On the Apparent Radius of Gyration of Linear Polymers and the Experimental Determination of the Excluded-Volume Parameter

A. J. Barrett*

Department of Mathematics and Computer Science, Royal Military College of Canada, Kingston, Ontario K7K 5L0, Canada

J. Skolnick†

Institute of Macromolecular Chemistry, Department of Chemistry, Washington University, St. Louis, Missouri 63130. *Received July 27, 1987; Revised Manuscript Received September 18, 1987*

ABSTRACT: The structure factor for linear polymers in the Θ state is given by the well-known Debye function. In a good solvent the chain is subject to excluded volume; however, the form of the structure factor still closely resembles that of the Debye function. As a result, one is tempted to interpret the structure factor as a Debye function whose argument is scaled by the radius of gyration of the swollen chain. We present here rigorous and numerical arguments which demonstrate that such an interpretation is legitimate only for small values of the argument. An asymptotic expression for the structure factor suggests a method of measuring the value of the excluded-volume variable Z by experiment.

1. Introduction

The theory of light scattering from linear polymers in dilute solution has been known since the work of Debye[1] and Zimm.[2] The extension of a macromolecule relative to that of a small particle is accounted for by the inclusion in the relevant equations of a *structure factor* or *form factor*, which may be measured by experiment. Debye[1] has provided a simple analytic expression for the structure factor of chains in the Θ state which permits the chain dimensions to be determined. If the chains are dissolved in a good solvent the dimensions will be swollen because of the excluded-volume effect. Under these circumstances the dimensions may still be ascertained by examining the structure factor in the limit of small wavevector q where

$$q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$$

In this equation λ represents the wavelength of the scattered radiation and θ the scattering angle. If, as sometimes happens (for instance in the case of SANS experiments), reliable data cannot be obtained for small q, then the interpretation of the structure factor becomes a serious problem.

Recently there have appeared a number of articles[3-5] which have made use of a quality known as the "apparent radius of gyration". This apparent radius of gyration is obtained by numerically fitting experimentally observed values of the structure factor to a Debye function in which the independent variable is scaled by an unknown factor. It is supposed that this unknown factor is independent of q and simply related to the expansion factor α_S^2 of the radius of gyration, where

$$\alpha_S^2 = \langle S^2 \rangle / \langle S^2 \rangle_0$$

In this equation, $\langle S^2 \rangle$ represents the mean-square radius of gyration of the chain. The 0 subscript indicates the Θ condition. In the remainder of this work we write for brevity $R_g = \langle S^2 \rangle^{1/2}$.

In this short study, we show that while it is possible to obtain good "fits" of the observed data to the Debye function, these do not provide, in general, reliable estimates of the true radius of gyration.

The particle structure factor for a polymer is defined to be

$$P(q) = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle e^{i\mathbf{q}\cdot(\mathbf{r}_i - \mathbf{r}_j)} \rangle \tag{1}$$

which may be approximated by

$$P(q) = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} e^{-q^2 \alpha_{ij}^2 |j-i|/6} \tag{2}$$

Here N represents the degree of polymerization and r_i the position of the ith monomer unit. We have made use of

$$\alpha_{ij}^2 = \frac{\langle R_{ij}^2 \rangle}{|j - i|}$$

the expansion factor of that part of the polymer joining skeletal units labeled i and j.

The definition may be written in the form of an integral as[6]

$$P(q) = \frac{1}{4} \int_{-1}^{1} \int_{-1}^{1} dx\, dy \exp\left[-\frac{\alpha^2(x,y)}{2\alpha_S^2} |y - x| u^2 \right] \tag{3}$$

The variable u^2 which appears in this equation is defined as the product of the mean-square radius of gyration and the square of the wavevector.

$$u^2 = q^2 \langle S^2 \rangle = q^2 R_g^2$$

For convenience, all bond lengths are taken as unity.

