(4) A. Dondos, P. Rempp, and H. Benoit, *Polymer*, **16**, 698 (1975).
(5) S. Krause, *J. Phys. Chem.*, **68**, 1948 (1964).
(6) H. Utiyama, K. Takenaka, M. Mizumori, M. Fukuda, Y. Tsunashima, and M. Kurata, *Macromolecules*, **7**, 515 (1974).
(7) H. Utiyama, K. Takenaka, M. Mizumori, and M. Fukuda, *Macromolecules*, **7**, 28 (1974).
(8) T. Tanaka, T. Kotaka, and H. Inagaki, *Macromolecules*, **7**, 311 (1974).
(9) J. Prud'homme and S. Bywater, *Macromolecules*, **4**, 543 (1971).
(10) J. G. Zilliox, J. E. L. Roovers, and S. Bywater, *Macromolecules*, **8**, 573 (1975).
(11) J. P. Cotton, D. Decker, H. Benoit, B. Farnoux, J. Higgins, J. Jannink, R. Ober, C. Picot, and J. des Cloizeaux, *Macromolecules*, **7**, 863 (1974).
(12) R. G. Kirste, W. A. Kruse, and J. Shelten, *J. Makromol. Chem.*, **162**, 299 (1972).
(13) D. G. H. Ballard, J. Shelten, and C. D. Wignall, *Eur. Polym. J.*, **9**, 965 (1973).
(14) J. P. Cotton, D. Decker, B. Farnoux, G. Jannink, R. Ober, and C. Picot, *Phys. Rev. Lett.*, **32**, 1170 (1974).
(15) R. G. Kirste and W. A. Kruse, *Polymer*, **16**, 120 (1975).
(16) J. P. Cotton, B. Farnoux, and G. Jannink, *J. Chem. Phys.*, **57**, 290 (1972).
(17) J. S. King, G. C. Summerfield, and R. Ullman, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **16**, 410 (1975).
(18) For example: F. Kohler, "The Liquid State", Verlag Chemie, Weinheim/Bergstr., Germany, 1972; Chapter 4, or H. Boutin and S. Yip, "Molecular Spectroscopy with Neutrons", MIT Press, Cambridge, Mass., 1968.
(19) A. S. Hyman, *Macromolecules*, **8**, 849 (1975).
(20) For example: M. B. Huglin, Ed., "Light Scattering from Polymer Solutions", Academic Press, New York, N.Y., 1972; or H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971.
(21) F. Zernicke and J. A. Prins, *Z. Phys.*, **41**, 184 (1927).
(22) P. Debye and H. Menke, *Phys. Z.*, 797 (1930).
(23) For example: C. Tanford, "Physical Chemistry of Macromolecules", Wiley, New York, N.Y., 1961.
(24) A. Peterlin, *J. Chem. Phys.*, **23**, 2464 (1955).
(25) A. J. Hyde, *Trans. Faraday Soc.*, **56**, 591 (1960).
(26) O. B. Ptitsyn, *Zh. Fiz. Khim.*, **31**, 1091 (1957); or ref 20, Chapter 7.
(27) J. Mazur and D. McIntyre, *Macromolecules*, **8**, 464 (1975).
(28) D. J. Coumou, *J. Colloid Sci.*, 408 (1960).
(29) J. H. O'Mara and D. McIntyre, *J. Phys. Chem.*, **63**, 1435 (1959).
(30) L. J. Fetters, *J. Res. Natl. Bur. Stand., Sect. A*, **70a**, 5, 421 (1966).
(31) G. E. Bacon, "Neutron Differaction", Oxford, 1962.
(32) J. Mazur, *Natl. Bur. Stand. (U.S.), Tech. Note*, in press.
(33) D. Y. Yoon and P. J. Flory, *Polymer*, **9**, 645 (1975).
(34) J. D. Matlack, A. L. Resnick, and R. J. Samuels, *J. Polym. Sci.*, **17**, 391 (1955).
(35) P. J. Flory, "Statistic Mechanics of Chain Molecules", Interscience, New York, N.Y., 1969.
(36) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **20**, 85 (1952).
(37) A. Oth and P. Doty, *J.* Phys. Chem., **56**, 43 (1952).
(38) W. Burchard, *Polymer*, **10**, 29 (1969).
(39) B. H. Zimm, *J. Chem. Phys.*, **16**, 1093 (1948).
(40) A. C. Albrecht, *J. Chem. Phys.*, **27**, 1014 (1957).
(41) Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

