Shape distributions of Gaussian molecules

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(13) Kholodenko, A.; Freed, K. F. *J. Chem. Phys.* **1983**, *78*, 7390.
(14) Kosmas, M.; Freed, K. F. *J. Chem. Phys.* **1978**, *69*, 3647.
(15) Adler, R.; Freed, K. F. *J. Chem. Phys.* **1980**, *72*, 4186.
(16) (a) Douglas, J.; Freed, K. F. *Macromolecules* **1984**, *17*, 2354. (b) Douglas, J. F.; Freed, K. F. "Polydispersity Corrections on Excluded Volume Dependence in Flexible Polymers", to appear in *J. Phys. Chem.*
(17) Douglas, J.; Freed, K. F. *Macromolecules* **1983**, *16*, 1800.
(18) Oono, Y.; Freed, K. F. *J. Chem. Phys.* **1981**, *75*, 993.
(19) Ohta, T.; Oono, Y. *Phys. Lett. A* **1982**, *A89*, 460.
(20) Ohta, T.; Oono, Y.; Freed, K. F. *J. Chem. Phys.* **1981**, *74*, 6458.
(21) Oono, Y.; Freed, K. F. *J. Phys. A* **1982**, *15*, 1931.
(22) Oono, Y.; Ohta, T. *Phys. Lett. A* **1981**, *85*, 480.
(23) Oono, Y.; Kohmoto, M. *J. Chem. Phys.* **1983**, *78*, 520.
(24) Lipkin, M.; Oono, Y.; Freed, K. *Macromolecules* **1981**, *14*, 1270.
(25) Miyake, A.; Freed, K. F. *Macromolecules* **1983**, *16*, 1228.
(26) Miyake, A.; Freed, K. F. *Macromolecules* **1984**, *17*, 678.
(27) (a) Freed, K. F. *J. Chem. Phys.* **1983**, *79*, 3121. (b) Nemirovsky, A. M.; Freed, K. F. "Excluded Volume Effects for Polymers in the Presence of Interacting Surfaces", submitted manuscript.
(28) The motivation for choosing this rescaling is the minimization of the errors involved in the ϵ-expansion procedure. Discussion of the rescaling is made in ref 11.
(29) Tanaka, G. *Macromolecules* **1980**, *13*, 1513.
(30) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(31) Stockmayer, W. H.; Albrecht, A. *J. Polym. Sci.* **1958**, *32*, 215.
(32) Weill, G.; des Cloizeaux, J. *J. Phys. (Orsay, Fr.)* **1979**, *40*, 99.
(33) Akcasu, A.; Han, C. *Macromolecules* **1979**, *12*, 276. We note that Mattice (preprint) has considered numerically the ratio $\alpha_{R^2}{}^2/\alpha_{S^2}{}^2$ in the self-avoiding limit for long chains and found in his simulations $\mu = 1.028$, which is in much better agreement with the RG theory.
(34) Daoud, M. Thesis, Université de Paris VI, Paris, France, 1977.
(35) Farnoux, B.; et al. *J. Phys. (Orsay, Fr.)* **1978**, *39*, 77.
(36) Cotton, J. P. *J. Phys. Lett.* **1980**, *41*, 231.
(37) Le Guillou, J.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.
(38) Lawrie, I. D. *J. Phys. A* **1976**, *9*, 435.
(39) Miyaki, Y.; Einaga, Y.; Hirosye, T.; Fujita, H. *Macromolecules* **1977**, *10*, 1356.
(40) Gobush, W.; Solc, K.; Stockmayer, W. H. *J. Chem. Phys.* **1974**, *60*, 12.
(41) Witten, T.; Shäfer, L. *J. Chem. Phys.* **1981**, *74*, 2582.
(42) (a) des Cloizeaux, J. *J. Phys. (Orsay, Fr.)* **1981**, *42*, 635. (b) des Cloizeaux, J.; Noda, T. *Macromolecules* **1982**, *15*, 1505.
(43) Kniewske, R.; Kulicke, W. M. *Makromol. Chem.* **1983**, *184*, 2173.
(44) Shimada, J.; Yamakawa, H. *J. Polym. Sci.* **1978**, *16*, 1927.
(45) Tanaka, G.; Imai, S.; Yamakawa, H. *J. Chem. Phys.* **1970**, *52*, 2639.
(46) (a) Norisuye, T.; Kawahara, K.; Teramoto, A.; Fujita, H. *J. Chem. Phys.* **1968**, *49*, 4330. (b) Kawahara, K.; Norisuye, T.; Fujita, H. *J. Chem. Phys.* **1968**, *49*, 4339.
(47) We use the value of $\Phi_0 = 2.51 \times 10^{23}$ calculated by Zimm (*Macromolecules* **1980**, *13*, 592) which is obtained in a numerical simulation where the usual preaveraging approximation is not employed. Experimental results for Φ_0 which are close to Zimm's values are frequently reported in the literature. The values of Φ_Θ and P_Θ, however, are not universal (see ref 1) so that it is best to regard these as phenomenological constants which are "reasonably" estimated by the Gaussian theory. There is still some controversy regarding his simulation so that it must be regarded as a tentative result (see ref 15).
(48) Tsitsilianis, C.; Pierri, E.; Dondos, A. *Polym. Lett.* **1983**, *21*, 685.
(49) Sarizin, D.; Francois, J. *Polymer* **1978**, *19*, 699.
(50) Suzuki, H. *Br. Polym. J.* **Dec 1982**, 137.
(51) Nishio, I.; Swislow, G.; Sun, S.; Tanaka, T. *Nature (London)* **1982**, *300*, 243.
(52) Tanaka, G. *Macromolecules* **1982**, *15*, 1028.
(53) Sun, S.; Nishio, I.; Swislo, G.; Tanaka, T. *J. Chem. Phys.* **1980**, *73*, 5971.
(54) Bauer, D.; Ullman, R. *Macromolecules* **1980**, *13*, 392.
(55) Perzynski, R.; Adam, M.; Delsanti, M. *J. Phys. (Orsay, Fr.)* **1982**, *43*, 129.
(56) Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4550.
(57) Abdel-Azim, A.; Huglin, M. *Polymer* **1982**, *23*, 1859.
(58) Shultz, A.; Flory, P. *J. Polym. Sci.* **1955**, *15*, 231.
(59) Noel, R.; Patterson, D.; Somcynsky, T. *J. Polym. Sci.* **1960**, *42*, 561.
(60) Simionescu, C. I.; Simionescu, B. C. *Makromol. Chem.* **1983**, *184*, 829.
(61) Matsumoto, T.; Nishioka, N.; Fujita, H. *J. Polym. Sci.* **1972**, *10*, 23.
(62) Akita, S.; Einaga, Y.; Miyaki, Y.; Fujita, H. *Macromolecules* **1976**, *9*, 774.
(63) Slagowski, E. Ph.D. Thesis, University of Akron, Akron, OH, 1972.
(64) Fakuda, M.; Fukutomi, M.; Kato, Y.; Hashimoto, T. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 871.
(65) Fox, T., Jr.; Flory, P. *J. Phys. Colloid Chem.* **1949**, *53*, 197.
(66) Berry, G. C. *J. Chem. Phys.* **1967**, *46*, 1338.
(67) Norisuye, T.; Kawahara, K.; Fujita, H. *Polym. Lett.* **1968**, *6*, 849.
(68) Noda, I.; Mizutani, K.; Kato, T. *Macromolecules* **1977**, *10*, 618.
(69) Ooms, G.; Mijnlieff, P.; Beckers, H. *J. Chem. Phys.* **1970**, *53*, 4123.
(70) Noda, I.; et al. *Macromolecules* **1970**, *6*, 787.
(71) Roovers, J.; Toporowski, P. M. *J. Polym. Sci., Phys. Ed.* **1980**, *18*, 1907.
(72) Barrett, A. *J. Phys. A* **1976**, *9*, L-33.