In general α^2 will be a function of the excluded-volume variable Z, where[7]

$$Z = (3/2\pi)^{3/2} N^{1/2} \beta$$

and β is a binary cluster integral. In the special case of no excluded volume, $Z = 0$ and $\alpha^2 = 1$. Then the integral of eq 3 can be performed exactly to give the Debye function:

$$P_{DB}(u) = \frac{2}{u^4} [e^{-u^2} - 1 + u^2]$$

Some researchers[8,9] have noted that even for $Z > 0$, that is for a non-Θ solution, the observed structure factor is essentially identical in shape with the Debye function. This is the origin of the "apparent radius of gyration". Suppose that in eq 3, the function $\alpha^2(x,y)$ is replaced by $\tilde{\alpha}^2$, a function of Z *only*, then $\tilde{\alpha}^2$ may be taken as the definition of the apparent expansion factor of the radius of gyration. If this is a legitimate procedure, it follows trivially from eq 3 that

† Alfred P. Sloan Foundation Fellow.

0024-9297/88/2221-1141$01.50/0

$$P(u) = P_{DB}(cu) \tag{4}$$

where

$$c^2 = \tilde{\alpha}^2/\alpha_S^2$$

It is clear that $\tilde{\alpha}^2$, like α_S^2, is a form of average of $\alpha^2(x,y)$, taken over the chain. We need to know, therefore, under which conditions $\alpha^2(x,y)$ may be replaced by a constant. We shall show that this may be done safely only for small or very large u. In the second case the apparent radius of gyration is considerably different from the true radius of gyration. We shall conclude that the apparent radius of gyration *may be used with care* for small qR_g. The rigorous results for the limits of small qR_g and large qR_g are linked by a numerical analysis based on a formula suggested in an earlier paper.[10]

2. Results in the Small u Regime

If $u = qR_g$ is sufficiently small, then the exponential in eq 3 may be expanded in series:

$$P(u) = 1 - \frac{u^2}{8\alpha_S^2}\int_{-1}^{1}\int_{-1}^{1} dx\, dy\, \alpha^2(x,y)|y-x| + \frac{u^4}{32(\alpha_S^2)^2}\int_{-1}^{1}\int_{-1}^{1} dx\, dy\, [\alpha^2(x,y)(y-x)]^2 + \ldots = 1 - \frac{u^2}{3} + B(Z)u^4 + \ldots \tag{5}$$

The coefficient of u^4 is not a constant but rather a function of Z. Comparing (5) with the expansion of the Debye function,

$$P_{DB}(u) = 1 - \frac{u^2}{3} + \frac{u^4}{12} + \ldots$$

we find that $\tilde{\alpha}^2 = \alpha_S^2$ to $\mathcal{O}(u^2)$. Whether or not the equality extends to higher order terms in u depends on how nearly constant $B(Z)$ and the higher order coefficients are. In section 4 we shall show that $B(Z)$ is in fact a slowly increasing function of Z and so for small values of u the apparent radius of gyration gives a good estimate of the true radius of gyration.

3. Results in the Large u Regime

The small u expansion presented in the previous section has been known for some time, indeed it forms part of the basis of the Zimm plot. Less is known about the behavior of the structure factor for large u, although it turns out that it is relatively simple to obtain useful results.

A glance at eq 3 shows that the integrand is a sharply peaked function for large values of u. This feature may be exploited, not only to simplify the integration but also to permit an accurate representation of the function $\alpha^2(x,y)$. Although the argument is not explicitly stated, α^2 is a function of the "local" excluded-volume variable z, where[10]

$$z = (3/2\pi)^{3/2}\frac{N^{1/2}\beta}{2^{1/2}}|x-y|^{1/2}$$

Note that this definition of z demonstrates the well-known property that small segments of the chain display less volume exclusion than longer segments. If the solvent or excluded-volume condition of the chain as a whole is characterized by Z, then the local excluded volume z is related to the chain excluded volume Z by[10]

$$z = \frac{|y-x|^{1/2}}{2^{1/2}}Z \tag{6}$$

It follows therefore that for *any* reasonable value of Z, the local excluded volume z will be small for small $|y-x|$. Now it is well-known that for small values of z, $\alpha^2(x,y)$ may be expanded in series:

$$\alpha^2(x,y) = 1 + C(x,y)z + \ldots$$

The perturbation coefficient C was worked out years ago by Teramoto, Kurata and Yamakawa[15] to be

$$C = \frac{4}{3}\left[\frac{8}{3} - 4\left(\frac{1+y}{y-x}\right)^{1/2} - 4\left(\frac{1-x}{y-x}\right)^{1/2} + \left(\frac{y-x}{2}\right)^{1/2} + \frac{8}{3}\left[\left(\frac{1+y}{y-x}\right)^{3/2} + \left(\frac{1-x}{y-x}\right)^{3/2} - \left(\frac{1-x}{y-x}\right)^{3/2} - \left(\frac{1-y}{y-x}\right)^{3/2}\right]\right]$$

for $y > x$. If $x > y$ then it is necessary to interchange x and y.