Conformation of Flexible Polymers Near an Impermeable Surface

Takeshi Tanaka

Laboratory of Polymer Separation and Characterization, Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611, Japan. *Received April 15, 1976*

ABSTRACT: Statistics on a random-flight chain which is bound on or near an impermeable, noninteracting planar surface with one end or both ends were developed. Probability densities of finding a given number of segments at respectively specified locations were obtained as functions of the location(s) of end segment(s). From these functions some new information about the conformational properties of flexible polymers near the surface was derived such as overall density distribution of segments and moments of segment distribution about the end segment and about the center of mass, all as functions of the location(s) of end segment(s). As for the so-called "tail" chain, the first-order coefficient of the perturbation theory of excluded-volume effects concerning the mean-square end-to-end distance was also derived.

The statistics of random flights near impermeable surfaces are important in understanding the behavior of flexible polymer molecules under various situations such as adsorption onto interfaces, stabilization of colloidal dispersions, partition equilibrium in gel permeation chromatography, and two-phase formation in crystalline polymers and in block copolymers. In particular, random-flight chains attached on a flat surface with one end ("tail" chain) or both ends ("loop" chain) are important as the simplest models. For these models the probability densities $f_n(Z_i)$ of finding the ith segment of a chain with size n at a normal-to-surface distance Z_i have been obtained by Hoeve,[1] Meier,[2] and Hesselink,[3] and the overall density distribution of segments has been calculated.[3] Recently, Lax[4] examined the effects of volume exclusion between segments on the function $f_n(Z_i)$ by a method of exactly enumerating the number of self-avoiding walks on a lattice.

In this paper we also deal with a random-flight chain near a planar surface. We first formulate the conditional probability densities $P_n(Z_i, Z_j, Z_k, \ldots)$ of finding series of segments $(i, j, k, \ldots)$ at respective positions $(Z_i, Z_j, Z_k, \ldots)$, when the chain is bound at given distance(s) from the surface with one end ("taillike" chain) or both ends ("looplike" chain). This generalization enables us to calculate various quantities of interest such as overall density distribution of segments as a function of the distance(s) of the end segment(s) from the surface, moments of segment distribution about the end segment and about the center of mass, and coefficients of perturbation theory of excluded-volume effects. The moments are important especially when we deal with radiation scattering from such molecules. The perturbation theory offers another approach to the excluded-volume problem. Some results on these points will be given below.

Formulation

Consider a random-flight chain with $n + 1$ segments (size n) serially numbered from 0 to n. Assuming an impermeable, noninteracting plane at $Z = 0$ of orthogonal coordinate system (X, Y, Z), we can write the conditional probability density $P_n(Z_n/Z_0)$ of finding the last (nth) segment at Z_n with the first (0th) segment fixed at $Z_0 \geq 0$, as[5,2]

$$P_n(Z_n/Z_0) = K_1 \{\exp[-\beta_{0n}(Z_0 - Z_n)^2] - \exp[-\beta_{0n}(Z_0 + Z_n)^2]\} \quad (1)$$

Here K_1 is the normalization constant given by

$$K_1 = (\beta_{0n}/\pi)^{1/2}/\mathrm{erf}(\beta_{0n}^{\ 1/2} Z_0) \quad (2)$$

$$\beta_{pq} = 3/[2(q-p)b^2],\ p < q \quad (3)$$

$$\mathrm{erf}(x) = (2/\pi^{1/2})\int_0^x \exp(-t^2)\,\mathrm{d}t \quad (4)$$

with b^2 being the mean-square segment length. Henceforth, we refer to such a chain as a "taillike" chain. A "tail" chain is a special case where $Z_0 = 0$, i.e., the 0th segment is bound *on* the surface.

