - 2C_3' s_3 (1-s_3^n)(1-s_3)^{-2} - 2C_4' s_4 (1-s_4^n)(1-s_4)^{-2} \} . \qquad (9)$$

For large n (9) gives $\langle r^2 \rangle$ proportional to n:

$$\langle r^2 \rangle \cong a^2 n (1+c)(1-b)/(1-c)(1+b) , \qquad (9a)$$

and for $b = -1$ (9) gives the length of the most stretched chain:

$$r^2 = a^2 n^2 (1+c)/2 \qquad \text{for even } n , \qquad (9b)$$

$$r^2 = a^2 n^2 (1+c)/2 + a^2 (1-c)/2 \qquad \text{for odd } n , \qquad (9c)$$

Of course the equation (9) includes the Kuhn's formula (1) as a special

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(2) C. P. Smyth, *J. Amer. Chem. Soc.* 53 (1931), 2988; 54 (1932), 2261.

case $b = 0$. Kubo's ingeneous intramolecular statistics in his first paper⁽³⁾ does not include this result, for his generalised theory cannot yet describe the doubly correlated chain rigorously.

The theoretical values are shown in Fig. 7. $\langle r^2 \rangle$ must be about three times larger than the Kuhn's value, for b is not 0 but about $-1/2$ at the ordinary temperature.

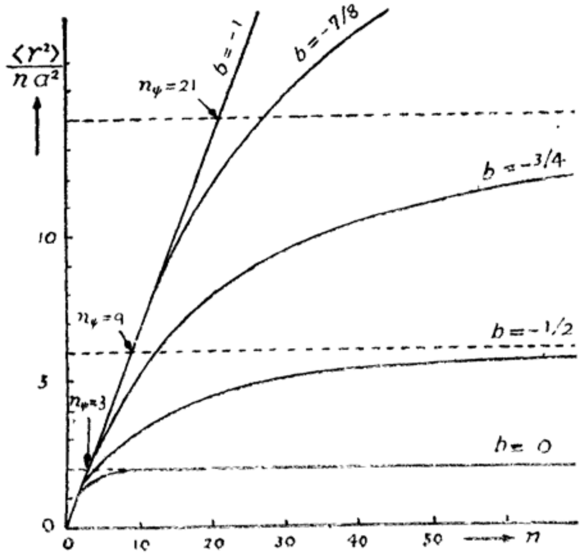

Fig. 7.

Apparent length r and Pseudosegment n_ψ of $C_{n+1}H_{2n+3}$

6. The moment of inertia. The moment of inertia about the axis (parallel to the Y axis) passing through the centre of, I_Y, is a significant quantity concerning the viscosity of the solution of the molecules.⁽⁴⁾ We define the quantity I as

$$I = \sum_{p=0}^{n} m \, | r_p - R |^2 , \qquad (10)$$

where r_p and R are the radius vectors of the p th atom and the centre of mass, m is the mass of the atom and subsequent atoms, CH_2 in paraffine. Then

$$3 \langle I_Y \rangle = 2 \langle I \rangle . \qquad (11)$$

I is obtained as follows: for any configuration

$$\mathbf{r}_p = \mathbf{r}_0 + \sum_{i=0}^{p-1} \mathbf{a}_i ,$$

$$\mathbf{R} = \sum_{p=0}^{n} \mathbf{r}_p / (n+1) = \mathbf{r}_0 + \sum_{i=0}^{n-1} (n-i) \, \mathbf{a}_i / (n+1) ,$$

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(3) R. Kubo, *J. Phys. Soc. Japan*, 2 (1947), 47: In the recent meeting of the physical society of Japan at Sept. 9, 1947 Kubo read the expansion of his theory to the doubly correlated chain and gave the approximating formulae of $\langle r^2 \rangle$ etc. for large n.

