

UNCLASSIFIED

AD _____

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION ALEXANDRIA, VIRGINIA

DOWNGRADED AT 3 YEAR INTERVALS:
DECLASSIFIED AFTER 12 YEARS
DCD DIR 5200.10



UNCLASSIFIED

THIS REPORT HAS BEEN DECLASSIFIED
AND CLEARED FOR PUBLIC RELEASE.

DISTRIBUTION A
APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

ONR Technical Report No. 1/3
Contract: Nonr 702(00) ✓
Project: NR 330-021

THE CALCULATION OF THE
PRINCIPAL POLARIZABILITIES
OF POLYMER CHAINS - I

by
Richard S. Stein

OFFICE OF NAVAL RESEARCH

Contract: Nonr 702(00)
Project: MR 330-024

Technical Report No. 1

THE CALCULATION OF THE
PRINCIPAL POLARIZABILITIES
OF POLYMER CHAINS - I

by

Richard S. Stein

Department of Chemistry
University of Massachusetts ✓
Amherst, Massachusetts

June 19, 1952

TABLE OF CONTENTS

	<u>Page</u>
<u>Letter of Transmittal</u>	1
<u>Abstract</u>	2
<u>Introduction</u>	3
Figure 1: The Statistical Chain and its Polarizabilities	4
<u>A Model for the Calculation of the Birefringence of a Simple Polymer Chain</u>	7
Figure 2: Configurations about a c-c bond.	8
Figure 3: The Coordinate System.	9
<u>The Numerical Evaluation of Q</u>	11
Table I: The Statistics of a Four Bond Carbon Chain	12
<u>Results of Preliminary Calculations</u>	14
Table II: The Results of Preliminary Polariza- bility Calculations	14
Figure 4: The Variation of Q and $(\pi_{ } - \pi_{\perp}) /$ $(b_1 - b_2)$ with n	15
<u>Restricted Rotation</u>	15
Table III: The Variation of Q, R^2 , and $(\pi_{ } - \pi_{\perp}) /$ $(b_1 - b_2)$ with degree of Restricted Rotation	19
Figure 5: A Plot of the Data of Table III	20
<u>Comparison with Experiment</u>	20
Table IV: A comparison of Theoretical and Ex- perimental Polarizability Differences	23

Table V: A Comparison of Several Determinations of the Principal Polarizabilities of Ethane	24
Figure 5a: The Vector Coordinates for the Bonds in Pentane	26
Table Va: The Coordinates of the Principal Polarizability Axis and the Difference Between Principal Polarizabilities for the Nine Configurations of Pentane	28
<u>Steric Hindrance and Interactions between Distant Portions of the Chain</u>	31
Figure 6: The Numbering of the Atoms in Pentane	31
Table VI: The Coordinates of the Carbon and Hydrogen Atoms in the Nine Configurations of Pentane	33
Table VIa: The Coordinates of the Carbon and Hydrogen Atoms in the Trans and the Gauche Configurations of Butane	34
Table VIb: The Squares of the Distances between Pairs of Hydrogen Atoms in Butane	34
Table VII: The Squares of the Distances between Pairs of Hydrogen Atoms in Butane	36

Table VIII: Pitzer's Classification of the
Configurations of the Paraffin
Hydrocarbons 37

Figure 7: The Variation of van der Waals'
Energy with R^2 38

Table IX: The Contributions to the Steric
Energy in Butane and Pentane 40

Table X: The Steric Energy Weighting Factors
for Butane and Pentane 41

References Cited 43

Distribution List 45



CHEMISTRY AND
CHEMICAL ENGINEERING

The Commonwealth of Massachusetts

University of Massachusetts

Amherst

June 19, 1952

Chief of Naval Research
Navy Department
Washington 25, D.C.

Ref: Contract No.: Nonr 702(00)
Project: 330-024

Dear Sir:

We are respectfully submitting Technical Report No. 1 in which the first phase of our theoretical consideration of the relationship between birefringence and molecular structure of large molecules.

This subject is being studied further, both from experimental and theoretical aspects, and we plan to publish additional reports on this same topic.

We shall welcome any comments or suggestions which any readers have to offer.

Respectfully submitted,

Richard S. Stein
Richard S. Stein
Asst. Prof. of Chemistry

RSS:ICP

ABSTRACT

The measurement of the principal polarizabilities of molecules is a useful method of studying their structure. Previous work has resulted in a relationship between the polarizabilities of large molecules and that of their "statistical segments". Values for the polarizabilities of the segments exist in the literature.

This paper is concerned with the calculation of principal polarizabilities of polymethylene hydrocarbons in terms of more detailed structural features; that is, bond polarizabilities, lengths, angles, and restricted rotation potentials. A tetrahedral lattice model for a polymer chain is used, and the polarizabilities for each configuration of the polymer are calculated. These are averaged for the cases of (a) equally probable orientation about the (c-c) bond, (b) preferred trans orientation, (c) steric hindrance, and (d) interaction between distant portions of the chain. The calculation is carried out for chains up to 6 bonds long (heptane).

A comparison of the predicted polarizabilities with those obtained from light scattering depolarization measurements is made.

THE CALCULATION OF THE PRINCIPAL POLARIZABILITIES OF POLYMER CHAINS I*

Richard S. Stein
Contribution from the Dept. of Chemistry
University of Massachusetts
Amherst, Massachusetts

Introduction

The calculation of the polarizabilities of simple molecules has been treated in several papers (1, 2, 3, 4, 5). Most of this work has utilized the Silberstein theory for calculating the interactions of polarizabilities of neighboring atoms (6). Denbigh (7) has recently shown that it is possible to formulate a table of bond polarizabilities in which both the polarizabilities of a bond along and perpendicular to the bond axis are given. These are calculated from light scattering depolarization and Kerr effect data on simple molecules. The use of these bond polarizabilities has greatly facilitated the calculation of the principal polarizabilities of covalently bonded organic molecules.

The calculation of the principal polarizabilities of a long chain organic molecule has been discussed by W. Kuhn (8) and L. R. G. Treloar (9). They use a model in which the actual polymer chain is replaced by an idealized chain consisting of so-called "statistical segments". These segments are thought of as being rigid (having no internal motion) and being freely orienting. That is, each statistical segment is thought to be connected to the adjoining segments by a joint which is completely flexible (like a ball and socket joint) so that the angle, θ , between 2 statistical segments may assume any value between 0 and 2π radians.

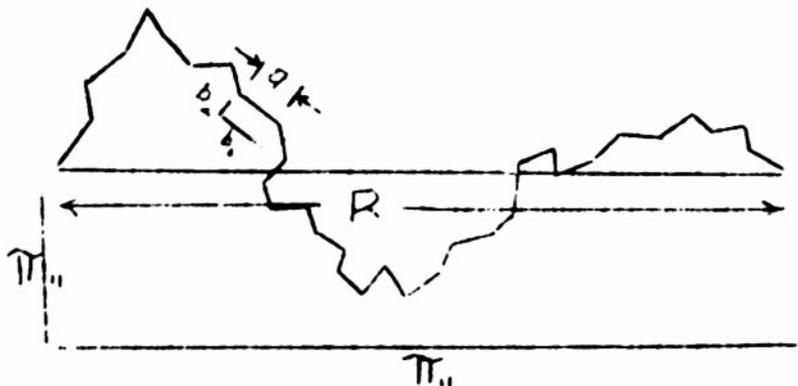
*This work is supported in part by the Office of Naval Research.

It is assumed that the chain ends are held fixed a distance R apart, and that intermediate parts of the chain are free to randomly assume all possible configurations consistent with this restriction. The segment is assigned polarizabilities, b_1 and b_2 along and perpendicular to the segment axis. Neglecting steric hindrance between segments, an equation is derived relating the principal polarizabilities of a polymer molecule to that of its segments.

$$(\bar{\pi}_{\parallel} - \bar{\pi}_{\perp}) = \frac{3}{5} n (b_1 - b_2) \left(\frac{R}{na} \right)^2 \quad (1)$$

where $\bar{\pi}_{\parallel}$ is the average polarizability of the chain (consisting of n statistical segments, each of length a) along the line joining chain ends, and $\bar{\pi}_{\perp}$ is the average polarizability perpendicular to this direction. (See Fig. 1).

Figure 1: The Statistical Chain and its Polarizabilities



It has been shown (10) for an unconstrained chain, that the average square distance between chain ends is given by

$$\bar{R}^2 = na^2 \quad (2)$$

If one assumes that the unconstrained chain is held at this length* so that

$$\bar{R}^2 = R^2$$

then

$$\bar{\Pi}_{11} - \bar{\Pi}_{22} = \frac{3}{5} (b_1 - b_2) \text{ seg.} \quad (3)$$

Then, if one sums the polarizabilities of all chains constituting a crosslinked high polymer consisting of ideal chains of this type which has been stretched by a factor α (length is α times the unstretched length) then the difference between the polarizability of the polymer sample along and perpendicular to the stretching direction is

$$P_1 - P_2 = \frac{3}{15} N_c (b_1 - b_2) \left(\alpha^2 - \frac{1}{\alpha} \right) \quad (4)$$

Using the Lorenz - Lorentz relationship, the difference between the refractive indices in these two directions is

$$\Delta = n_1 - n_2 = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \frac{2\pi}{45} N_c (b_1 - b_2) \left(\alpha^2 - \frac{1}{\alpha} \right) \quad (5)$$

where \bar{n} is the average refractive index, and N_c is the number of "crosslinking points" at which chains are joined together.

The quantity, Δ is defined as the birefringence of the polymer.