It is possible to expand the coefficient C as a Taylor series in $|y-x|^{1/2}$ (some care must be exercised since C is not analytic at $y = x$; however, this does not cause any fundamental difficulties). Retaining only the leading term, we find

$$\alpha^2(x,y) = 1 + \frac{32}{9(2^{1/2})}|y-x|^{1/2}Z \tag{7}$$

Here we have made use of the limit of C for a subchain with two infinitely long attached end chains and have expressed z in terms of the excluded volume for the complete chain Z according to eq 6. See ref 10.

If we retain only the first term in Z, then it is possible to replace the true $\alpha^2(x,y)$ by a function of the relative variable $t = |y-x|/2$. Note that this is *not* possible in general since $\alpha^2(x,y)$ is a function of *both* $|x-y|$ *and* x. Equation 3 may now be written:

$$P(u) = 2\int_0^1 dt\,(1-t)\exp\left[-\frac{\alpha^2(t)}{\alpha_S^2}tu^2\right]$$

Expanding the exponential about $\alpha^2(t)/\alpha_S^2 = 1$, we obtain the following expression:

$$P(u) = 2\sum_{n=0}^{\infty}\frac{(-1)^n u^{2n}}{n!}\int_0^1 dt\,(1-t)t^n e^{-tu^2}\left(\frac{\alpha^2(t)}{\alpha_S^2} - 1\right)^n \tag{8}$$

The binomial may be expanded as follows, making use of (7):

$$\left(\frac{\alpha^2(t)}{\alpha_S^2} - 1\right)^n = \frac{1}{(\alpha_S^2)^n}\left[(1-\alpha_S^2)^n + \frac{32n}{9}(1-\alpha_S^2)^{n-1}t^{1/2}Z + \ldots\right]$$

Note that while the "full" α_S^2 appears in this expansion, $\alpha^2(t)$ is correct only to $\mathcal{O}$ Useful expressions may be obtained from eq 8 in two ways. First note that if the binomial expression is substituted into (8), then the $n = 0$ term of the sum corresponds to the Debye function. It is therefore possible to compute corrections to the Debye functional form by evaluating as many of the subsequent terms as desired. If the $n = 1$ term is evaluated with α_S^2 replaced by its first-order approximation

$$\alpha_S^2 = 1 + \frac{134}{105}Z$$

Table I
Computed and Asymptotic Estimates of $P(u)$ for Various Z

	$Z = 0$			$Z = 0.1$		
u	$P(u)^a$	P^b	P^c	P^a	P^b	P^c
0	1	1		1	1	
0.1	0.997	0.997		0.997	0.990	
0.5	0.922	0.922		0.922	0.914	
1.0	0.736	0.736	2	0.736	0.717	1.12
5.0	0.0768	0.768	0.0800	0.0803	0.0791	0.0803
10.0	0.0198	0.0198	0.0200	0.0212	0.0212	0.0212
20.0	0.00499	0.00499	0.00500	0.00544	0.00545	0.00544
100.0	0.00020	0.00020	0.00020	0.00022	0.00022	0.00022
	$Z = 1.0$			$Z = 10.0$		
u	$P(u)^a$	P^b	P^c	P^a	P^b	P^c
0	1	1		1	1	
0.1	0.997	0.966		0.997	0.946	
0.5	0.922	0.885		0.922	0.861	
1.0	0.738	0.642		0.740	0.581	
5.0	0.0910	0.0882		0.0994	0.0956	
10.0	0.0262	0.0267	0.0131	0.0310	0.0313	
20.0	0.00724	0.00726	0.00598	0.00941	0.00875	
100.0	0.00033	0.00031	0.00033	0.00054	0.00038	0.00005

[a] Calculated value of $P(u)$. [b] Equation 9. [c] Equation 10.

then $P(u)$ may be approximated by a simple rational function in Z.