(4) H. Kramers, *J. Chem. Phys.*, 14 (1946), 415; P. Debye, ibid., 636.

$$\mathbf{r}_p-\mathbf{R} = \left\{ \sum_{i=0}^{p-1} (1+i)\, \mathbf{a}_i - \sum_{i=p}^{n-1})n-i)\, \mathbf{a}_i \right\} / (n+1)\,,$$

$$\sum_{p=0}^{n} (\mathbf{r}_p-\mathbf{R})^2 = \left\{ \sum_{i=0}^{n-1} (1+i)\,(n-i)\,(\mathbf{a}_i\,\mathbf{a}_i) + 2 \sum_{k=1}^{n-1} \sum_{j=0}^{k-1} (1+j)(n-k)(\mathbf{a}_j\,\mathbf{a}_k) \right\} / (n+1).$$

Meaning over all the configurations we have

$$\langle I \rangle = wa^2\{n\,(n+1)\,(n+2) + 2 \sum_{i=1}^{n-1} (n-i)(n-i+1)(n-i+2)\langle \cos \rho_i \rangle\} \,/\, 6(n+1)\,. \tag{12}$$

Using (5) it leads to

$$\langle I \rangle = m\,a^2 [n(n+1)\,(n+2) + 2 \sum C\,\{(n+1)\,n\,(n-1)\,s\,(1-s)^{-1} - (n-1)ns^2(1-s)^{-2} + (n-1)s^3(1-s)^{-3} - (1-s^{n-1})s^4(1-s)^{-4}\}]/6(n+1), \tag{13}$$

where $\sum$ is summed up for s_3 and s_4, C_3 and C_4. $\langle I \rangle / ma^2 n^2$ plotted against n gives a similar curve to that of $\langle r^2 \rangle$. For large n (13) becomes

$$\langle I \rangle \cong ma^2 n^2 (1+c)\,(1-b)\,/\,6(1-c)\,(1+b) = \langle r^2 \rangle\, mn/6. \tag{14}$$

Combinating (14) with (11) we find

$$\langle I_T \rangle \cong \langle r^2 \rangle\, mn/9\,. \tag{15}$$

The equation can be derived much more generally. If b is not -1 and n is so large that (8) is approximately rewritten that

$$\langle r^2 \rangle \cong na^2\,(1 + 2 \sum \langle \cos \rho_i \rangle\,)\,,$$

then (12) is also approximately rewritten that

$$\langle I \rangle \cong ma^2 n^2\,(1 + 2 \sum \langle \cos \rho_i \rangle\,)/6\,.$$

Therefore one obtains (14) and (15).

7. The relation between $\langle \cos \varphi \rangle$ and temperature. We have carried out mathematical treatment. Now some physical discussions will be made on the mathematical results.

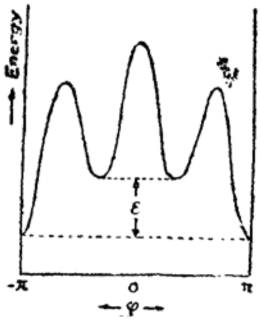

Fig. 8.

The distribution of rotational isomers round the bond-axis is somewhat complicated. Our results, however, find out that the mean value of cosine of rotation angle φ can describe such physical quantities as $\langle r^2 \rangle$, $\langle \mu^2 \rangle$ and $\langle I \rangle$ rigorously. Our formulae are derived without approximation under three conditions (2), which are probably satisfied by real molecules to a sufficient extent.

The potential curve round the bond-axis shown in Fig. 8 with three peaks and three valleys.⁽⁵⁾ Separating into quantum states q we can estimate the distribution probability w_q for each state and $\langle \cos \varphi \rangle$ will be given by $\sum_q w_q \cos \varphi_q$.

But a preliminary estimation is tried here. Only three states at the bottoms of the valleys are regarded as the principal states and others are neglected, for the molecules,

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(5) Mizushima and colaborators, series of papers on "internal rotation" in *Sci. Papers Inst. Phys. Chem. Research* (Tokyo).

in fact, takes chiefly the three states, which are called t, g, and g' respectively corresponding $\varphi = \pi$, $\pi/3$, and $-\pi/3$. The energy of g state is equal to that of g' state and higher that t state. Let ε be the difference. Then the distribution probability w_q are given by the Boltzmann's statistics:

$$w_t = 1/\{1+2\exp(-\varepsilon/kT)\}\,.$$
$$w_g = w_{g'} = \exp(-\epsilon/kT)/\{1+2\exp(-\epsilon/kT)\}\,, \qquad (16\text{ b})$$

where k is the Boltzmann's constant and T is the absolute temperature. Then

$$b = \langle\cos\varphi\rangle = \sum w\cos\varphi = \{-1+\exp(-\epsilon/kT)\}/\{1+2\exp(-\varepsilon/kT)\}\,. \qquad (17)$$