By using the same sort of assumptions^{10,11}, Kuhn (11) and others (12, 13, 14, 15) have calculated the tensile stress, σ , on a stretched ideal rubber. This is

$$\sigma = N_c k T \left(\alpha^2 - \frac{1}{\alpha} \right) \quad (6)$$

*It may be shown that if one does not make this assumption, but averages over all possible values of R for the unconstrained chain, one arrives at the same result.

where k is Boltzmann's constant and T is the absolute temperature. σ is in units of dynes per square centimeter of attained cross-sectional area. Thus, the stress - optical coefficient would be

$$B = \frac{\Delta}{\sigma} = 2\pi \frac{(\bar{n}^2 - 2)^2 (b_1 - b_2)}{45 \pi kT} \quad (7)$$

This quantity is independent of elongation and number of crosslinking points. Therefore, by measuring B and \bar{n} , $(b_1 - b_2)$ may be determined. Values for this quantity for several polymers have been tabulated by Stein and Tobolsky (16).

The next problem is to relate this quantity to the properties of the chain itself. The birefringence of this hypothetical statistical segment must be related to the polarizabilities and configuration of the bonds constituting the polymer.

One approach to this problem which was made by Treloar (17) is to calculate the birefringence of the monomer unit Δ_m (defined as the difference between the refractive index of the monomer unit along the axis of symmetry of the monomer and the average monomer refractive index perpendicular to this direction). The polymer chain may then be characterized by a parameter, Z , defined as

$$Z = \frac{(b_1 - b_2)}{\Delta_m} \quad (8)$$

Z may be regarded as a measure of the number of monomer units per statistical segment. It is a function of:

- a) The amount of internal rotation within a monomer unit.
- b) The angle and degree of free rotation occurring about the bond joining the monomers together.

c) Steric factors affecting chain rigidity.

Thus, Z is principally a function of the stiffness of the chain. Values of this parameter have been calculated by Treloar for Hevea rubber and by Stein and Tobolsky (16) for other polymers.

It would be desirable to be able to characterize the polymer chain in greater detail than is possible by this rather poorly defined parameter. For example, it would be desirable to be able to calculate from birefringence measurements, the ratio R^2/R_0^2 (where R_0^2 is the mean-square end-to-end length on the basis of ideal chain statistics with free rotation about all bonds), as well as other properties of polymer chains. This would enable one to compare chain dimensions determined in this manner with those determined by other techniques. In this manner, it would be possible to compare for example, the r.m.s. length of a chain in solution with its length in the solid polymer. This would be of great help in the understanding of the properties of solid polymers.

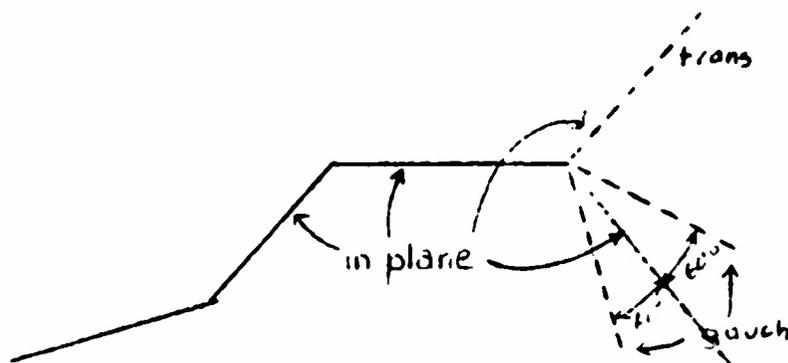
A Model for Calculating the Birefringence of a Simple Polymer Chain

The method which we shall follow is very similar to that used by King (18) in his calculation of some of the properties of polymer chains. He has been able to carry out his calculations of R^2 for rather long chains using punched card computing machinery. Our calculations of R^2 should check with his and ~~our~~^{are} just incidental to the birefringence calculation.

For the preliminary calculation, a very simple chain model will be considered, consisting of only carbon atoms joined together in a linear chain. The (c-c) bonds will be at the usual tetrahedral angle

with each other. In the first consideration, side groups will be neglected. It is hoped that these shall be included in future calculations.

Figure 2: Configurations about a c-c bond.



As is known (19), rotation about the (c-c) bond is restricted. There are three equilibrium positions (Fig. 2), the trans, and two "gauch". As a first approximation one might consider the case in which all these positions are equally probable. Then one might consider the more realistic situation in which the trans is more probable than the gauch. The potential is such that at all but very high temperatures, most time is spent in the equilibrium positions, so that in considering properties like birefringence that depend upon averages over all configurations, it is a very good approximation to assume that the bonds are only found in these equilibrium positions.

The height of the barrier restricting rotation is about 3000 cal/mole. At room temperature, the probability of finding a c-c bond at an equilibrium position will be $\exp(3000/RT)$ or 150 times that of finding it half way in between two equilibrium positions.

Let the i^{th} bond be represented by a vector σ_i of length $\sqrt{3}$. If we locate these vectors with respect to a right handed cartesian coordinate system (Fig. 3) ^{and} assume that the first bond makes equal angles with all three coordinate axes, then its coordinates will be (1,1,1). Then the second bond vector, σ_2 , is to be at a tetrahedral angle to the first, and the second bond is in an equilibrium position, its coordinates must be either $(\bar{1},1,1)$, $(1,\bar{1},1)$ or $(1,1,\bar{1})$. Thus, as has been shown by Tobolsky, Powell, and Eyring (20), the end points of all of these vectors will fall on the lattice points of a diamond lattice, and the possible projections of any vector will each be either (+1) or (-1) and the signs may be obtained from the three projections of the preceding vector by changing the sign of one and only one of the coordinates of the remaining (N-2) vectors.

The so-called displacement vector, R , of the chain connecting the first carbon atom with the last is then given by the vector sum

$$R = \frac{a}{\sqrt{3}} \sum_i \sigma_i \quad (9)$$

where $a/\sqrt{3}$ is the bond length of a C-C bond. The square of the length of the displacement vector is

$$R^2 = R \cdot R = \frac{a^2}{3} \left(1 + \sum_i \sum_j (\sigma_i \cdot \sigma_j) \right) \quad (10)$$

Applying the statistics of the diamond lattice, Tobolsky, Powell, and Eyring derive an equation (20) for a tetrahedral lattice from which one may obtain the equation for R^2

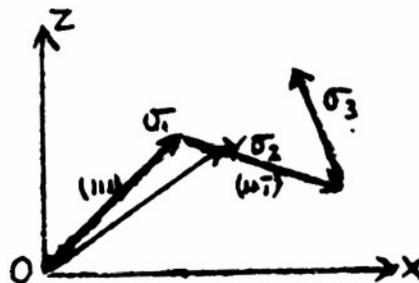


Figure 3: The Coordinate System.

$$R^2 = a^2 \sum_{p=0}^N \left[\frac{1}{2} \left(\frac{2}{3} \right)^{N-1} \left(\sum_{x=1}^{N-p} \frac{N+2x}{2^{2x}} \frac{(N-p-1)! (p-1)! (2p-N)^2}{(p-x)! (N-p-x)! x! (x-1)!} \right) \right] \quad (11)$$

The calculation of the polarizability of a polymer chain follows somewhat similar lines. If the i^{th} bond having polarizabilities b_1 and b_2 lies at the polar angles θ_i and ϕ_i with respect to the coordinate axes (Fig. ^{3a} ~~3b~~, the contribution of this bond to the polarizabilities along the coordinate axes are (7)

$$\begin{aligned} (P_x)_i &= b_1 \cos^2 \theta_i + b_2 \sin^2 \theta_i \\ &= (b_1 - b_2) \cos^2 \theta_i + b_2 \end{aligned} \quad (12)$$

$$\begin{aligned} (P_y)_i &= (b_1 - b_2) \sin^2 \theta_i \cos^2 \phi_i + b_2 \\ &= (b_1 - b_2) \cos^2 \phi_i - (b_1 - b_2) \cos^2 \theta_i \cos^2 \phi_i + b_2 \end{aligned} \quad (13)$$

$$\begin{aligned} (P_z)_i &= (b_1 - b_2) \sin^2 \theta_i \sin^2 \phi_i + b_2 \\ &= (b_1 - b_2) \sin^2 \phi_i - (b_1 - b_2) \cos^2 \theta_i \sin^2 \phi_i + b_2 \end{aligned} \quad (14)$$

The coordinate system may be chosen so that the X axis lies along the displacement vector of the chain. The total polarizability of the chain may then be found by summing the polarizabilities of the constituent bonds. The average polarizabilities are then found by averaging over θ and ϕ , eg.

$$\overline{\Pi_{11}} = \overline{\sum_i (P_x)_i} = (b_1 - b_2) \overline{\sum_i \cos^2 \theta_i} + nb_2 \quad (15)$$

$$\begin{aligned} \overline{\Pi_{11}} &= \overline{\sum_i (P_{y1})_i} = (b_1 - b_2) \overline{\sum_i \cos^2 \phi_i} \\ &= (b_1 - b_2) \overline{\sum_i \cos^2 \theta_i \cos^2 \phi_i} + nb_2 \end{aligned} \quad (16)$$