Shape Distributions for Gaussian Molecules†

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ABSTRACT: The general solution for the distribution function of the gyration tensor for Gaussian molecules in k-dimensional space is given in terms of zonal polynomials. The distribution for two-dimensional rings is reviewed, and that for three-dimensional ellipsoids of revolution is formulated so as to reduce the calculation to a sum of one-dimensional integrals.

Introduction

The distributions of shapes of linear chains in three dimensions and of both linear and circular chains in two dimensions have been studied by Šolc, Stockmayer, and Gobush in a series of original papers.[1–3] Since its inception, the theory of these distributions has seemed to be formidable, but it has nonetheless attracted some attention because of potential applications to rubber elasticity[4,5] and to solution thermodynamics.[6,7]

The gyration tensor **S** for a system of particles with masses m_i, $1 \le i \le n$, is defined as

$$\mathbf{S} = M^{-1}\mathbf{X}\mathbf{M}\mathbf{X}' \tag{1}$$

If the particles are imbedded in a k-dimensional space, **X** is a $k \times n$ matrix of coordinates in an arbitrarily oriented frame with origin at the center of mass, $\mathbf{X}'$ is the transpose

†Dedicated to Professor Walter H. Stockmayer on the occasion of his 70th birthday.

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of $\mathbf{X}$, $\mathbf{M} = \mathrm{diag}\,(m_1,m_2,...,m_n)$ and $M = \mathrm{tr}\,(\mathbf{M})$ = total mass. For present purposes, all particles will have the same mass, and eq 1 reduces to

$$\mathbf{S} = n^{-1}\mathbf{X}\mathbf{X}' \tag{2}$$

The shape distribution of the mechanical system is determined by the probability distribution of the principal components (eigenvalues or latent roots) of $\mathbf{S}$ when some potential acts between the particles. The Gaussian model is a useful starting point for this problem; the corresponding potential is harmonic with zero mean and is additive over bonded pairs of mass elements. These interactions are the equivalent bonds in the spring-bead model. In this approximation, the effective potential of mean force $\beta\mathbf{V}(\mathbf{X})$ for a molecule of arbitrary connectivity is

$$\beta\mathbf{V}(\mathbf{X}) = \gamma\,\mathrm{tr}\,(\mathbf{X}\mathbf{K}\mathbf{X}') = \mathrm{tr}\,(\mathbf{X}\mathbf{K}_\gamma\mathbf{X}') \tag{3}$$

where $\beta = 1/k_\mathrm{B}T$, $\gamma = k/2\langle l^2\rangle_0$, and $\mathbf{K}_\gamma = \gamma\mathbf{K}$ is a Kirchhoff matrix. (The notation used here follows that of a previous review of the literature on the distribution of the radius of gyration.[8])

The highest order probability distribution that is sought is for k unequal principal components of $\mathbf{S}$, and this can be written as

$$P(\mathbf{S})\,\mathrm{d}\mathbf{S} = (\mathrm{d}\mathbf{S}/Z)\int...\int \mathrm{etr}\,(-\mathbf{X}\mathbf{K}_\gamma\mathbf{X}')\delta(\mathbf{X}\mathbf{J}')\,\mathrm{d}\mathbf{X}/\mathrm{d}\mathbf{S} \tag{4}$$

where Z is the configuration integral, etr $(\cdot) = \exp[\mathrm{tr}\,(\cdot)]$, $\mathrm{d}\mathbf{X} = \prod_{i=1}^{n}\prod_{\alpha=1}^{k}\mathrm{d}x_i^\alpha$, and $\mathrm{d}\mathbf{S} = \prod_{\alpha\le\beta}\mathrm{d}S_{\alpha\beta}$. The δ function, with $\mathbf{J} = (1,1,...,1)$, fixes the origin of coordinates at the center of mass. The integral in eq 4 occurs in multivariate statistics,[9] as has been communicated to the author by Richards.[10] This theory is used here to solve, as far as is generally possible, eq 4 and its lower dimensional analogues.