$$P(u) = P_{DB}(u) + \frac{268Z}{(105 + 134Z)u^4}[u^2 - 2 + e^{-u^2}(u^2 + 2)] - \frac{2240Z}{(315 + 402Z)u^4}\left[e^{-u^2}\left(\frac{15}{4} + u^2\right) + \left(\frac{3u}{4} - \frac{15}{8u}\right)\pi^{1/2}\,\mathrm{erf}\,(u)\right] \quad (9)$$

As can be seen from Table I, the rational function approximation provides reasonable estimates for $P(u)$ over a wide range of values of u and Z. However, for large Z it gives a correction to the Debye function which is independent of Z and this is incorrect. A rigorous expansion for $P(u)$ to $\mathcal{O}(Z)$ is obtained if α_S^2 is replaced by 1, but this does not yield a very useful approximation.

An asymptotic expression valid in the limit of large u is obtained by noting that the dominant contribution to the integral in (8) comes from the neighborhood of $t = 0$. By considering only the least powers of t for each value of n and by extending the upper limit of the integrals to $+\infty$, it becomes possible to perform all the integrals and summations. The result is

$$P(u) \sim \frac{2\alpha_S^2}{u^2} - \frac{16\pi^{1/2}Z}{3}\left(\frac{\alpha_S^2}{u^2}\right)^{3/2} + \mathcal{O}(u^{-4}) \quad (10)$$

This asymptotic expansion demonstrates immediately that $P(u) \neq P_{DB}(cu)$, since the latter contains no odd powers of u. Furthermore, we see that in the limit of large u, $P(u)$ is given by the single term arising from the approximation $\alpha^2(x,y) = 1$, which means that $c^2 = 1/\alpha_S^2$ and $\tilde{\alpha}^2 = 1$. It follows that the assumption of equality of the apparent and a true radii of gyration is *totally without foundation* in the region of large u. Expression 10 should be compared with that derived by Utiyama, Tsunashima, and Kurata[11] by using the Domb–Gillis–Wilmers[12] distribution function:

$$P(u) = c_1u^{-5/6} + c_2u^{-5/3} + \ldots \quad (11)$$

The explicit values of c_1 and c_2 etc. are quoted in ref 13, which also contains other pertinent references.

Expression 11 is valid for large u *and* large Z, while expression 10 should be valid for $Z\alpha_S/u$ sufficiently small. The essential difference between the two expressions arises because eq 11 is derived by direct application of the Domb–Gillis–Wilmers distribution to (1), whereas approximation (2) presupposes a near-Gaussian distribution function.

4. Numerical Results

While the rigorous results obtained in the previous two sections are useful, they reveal very little about the behavior of $P(u)$ in the region of intermediate u. We can expect, qualitatively, that the behavior of P will be such that $\tilde{\alpha}^2$ decreases steadily from α_S^2 to unity; however, the only effective means of estimating $P(u)$ in the intermediate regime is by numerical approximation. An approximate expression for $\alpha^2(x,y)$, based on the Domb–Joyce model,[14] has been proposed in a previous article,[10] and it is not a particularly difficult matter to evaluate the integrals of (3) numerically. Care must be taken when u becomes large since the usual Gaussian quadrature methods are not precise for sharply peaked functions. This problem can be circumvented by writing $|y - x| = 1/t^3$ in the inner integral. One of the integral limits then becomes infinite and the other can be made zero by a simple change of variable. The result is an integral which may be evaluated by using the Gauss–Laguerre quadrature (see, e.g., ref 16). Values of $P(u)$ obtained by this method are displayed in Table I for $Z = 0$, $Z = 0.1$, $Z = 1$, and $Z = 10$. The approximations given by the rational function (9) and the asymptotic representation (10) are given for comparison. It can be seen (Table I) that the numerical estimates interpolate smoothly between the rigorously established values for small and large u. For very large values of u, the asymptotic estimates are probably more accurate than the numerical ones.

It is interesting to consider the result of fitting computed values of $P(u)$ to a Debye functional form. We have done this for a number of values of Z and have found that the fits are very close indeed. However, the values of $\tilde{\alpha}^2$ thus obtained are always somewhat low, even for small values of Z. This is not surprising, since an examination of Table I indicates that $P(u)$ differs from $P_{DB}(u)$ even for fairly small values of u, and the region of identity diminishes with increasing Z.