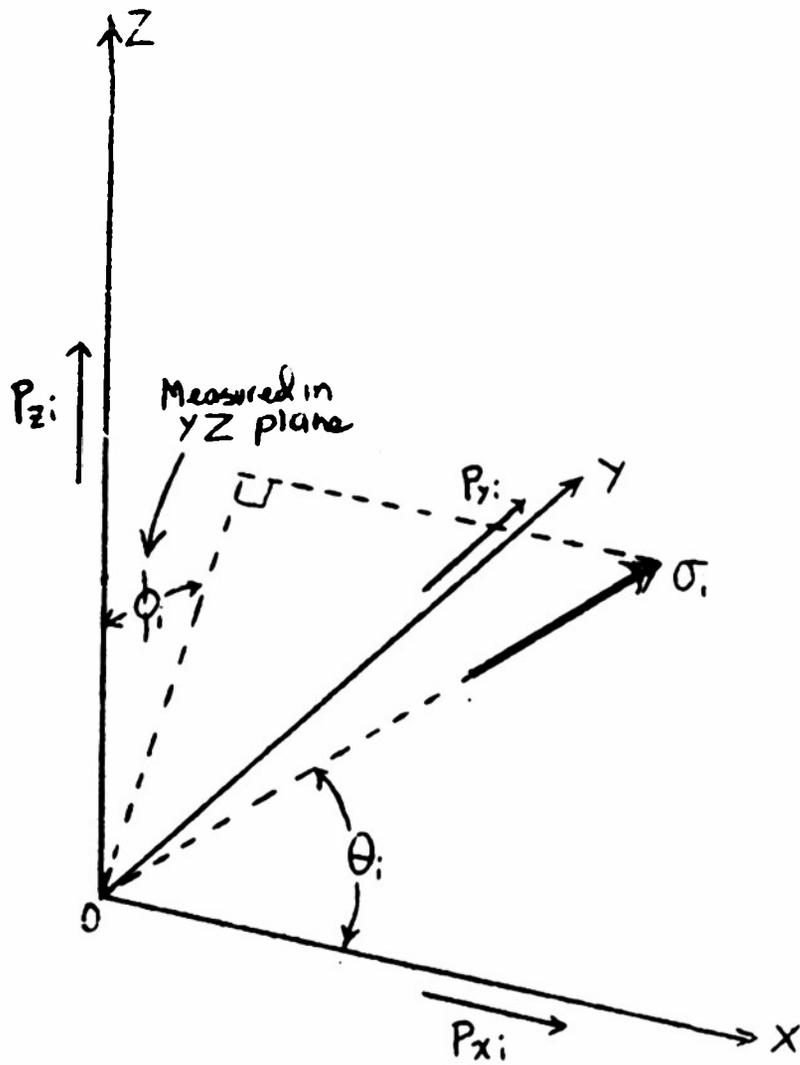


Figure 3a - The Angular Coordinates for Locating the Bond Vectors

If the chain is symmetrically disposed about the displacement vector, then all values of ϕ will be equally probable and

$$\overline{\cos^2 \phi} = \frac{1}{2}$$

so

$$\overline{\Pi_1} = \frac{1}{2} (b_2 - b_1) \overline{\sum \cos^2 \theta_1} + \frac{\Pi_1 (b_1 + b_2)}{2} \quad (17)$$

also

$$\overline{\sum (P_z)_1} = \overline{\sum (P_x)_1} = \overline{\Pi_1}$$

and

$$\overline{\Pi_1} - \overline{\Pi_1} = \frac{1}{2} (b_1 - b_2) (3 \overline{\sum \cos^2 \theta_1} - \Pi_1) \quad (18)$$

Thus, the calculation of the polarizability of the chain is dependent on the calculation of $\overline{\sum \cos^2 \theta_1}$.

Now from the definition of the scalar product of two vectors

$$\sigma_1 \cdot R = |\sigma_1| |R| \cos \theta_1 \quad (19)$$

so

$$\cos^2 \theta_1 = \frac{(\sigma_1 \cdot R)^2}{(\sigma_1)^2 |R|^2} = \frac{(\sigma_1 \cdot R)^2}{3 R^2} \quad (20)$$

and

$$\overline{\sum \cos^2 \theta_1} = \overline{\sum \frac{(\sigma_1 \cdot R)^2}{3 R^2}} = Q \quad (21)$$

where R is given by eq (9). This sum must be averaged over all possible combinations of σ_1 's possible for the chain.

The Numerical Evaluation of Q

Q may be evaluated, at least for short chains, as is illustrated in the following example:

Results of Preliminary Calculations

Q has been calculated to date for carbon chains up to 7 bonds (8 atoms) in length. The results of these calculations are summarized in Table II. The quantity $(\pi_{11} - \pi_{12}) / (b_1 - b_2)_{cc}$ is the ratio of the polarizability difference of the chain to that of the c-c bond. This is equal to $\frac{1}{2} (3Q - n)$ according to equation (18).

The quantity $(b_1 - b_2)_{seg} / (b_1 - b_2)_{c-c}$ in the next column is the ratio of the polarizability differences of the statistical

Table II

The Results of Preliminary Polarizability Calculations

N		No. of configurations	Q	$\frac{\pi_{11} - \pi_{12}}{(b_1 - b_2)_{cc}}$	$\frac{(b_1 - b_2)_{seg}}{(b_1 - b_2)_{cc}}$	$\frac{-2}{R}$	$(R^2) = 6R$
1	1.00	1	1.00	1.00	1.667	3	5
2	1.33	1	1.33	.99	1.65	8	12
3	4.75	3	1.58	.87	1.45	13.7	18
4	16.86	9	1.87	.80	1.33	19.6	24
5	58.64	27	2.17	.76	1.27	25.1	30
6	194.06	81	2.40	.60	1.00	31.3	36

segment to that of the c-c bond. It is obtained by dividing

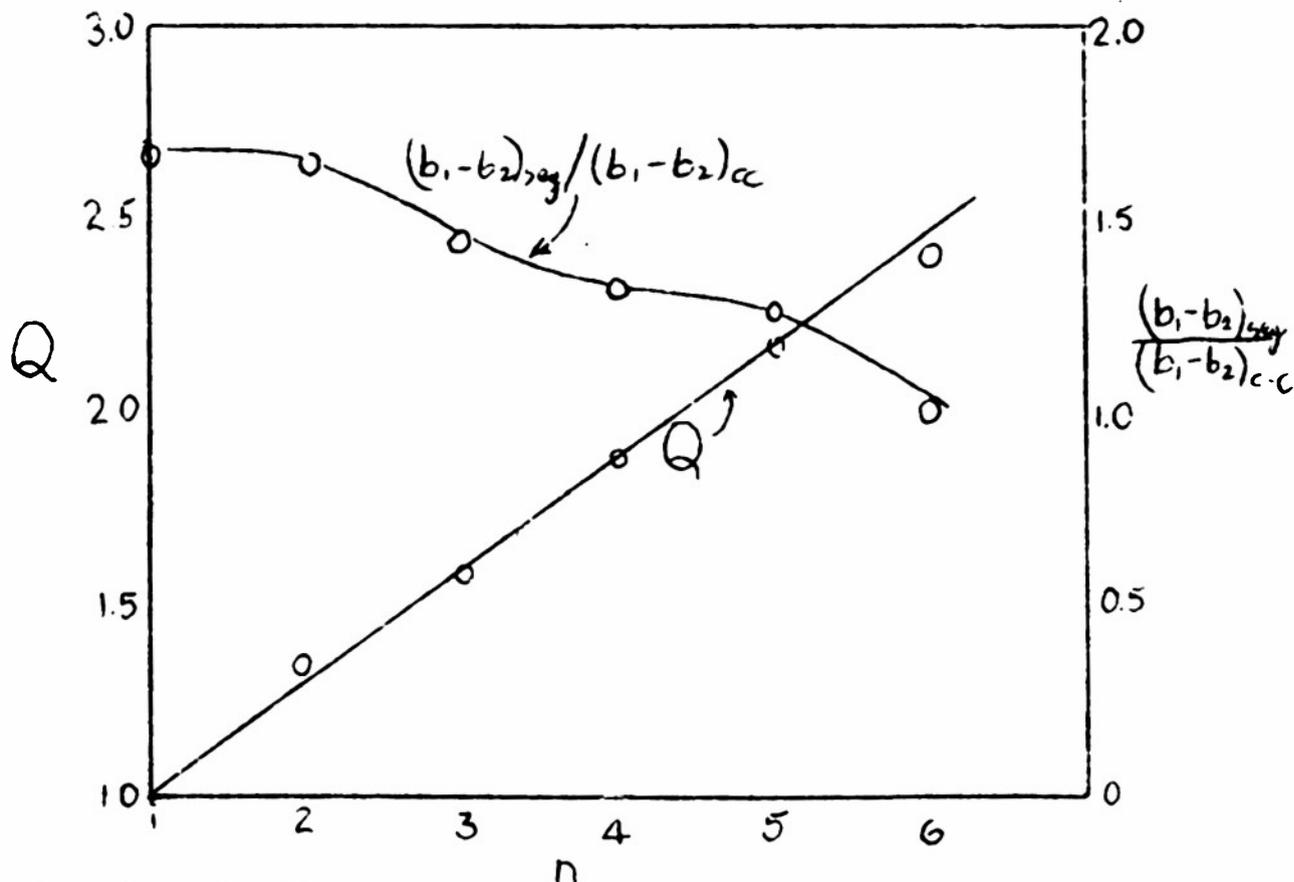
$(\pi_{11} - \pi_{12}) / (b_1 - b_2)_{cc}$ by

$$\frac{\pi_{11} - \pi_{12}}{(b_1 - b_2)_{seg}} = \frac{3}{5}$$

(from equation (3)). If one assumes that no internal motion occurs within a statistical segment, this quantity ought to be proportional to the number of c-c bonds per statistical segment. The statistical

theory would predict that this quantity should be a constant for long chains. It is plotted against n in Fig. (4). It is obvious that for the short chains considered here, this is not so. The calculation must be carried out for greater values of n in order to test this hypothesis and determine the constant. This is being done at present and the results will be included in a later report.

Figure 4: The Variation of Q and $(b_1 - b_2)_{\text{c-c}} / (b_1 - b_2)_{\text{c-c}}$ with n



Restricted Rotation

In the preceding discussion, it was assumed that the three equilibrium positions of rotation about the c-c bond were equally probable. This is not so, for the trans or the gauche positions may be more probable depending upon chain substituents. In the case of a

hydrocarbon chain, it has been shown that the trans is more probable. The result of this is that the chain will be more stretched out than in the "equal probability" case. Both R^2 and the chain polarizabilities will be affected.

