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Citation: *The Journal of Chemical Physics* **15**, 412 (1947); doi: 10.1063/1.1746540

View online: <http://dx.doi.org/10.1063/1.1746540>

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Average Square Length and Radius of Unbranched Long-Chain Molecules with Restricted Internal Rotation

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(Received March 27, 1947)

EYRING¹ has derived a well-known formula for the average square length of an unbranched long-chain molecule with n bonds, each of length σ , with a fixed valence angle θ between successive bonds, and *free internal rotation* about each bond, and Debye² has given a formula for the average square radius of the molecule. These quantities appear as parameters in theories of the physical properties (elasticity, intrinsic viscosity, streaming double refraction, etc.) of long-chain molecules. However, the assumption of free rotation is now known to be inadequate for a quantitative treatment of properties affected by internal rotation. In actual molecules in which rotations occur, the latter are, in general, partially restricted by potential functions with one or more minima separated by intervening maxima (potential barriers).

The only published attempt to calculate the effect of a restricting potential of which the writer is aware, is that of Bresler and Frenkel,³ who, however, considered only the special case of small torsional oscillations about the equilibrium configuration.⁴ Their treatment fails for large oscillations or for potential functions with more than one minimum, so that they have not in fact treated restricted *rotation*.

The present communication reports formulas for the average square length and radius of an unbranched long-chain molecule for the case in which the rotation about each bond is restricted by the same potential function $V(\phi)$ (ϕ =angle

of rotation, defined so that $\phi=0(\pi)$ for the planar *trans* (*cis*) configuration of three successive bonds). It is assumed that there are no interactions between different rotations (because of terms in the potential function or of steric hindrance), but there are no restrictions on the form of the function $V(\phi)$, or on the extent of the rotation. The exact solution has been obtained in a very general form which allows also for variation of the bond angle and bond length. However, in actual molecules the effect of these latter variations on the length and radius should be much less important than that of internal rotation. Only the formulas for restricted internal rotation will be presented here, and, in addition, only the approximate formulas valid for long chains. The derivation (which is based on Eyring's method¹) and the general solution will be presented in a subsequent paper.

According to classical statistics, the probability that a given bond rotation lies in the range $(\phi, \phi+d\phi)$ is $p(\phi)d\phi$, where

$$p(\phi) = C \exp[-V(\phi)/kT] \quad (1)$$

and C has a value such that,

$$\int_{-\pi}^{\pi} p(\phi) d\phi = 1. \quad (2)$$

k is Boltzmann's constant and T is the absolute temperature. The average square length and radius depend on the function $V(\phi)$, and on the temperature, only through the two parameters, a and b , defined by the equation,

$$\begin{Bmatrix} a \\ b \end{Bmatrix} = \int_{-\pi}^{\pi} p(\phi) \begin{Bmatrix} \cos\phi \\ \sin\phi \end{Bmatrix} d\phi. \quad (3)$$

a and b are clearly the average values of $\cos\phi$ and $\sin\phi$, respectively. The solution has been obtained for the general case, $a \neq 0$, $b \neq 0$. However the only case likely to be of physical interest is that corresponding to an *even* potential function, $V(\phi) = V(-\phi)$, for which $b = 0$.

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¹ H. Eyring, Phys. Rev. **39**, 746 (1932); E. Gorin, J. Walter, and H. Eyring, J. Am. Chem. Soc. **61**, 1885 (1939); see also, F. T. Wall, J. Chem. Phys. **11**, 67 (1943).

² P. Debye, J. Chem. Phys. **14**, 636 (1946).

³ S. E. Bresler and J. I. Frenkel, Acta Physicochimica U.R.S.S. **11**, 485 (1939). In English.

⁴ R. Simha, in reviewing the present paper, has brought to the attention of the author a paper by B. H. Zimm, R. S. Stein, and P. Doty (Polymer Bulletin, Vol. 1, October 1945, page 109 and Eq. (64)) in which brief mention is made of a treatment of this problem by Debye. It is not immediately clear whether the result quoted agrees with Eq. (4) of the present paper.