The theory to be presented differs somewhat from that formulated by Šolc.[2,3] It is more direct than his method, but it gives equivalent results. The problems considered under each heading are as follows: (I) the general k-dimensional problem, i.e., solution of eq 4; (II) the formulation of eq 4 in Eckart coordinates; (III) the asymptotic distribution for the general case; (IV) two-dimensional rings; and (V) two equal components of $\mathbf{S}$ in three dimensions, i.e., ellipsoids of revolution.

I. The General Problem

The probability distribution of $\mathbf{S}$, $P(\mathbf{S})\,\mathrm{d}\mathbf{S}$, may be formulated as an integral over the configuration space in two different ways. The first, to be considered in this section, is had by restricting the configuration integral to yield zero when $\mathbf{S} \neq n^{-1}\mathbf{X}\mathbf{X}'$. The other method, described in the next section, makes use of Eckart coordinates. The constraint is written as

$$P(\mathbf{S})\,\mathrm{d}\mathbf{S} = (\mathrm{d}\mathbf{S}/Z)\int\delta(\mathbf{S} - n^{-1}\mathbf{X}\mathbf{X}')\delta(\mathbf{X}\mathbf{J}')\,\mathrm{etr}\,(-\mathbf{X}\mathbf{K}_\gamma\mathbf{X}')\,\mathrm{d}\mathbf{X} \tag{5}$$

To solve eq 5, convert to normal coordinates[8] $\mathbf{Q} = \mathbf{X}\mathbf{T}'$, $\mathbf{T} \in \mathrm{SO}(n)$, chosen such that $\mathbf{T}\mathbf{K}_\gamma\mathbf{T}' = \Lambda = \mathrm{diag}\,(0,\gamma\lambda_1,...,\gamma\lambda_{n-1}) = \mathrm{diag}\,(0,\Lambda_\gamma)$. [The orthogonal group of $n \times n$ matrices is denoted by $\mathrm{O}(n)$; $\mathrm{SO}(n)$ is the subgroup of $\mathrm{O}(n)$ consisting of matrices with determinant +1.] The Jacobian of the transformation is +1. Since $\mathbf{K}_\gamma$ has a single zero eigenvalue if the molecule is connected, and since $\mathbf{T}$ contains a constant row, proportional to $\mathbf{J}$, we have

$$P(\mathbf{S})\,\mathrm{d}\mathbf{S} = (\mathrm{d}\mathbf{S}/Z)\int\delta(\mathbf{S} - n^{-1}\mathbf{Q}_0\mathbf{Q}_0')\,\mathrm{etr}\,(-\mathbf{Q}_0\Lambda_\gamma\mathbf{Q}_0')\,\mathrm{d}\mathbf{Q}_0 \tag{6}$$

where $\mathbf{Q}_0$ is $k \times (n-1)$, as obtained from $\mathbf{Q}$ by deletion of the coordinates corresponding to the center of mass motion.

The δ function is expressed as the Fourier integral

$$\delta(\mathbf{S} - n^{-1}\mathbf{Q}_0\mathbf{Q}_0') = (2\pi)^{-k(k+1)/2}\int\mathrm{etr}\,(i\mathbf{Y}\mathbf{S} - in^{-1}\mathbf{Y}\mathbf{Q}_0\mathbf{Q}_0')\,\mathrm{d}\mathbf{Y} \tag{7}$$

where $\mathrm{d}\mathbf{Y} = \prod_{\alpha\le\beta}\mathrm{d}y_{\alpha\beta}$, and

$$\mathbf{Y} = \begin{bmatrix} y_{11} & {}^1\!/_2 y_{12} & \cdots & {}^1\!/_2 y_{1k} \\ {}^1\!/_2 y_{12} & y_{22} & \cdots & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ {}^1\!/_2 y_{1k} & \cdot\;\cdot\;\cdot & \cdot\;\cdot & \cdot\, y_{kk} \end{bmatrix} \tag{8}$$

Let $\mathbf{q} = (q_1^1,q_2^1,...,q_{n-1}^1,q_1^2,q_2^2,...,q_{n-1}^k)$ be the row form of $\mathbf{Q}_0$. It is easy to show that if $\mathbf{Q}_0 \to \mathbf{A}\mathbf{Q}_0\mathbf{B}$, with $\mathbf{A}$ a $k \times k$ and $\mathbf{B}$ an $(n-1) \times (n-1)$ matrix, $\mathbf{q} \to \mathbf{q}(\mathbf{A}' \otimes \mathbf{B})$. It is apparent also that $\mathrm{d}\mathbf{Q}_0 = \mathrm{d}\mathbf{q}$. Insert eq 7 into eq 6, collect terms, and integrate over $\mathrm{d}\mathbf{q}$ to get

$$P(\mathbf{S})\,\mathrm{d}\mathbf{S} = \mathrm{d}\mathbf{S}\int\mathrm{etr}\,(i\mathbf{Y}\mathbf{S})|1 + in^{-1}\mathbf{Y} \otimes \Lambda_\gamma^{-1}|^{-1/2}\,\mathrm{d}\mathbf{Y} \tag{9}$$