It has been shown by W. J. Taylor (21) and others that the potential energy accompanying rotation about a c-c bond may be described as a function of the angle ϕ describing the rotation by an equation of the form

$$V(\phi) = \frac{1}{2} V_m \left[X(1 - \cos \phi) + (1 - X)(1 - \cos 3\phi) \right] \quad (22)$$

where for normal paraffin hydrocarbons $X = .26$ and $V_m = 4100$ cal/mole.

For long chains containing n bonds of length a , Taylor shows that

$$R^2 = na^2 \left[\frac{1 + \cos \theta}{1 - \cos \theta} \right] \left[\frac{1 + b}{1 - b} \right] \quad (23)$$

where θ is the valence angle between bonds of the chain and b is the average value of $\cos \phi$ which is calculated from

$$b = \frac{\int_0^{2\pi} \cos \phi e^{-V(\phi)/kT} d\phi}{\int_0^{2\pi} e^{-V(\phi)/kT} d\phi} \quad (24)$$

By combining equations (22) and (24), Taylor is able to obtain a plot of $\frac{1+b}{1-b}$ against V_m/Rt which is useful for calculating the dependency of the dimensions of a polymer chain on the potential opposing rotation.

By applying these concepts to our model for calculating polarizabilities, the effect of restricted rotation upon these may be calculated. In this calculation, it is assumed, as before that the bond spends most of its time in one of the three rotational equilibrium positions, so

that only these need be considered.

Suppose that the energies of the trans and the gauche positions are V_t and V_g respectively. These correspond to $\phi = 0^\circ$ and $\phi = 120^\circ$ and may be calculated from eq (22)

$$\begin{aligned} V_t &= 0 \\ V_g &= \frac{1}{2} V_m (X(1 - \cos 120^\circ)) = .75V_m X \end{aligned} \quad (25)$$

The total energy of a chain may be characterized by the number of pairs of alternate bonds which are in the trans configuration with respect to each other (n_t). The number of pairs in the gauche configuration is then

$$n_g = (n - 2) - n_t \quad (26)$$

since the total number of alternate pairs is $n-2$, n being the number of bonds in the chain.

The total configurational energy of a configuration is then

$$E = n_t V_t + n_g V_g \quad (27)$$

The probability of a configuration is then given by Boltzman's relationship

$$\begin{aligned} W &= c e^{-E/kT} = c e^{-(n_t V_t + n_g V_g)/kT} \\ &= c e^{-n_t V_t/kT} e^{-n_g V_g/kT} \\ &= \omega_t^{n_t} \omega_g^{n_g} \\ &= \omega_t^{n_t} \omega_g^{(n-2)-n_t} \\ &= \left(\frac{\omega_t}{\omega_g}\right)^{n_t} \omega_g^{n-2} \end{aligned} \quad (28)$$

where

$$\omega_t = c^{1/2} e^{-V_t/kT}, \quad \omega_g = c^{1/2} e^{-V_g/kT}$$

For a given value of n , ω_g^{n-2} will be the same for all configurations and will be included in the normalizing constant, K_n , as

$$W = K_n \left(\frac{\omega_t}{\omega_g} \right)^{n_t} \quad (29)$$

where
$$\frac{\omega_t}{\omega_g} = e^{-(V_t - V_g)/kT} = e^{.75 V_m x / RT}$$

In calculating R^2 and Q , the configurations must be weighted with these probability factors; thus

$$R^2 = \frac{\sum_j W_j R_j^2}{\sum_j W_j} = \frac{\sum_j \left(\frac{\omega_t}{\omega_g} \right)^{n_{tj}} R_j^2}{\sum_j \left(\frac{\omega_t}{\omega_g} \right)^{n_{tj}}} \quad (30)$$

and

$$Q = \frac{\sum_j \left[\left(\frac{\omega_t}{\omega_g} \right)^{n_{tj}} \sum_i \frac{(\sigma_i \cdot R)^2}{3 R^2} \right]}{\sum_j \left(\frac{\omega_t}{\omega_g} \right)^{n_{tj}}} \quad (31)$$

The subscript j refers to the j^{th} configuration, and the sum is over all 3^{n-2} configurations. Eq (31) reduces to eq (21) in the limit where

$$\omega_t = \omega_g$$

The value of n_t for a given configuration is readily obtained by inspection of the coordinates of the σ 's. A group of 3 σ 's will represent a trans configuration of the coordinates if the first and third are the same. One need merely count the number of groupings of this type in a given configuration. For example, referring to

configuration #1 in table I, O_1 and O_3 have the same coordinates as do O_2 and O_4 . Therefore, $n_t = 2$ for this configuration. The values of n_t for the various configurations for $n = 4$ are listed in the last column of this table.

The calculation of Q with restricted rotation might be illustrated in this case of $n = 4$. In the absence of preferred orientation, where $(\omega_t/\omega_g) = 1$, Q is obtained by averaging the $(O_i R)^2/3R^2$ values and was found to be 1.87.

Consider the case in which the trans configuration is twice as probable as the gauche. This corresponds to $(V_g - V_t)/RT = .69$. Then using eq. (31)

$$Q = \frac{2^2 \times 2.66 + 4 (2^1 \times 2.22) + 4 (2^0 \times 1.33)}{2^2 + 4 \times 2^1 + 4 \times 2^0} = 2.10$$

The calculation has been carried out for $n = 6$ for several values of (ω_t/ω_g) . These are presented in Table III.

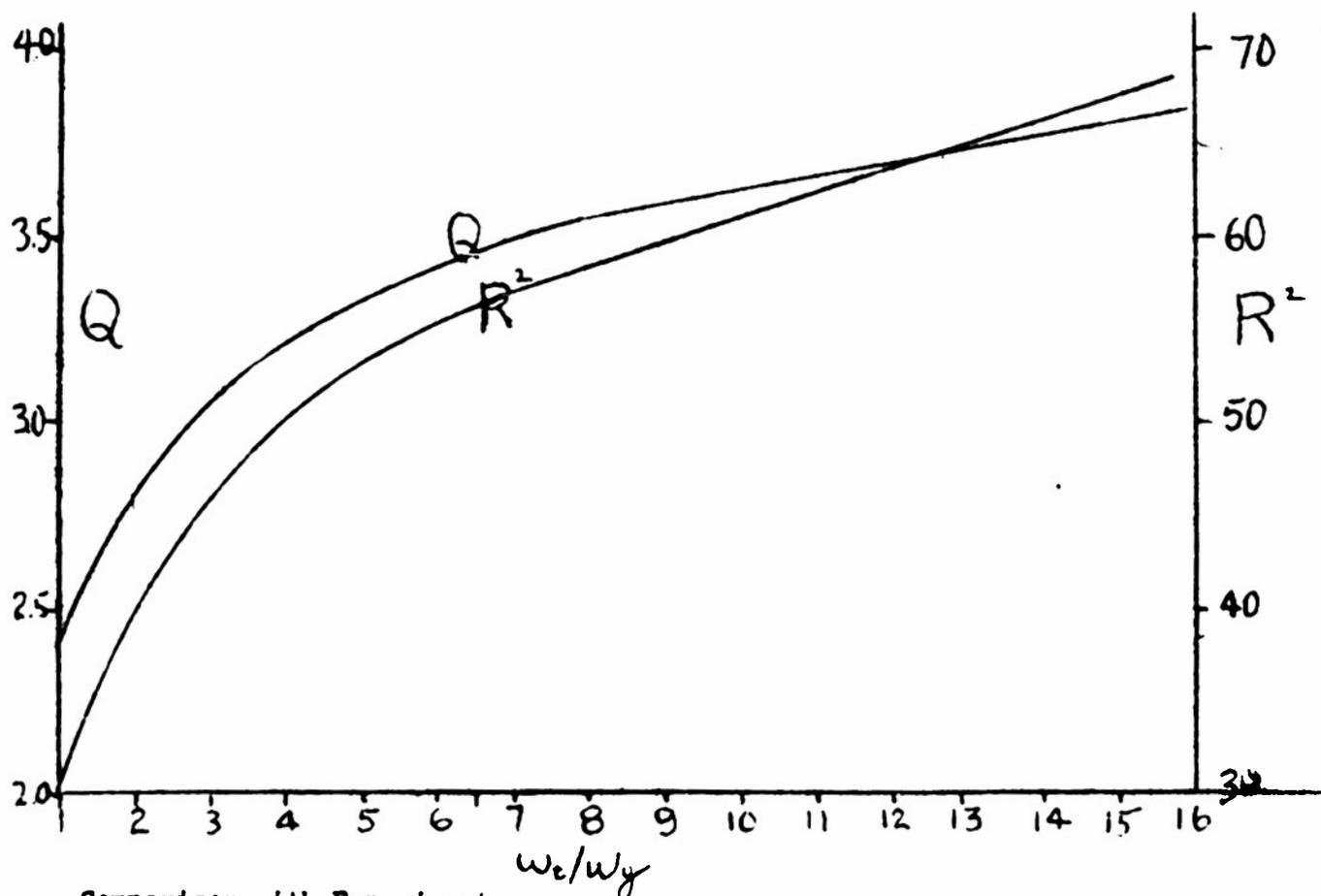
Table III

(ω_t/ω_g)	$\frac{E_g - E_t}{RT}$	R^2	Q	$\frac{\pi_{ } - \pi_{\perp}}{(b_1 - b_2)_{cc}}$
1	0	31.3	2.40	.60
2	.69	41.0	2.86	1.29
4	1.38	51.1	3.24	1.86
10	2.30	61.5	3.61	2.42
∞	∞	72	4.00	3.00

As can be seen, as the energy difference between the gauche and trans positions increases, the chain tends to be more stretched out,

so that both its R^2 and its polarizability difference increases. The values for $(\lambda/\lambda_g) = \infty$ correspond to the completely stretched out chain. It is apparent that the measurement of the polarizability difference of a chain of a given size could serve as a measure of the restricted rotation potential. The data of Table III are plotted in Fig (5).