Analogously the bivariate conditional probability density $P_n(Z_i, Z_n/Z_0)$ of finding the i- and nth segments at Z_i and Z_n, simultaneously, with the 0th segment fixed at Z_0 can be written as

$$P_n(Z_i, Z_n/Z_0) = K_2 P_i(Z_i/Z_0)\{\exp[-\beta_{in}(Z_i - Z_n)^2] - \exp[-\beta_{in}(Z_i + Z_n)^2]\} \quad (5)$$

where $P_i(Z_i/Z_0)$ refers to a chain with size i, and the normalization factor K_2 is obtained by integrating eq 5 with respect to Z_i over $Z_i = 0$ to ∞ and comparing the result with eq 1. Proceeding in this manner, we obtain the conditional probability density of any order as below:

$$P_n(Z_i, Z_j, \ldots, Z_m, Z_n/Z_0) = [\mathrm{erf}(\beta_{0n}{}^{1/2}Z_0)]^{-1}(Q_{0i}Q_{ij}\ldots Q_{mn}) \quad (6)$$

$$Q_{pq} = (\beta_{pq}/\pi)^{1/2}\{\exp[-\beta_{pq}(Z_p - Z_q)^2] - \exp[-\beta_{pq}(Z_p + Z_q)^2]\} \quad (7)$$

$$(p < q) = (0 < i < j < \ldots < m < n)$$

In particular, defining the function f_n as

$$f_n = \lim_{Z_0 \to 0} P_n \quad (8)$$

then we have

$$f_{n,\mathrm{tail}}(Z_i, Z_j, Z_k, \ldots, Z_m, Z_n) = 2\beta_{0n}{}^{-1/2}\beta_{0i}{}^{3/2}Z_i \exp(-\beta_{0i}Z_i{}^2)(Q_{ij}Q_{jk}\ldots Q_{mn}) \quad (9)$$

Equations 6 and 9 are the normalized probability densities of taillike and tail chains, respectively. When the position of the nth segment is not specified, we find on integration of eq 6 and 9 with respect to Z_n that Q_{mn} in those equations are to be replaced with $\mathrm{erf}(\beta_{mn}{}^{1/2}Z_m)$.

The corresponding expression for "looplike" chains with the first and last segments fixed at Z_0 and Z_n (both ≥ 0), respectively, is given as

$$P_n(Z_i, Z_j, \ldots, Z_m/Z_0, Z_n) = P_n(Z_i, Z_j, \ldots, Z_m, Z_n/Z_0)/P_n(Z_n/Z_0) = (Q_{0i}Q_{ij}\ldots Q_{mn})/Q_{0n} \quad (10)$$

Again, letting $Z_0 \to 0$ and $Z_n \to 0$, we have

$$f_{n,\mathrm{loop}}(Z_i, Z_j, Z_k, \ldots, Z_l, Z_m) = (4/\pi^{1/2})(\beta_{0i}\beta_{mn}/\beta_{0n})^{3/2}[Z_i \exp(-\beta_{0i}Z_i{}^2)] \times (Q_{ij}Q_{jk}\ldots Q_{lm})[Z_m \exp(-\beta_{mn}Z_m{}^2)] \quad (11)$$

for the normalized probability density of loop chains.

Expressions equivalent to $f_{n,\mathrm{tail}}(Z_i)$ and $f_{n,\mathrm{loop}}(Z_i)$ have been obtained by Hesselink[3] and by Hoeve,[1] respectively, through a somewhat more complicated procedure based on a lattice-walk model.

Overall Density Distribution of Segments

The overall density distribution of segments of taillike chains, $\rho_n(Z/Z_0)$, normalized to unity is given as

$$\rho_n(Z/Z_0) = (n+1)^{-1}\sum_i P_n(Z_i/Z_0) \quad (12)$$

Putting eq 6 into eq 12, converting the summation to an integral, and setting $Z_i = Z$ for all i, we have

$$\rho_n(Z/Z_0) = (\beta_{0n}/\pi)^{1/2}[(n+1)\,\mathrm{erf}(\beta_{0n}{}^{1/2}Z_0)]^{-1} \times \int_0^n \mathrm{erf}(\beta_{in}{}^{1/2}Z)\{\exp[-\beta_{0i}(Z_0 - Z)^2] - \exp[-\beta_{0i}(Z_0 + Z)^2]\}\,\mathrm{d}i \quad (13)$$