Numerical techniques may be applied to estimate the Z dependence of the coefficient $B(Z)$ of u^4 in the expression of $P(u)$. If the integral in (5) is evaluated numerically, we find that the coefficient varies slowly indeed, increasing from $B = {}^1/_{12}$ at $Z = 0$ to approximately 1.07 times that value at $Z = 50$. For small u, therefore, we conclude that the factor c in eq 4 is approximately unity and that in this region $P(u)$ and $P_{DB}(u)$ are almost the same function. This is borne out by the numerical calculations presented in Table I.

5. Experimental Measurement of Z

Equation 10 may be multiplied by q^2 and u_0^3 respectively to give two equations which are linear in the limit of large q:

$$q^2P(q) = \frac{2}{R_{g0}^2} - \frac{16\pi^{1/2}Z}{3R_{g0}^3}\left(\frac{1}{q}\right) \quad (12)$$

$$u_0^3P(q) = 2u_0 - \frac{16\pi^{1/2}Z}{3} \quad (13)$$

If qR_g is large enough, then $q^2P(q)$ is linear in $1/q$, and the resulting straight line has an intercept which yields R_{g0} and a slope which yields Z. Similarly $u_0^3P(q)$ is linear in $u_0 = qR_{g0}$ with a slope of 2 and an intercept which yields Z. This is an interesting circumstance since it has long been considered that Z cannot be directly measured by experiment. One can now envision an experiment from which all three

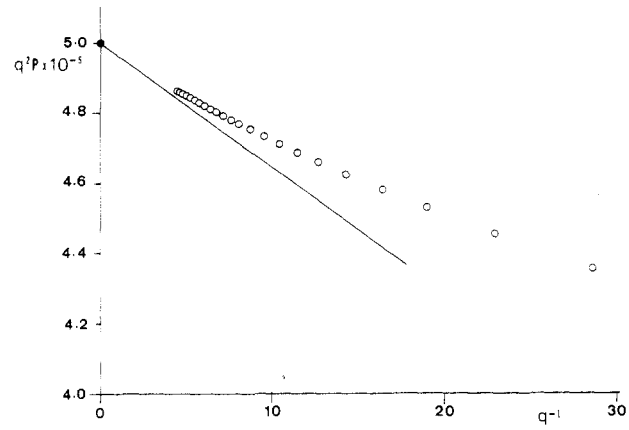

Figure 1. Extrapolation of q^2P versus $1/q$ to show estimation of R_{g0}: (○) calculated values; (●) extrapolated value. Solid line: asymptotic approximation, eq 12.

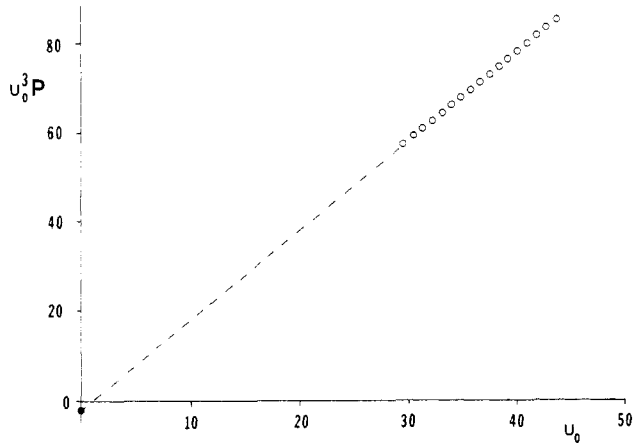

Figure 2. Extrapolation of $u_0{}^3P$ versus to u_0 to show estimation of Z: (○) calculated values; (●) extrapolated value.

pertinent quantities, R_{g0}, R_g, and Z, may be obtained at once. The unperturbed radius of gyration R_{g0} may be measured by application of (12) to large q measurements, and Z may be determined by application of (13) in the same regime. Finally, values of R_g can be obtained in the usual manner from measurements in the small q region, and the three quantities R_g, R_{g0}, and Z can be used to test the consistency of theoretical predictions.

Typical measurements are illustrated in Figures 1 and 2 for a hypothetical experiment on a polymer with R_{g0} = 200 Å and Z = 0.3. It is supposed that for this experiment, u_{max} = 50. The plotted points are computed by the use of eq 3 as described in the previous section; the solid curve in Figure 1 represents eq 12. The extrapolation to estimate R_{g0} (Figure 1) can conveniently be done by using simple linear or quadratic least-squares fitting. Note that the calculated points do not extrapolate to the expected theoretical value but rather to a point beside it. However, this results in an error of less than $^1/_2$% in the estimate of R_{g0}.