Figure 5: A Plot of the Data of Table III.



Comparison with Experiment

The two usual methods for studying the electric anisotropy of a small molecule are measurements of (a), the Kerr Effect (22, 23, 24), and (b), the depolarization of scattered light (25, 26).

The data for the latter method seems more complete and will be

used in the present comparison.

If light is scattered by a gas consisting of isotropic molecules, it ought to be completely plane polarized (27). If the molecules are anisotropic, polarization will not be complete, and the depolarization may be defined as

$$\rho = \frac{\text{Intensity of Horizontally Polarized Light}}{\text{Intensity of Vertically Polarized Light}} \quad (32)$$

(The horizontal plane is a plane containing the paths of the incident and scattered rays).

This ratio is measured, using unpolarized incident light and measuring the scattering at an angle of 90° from the incident light beam.

Krishnan has shown (26) that for small molecules, ρ may be related to the polarizability difference of the scattering molecule by the relationships

$$\delta = \frac{(\alpha_1 - \alpha_2)^2}{(\alpha_1 + 2\alpha_2)^2} \quad (33)$$

$$\text{where } \delta = \frac{5\rho}{6 - 7\rho} \quad (34)$$

where α_1 and α_2 are the principal polarizabilities parallel and perpendicular to the axis of symmetry of a cylindrically symmetrical molecule. Values of these quantities for a large number of molecules have been compiled by Cabannes (25) (29). They have been modified by Bhagavantam (28) on the basis of more recent measurements by Parthasarathy (30), Ananthakrishnan (31) and Volkman (32, 33). Values of ρ for

n-paraffin hydrocarbons from ethane to octane which were adopted by Cabannes as well as the so called most probable values adopted by Bhagavantam are listed in Table IV.

$(\alpha_1 + 2\alpha_2)$ is simply three times the average bond polarizability, and values of this quantity (calculated from molar refraction data (7)) are listed in Table IV.

$(\alpha_1 - \alpha_2)$ values calculated from both sets of f 's are also listed. The author has somewhat more faith in the values calculated from Cabannes's f 's. The reason is apparent upon examining Table V in which $(\alpha_1 - \alpha_2)$ for ethane determined by several workers by different methods is listed. It would seem that the value adopted by Bhagavantam is somewhat out of line with other independent determinations. In view of this uncertainty, however, it would seem as though there would be a possible error in the experimental values of $(\alpha_1 - \alpha_2)$ of at least $\pm 10\%$.

In order to compare the experimentally measured difference of principal polarizabilities with theory, it is necessary to be able to calculate the principal polarizability of each configuration. The experimental quantity $(\alpha_1 - \alpha_2)$ is then identified with the average of these.

The polarizability of a molecule along any axis may be calculated. For an anisotropic molecule, its value will depend upon the relative direction of the axis. For some particular direction, the polarizability will be a maximum, and is called a principal polarizability α_1 . For a cylindrically symmetrical molecule, the polarizability in any direction perpendicular to this will be the same and is the second

Table IV

Substance	$\rho \times 10^3$ (Bhagavantam)	$\rho \times 10^3$ (Cabannes)	$(\alpha_1 + 2\alpha_2) \times 10^{24}$	$(\alpha_1 - \alpha_2) \times 10^{25}$ exp. (Bhagavantam)	$(\alpha_1 - \alpha_2) \times 10^{25}$ exp (Cabannes)	$(\alpha - \alpha) \times 10^{25}$ free rot.	$(\alpha - \alpha) \times 10^{25}$ rest.rot.	$(\alpha - \alpha) \times 10^{25}$ interact.
Ethane	0.5	1.6	13.62	8.2	16.0	15.0	15.0	15.0
Propane	0.7	1.6	19.44	14.94	17.5	14.4	14.4	14.4
Butane	0.9	1.7	25.26	21.99	30.4	14.2	80.6	20.1
Pentane	1.3	1.3	31.08	32.55	32.55	16.7	22.8	23.0
Hexane	1.5	1.5	36.90	41.7	41.7	-	-	-
Heptane	1.6	1.6	42.72	49.8	49.8	-	-	-
Octane	1.8	1.8	48.54	60.0	60.0	-	-	-

Table V

Source	$\alpha_1 \times 10^{25}$	$\alpha_2 \times 10^{25}$	$(\alpha_1 - \alpha_2) \times 10^{25}$
Depolarisation (H.A. Stuart, Molekul- struktur (29))	56	40	16
Kerr Constant (Stuart & Volkman (1934)(33))	56.5	39.7	16.8
Kerr Constant (Breazeale (1935)(34))	55.4	40.3	15.1
Depolarisation (Ananthakrishnan)(1935) (30)(value adopted by Bhagavantam))	51.0	42.5	8.5

principal polarizability, α_2 .

In order to determine this axis of maximum polarizability, it is necessary to calculate the polarizability as a function of the direction of the axis. If M is a vector along the axis and θ_{ik} is the angle between the i^{th} bond of type k and this vector, the average difference between principal polarizabilities will be given as in equation (18) by

$$(\alpha_1 - \alpha_2) = \left\langle \frac{1}{2} \sum_k [(b_1 - b_2)_k (3 \sum_i \cos^2 \theta_{ik} - n_k)] \right\rangle_{av}$$

(The index, k , indicates the type of bond, eg. (C-C), (C-H), etc.). The average is over all configurations. Then

$$(\alpha_1 - \alpha_2) = \left\langle \frac{3}{2} [(b_1 - b_2)_{C-C} Q_{M(C-C)} + (b_1 - b_2)_{C-H} Q_{M(C-H)}] - \frac{1}{2} [n_{C-C} (b_1 - b_2)_{C-C} + n_{C-H} (b_1 - b_2)_{C-H}] \right\rangle_{av}$$

where

$$Q_{M(C-C)} = \sum_i \cos^2 \theta_i$$

$$= \sum_i \frac{(\sigma_i \cdot M)^2}{3 M^2}$$

the sum being taken over all C-C bonds in a given configuration,
and

$$Q_{M(C-H)} = \sum \frac{(\sigma_c M)^2}{3 M^2}$$

the sum being taken over all C-H bonds.

n_{C-C} and n_{C-H} are the number of (C-C) and (C-H) bonds in the molecule.

Assume that the coordinates of M are (1, y, z). (Only 2 coordinates need be taken as variable since only the direction of M need be determined. Its length is arbitrary.)

Q_i may then be calculated for any configuration. For illustration, consider the case of pentane in configuration No. 2 of Table I. From Donbigh (7) we have

Bond	$b_1 \times 10^{25}$	$b_2 \times 10^{25}$	$(b_1 - b_2) \times 10^{25}$
C-C	18.8	0.2	18.6
C-H	7.9	5.8	2.1

Therefore, since $n_{C-C} = 4$ and $n_{C-H} = 12$

$$(\alpha_1 - \alpha_2) \times 10^{25} = 27.9 Q_M(C-C) + 3.2 Q_M(C-H) - 49.8$$

The values of y and z giving rise to a direction of M corresponding to a maximum polarizability difference are then found by partial differentiation with respect to y and z and setting the derivatives equal to zero.

$$\frac{\partial (\alpha_1 - \alpha_2)}{\partial y} \times 10^{25} = 0 = 27.9 \frac{\partial Q_M(C-C)}{\partial y} + 3.2 \frac{\partial Q_M(C-H)}{\partial y} \quad (34a)$$

and

$$\frac{\partial (\alpha_1 - \alpha_2) \times 10^{25}}{\partial z} = 0 = 27.9 \frac{\partial Q_{M(C-C)}}{\partial z} + 3.2 \frac{\partial Q_{M(C-H)}}{\partial z} \quad (34b)$$

In Figure 5a, a diagram for configuration No.2 of pentane is given in which the coordinates for the σ 's for all of the bonds are indicated.

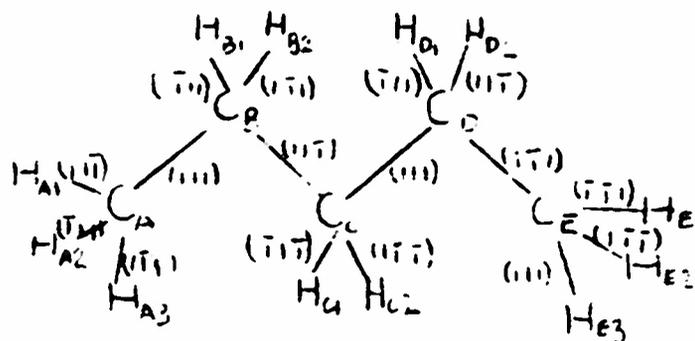


Figure 5a

(A discussion of the method for the determination of the σ 's for the (C-H) bonds is to be found on pages 30 to 34)

The four σ_{C-C} 's are (111), (11 $\bar{1}$), (1 $\bar{1}$ 1), and (1 $\bar{1}\bar{1}$). Therefore

$$\begin{aligned} Q_{M(C-C)} &= \frac{[(111) \cdot (1yz)]^2 + [(11\bar{1}) \cdot (1yz)]^2 + [(1\bar{1}1) \cdot (1yz)]^2 + [(1\bar{1}\bar{1}) \cdot (1yz)]^2}{3[1+y^2+z^2]} \\ &= \frac{(1+y+z)^2 + (1+y-z)^2 + (1+y+z)^2 + (1-y+z)^2}{3[1+y^2+z^2]} \\ &= \frac{4}{3} + \frac{4}{3} \frac{y+z}{1+y^2+z^2} \end{aligned}$$