This integration can be performed through the Laplace folding operation to give

$$\rho_n(Z/Z_0) = [2\beta^{1/2}/\mathrm{erf}(\beta^{1/2}Z_0)][p_1\,\mathrm{erf}(p_1) + p_2\,\mathrm{erf}(p_2) - p_3\,\mathrm{erf}(p_3) - p_4\,\mathrm{erf}(p_4) + \pi^{-1/2}(e^{-p_1{}^2} + e^{-p_2{}^2} - e^{-p_3{}^2} - e^{-p_4{}^2})] \quad (14)$$

$$p_1 = \beta^{1/2}|Z - Z_0|,\ p_2 = \beta^{1/2}(2Z + Z_0)$$

$$p_3 = \beta^{1/2}(Z + Z_0),\quad p_4 = \beta^{1/2}(|Z - Z_0| + Z)$$

where, henceforth, $\beta = \beta_{0n} = 3/(2nb^2)$. For $Z_0 \to 0$, eq 14 converges to the distribution of tail chains given previously;[3]

$$\rho_{n,\mathrm{tail}}(Z) = 2(\pi\beta)^{1/2}[\mathrm{erf}(2\beta^{1/2}Z) - \mathrm{erf}(\beta^{1/2}Z)] \quad (15)$$

The density distribution of looplike chains $\rho_n(Z/Z_0, Z_n)$ can be calculated similarly. The result is

$$\rho_n(Z/Z_0, Z_n) = (\beta/Q_{0n})[\mathrm{erf}(q_1) + \mathrm{erf}(q_2) - \mathrm{erf}(q_3) - \mathrm{erf}(q_4)] \quad (16)$$

$$q_1 = \beta^{1/2}(|Z - Z_0| + Z + Z_n)$$

$$q_2 = \beta^{1/2}(|Z - Z_n| + Z + Z_0)$$

$$q_3 = \beta^{1/2}(|Z - Z_0| + |Z - Z_n|)$$

$$q_4 = \beta^{1/2}(2Z + Z_0 + Z_n)$$

Again, for $Z_0 \to 0$ and $Z_n \to 0$, we have

$$\rho_{n,\mathrm{loop}}(Z) = 8\beta Z \exp(-4\beta Z^2) \quad (17)$$

for the distribution of loop chains.[3]

In Figures 1 and 2 respectively eq 14 and 16 are plotted against Z for a few values of Z_0 ($= Z_n$, for looplike chains). As Z_0 increases from zero, both $\rho_n(Z/Z_0)$ and $\rho_n(Z/Z_0, Z_n)$ apparently become somewhat sharper than the $Z_0 = 0$ curves, as indicated by the peak heights. With further increase of Z_0, both curves become broader again approaching the symmetrical curves for the free chains.[6] Very crudely, the curves become almost indistinguishable from those of the free chains for $Z_0 > 1.0(nb^2)^{1/2}$ (for taillike chains) and $Z_0 > 0.7(nb^2)^{1/2}$ (for looplike chains).

Moments of Segment Distribution

The first and second moments $\langle Z\rangle_{(0)}$ and $\langle Z^2\rangle_{(0)}$ of segment distribution about the first segment are given by

$$\langle Z\rangle_{(0)} = \int_0^\infty (Z - Z_0)\rho_n(Z)\,\mathrm{d}Z \quad (18)$$

$$\langle Z^2\rangle_{(0)} = \int_0^\infty (Z - Z_0)^2\rho_n(Z)\,\mathrm{d}Z \quad (19)$$

with ρ_n given by eq 14 and 15 for taillike chains and by eq 16 and 17 for looplike chains. Analytical results of the above integrations are not given here due to their complexity. In Figures 3 and 4, $\langle Z\rangle_{(0)}$ and $\langle Z^2\rangle_{(0)}$ are plotted against Z_0 for taillike chains and looplike chains (with $Z_0 = Z$), respectively. For both models, the first moment $\langle Z\rangle_{(0)}$ naturally decreases monotonously to zero with increasing Z_0, while the second moment $\langle Z^2\rangle_{(0)}$ decreases at first and, going through a minimum, increases to approach the value for the free chain.

The second moment $\langle Z^2\rangle_{(G)}$ about the center of mass is given by

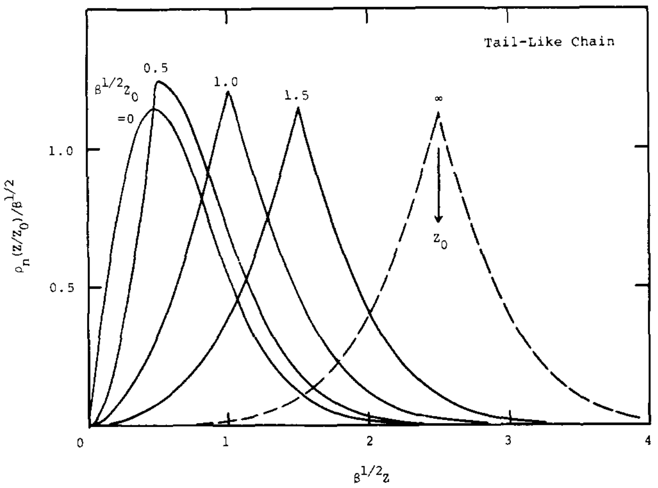

Figure 1. Overall density distribution of segments of taillike chains, $\rho_n(Z/Z_0)$, vs. normal-to-surface distance Z. The first segment is fixed at Z_0 as indicated in the figure; $\beta = 3/(2nb^2)$.