The extrapolation to estimate Z (Figure 2) is also straightforward; however, it is necessary to take great care to ensure that sufficiently large values of u_0 are used so that the linear region is truly obtained. If it assumed that the points satisfy the equation

$$y = 2x + y_0$$

then the intercept y_0 is estimated by

$$\frac{1}{m}[\Sigma y_i - 2\Sigma x_i]$$

where the sum is taken over the last m points. This calculation is, unfortunately, much more sensitive to error than the previous one; small errors in the measured points will result in relatively large errors in the intercept and hence in the estimate of Z.

Note that effects of concentration have not been considered. One supposes that a device similar to the Zimm plot will be adequate to deal with this aspect of the measurements.

6. Conclusions

We have examined the structure function $P(u)$ for excluded-volume chains and have concluded that, except for small values of the argument u, this function differs from the Debye function $P_{DB}(u)$. In particular, for large u, P has the behavior of a Debye function associated with a much smaller chain. Estimates of the dimensions of excluded-volume chains obtained by fitting P to a Debye functional form are therefore not reliable, despite the fact that the two functions are remarkably similar in shape. The results we present here are for simple chains at infinite dilution, but there is no question that they may also be applied to some extent to other situations. For instance it is clear that the difference between the structure factor and the Debye function will be increased if end chains are attached to the chain in question. The effect will indeed be similar to an increase in Z. It is difficult to say what the effect of increased concentration will be on the form of $P(u)$. In concentrated solutions, as is the case for the work of Lodge et al.,[5] the chains are well described by Gaussian statistics and one would expect the Debye function to be perfectly adequate in this case. However, in general, this is a difficult question which deserves further study.

We have obtained a rigorous asymptotic expression for P which suggests a means of measuring the quantities R_{g0}, R_g, and Z, all from a single experiment. We have avoided any discussion of the experimental difficulties which will accompany any such measurement but put our formula forward in the hope that it will eventually prove useful.

We note finally that it should not be difficult to extend the above results to chains with more complicated geometries, notably ring and branched polymers. The asymptotic results, for instance, require only that a perturbation series be developed. We note in passing that the leading term in eq 10 is independent of chain configuration or of the presence or absence of excluded volume. This expression may therefore be applied to any polymer whatsoever in dilute solution.

Acknowledgment. We are grateful to Dr. T. P. Lodge for helpful discussions and to Professor W. H. Stockmayer for bringing ref 13 to our attention. This work has been supported, in part, by the Department of National Defense, Canada, Grant ARP3610-656, and, in part, by Grant GM37408 from the Division of General Medical Science, United States Public Health Service.

References and Notes

(1) Debye, P. *J. Phys. Colloid Chem.* **1947**, *51*, 18.
(2) Zimm, B. H. *J. Chem. Phys.* **1947**, *16*, 1093, 1099.
(3) Matsushita, Y.; Noda, I.; Nagasawa, M.; Lodge, T. P.; Amis, E. J.; Han, C. C. *Macromolecules* **1984**, *17*, 1785.
(4) King, J. S.; Boyer, W.; Wignall, G. D.; Ullman, R. *Macromolecules* **1985**, *18*, 709.
(5) Lodge, T. P.; Hermann, K. C.; Landry, M. R. *Macromolecules* **1986**, *19*, 1996.
(6) Barrett, A. J. *Macromolecules* **1985**, *18*, 2441.
(7) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(8) Witten, T. A. Schaefer, L. *J. Chem. Phys.* **1981**, *74*, 2582.
(9) Ohta, T.; Oono, Y.; Freed, K. F. *Phys. Rev. A* **1982**, *25*, 2801.
(10) Barrett, A. J. *Macromolecules* **1984**, *17*, 1561.

(11) Utiyama, H.; Tsunashima, Y.; Kurata, M. *J. Chem. Phys.* **1971**, *55*, 3133.
(12) Domb, C.; Gillis, J.; Wilmers, G. *Proc. Phys. Soc. (London)* **1965**, *85*, 625.
(13) Tsunashima, Y.; Kurata, M. *J. Chem. Phys.* **1986**, *84*, 6432.
(14) Domb, C.; Joyce, G. S. *J. Phys. C* **1972**, *5*, 956.
(15) Teramoto, E.; Kurata, M.; Yamakawa, H. *J. Chem. Phys.* **1958**, *28*, 785.
(16) Davis, P. J.; Rabinowitz, P. *Methods of Numerical Integration*; Academic: New York, 1975.