Then

$$\frac{\partial Q_{M(C-C)}}{\partial y} = \frac{4}{3} \frac{(1 - y^2 + z^2 - 2yz)}{(1 + y^2 + z^2)^2}$$

and

$$\frac{\partial Q_{M(C-H)}}{\partial z} = \frac{4}{3} \frac{(1 + y^2 - z^2 - 2yz)}{(1 + y^2 + z^2)^2}$$

The Q_i 's for the (C-H) bonds are found in a similar way, summing over the twelve \mathcal{J} 's for those bonds.

$$Q_{M(C-H)} = 4 \left(1 - \frac{2}{3} \frac{y+z}{1+y^2+z^2} \right)$$

$$\therefore \frac{\partial Q_{M(C-H)}}{\partial y} = -\frac{8}{3} \frac{(1 - y^2 + z^2 - 2yz)}{(1 + y^2 + z^2)^2}$$

$$\frac{\partial Q_{M(C-H)}}{\partial z} = \frac{8}{3} \frac{(1 + y^2 - z^2 - 2yz)}{(1 + y^2 + z^2)^2}$$

Then equation (3a) gives

$$27.9 \left[\frac{4}{3} \frac{(1 - y^2 + z^2 - 2yz)}{(1 + y^2 + z^2)^2} \right] + 3.2 \left[-\frac{8}{3} \frac{(1 - y^2 + z^2 - 2yz)}{(1 + y^2 + z^2)^2} \right] = 0$$

Since the denominator is not infinite,

$$(1 - y^2 + z^2 - 2yz) = 0$$

Similarly, from Eq. (3b) one gets

$$(1 + y^2 - z^2 - 2yz) = 0$$

The values for y and z corresponding to the simultaneous solution of these equations are the coordinates determining M for maximum (or minimum) polarizability. These are:

$$y = z = \sqrt{2}/2$$

Table Va

Config. No.	Coordinates of M	$Q_M(\text{C-C})$	$Q_M(\text{C-H})$	$(\alpha_1 - \alpha_2) \times 10^{25}$
1	(1, 1, 0)	2.66	1.33	28.9
2	(1, $\sqrt{2}/2$, $\sqrt{2}/2$)	2.27	2.12	20.3
3	(1, $\sqrt{2}$, 1)	2.27	2.12	20.3
4	isotropic	1.33	4.00	0
5	(1, $\sqrt{2}/2$, $-\sqrt{2}/2$)	2.27	2.12	20.3
6	(1, $\sqrt{2}$, 1)	2.27	2.12	20.3
7	isotropic	1.33	4.00	0
8	(1, $\sqrt{2}/2$, $\sqrt{2}/2$)	2.27	2.12	20.3
9	(1, $\sqrt{2}$, -1)	2.27	2.12	20.3

Thus, $M = (1, \sqrt{2}/2, \sqrt{2}/2)$, and the Q_M 's for this configuration are:

$$Q_M(\text{C-C}) = 2.27$$

$$Q_M(\text{C-H}) = 2.12$$

Then for this configuration $(\alpha_1 - \alpha_2) = 20.3 \times 10^{-25}$

This procedure must be carried through for each configuration, and the results must be averaged to obtain $(\alpha_1 - \alpha_2)$. This has been done for pentane. The results are summarized in Table Va.

The average $(\alpha_1 - \alpha_2)$ for the case in which all configurations are weighted equally is listed in the column of Table IV labeled $(\alpha_1 - \alpha_2)$ (free rot.). It is seen that the calculated value is far above the experimental and well outside the estimated error (about $\pm 10\%$ for each). This would indicate that the chains are more stretched out than would be expected for "free rotation".

In order to take into account restricted rotation, one must weight trans configurations more heavily using a modification of equation (31)

$$\overline{(\alpha_1 - \alpha_2)} = \frac{\sum_j (\alpha_1 - \alpha_2)_j \left(\frac{\omega_t}{\omega_g}\right)_j^{n_{tj}}}{\sum_j \left(\frac{\omega_t}{\omega_g}\right)_j^{n_{tj}}}$$

Using the constants in equation (22) which Taylor assigns for paraffin chains, one finds that the energy of the trans position is 800 cal./mole less than that for the gauche. From equation (29) one may then calculate

$$\frac{\omega_t}{\omega_g} = e^{800/RT} = 3.8$$

for $T = 300^\circ \text{K}$. The values of $\overline{(\alpha_1 - \alpha_2)}$ which were calculated from this are listed in the next column of Table IV. They are still appreciably smaller than the experimental values.

The conclusion which must be drawn from our interpretation of this data is that the paraffin chains are more stretched out than would be predicted from statistical theory.

This is in contradiction to the findings of McCoubrey, McCrea, and Ubbelohde who have studied the dimensions of these compounds by measuring the viscosity of their vapors. They interpret their data as indicating that the "n-paraffins occupy a volume corresponding to coiling into close packed configurations". They also find from the temperature dependency of gas viscosity that the molecules seem to slightly increase in size with increasing temperature instead of decreasing as would be expected from the Taylor potential.

It is suggested that a measurement of the temperature dependency

of either the depolarization factor or the Kerr constant for these n-paraffins would be of use in deciding whether the dimensions of the molecule actually do increase or decrease with increasing temperature.

Some possible reasons for the apparent inadequacy of the statistical theory are:

- (1) The potential for rotation about the c-c bond is not correct.
- (2) Some configurations are excluded because of steric effects.
- (3) Interactions between more distant parts of the chain have been neglected.

Ubbelohde has considered some other shapes for the potential energy function than that of equation (22) which would give less temperature dependency of R (36). It would seem, however, that the potential energy function cannot be greatly modified and still give consistent agreement with thermodynamic, dipole moment, spectroscopic, and other data. This possibility, however, should be investigated further, both theoretically and experimentally.

If steric effects are taken into account, they are certainly going to modify the theory. The excluded configurations are going to be more tightly coiled ones, so that their omission will result in a larger R and larger polarizability difference.

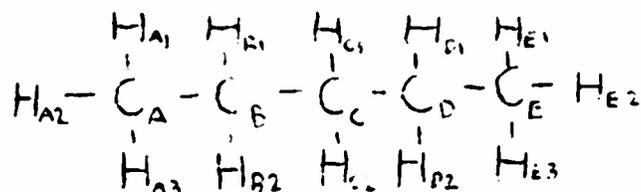
The third factor, interaction between distant portions of the chain, seems most promising. It would seem that van der Waals attraction would favor the more tightly coiled configurations. The temperature dependency of this effect would be in the opposite direction from that of restricted rotation. However, van der Waals

repulsion between hydrogens which are very close would produce the opposite effect.

Steric Hindrance and Interaction Between Distant Portions of the Chain

In order to consider these effects, it is necessary to include the hydrogens as well as the carbons in the chain model. This may be readily done if one makes the approximation (as has been done by King (18)) that the length of the C-C and the C-H bonds are the same. Actually they are 1.54 \AA and 1.09 \AA respectively. By doing this, both the hydrogens and the carbons will lie on tetrahedral lattice points, and distances between the hydrogens may be readily calculated. In cases where the interaction energy is critically dependent upon the distance, we shall see that it is possible to correct for this approximation.

Figure 6: The Numbering of the Atoms in Pentane.



We shall consider the interactions occurring in pentane. We shall identify the carbon and hydrogen atoms by the symbols indicated in Figure (6). The coordinates of possible lattice vectors connecting a carbon with its hydrogens may be obtained from the coordinates of the vector connecting the carbon with the preceding one by the same rules as were previously introduced on page (9). For example, suppose

the coordinates of O_3 connecting C_C with C_D are $(\bar{1}\bar{1}\bar{1})$. The possible coordinates of O_4 connecting C_D with C_E are then $(1\bar{1}\bar{1})$, $(\bar{1}\bar{1}\bar{1})$, or $(\bar{1}\bar{1}\bar{1})$. In the configuration in which O_4 is $(\bar{1}\bar{1}\bar{1})$, (Configuration No. 4 of Table I), the remaining possibilities for vectors connecting C_D with its two hydrogens, H_{D1} and H_{D2} are $(1\bar{1}\bar{1})$ and $(\bar{1}\bar{1}\bar{1})$. The coordinates of any atom of the chain with respect to the origin (which, as before, is taken as carbon atom C_A) are the components of the vector leading from the origin to the atom. This is equal to the sum of all of the bond vectors connecting C_A with the atom. For example, for atom H_{D2} in the above configuration, this will be

$$O_1 + O_2 + O_3 + O_{32} = (111) + (1\bar{1}\bar{1}) + (\bar{1}\bar{1}\bar{1}) + (1\bar{1}\bar{1}) = (42\bar{2})$$

The coordinates of all of the atoms in the nine configurations of pentane are listed in Table VI, while those for the trans and one of the gauche configurations of butane are given in Table VI a. (It is not necessary to consider the second gauche configuration as it is a mirror image of the first.)

Any configuration in which two atoms have the same coordinates is prohibited. This occurs in configurations number 6 and 8.

In order to take into account the interactions between the atoms in the remaining configurations, the distances between them must be known. The coordinates of the vector connecting any two atoms may be found by subtracting the coordinates of the first from those of the second. For example, the vector connecting atoms H_{B1} and H_{E3} in configuration 4 of pentane has the coordinates $(5\bar{1}\bar{1}) - (42\bar{2}) = (5\bar{3}\bar{3})$. The square of the length of this vector is then the sum of the squares of the components, which is 43.