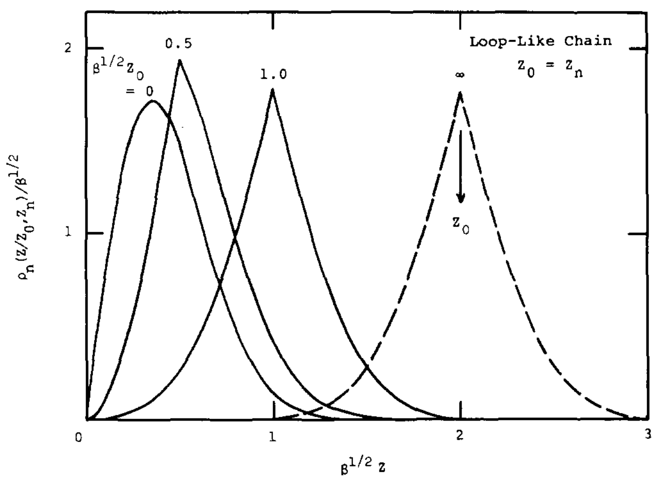

Figure 2. Overall density distribution of segments of looplike chains, $\rho_n(Z/Z_0, Z_n)$, vs. normal-to-surface distance Z. The first and last segments are fixed at Z_0 (=Z_n) as indicated in the figure; $\beta = 3/(2nb^2)$.

$$\langle Z^2\rangle_{(G)} = (n+1)^{-2} \sum\sum_{i<j} \int_0^\infty \int_0^\infty \times (Z_i - Z_j)^2 P_n(Z_i, Z_j)\, dZ_i\, dZ_j \quad (20)$$

with P_n given by eq 6 and 9 for taillike chains and by eq 10 and 11 for looplike chains. Converting the summations to integrals and carrying out the quadruple integration,[7] we have the results shown in Figures 3 and 4. Again, we have chosen the case of $Z_0 = Z_n$ for looplike chains. It can be seen that with both models $\langle Z^2\rangle_{(G)}$ goes through a minimum. The behavior of $\langle Z^2\rangle_{(G)}$ and $\langle Z^2\rangle_{(0)}$ corresponds to the before-mentioned sharpening effect of the density distribution curves in an intermediate range of Z_0.

The mean-square radius of gyration $\langle S^2\rangle$ of taillike chains is obtained by summing $\langle Z^2\rangle_{(G)}$ and the other two components $\langle X^2\rangle_{(G)}$ and $\langle Y^2\rangle_{(G)}$, both being $nb^2/18$. The maximum and minimum values of $\langle S^2\rangle$ are: $\langle S^2\rangle/\langle S^2\rangle_f = 1.02_9$ ($Z_0 = 0$) and 0.95_5 ($Z_0 \sim 0.73(nb^2)^{1/2}$), respectively, where $\langle S^2\rangle_f$ (=$nb^2/6$) is the value for the free chain. The corresponding ratios of the mean-square end-to-end distances $\langle R^2\rangle/\langle R^2\rangle_f$ are 4/3 ($Z_0 = 0$) and 0.914 ($Z_0 = 0.74(nb^2)^{1/2}$), respectively, showing that the chain can be significantly elongated (for small Z_0) or contracted (for an intermediate range of Z_0) due to the barrier,