where use has been made of

$$Z = \pi^{k(n-1)/2}|\Lambda_\gamma|^{-k/2} \tag{10}$$

Since $\mathbf{Y}$ is symmetric, $\mathbf{Y} = hyh'$, $h \in \mathrm{SO}(k)$ and $\mathbf{y} = \mathrm{diag}\,(y_1,...,y_k)$. The volume element in polar $(\mathbf{y},h)$ variables is computed with the following procedure. The metric $\mathrm{d}\xi^2 = \mathrm{d}\mathbf{x}\,\mathbf{G}\,\mathrm{d}\mathbf{x}'$, with $\mathbf{G}$ an $m \times m$ matrix and $\mathbf{x}$ a $1 \times m$ vector, has an associated volume element $\mathrm{d}V = |G|^{1/2}\prod_\alpha \mathrm{d}x_\alpha$. Consider

$$\mathrm{d}\xi^2 = \mathrm{tr}\,(\mathrm{d}\mathbf{Y}\,\mathrm{d}\mathbf{Y}') = \mathrm{tr}\,(\mathrm{d}\mathbf{Y}\,\mathrm{d}\mathbf{Y}) = \sum_\alpha \mathrm{d}y_{\alpha\alpha}^2 + {}^1\!/_2\sum_{\alpha<\beta}\mathrm{d}y_{\alpha\beta}^2 \tag{11}$$

This metric has a natural volume element $\mathrm{d}V = 2^{-k(k-1)/4}\prod_{\alpha\le\beta}\mathrm{d}y_{\alpha\beta}$. In terms of polar coordinates, $\mathrm{d}\mathbf{Y} = \mathrm{d}h\,yh' + h\,\mathrm{d}y\,h' + hy\,\mathrm{d}h' = h(\mathrm{d}y + \delta hy - y\delta h)h'$, with $\delta h = h'\,\mathrm{d}h = -\mathrm{d}h'\,h = -\delta h'$ since $h'h = 1$. Substitute this expression for $\mathrm{d}\mathbf{Y}$ into eq 11 to find

$$\mathrm{d}\xi^2 = \mathrm{tr}\,[\mathrm{d}\mathbf{y}^2 + (\delta h\mathbf{y} - \mathbf{y}\delta h)^2] = \sum_{\alpha=1}^{k}\mathrm{d}y_\alpha^2 + 2\sum_{\alpha<\beta}(y_\alpha - y_\beta)^2\delta h_{\alpha\beta}^2 \tag{12}$$

The volume element is thus

$$\prod_{\alpha\le\beta}\mathrm{d}y_{\alpha\beta} = 2^{(k-1)(k-2)/2}\prod_{\alpha\le\beta}|y_\alpha - y_\beta|\prod_\alpha\mathrm{d}y_\alpha\,\mathbf{d}h \tag{13}$$

where $\mathbf{d}h$ is the (unnormalized) Haar measure on $\mathrm{SO}(k)$.[9] [On the last point: $\mathrm{tr}\,(\mathrm{d}h\,\mathrm{d}h') = \mathrm{tr}\,(h'\,\mathrm{d}h\,\mathrm{d}h'\,h) = \mathrm{tr}\,(\delta h\delta h')$, with volume element $\mathbf{d}h$. This is both left and right invariant, since for any fixed $h_1,h_2 \in \mathrm{SO}(k){:}h \to h_1hh_2$ we have $\mathrm{tr}\,(h_1\,\mathrm{d}h\,h_2h_2'\,\mathrm{d}h'\,h_1') = \mathrm{tr}\,(\mathrm{d}h\,\mathrm{d}h')$.] In eq 13, a factor of 2^{k-1} has been divided out because of symmetry (see ref 9, p 104). Equation 9 now becomes

$$P(\mathbf{S})\,\mathrm{d}\mathbf{S} = \frac{\mathrm{d}\mathbf{S}}{2^{2k-1}\pi^{k(k+1)/2}}\int\mathrm{etr}\,(ihyh'\mathbf{S})|1 + in^{-1}\mathbf{y} \otimes \Lambda_\gamma^{-1}|^{-1/2}\prod_{\alpha<\beta}|y_\alpha - y_\beta|\prod_\alpha\mathrm{d}y_\alpha\,\mathbf{d}h \tag{14}$$

The last two steps to the general solution are to reduce $\mathrm{d}\mathbf{S}$ and to compute the integral over $\mathrm{SO}(k)$.

Since $\mathbf{S}$ is symmetric, it is the case that $\mathbf{S} = h_1'\mathbf{S}_\mathrm{d}h_1$, $h_1 \in \mathrm{SO}(k)$ and $\mathbf{S}_\mathrm{d} = \mathrm{diag}\,(S_1,S_2,...,S_k)$. All S_α are presumed to be distinct. Use again the calculation from eq 11 to eq 12 for tr (dS dS) to get

$$\mathrm{d}\mathbf{S} = 2^{1-k} \prod_{\alpha<\beta} |S_\alpha - S_\beta| \prod_\alpha \mathrm{d}S_\alpha \, \mathrm{d}\mathbf{h} \tag{15}$$

so that the polar form of $P(\mathbf{S})\,\mathrm{d}\mathbf{S}$ is

$$P(\mathbf{S})\,\mathrm{d}\mathbf{S} = P(\mathbf{S}_\mathrm{d}) \prod_{\alpha<\beta} |S_\alpha - S_\beta| \prod_\alpha \mathrm{d}S_\alpha \, \mathrm{d}\mathbf{h} \tag{16}$$