Table VI

Config. No.	C _A	H _{A1}	H _{A2}	H _{A3}	C _B	H _{B1}	H _{B2}	C _C	H _{C1}	H _{C2}	C _D	H _{D1}	H _{D2}	C _E	H _{E1}	H _{E2}	H _{E3}
1	000	III	III	III	111	022	202	220	13I	31I	331	242	422	440	35I	53I	55I
2	000	III	III	III	111	022	202	220	13I	31I	331	242	440	422	313	533	511
3	000	III	III	III	111	022	202	220	13I	31I	331	422	440	242	353	133	151
4	000	III	III	III	111	022	202	220	13I	331	31I	202	422	400	311	511	5II
5	000	III	III	III	111	022	202	220	13I	331	31I	202	400	422	333	513	53I
6	000	III	III	III	111	022	202	220	13I	331	31I	422	400	202	313	113	1II
7	000	III	III	III	111	022	202	220	31I	331	13I	242	040	040	151	131	15I
8	000	III	III	III	111	022	202	220	31I	331	13I	242	040	022	113	133	1II
9	000	III	III	III	111	022	202	220	31I	331	13I	242	040	242	153	333	35I

Table VI a

Configuration	C _A	H _{A1}	H _{A2}	H _{A3}	C _B	H _{B1}	H _{B2}	C _C	H _{C1}	H _{C2}	C _D	H _{D1}	H _{D2}	H _{D3}
Trans	000	III	III	III	III	022	202	220	13I	3II	33I	2I2	422	4I0
Gauch	000	III	III	III	III	022	202	220	13I	33I	3II	202	422	400

Table VIb

Atom Pair	A1 C1	A1 C2	A2 C1	A2 C2	A3 C1	A3 C2	B1 C1	B1 C2	B2 C1	B2 C2	A1 D1	A1 D2	A1 D3	A2 D1	A2 D2	A2 D3	A3 D1	A3 D2	A3 D3	
Conf. Ec. Trans	24	24	16	8	8	16	11	19	19	11	35	35	51	35	27	35	27	27	35	35
Gauch	24	32	16	24	8	24	11	11	19	11	19	43	27	3	19	11	11	27	27	27

Since the hydrogen atoms will approach each other much more closely than do the carbons, the interactions between these will be of principal importance, and will be the only ones considered here. The squares of the lengths of the vectors connecting all pairs of hydrogens in butane are given for the two configurations in Table VI b. Distances are given in lattice units in which the (C-C) bond has a length of $\sqrt{3}$. R^2 in (angstroms)² may be obtained by multiplying by $(1.54)^2/3$.

Distances between hydrogens on atoms A and B and those on atoms C and D are not given because the same set of distances occur in all configurations (because of the symmetry of the CH₃ groups) so that no differences in interaction occur.

Distances between hydrogens on atoms B and D are not given because (by symmetry) they will be the same as those between hydrogens on atoms A and C so that these may be included twice.

On carrying out the same process for pentane, one finds that nine configurations fall into one of four classes:

- Class (a) — Configuration No. 1
- Class (b) — Configurations No. 2, 3, 5, and 9
- Class (c) — Configurations No. 4 and 7
- Class (d) — Configurations No. 6 and 8

All configurations within a given class have the same set of R^2 's and have the same interaction energy. Class (d) is that of the excluded configurations (which need not be considered) in which two hydrogens would occupy the same lattice site. In Table VII, R^2 's are given for one member of each permitted class.

Table VII.

Atom Pair	R ² for Config. No.			Atom Pair	R ² for Config. No.		
	1	2	4		1	2	4
A1-C1	24	24	24	B1-D1	8	8	24
A1-C2	24	24	32	B1-D2	16	24	32
A2-C1	16	16	16	B2-D1	16	16	16
A2-C2	8	8	24	B2-D2	8	24	24
A3-C1	8	8	8	A1-E1	56	24	16
A3-C2	16	16	24	A1-E2	56	56	40
C1-E1	8	24	24	A1-E3	76	40	40
C1-E2	16	32	24	A2-E1	40	24	8
C1-E3	24	24	32	A2-E2	32	0	24
C2-E1	16	16	16	A2-E3	56	24	16
C2-E2	8	24	8	A3-E1	32	32	24
C2-E3	24	8	24	A3-E2	40	56	40
A1-D1	35	35	19	A3-E3	56	40	40
A1-D2	35	51	43	B1-C1	11	11	11
A2-D1	35	35	3	B1-C2	19	19	11
A2-D2	27	35	19	B2-C1	19	19	19
A3-D1	27	27	11	B2-C2	11	11	11
A3-D2	35	35	27	C1-D1	11	11	11
B1-E1	27	11	19	C1-D2	19	11	11
B1-E2	35	27	27	C2-D1	19	19	19
B1-E3	35	27	43	C2-D2	11	11	11
B2-E1	35	3	3				
B2-E2	27	19	11				
B2-E3	35	11	19				

Table VIII[†]

Substance	No. of configurations with steric energy						
	0	a	2a	3a	4a	5a	∞
Butane	1	2	0	0	0	0	0
Pentane	1	4	2	0	0	0	2
Hexane	1	6	8	2	0	0	10
Heptane	1	8	18	12	2	0	40
Octane	1	10	32	38	16	2	144

[†]Reproduced from K. Pitzer, J. Chem. Phys., 8, 711 (1940).

This classification is similar to that made by Pitzer (37). Table VIII is reproduced from his paper. E_1 (steric) = 0 corresponds to the stretched out configuration $E_1 = a$ corresponds to one lattice distance interaction, $E_1 = 2a$, to 2 interactions per configuration, etc. $E_1 = \infty$ corresponds to a prohibited configuration. The number of interactions was determined by Pitzer by examining a model. Our method is somewhat more satisfactory because:

a) We have available simultaneously, the steric energy, the value of R^2 (between ends) and the value of $\sum (O_i \cdot R)^2 / 3R^2$ for each configuration, so that we may obtain weighted averages of R^2 and Q .

b) Table VII gives actual interatomic distances which permit an evaluation of the interaction energy, a , from van der Waals force theory.

c) All of the relevant interatomic distances are given. Thus the smaller interactions between other than the closest atoms may be included to give a more accurate value for the steric energy.

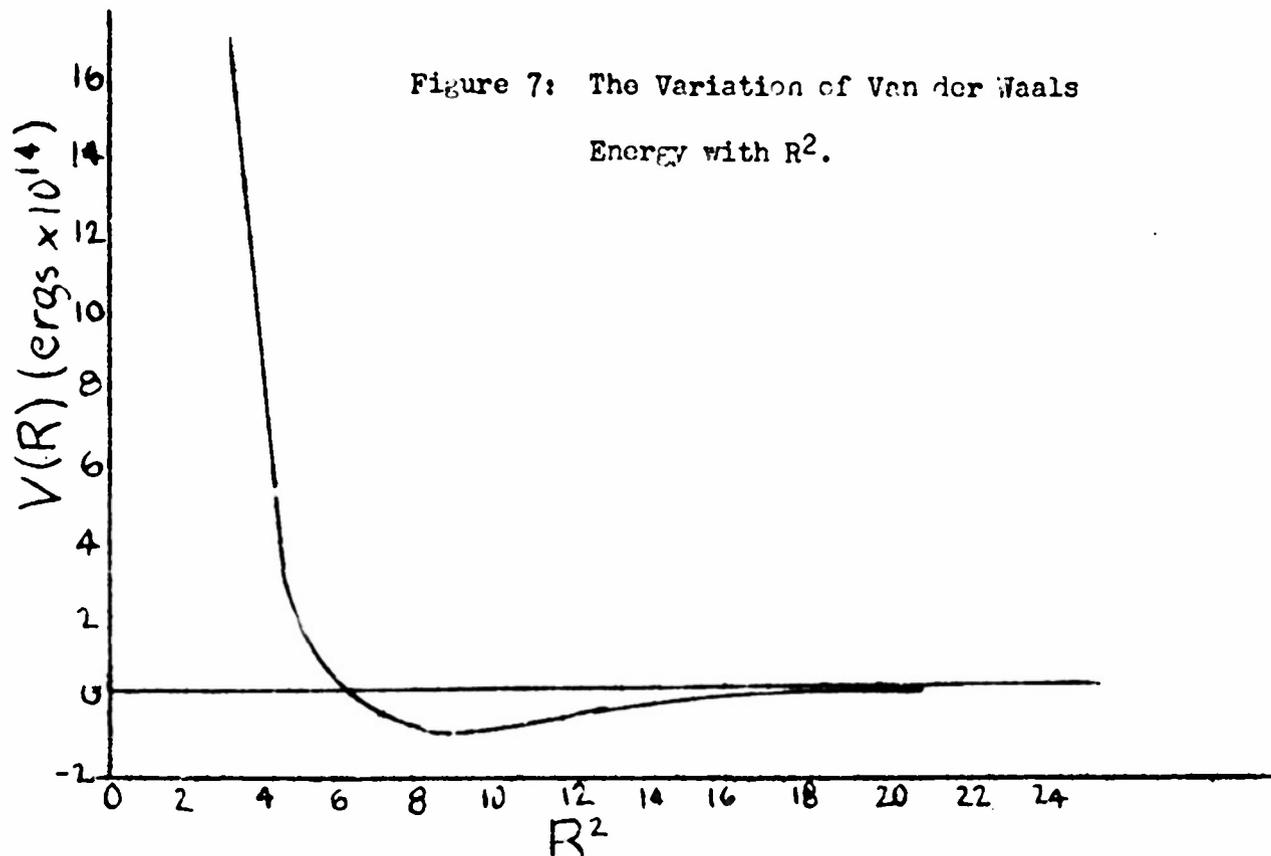
The calculation of the steric energy may be made on the basis of a knowledge of the dependency of van der Waals energy on interatomic distance. For this purpose, we have made use of the equation employed by Müller (38) for the calculation of the lattice energy of crystals of the n-paraffins.

$$V = -\frac{4.31 \times 10^{-12}}{r^6} + 7.7 \times 10^{-10} e^{-4.58r} \quad (35)$$

where: V is the interaction energy in ergs per molecule

r is the distance between centers of hydrogen atoms in Angstrom units.