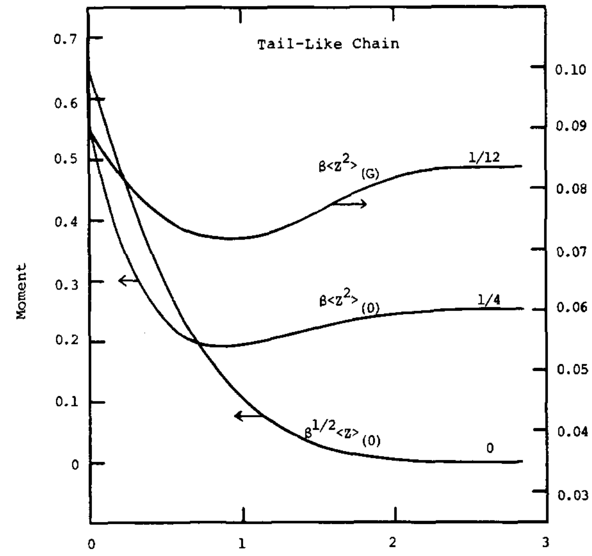

Figure 3. First and second moments, $\langle Z\rangle_{(0)}$ and $\langle Z^2\rangle_{(0)}$, about the first segment, and second moment $\langle Z^2\rangle_{(G)}$ about the center of mass of taillike chains vs. normal-to-surface distance of the first segment Z_0; $\beta = 3/(2nb^2)$. Figure attached to each curve is the limiting value for $Z_0 = \infty$ (i.e., a free chain).

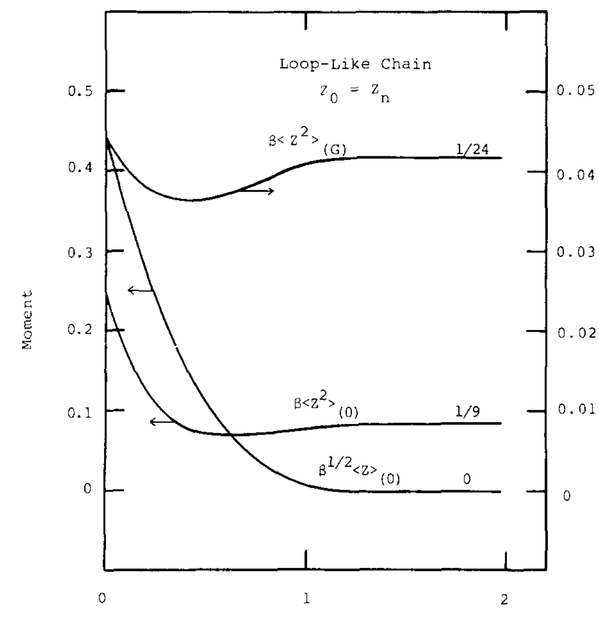

Figure 4. First and second moments, $\langle Z\rangle_{(0)}$ and $\langle Z^2\rangle_{(0)}$, about the first segment, and second moment $\langle Z^2\rangle_{(G)}$ about the center of mass of looplike chains vs. normal-to-surface distance Z_0 (=Z_n) of the first (and last) segment; $\beta = 3/(2nb^2)$. Figure attached to each curve is the limiting value for $Z_0 = Z_n = \infty$ (i.e., a free ring chain).

even though the value of $\langle S^2\rangle$ is nearly insensitive to such effects. A similar conclusion is obtained for looplike chains. Thus, $\langle S^2\rangle/\langle S^2\rangle_f$ is close to unity for any Z_0 for a chain terminally bound on or near, for example, the outside surface of a sphere, whereas the ratio for a chain bound to the inside surface would become considerably smaller than unity in certain cases.

The information obtained in this section should be useful[8] when, for example, one deals with the radiation scattering from colloidal dispersions such as block copolymer micelles.[9]

First-Order Perturbation Theory. End-to-End Distance of Tail Chain

The first-order coefficient C_1 of the perturbation theory of excluded volume effects concerning the mean-square end-to-end distance $\langle R^2 \rangle$ is given by[10]

$$C_1 = (2\pi b^2/3)^{3/2}/[\langle R^2 \rangle_0 (n+1)^{1/2}] \times \sum_{i<j}\sum \int R^2[P(\mathbf{0}_{ij})P(\mathbf{R}) - P(\mathbf{0}_{ij}, \mathbf{R})]\, d\mathbf{R} \quad (21)$$

where $\langle R^2 \rangle_0$ ($=4nb^2/3$, for the tail chain) is the unperturbed dimension, and $P(\mathbf{0}_{ij}, \mathbf{R})$, for example, is the probability density that the vector distance between the i- and jth segments is zero and the end-to-end vector is $\mathbf{R}$, simultaneously. Expressing eq 21 in an orthogonal coordinate system, applying eq 9 to the Z components of the probability functions, and carrying out the rather lengthy integration with respect to the coordinates, we have the following expression for the tail chain;

$$C_1 = \frac{1}{n+1}\sum_{i<j}\sum \left[\frac{1}{(j-i)^{1/2}(n-j+i)^{1/2}} - \frac{j^2+2ij-i^2}{(j+3i)^2[n(j+3i)-(i+j)^2]^{1/2}}\right] \quad (22)$$