This is further simplified by integration over SO(k), with volume[9] $V[\mathrm{SO}(k)] = 2^{k-1}\pi^{k^2/2}/\Gamma_k(k/2)$, where

$$\Gamma_k(a) = \pi^{k(k-1)/4} \prod_{i=1}^{k} \Gamma[a - (i-1)/2], \quad \mathrm{Re}\,(a) > (k-1)/2$$

to give

$$P(\mathbf{S})\,\mathrm{d}\mathbf{S} = \boldsymbol{P}(\mathbf{S}_\mathrm{d}) \prod_{\alpha<\beta} |S_\alpha - S_\beta| \prod \mathrm{d}S_\alpha \tag{17}$$

with

$$\boldsymbol{P}(\mathbf{S}_\mathrm{d}) = C_k^{-1} \int \mathrm{etr}\,(ihyh'\mathbf{S}_\mathrm{d}) |1 + in^{-1}\mathbf{y} \otimes \Lambda_\gamma^{-1}|^{-1/2} \prod_{\alpha<\beta} |\, y_\alpha - y_\beta| \prod_\alpha \mathrm{d}y_\alpha \, \mathrm{d}\mathbf{h} \tag{18}$$

$$C_k = 2^{2k-1}\pi^{k(k+1)/4} \prod_{\alpha=1}^{k} \Gamma(\alpha/2) \tag{19}$$

In eq 18, use has been made of the left invariance of $\mathbf{dh}$, and the replacement $h_1 h \rightarrow h$ has been made in etr $(\cdot)$.

In the final step of this section, the integral over SO(k) in eq 18 will be computed. Šolc[2] calculated all terms in the expansion of etr $(\cdot)$ in terms of β functions for $k = 3$. The author, in hopes of eliciting a more compact solution to the integral over SO(3), posed this problem in the mathematical literature.[11] Its solution for all k was communicated to me by Richards,[10] who also pointed out that the same problem was earlier posed by Satake.[12] For $k = 2$ the integral is accomplished in terms of elementary functions in section IV. Here we are interested in the general case, $k > 2$, and so have to be content with a more complicated result. It follows from the work of James[9,13] that

$$\int_{\mathrm{SO}(k)} \mathrm{etr}\,(ihyh'\mathbf{S}_\mathrm{d})\,\mathrm{d}\mathbf{h} = V[\mathrm{SO}(k)] \sum_{m=0}^{\infty} \frac{i^m}{m!} \sum_\mu \frac{C_\mu(\mathbf{y}) C_\mu(\mathbf{S}_\mathrm{d})}{C_\mu(\mathbf{1}_k)} \tag{20}$$

where $C_\mu(X)$ is a zonal polynomial of degree m in the eigenvalues or latent roots of X. These polynomials are not known in their entirety, but there is an algorithm for their computation.[9,14] In eq 20, $\mu = (m_1, m_2, ..., m_k)$ is a partition of m into no more than m parts such that $m_j \geq 0$ and $\sum_j m_j = m$. Furthermore, $[\mathrm{tr}\,(X)]^m = \sum_\mu C_\mu(X)$, as easily follows from eq 20 if either $\mathbf{y}$ or $\mathbf{S}_\mathrm{d}$ is a multiple of $\mathbf{1}_k$.

In particular, for $k = 3$, we have finally

$$\boldsymbol{P}(\mathbf{S}_\mathrm{d}) = (2\pi)^{-2} \int \sum_{m=0}^{\infty} (i^m/m!) \sum_\mu \frac{C_\mu(\mathbf{y}) C_\mu(\mathbf{S}_\mathrm{d})}{C_\mu(\mathbf{1}_3)} |1 + in^{-1}\mathbf{y} \otimes \Lambda_\gamma^{-1}|^{-1/2} |y_1 - y_2||y_1 - y_3||y_2 - y_3| \,\mathrm{d}y_1\,\mathrm{d}y_2\,\mathrm{d}y_3 \tag{21}$$

The range of integration is $-\infty < y_3 < y_2 < y_1 < \infty$. This equation will not be useful for computations until a means is found to evaluate the sum over the zonal polynomials in terms of more rapidly convergent functions. One possibility is to extract $\exp[(i/3)\,\mathrm{tr}\,(\mathbf{y})\,\mathrm{tr}\,(\mathbf{S}_\mathrm{d})]$ from the sum in eq 21 and perhaps also to use a cumulant expansion. These notions are not pursued here.

The result, eq 21, is disappointing in the respect that it is complicated. However, it represents the most that can be done with the exact general solution at the present time. Its complexity motivates attempts to formulate the problem differently and to look for simplifications for special cases.

II. Formulation in Eckart Coordinates

If eq 4 is reduced to a normal-coordinate version, as in eq 6, one obtains

$$P(\mathbf{S})\,\mathrm{d}\mathbf{S} = (\mathrm{d}\mathbf{S}/Z) \int \mathrm{etr}\,(-\mathbf{Q}_0 \Lambda_\gamma \mathbf{Q}_0')\,\mathrm{d}\mathbf{Q}_0/\mathrm{d}\mathbf{S} \tag{22}$$

This will now be expressed in polar or Eckart[15,16] coordinates. The polar decomposition $\mathbf{Q}_0 = h\sigma\mathbf{V}$, with $h \in \mathrm{SO}(k)$, $\sigma = \mathrm{diag}\,(n^{1/2}S_1^{1/2}, n^{1/2}S_2^{1/2}, ..., n^{1/2}S_k^{1/2})$ and $\mathbf{V} = \mathbf{V}_{k,n-1}$, follows from the Autonne–Eckart–Young theorem.[17] The space spanned by the matrices $\mathbf{VV}' = \mathbf{1}_k$ is a Stiefel manifold;[9,18] it is isomorphic to the coset space $\mathrm{O}(n-1)/\mathrm{O}(n-1-k)$[18] of dimension $k(2n - 3 - k)/2$. Using the invariance of the trace to cyclic permutations, we have etr $(-\mathbf{Q}_0\Lambda_\gamma\mathbf{Q}_0') = \mathrm{etr}\,(-n\mathbf{S}_\mathrm{d}\mathbf{V}\Lambda_\gamma\mathbf{V}')$.