A plot of $V(R)$ against R^2 (in lattice units) is given in Figure (7). It is apparent that the interaction energy becomes quite high for R^2 's less than about 6. The two smallest R^2 's in Table VII are 3 and 8. It is apparent that Pitzers consideration of only the $R^2 = 3$ interaction is a good approximation.



The values for the steric energies are obtained for each configuration by adding the values of $V(R)$ for all the R 's. For the $R^2 = 3$ interaction, it is necessary to correct for the assumed identity of the C - C and C-H bond length because of the rapid variation of $V(R)$ with R in this region. Upon doing this, one finds that the actual value of R^2 is 4.5 which corresponds to $V(R) = 4.5 \times 10^{-14}$ ergs/molecule or 650 calories per mole. Considering the approximations involved, this is in good agreement with the value of $a = 800$ cal./mole which Pitzer found to give best agreement between experimental and theoretical entropies.

In Table IX, F (the number of times a given R^2 occurs in a configuration), $V(R)$ (corresponding to that R^2), and E (the contribution of this R^2 interaction to the total potential) are listed. The results of this calculation are summarized in Table X.

The reason for favoring the trans configurations in the restricted rotation model is apparent from this model. The principal contribution to the steric energy is the repulsive energy arising from an $R^2 = 3$ type interaction. It is apparent (from tables I and VII) that an interaction of this type occurs between the hydrogens on two carbons which are separated by two carbons whenever the three intervening (C-C) bonds are in a gauche configuration. The number of such interactions may be counted by counting the number of gauche (or trans) configurations. This has been pointed out by Pitzer and by Taylor. It is believed that the treatment used here is more satisfactory in that all of the interactions are considered instead of just the $R^2 = 3$ type. While there is not a great difference between the results of the two methods of approach

Table IX

R ²	V(R) x 10 ¹⁴ ergs	Butane				Pentane					
		Trans		Gauged		#1		#2		#3	
		F	E	F	E	F	E	F	E	F	E
3	+4.5	0	0	1	+4.5	0	0	1	+4.5	2	+9.0
8	-0.86	4	-3.44	2	-1.72	6	-5.16	4	-3.44	3	-2.58
11	-0.58	2	-1.16	5	-2.90	4	-2.32	7	-4.06	8	-4.64
16	-0.21	4	-0.84	2	-0.42	6	-1.26	4	-0.84	5	-1.05
19	-0.13	2	-0.26	3	-0.39	4	-0.52	4	-0.52	6	-0.78
24	-0.06	4	-0.24	6	-0.36	4	-0.24	10	-0.60	10	-0.60
27	-0.04	2	-0.08	3	-0.12	4	-0.16	3	-0.12	2	-0.08
32	-0.02	0	0	2	-0.04	2	-0.04	2	-0.04	3	-0.06
35	-0.02	6	-0.12	0	0	8	-0.16	4	-0.08	0	0
40	-0.01	0	0	0	0	2	-0.02	3	-0.03	4	-0.04
43	-0.01	0	0	1	-0.02	0	0	0	0	2	-0.02
51	-0.00	1	-0.00	0	0	0	0	1	-0.00	0	0
56	-0.00	0	0	0	0	4	-0.00	2	-0.00	0	0
76	-0.00	0	0	0	0	1	-0.00	0	0	0	0
Total			-6.14		-1.5		-9.88		-5.2		-0.9

here, the difference will become increasingly greater for longer molecules and those with side groups. For these, there will be a larger number of forbidden configurations; also R² = 3 type interactions can occur between hydrogens on carbons that are more distant than those considered here. These would not be included by simply counting the number of trans configurations.

Table I

Substance	Steric Energy		exp[-V(steric)/RT] T = 25° C.
	Ergs/molecule x 10 ¹⁴	Cal./mole	
Butane			
Trans	- 6.1	- 880	4.4
Gauch	- 1.5	- 220	1.4
Pentane			
Conf. 1	- 9.9	-1130	11.2
2,3,4,9	- 5.2	- 750	3.5
4,7	- 0.9	- 130	1.2
6,8	0	0	0

The calculation of the averages of R^2 and $(\alpha_1 - \alpha_2)$ is done by weighting the configurations with a Boltzman factor $\exp[-V(\text{steric})/RT]$

Thus:

$$\overline{R^2} = \frac{\sum_j [R_j^2 \exp(-V(\text{steric})_j/RT)]}{\sum_j [\exp(-V(\text{steric})_j/RT)]}$$

$$\overline{(\alpha_1 - \alpha_2)} = \frac{\sum_j [(\alpha_1 - \alpha_2)_j \exp(-V(\text{steric})_j/RT)]}{\sum_j [\exp(-V(\text{steric})_j/RT)]}$$

The weighting factors for $T = 25^\circ \text{C}$ are listed in the last column of Table I.

The values of $(\alpha_1 - \alpha_2)$ which were calculated by this means are listed in the last column of Table IV. These are still somewhat below the experimental values.

It should be pointed out that the experimental values for some of the

hydrocarbons are higher than the $(\alpha_1 - \alpha_2)$ values for the completely stretched out configuration (27.7 for butane and 28.9 for pentane), so that no method of averaging or weighting of configurations could give the experimental value. The difficulty is evidently that the experimental value is too high.

It would be of great interest to obtain better experimental values of $(\alpha_1 - \alpha_2)$ for these and other compounds, either by depolarisation or Kerr Effect, in order to better verify the correctness of these theoretical considerations. A knowledge of these interactions which govern the shape of the hydrocarbon chain would be of direct application in the study of the properties of polymeric substances.

References

(References are listed in order of their appearance)

1. M. Born, "Dynamic der Krystalgitter" (1915).
2. W. L. Bragg, Proc. Ry. Soc., 105, 370 (1924).
3. W. H. Zacharissen, J. Chem. Phys. 1, 640 (1933).
4. C. V. Raman, Nature, 114, 49 (1924).
5. S. Bhagavantam, Proc. Roy. Soc., 107, 684 (1924).
6. Silberstein, Phil. Mag, 33, 92, 215 and 521 (1917).
7. K. G. Denbigh, Tran. Far. Soc., 36, 936 (1940).
8. W. Kuhn and F. Grün, Koll. Z., 101, 248 (1942).
9. L. R. G. Treloar, Trans. Far. Soc., 43, 277 (1947).
10. H. Eyring, Phys. Rev. 39, 746 (1932).
11. W. Kuhn, Koll, Zeit., 76, 253 (1936); 87, 3 (1939); 68, 2 (1934).
12. L. R. G. Treloar, Trans. Far. Soc., 39, 36 (1943); 39, 241 (1943).
13. H. James and E. Guth, J. Chem. Phys., 15, 6601 (1947); 11, 455 (1943).
14. F. T. Wall, J. Chem. Phys., 10, 485 (1942).
15. Flory and Rehner, J. Chem. Phys., 11, 512 (1943).
16. R. S. Stein and A. V. Tobolsky, Plastics Laboratory Technical Report 18a, Princeton Univ. (1950).
17. L. R. G. Treloar, "The Physics of Rubber Elasticity", Oxford (1949), p. 147.
18. G. King, Technical Report No. 1 to Office of Naval Research Contract N6-onr-228 T.O. II, Project NR 033 243.
19. For a review, see K. S. Pitzer, Chem. Rev., 27, 39 (1940).
20. A. V. Tobolsky, R. Powell, and H. Eyring, "Elastic-Viscous Properties of Matter" in Burt & Grummit, "The Chemistry of Large Molecules", Interscience, New York (1943) p. 156.
21. W. J. Taylor, J. Chem. Phys., 16, 257 (1948).

22. Kerr, Phil Mag 50, 337 (1875).
23. Langevin, Jour. d. Phys., 7, 249 (1910).
24. Raman and Krishnan, Phil. Mag. 3, 724 (1927).
25. J. Cabannes, "La diffusion moleculaire de la Lumiere", Presses Univ. France, Paris (1929).
26. R. Krishnan, Proc. Ind. Acad. Sci. 1A, 212 (1934); 717, 782 (1935); 3, 211 (1936); 5A, 94, 305, 407, 409, 551 (1937); 7A 21, 91, 98 (1938).
27. A review of theory. B. H. Zimm, R. S. Stein, and P. Doty, Polymer Bulletin, 1, 90 (1945).
28. S. Bhagavantam, "Scattering of Light and the Raman Effect", Chemical Publishing Co., Brooklyn (1942) p.54.
29. H. A. Stuart, "Moloculestruktur" Julius Springer, Berlin (1934).
30. Parthasarthy, Ind. J. Physics, 7, 139 (1932).
31. Ananthakrishnan, Proc. Ind. Acad. Sci., A2, 153 (1935).
32. Volkmann, Ann. Physik., 24, 457 (1935).
33. Stuart and Volkmann, Physik Z., 35, 988 (1934).
34. Brezeale, Phys. Rev., 48, 237 (1935), 49, 625 (1936).
35. J. C. McCoubrey, J. N. McCrea, and A. R. Ubbelohde, J. Chem. Soc., 439, 1961 (1951).
36. A. R. Ubbelohde and Miss. I. Woodward, Trans. Far. Soc., 48, 113 (1952).
37. K. Pitzer, J. Chem. Phys., 8, 711 (1940).
38. A. Müller, Proc. Roy. Soc., A154, 624 (1936); A178, 227 (1941).