Only the result for $b=0$ is reported here. The case of free rotation corresponds to $V(\phi)=0$, $a=b=0$. An important special case is that of a potential function with m -fold symmetry, $m \geq 2$, so that $V(\phi)=V(\phi+2\pi/m)$. In this case it is easily shown from Eq. (3) and Lagrange's trigonometric identity that $a=b=0$, so that the length and radius have the same values as for free rotation, as has been pointed out by Gorin, Walter, and Eyring.¹

It is assumed that the n bonds join $(n+1)$ point masses, or atoms, of equal mass. For each possible configuration of the molecule there may be defined: (1) the *length*, L , equal to the distance from the first to the $(n+1)$ th atom; (2) the *radius*, R , equal to the root-mean-square value of the $(n+1)$ radii from the center of mass to the $(n+1)$ atoms. A given configuration is defined (for a fixed valence angle θ) by the values of the ϕ 's for each of the $(n-2)$ internal rotations. The probability of occurrence of the given configuration is taken to be the product of $(n-2)$ functions $p(\phi)$, one for each rotation (corresponding to the assumption that the potential energy is separable). An average of a quantity over all configurations, each weighted according to its probability of occurrence, will be denoted by the notation $\langle \rangle$.

For sufficiently large values of n , the average square length and radius are very nearly proportional to n , just as for free rotation, but the constant of proportionality is altered by the restricting potential. The approximate equations for large n are,⁵

$$\langle L^2 \rangle = \sigma^2 \left(\frac{1+\alpha}{1-\alpha} \right) \left(\frac{1+a}{1-a} \right) n, \quad (4)$$

$$\langle R^2 \rangle = \frac{1}{6} \langle L^2 \rangle \quad (5)$$

⁵ Equations equivalent to Eqs. (4) and (5) have been obtained by the writer by another method of calculation for the following special case: $\theta=109^\circ 28'$; $\phi=0, \pm(2\pi/3)$ (with unequal probabilities for the 0 and $\pm(2\pi/3)$ positions). These equations were contained in an unpublished manuscript completed September 30, 1944.

where $\alpha=\cos\theta$ and a is given by Eq. (3). Equation (5) is that given by Debye;² that is, the ratio of the radius to the length is unchanged to this approximation. For free rotation, $a=0$, and Eq. (4) reduces to the result reported previously.¹ The fractional errors in $\langle L^2 \rangle$ and $\langle R^2 \rangle$, as calculated from Eqs. (4) and (5), are of the order of magnitude of $(1/n)$ for values of α , a , and n , such that

$$n|\lambda_1^n| < 1, \quad n|\lambda_2^n| < 1 \quad (6)$$

where

$$\begin{cases} \lambda_1 \\ \lambda_2 \end{cases} = \frac{1}{2} \{ \alpha(1-a) \pm [\alpha^2(1-a)^2 + 4a]^{\frac{1}{2}} \}. \quad (7)$$

Also $|\lambda_1| < 1$ and $|\lambda_2| < 1$ for $|\alpha| < 1$ and $|a| < 1$, so that conditions (6) are satisfied for sufficiently large n except in the limiting cases, $|\alpha|=1$ or $|a|=1$.

According to Eqs. (4) and (5), $\langle L^2 \rangle$ and $\langle R^2 \rangle$ are functions of the temperature, through the parameter a . As the temperature increases the rotation becomes less restricted, and $|a|$ decreases. As a result, $\langle L^2 \rangle$ and $\langle R^2 \rangle$ decrease (increase), if a is positive (negative), resulting qualitatively from the increasing probability of more (less) coiled configurations. There is no temperature coefficient in the case of free rotation ($a=0$).

Returning now to the results of Bresler and Frenkel³ (hereafter referred to as BF) it will be seen that Eq. (4) is not in agreement with Eq. (35) of BF, which it should include as a special case. The writer is confident that Eq. (4) is correct, since it is obtained by an exact calculation. There are a number of approximations in the derivation of Eq. (35) of BF. The equivalent of Eq. (4) has been obtained by another method of calculation for a special case,⁶ and Eq. (4) also yields the correct result for free rotation.⁶

⁶ Note added in proof: C. Sadron, J. chim. physique **43**, 12 (1946), in a paper which became available to the writer after the present paper was submitted for publication, has given an approximate formula for $\langle L^2 \rangle$ for the case of *nearly free* rotation which agrees with the form assumed by Eq. (4) for this special case ($|a| \ll 1$).