The volume element is obtained by a procedure similar to that used to obtain eq 13. Let $\mathrm{d}\xi^2 = \mathrm{tr}\,(\mathrm{d}\mathbf{Q}_0\,\mathrm{d}\mathbf{Q}_0')$; also $\mathrm{d}\mathbf{Q}_0 = \mathrm{d}h\,\sigma\mathbf{V} + h\,\mathrm{d}\sigma\,\mathbf{V} + h\sigma\,\mathrm{d}\mathbf{V}$. The volume element becomes[5,9]

$$\mathrm{d}\mathbf{Q}_0 = 2^{1-2k} n^{k(n-1)/2} |\mathbf{S}_\mathrm{d}|^{(n-k-2)/2} \prod_{\alpha<\beta} |S_\alpha - S_\beta| \prod_\alpha \mathrm{d}S_\alpha \,\mathrm{d}\mathbf{h}\,\mathrm{d}\mathbf{V} \tag{23}$$

$$\mathrm{d}\mathbf{Q}_0/\mathrm{d}\mathbf{S} = n^{k(n-1)/2} 2^{-k} |\mathbf{S}_\mathrm{d}|^{(n-k-2)/2}\,\mathrm{d}\mathbf{V} \tag{24}$$

with use of eq 15. The distribution function, eq 22, is obtained as

$$P(\mathbf{S})\,\mathrm{d}\mathbf{S} = \mathrm{d}\mathbf{S} |\Lambda_\gamma|^{k/2} (n/\pi)^{k(n-1)/2} 2^{-k} |\mathbf{S}_\mathrm{d}|^{(n-k-2)/2} \int_{\mathbf{VV}'=1} \mathrm{etr}\,(-n\mathbf{S}_\mathrm{d}\mathbf{V}\Lambda_\gamma\mathbf{V}')\,\mathrm{d}\mathbf{V} \tag{25}$$

Use of eq 15 for the factor $\mathrm{d}\mathbf{S}$ on the right shows that $P(\mathbf{S})\,\mathrm{d}\mathbf{S} = 0$ whenever $S_\alpha = S_\beta$, and the determinantal factor $|\mathbf{S}_\mathrm{d}|^{(n-k-2)/2}$ guarantees that $P(\mathbf{S})\,\mathrm{d}\mathbf{S} = 0$ whenever $S_\alpha = 0$ for all $k < n - 2$. Configurations with two equal axes, or one that vanishes, exist on subspaces of the space of all ellipsoids, and they have zero measure in the latter space. To obtain information on these subspaces requires either a different approach, as will be seen in section V, or a careful analysis of eq 25, in the case that $\mathbf{S}_\mathrm{d}$ is degenerate.

The volume of $\mathbf{V} = \mathbf{V}_{k,n-1}$ can be shown[9] to be

$$V[\mathrm{O}(n-1)]/V[\mathrm{O}(n-k-1)] = 2^k \pi^{k(2n-k-1)/4} \Big/ \prod_{i=1}^{k} \Gamma[(n-i)/2] \tag{26}$$

Use of this equation gives the first-order term[5] in the series expansion of $P(\mathbf{S})\,\mathrm{d}\mathbf{S}$ from eq 25. More can be done, however. Multiply and divide eq 25 by $V[\mathrm{O}(n-k-1)]$ and take the factor in the numerator under the sign of integration. Expand $\mathbf{V}$ to all of $H \in \mathrm{O}(n-1)$ by adding the appropriate orthonormal rows, and similarly expand $\mathbf{S}_\mathrm{d}$ to an $(n-1) \times (n-1)$ matrix $\mathbf{S}_{n-1}$ by adding zeros. In so doing, $\mathrm{tr}\,(\mathbf{S}_\mathrm{d}\mathbf{V}\Lambda_\gamma\mathbf{V}') = \mathrm{tr}\,(\mathbf{S}_{n-1}H\Lambda_\gamma H')$. The integral in eq 25 becomes

$$V[\mathrm{O}(n-k-1)]^{-1} \int_{\mathrm{O}(n-1)} \mathrm{etr}\,(-n\mathbf{S}_{n-1}H\Lambda_\gamma H')\,\mathrm{d}H = \frac{V[\mathrm{O}(n-1)]}{V[\mathrm{O}(n-k-1)]} \sum_{m=0}^{\infty} \frac{(-n)^m}{m!} \sum_\mu \frac{C_\mu(\mathbf{S}_{n-1}) C_\mu(\Lambda_\gamma)}{C_\mu(\mathbf{1}_{n-1})} \tag{27}$$

by application of the results referred to at eq 20 above. The zonal polynomials $C_\mu(\mathbf{S}_{n-1})$ vanish if m is partitioned into more than k nonzero parts, since then all terms have at least one of the zero entries of $\mathbf{S}_{n-1}$. The complete series solution for $P(\mathbf{S})\ d\mathbf{S}$ is thus

$$P(\mathbf{S})\ d\mathbf{S} = \frac{d\mathbf{S}\ n^{k(n-1)/2}|\mathbf{\Lambda}_\gamma|^{k/2}|\mathbf{S}_d|^{(n-k-2)/2}}{\pi^{k(k-1)/4}\prod_{\alpha=1}^{k}\Gamma\left(\frac{n-\alpha}{2}\right)}\sum_{m=0}^{\infty}\frac{(-n)^m}{m!}\sum_{\mu}\frac{C_\mu(\mathbf{S}_{n-1})C_\mu(\mathbf{\Lambda}_\gamma)}{C_\mu(1_{n-1})} \quad (28)$$

This is, unfortunately, only slowly convergent, and so is not very useful for applications other than those related to collapsed configurations.