Converting the summations to integrals, we arrive at[7]

$$\alpha^2 = \langle R^2 \rangle / \langle R^2 \rangle_0 = 1 + C_1 z + \ldots$$
$$C_1 = 1.26 \quad (23)$$

where z is the usual excluded-volume parameter.[10]

The value of C_1 is slightly smaller than the corresponding value of 4/3 for the free chain,[10] indicating that the excluded-volume effect is less significant in the tail chain. This would correspond to the fact that the tail chain is more elongated than the free chain, thereby resulting in a smaller chance of mutual interference of segments. However, the difference is trivial at least for small z. For large z, it might be of some significance to convert eq 23 to a third-power type equation following the method of Fixman.[11] The result is

$$\alpha^3 - 1 = 1.89z \quad (24)$$

Through comparison of eq 24 with the corresponding equation for the free chain,[11] i.e., $\alpha^3 - 1 = 2z$, we can estimate that the difference in α^2 is less than a few percent even for z as large as 10.

From the above and before-mentioned implication, it is expected that the coefficient C_1 for a taillike chain would be slightly larger than that for the free chain in a certain range of Z_0. This difference should be trivial as well. It is also possible to make similar calculations on, for example, the mean-square radius of gyration $\langle S^2 \rangle$. However, in view of the fact that $\langle S^2 \rangle$ is less sensitively influenced by the barrier than $\langle R^2 \rangle$, the difference between the taillike chain and the free chain should be less significant in $\langle S^2 \rangle$ than in $\langle R^2 \rangle$ as for the excluded-volume effects also. Thus, for most purposes, the excluded-volume effects in taillike chains may be adequately taken into account by multiplying the segment length b by α_f, which is the expansion factor for the corresponding free chain concerning the quantity in question. The situation is different for looplike chains, in which segments are more densely populated than in taillike chains. However, if we choose a suitable chain (a circular chain, for example) as the reference, the same conclusion might apply.

Acknowledgment. The author is greatly indebted to Professor G. C. Berry for his critical reading of the manuscript and valuable comments. Thanks are also due to Professors H. Inagaki and T. Kotaka for their useful suggestions and discussions.

References and Notes

(1) C. A. J. Hoeve, *J. Chem. Phys.*, **43**, 3007 (1965).
(2) D. J. Meier, *J. Phys. Chem.*, **71**, 1861 (1967).
(3) F. Th. Hesselink, *J. Phys. Chem.*, **73**, 3488 (1969).
(4) M. Lax, *Macromolecules*, **8**, 947 (1975).
(5) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids", 2d ed., Oxford University Press, London, 1959.
(6) The density distribution of a free chain with the first segment fixed at $Z = 0$ is given by $\rho_n(Z)/\beta^{1/2} = (2/\pi^{1/2})\exp(-\beta Z^2) - 2\beta^{1/2}|Z|[1 - \mathrm{erf}(\beta^{1/2}|Z|)]$, and that of a free chain with the first and last segments fixed at $Z = 0$ (a circular chain) by $\rho_n(Z)/\beta^{1/2} = \pi^{1/2}[1 - \mathrm{erf}(2\beta^{1/2}|Z|)]$.
(7) Numerical calculations were made by a Monte Carlo method, whenever necessary. The results are correct to ±1%.
(8) The implication of the tail chain has been utilized for investigation of block copolymer solutions. See, T. Tanaka, T. Kotaka, and H. Inagaki, *Macromolecules*, **7**, 311 (1974); **9**, 561 (1976). In these papers a hypothetical block copolymer model is referred to, which is based on the approximately correct distribution of Meier[2,3] instead of the correct distribution $f_{n,\mathrm{tail}}(Z_i)$. On this point, see, T. Tanaka, T. Kotaka, and H. Inagaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, **54**, 91 (1976).
(9) Light scattering from block copolymer micelles will be discussed elsewhere in detail.
(10) See, for example, M. Fixman, *J. Chem. Phys.*, **23**, 1656 (1955).
(11) M. Fixman, *J. Chem. Phys.*, **36**, 306, 3132 (1962).