Short Polymer Chain Statistics and the Relationship to End to End Electronic Excitation Transport: Random Walks with Variable Step Lengths

M. B. Zimmt,† K. A. Peterson, and M. D. Fayer*

Department of Chemistry, Stanford University, Stanford, California 94305.
Received July 8, 1987

ABSTRACT: The problem of the distribution of distances between the ends of a polymer chain for short chains (a small number of statistical segments) is considered. A formalism developed by Rayleigh is utilized to calculate the exact end to end distribution functions for random walks with a small number of steps and variable step lengths. In particular, distribution functions for walks in which the first and last step differ in length from the intervening steps are obtained. These are used as models for low molecular weight polymers in which the first and last statistical segments are different from internal segments because of chain end effects or chromophores attached to the chain termini. The results are used to calculate the ensemble averaged time dependence of end to end electronic excitation transport. $G^s(t)$, the part of the transport Green function which yields the time-dependent fluorescence depolarization observable, is calculated with exact random walk distribution functions and approximate distribution functions. It is demonstrated that the results are similar but that experiments which examine several distance ranges have the capability of distinguishing the distribution functions.

I. Introduction

Flory investigated various statistical mechanics models to describe the properties of chain molecules.[1] He concluded that a Gaussian spatial distribution function provides an adequate description of *n*-alkanes longer than 50–75 bonds. This class of polymers is modeled as freely jointed chains. Properties such as the distribution of end to end distances or the ensemble averaged root-mean-square radius of gyration can be obtained from the Gaussian description of the polymer chains. For any chain in which the directional correlation between bonds exists over a finite distance, the distribution function converges to a Gaussian expression in the limit of an infinitely long chain.

The Gaussian distribution function is a result of the application of the theory of random walks to the description of long freely jointed chain polymers.[2] For an ensemble of walkers executing random walks about an origin, the average spatial probability distribution of finding a walker a distance R from the origin for long walks is given by a Gaussian. In the polymer problem, the step size in the walk is the length of a statistical segment, i.e., the average distance required for the loss of directional correlation of the bonds in the polymer backbone.[3]

The Gaussian distribution function may not provide an accurate description of the spatial properties, for example, the end to end distance distribution, of short polymer chains (less than ten statistical segments). The equilibrium radial distribution function for the vector connecting the ends of a polymer chain is important to the description of the configurational statistics of chain molecules and for the interpretation of polymer properties, such as rubber elasticity. The distribution of end to end distances for low molecular weight chains cannot be calculated by using the same Gaussian function (with appropriate changes for molecular weight) which accurately describes the end to end distances of high molecular weight chains. There are two reasons for this. First, short chains lack a sufficient number of statistical segments to achieve the Gaussian form. The distribution of end points for an ensemble of walks of N steps where N is a small integer is not accurately given by a Gaussian. In 1919, Rayleigh derived exact expressions for the end to end distribution functions of N step random walks ($N < 7$) of constant step size.[4] He also derived accurate approximations for the distribution function when N is larger. However, Flory pointed out that even if one properly employs the mathematics of short random walks to obtain the non-Gaussian description of the short wak, there can be a second problem. The freely jointed chain model ignores the perturbation introduced by chain end effects.[5] These effects are important for very short chains. They arise because the ends of a chain do not have the same configurational constraints as interior portions of the chain. An additional practical problem arises because many experimental approaches for the determination of end to end distribution functions employ polymers with molecular probes attached to the chain termini. The relevant quantity in these experiments is the probe-to-probe distance, which is identical with the polymer end to end distance only in the case of nonperturbing point probes.

For both short polymer chains and end-tagged polymers, a more appropriate description of the desired distribution function can be obtained with a freely jointed chain model employing two or more statistical segment (step) lengths: one representing the terminal chain segments and a second corresponding to the inner statistical segments. Such distribution functions enable consideration of both chain

†Permanent address: Chemistry Department, Brown University, Providence, RI 02912.

0024-9297/88/2221-1145$01.50/0