III. Asymptotic Distribution for Linear Chains

An asymptotic expansion for eq 25 can be obtained by application of known results when all S_α are large, and when the λ_i are nondegenerate. First order the matrices $\mathbf{S}_d = \text{diag}\ (S_1,S_2,...,S_k)$ and $\mathbf{\Lambda}_\gamma = \gamma\ \text{diag}\ (\lambda_1,\lambda_2,...,\lambda_{n-1})$ such that $S_1 > S_2 > ... > S_k$ and $\lambda_1 < \lambda_2 < ... < \lambda_{n-1}$. Complete $\mathbf{S}_d$ to $\mathbf{S}_{n-1}$, with $S_1 > S_2 > ... > S_k > S_{k+1} = S_{k+2} = ... = S_{n-1} = 0$, and $\mathbf{V} \rightarrow H$ as in the passage from eq 25 to eq 27. The asymptotic form of the integral in eq 27 is given by Muirhead as Theorem 9.5.4. We have

$$P(\mathbf{S})\ d\mathbf{S} \sim \text{constant}\ \exp(-\gamma n \sum_{\alpha=1}^{k}\lambda_\alpha S_\alpha)\prod_{\alpha<\beta}^{k}|S_\alpha - S_\beta|^{1/2}\prod_{\alpha=1} S_\alpha^{-1/2}\ dS_\alpha \quad (29)$$

in principal axes, with

$$\text{constant} = \frac{(\gamma n)^{k(k+1)/4}\prod_{j=1}^{n-1}\lambda_j^{k/2}}{\prod_{\alpha=1}^{k}\Gamma(\alpha/2)\prod_{\alpha<\beta}|\lambda_\alpha - \lambda_\beta|^{1/2}\prod_{j=k+1}^{n-1}\prod_{\alpha=1}^{k}|\lambda_j - \lambda_\alpha|^{1/2}} \quad (30)$$

The λ_j are given by[8]

$$\lambda_j = 4\sin^2 \pi j/2n \quad (31)$$

for the linear chain. Throughout this section, $\lambda_\alpha = \lambda_j$ for $1 \le j \le k$ where clarity dictates.

Equation 29 is satisfactory in the respect that the most probable, highly extended, configurations in two and three dimensions have all but one component of $\mathbf{S}$ equal to zero. The highly extended linear chain is most likely straight, and thus the mathematics of the Gaussian chain does not contradict physical principles. Quite the opposite is true in four or more dimensions, and this fact is profound.

It is not difficult to show that an extremum of eq 29, should one exist at $S_\alpha = S_\alpha^*$, $1 \le \alpha \le k$, must satisfy the equations

$$\gamma n \sum_{\alpha=1}^{k}\lambda_\alpha S_\alpha^* = k(k-3)/4$$

$$\sum_{\alpha=1}^{k}(2\gamma n\lambda_\alpha + 1/S_\alpha^*) = 0$$

The first cannot be satisfied for $S_\alpha^* > 0$ for $k < 4$, and the second can never be satisfied for $S_\alpha^* > 0$. There is never an extremum in the asymptotic region, but clearly the cases $k \le 3$ and $k > 3$ are different. The factor $\prod|S_\alpha - S_\beta|^{1/2}\prod S_\alpha^{-1/2}$ may be written as follows for $k \le 4$:

$k = 2$

$$(1/S_2 - 1/S_1)^{1/2}$$

$k = 3$

$$|(1 - S_2/S_1)(1 - S_3/S_2)(S_1/S_3 - 1)|^{1/2}$$

$k = 4$

$$|(S_1 - S_2)(S_1 - S_3)(1 - S_4/S_1)(1 - S_3/S_2)(S_2/S_4 - 1) \times (1 - S_4/S_3)|^{1/2}$$

For $k = 2$, $S_2 \rightarrow 0$ for fixed S_1 maximizes the probability. For $k = 3$, $S_2 \rightarrow S_3 \rightarrow 0$ such that $S_3/S_2 \rightarrow 0$ for fixed S_1 will be most probable. In the last case, $S_3 \rightarrow S_4 \rightarrow 0$ such that $S_4/S_3 \rightarrow 0$ for fixed S_1 *and* S_2 will define a subspace with high probability.

There are implications here for the excluded volume problem. Suppose that a repulsive interaction between segments is acting so as to favor configurations with a large radius of gyration in any dimension. In two and three dimensions the chain tends to become one-dimensional, i.e., it straightens out. In four dimensions it still remains a coil, albeit one that is most likely found near a subspace of two dimensions. In four or more dimensions the maximal dimension repulsive interaction is therefore ineffective in expanding the chain, and the perturbation of the random flight dimensions is nil.

IV. Distributions in Two Dimensions[3]

In two dimensions the integral over SO(2) in eq 18 can be accomplished in terms of a Bessel function, and if the λ_i are doubly degenerate the integrals over the y_α can then be done with use of the residue theorem. This provides a convenient starting point for numerical integrations in the general case, and the solution is reducible to a sum of terms in a simple one-dimensional integral in the special case of a circular chain.