When T is infinity, b is 0 and the quantities $\langle r^2\rangle$ etc. shows equal values to those of Kuhn's free rotation model. When T' is 0, b is -1, and the molecule takes the most stretched form, so $\langle r^2\rangle$ and $\langle I\rangle$ become the largest. With the elevation of temperature b increases and $\langle r^2\rangle$ and $\langle I\rangle$ become smaller and $\langle\mu\rangle$ larger.

ε must be about 1 kilocalorie per mole, if b is $-1/2$ at the ordinary temperature as seen in Fig. 6.

8. **Pseudosegment.** In Fig. 7 the value $\langle r^2\rangle/a^2 n$ for small n is on the line $b = -1$, which shows the most stretched form, and the value for large n approach the horizontal line asymptotically.

Let n_ψ be the abscissa of the cross point of the two lines. The equation of two lines are

$$\langle r^2\rangle\,/\,a^2 n = n(1+c)\,/\,2 \qquad \text{for } b = -1, \qquad (9\text{ b})\ (18)$$
$$\langle r^2\rangle\,/\,a^2 n = (1+c)\,(1-b)\,/\,(1-c)\,(1+b) \quad \text{for } n = \infty. \qquad (9\text{ a})\ (19)$$

So we get n_ψ equating the two formulae:

$$n_\psi = 2(1+c)\,(1-b)\,/\,(1-c)\,(1+b). \qquad (20)$$

n_ψ is the function of b and accordingly of T.

We divide the n-membered chain every n_ψ element. The number of divided parts n' is

$$n' = n/n_\psi\,. \qquad (21)$$

If each part is stretched forth, the ordinate of the cross point gives its length a':

$$a' = a n_\psi\,\{(1+c)\,/\,2\}^{1/2}. \qquad (22)$$

Here the chain is transformed into a chain with n' members of length a'. If the direction of each member is independent of any other members, the distance r between the both ends is given as a special case of (8) in which $\langle\cos\rho_i\rangle = 0$:

$$\langle r^2\rangle = n' a'^2 \qquad (23)$$

Putting (21), (22) in (23) we have

$$\langle r^2\rangle = na^2 n_\psi(1+c)/2\,.$$

The use of the value of n_ψ (20) gives

$$\langle r^2\rangle = na^2(1+c)(1-b)/(1-c)(1+b)\,.$$

It is the formula for the transformed chain without approximation, but is the same as the approximate formula (19) for the original chain.

We can use the transformed chain, in which the part composed of n_ψ elements moves independently of other parts, instead of the original one, in which every element moves depending on other elements.

This transformation simplifies the theory from the problem of Markoff's chain to that of independent variables. However it is only a model which can give the equal value of $\langle r^2\rangle$, and there is no groups of n_ψ elements moving together as a unit, but every element moves as a unit. Therefore n_ψ is named 'psedosegment'.

In theories of chain molecules the assumption of a certain magnitude of segment moving together as a unit may coincide with some experiments, but this coincidence cannot prove the assumption to be real. In this case above told the adoptation of n_ψ as a unit will succeed in dealing with quantities concerning $\langle r^2\rangle$, but may fail in dealing with other quantities. In fact the psendosegment similarly calculated for $\langle I\rangle$ is twice large as that for $\langle r^2\rangle$.

9. Summary. W. Kuhn's free rotation model for the problems on the configuration of long chain molecules must be seriously revised according to the recent progress of the physics of the molecular structure. We explain that several physical properties of chain molecules like paraffine can be expressed as the functions of the mean value of cosine of rotation angle.

One of the mathematical results, the series of the calculated values of dipole moment of $X(CH_2)_nX$, wins a fine coincidence with the experiment and shows the propriety of this theory.

We give the moment of inertia and the distance of the both ends of the chain molecule with its temperature dependence. These values are given also subject to an assumption of existence of segments, which are named here 'psedosegments' because of their apparent and false existence.

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