Let the group SO(2) be spanned by the matrices

$$\mathrm{h} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

with $d\mathbf{h} = d\theta$. Then tr $(hyh'\mathbf{S}) = y_+s^2 + y_-\Delta\cos 2\theta$, where $y_\pm = (y_1 \pm y_2)/2$, $s^2 = S_1 + S_2$, and $\Delta = S_1 - S_2$. Equation 18 becomes

$$\boldsymbol{P}(\mathbf{S}_d) = \pi^{-2}\int_{-\infty}^{\infty}dy_+\int_0^{\infty}y_-\ dy_-\int_0^{\pi}d\theta\ F_+F_-\ \exp[iy_+s^2 + iy_-\Delta\cos 2\theta] \quad (32a)$$

where

$$F_\pm = \prod_{j=1}^{n-1}[1 + i(y_+ \pm y_-)/\gamma n\lambda_j]^{-1/2} \quad (32b)$$

Integrating over SO(2) gives

$$\boldsymbol{P}(\mathbf{S}_d) = \pi^{-1}\int_{-\infty}^{\infty}dy_+\ \exp(is^2y_+)\int_0^{\infty}y_-\ dy_-\ J_0(\Delta y_-)F_+F_- \quad (33)$$

This result is equivalent to that obtained by Šolc and Gobush.[3]

If the molecule of interest is a ring with an odd number of equivalent bonds, the eigenvalues are doubly degenerate; the distinct values are given by[8]

$$\lambda_j = 4\sin^2 \pi j/n, \qquad 1 \le j \le (n-1)/2 \quad (34)$$

The $F_\pm$ functions in eq 33 become

$$F_\pm \rightarrow G_\pm = \prod_{j=1}^{(n-1)/2}(1 + i(y_+ \pm y_-)/\gamma n\lambda_j)^{-1} \quad (35)$$

so that the branch points of the $F_\pm$ functions are replaced by simple poles. To compute the integral, first make a partial fraction expansion of $G_\pm$ to obtain

$$G_\pm = |-in\mathbf{\Lambda}_\gamma|\sum_{j=1}^{(n-1)/2}A_j/[y_+ - (i\gamma n\lambda_j \mp y_-)] \quad (36)$$

where

$$(A_j)^{-1} = \prod_{k\neq j} [i\gamma n(\lambda_j - \lambda_k)] \quad (37)$$

When the right of eq 36 is reduced to the common denominator form, the coefficient of $y_+^{(n-3)/2}$ is $\sum A_j$, and it follows that

$$\sum_{j=1}^{(n-1)/2} A_j = 0 \quad (38)$$

which is helpful in sequel.

The contour for the y_+ integral in eq 33 is closed in the upper half-plane with a semicircle at infinity. The integrand has simple poles at $y_+ = i\gamma n\lambda_j \pm y_-$, and the result of application of the residue theorem is

$$P(\mathbf{S}_d) = i|-in\Lambda_\gamma|^2 \sum_j \sum_k A_j A_k \int_0^\infty dy_- \; J_0(\Delta y_-) \frac{(2y_-)[e_k \exp(is^2y_-) - e_j \exp(-is^2y_-)]}{2y_- - i\gamma n(\lambda_j - \lambda_k)} \quad (39)$$

with $e_j = \exp(-\gamma n\lambda_j s^2)$. Since $x/(x-a) = 1 + a/(x-a)$, and because of eq 38, this reduces to

$$P(\mathbf{S}_d) = -(\gamma n/2)|-in\Lambda_\gamma|^2 \sum_j \sum_k A_j A_k (\lambda_j - \lambda_k) \int_0^\infty dy \; J_0(\Delta y) \frac{[e_k \exp(is^2y) - e_j \exp(-is^2y)]}{y - i\beta_{jk}} \quad (40)$$

with $\beta_{jk} = \gamma n(\lambda_j - \lambda_k)/2$ and the subscript on y_- has been dropped.

The bracketed factor in eq 40 is written as $2i(e_je_k)^{1/2} \sin [s^2(y - i\beta_{jk})]$, and then use is made of

$$\frac{\sin [s^2(y - i\beta_{jk})]}{y - i\beta_{jk}} = \int_0^{s^2} \cos [(y - i\beta_{jk})t] \, dt$$

on combining terms for $j > k$ and $j < k$, one finds

$$P(\mathbf{S}_d) = \gamma n|-in\Lambda_\gamma|^2 \sum_{j>k} \sum A_j A_k (e_j e_k)^{1/2} (\lambda_j - \lambda_k) \int_0^{s^2} \sinh (\beta_{jk} t) \, dt \int_0^\infty J_0(\Delta y) \sin (ty) \, dy \quad (41)$$

A standard result is[19]

$$\int_0^\infty J_0(\Delta y) \sin (ty) \, dt = 0, \quad 0 < t < \Delta$$

$$= (t^2 - \Delta^2)^{-1/2}, \quad 0 < \Delta < t$$

with which eq 41 becomes

$$P(\mathbf{S}_d) = -(\gamma n)^3 \sum_{j>k} \sum B_j B_k (\lambda_j - \lambda_k) \exp[-\gamma n(\lambda_j + \lambda_k)s^2/2] \int_\Delta^{s^2} \frac{\sinh (\beta_{jk} t)}{(t^2 - \Delta^2)^{1/2}} \, dt \quad (42)$$

where

$$B_j = \lambda_j / \prod_{k \neq j} (1 - \lambda_j/\lambda_k)$$

These factors alternate in sign, so that the leading term in eq 42 is positive. The integral in this equation is not susceptible to further nontrivial reduction, but it can be expressed as a relatively simple double sum, and it should be easy to evaluate by numerical quadrature. The result of Šolc and Gobush[3] is expressed as an infinite sum, which is equivalent to a series expansion of the integral in eq 42. Since the evaluation of any of these equations is likely to be done with the use of a computer, it is just as well that a numerical quadrature rather than a series is left in the results.

The special case $n = 3$, for which the one distinct eigenvalue is $\lambda = 3$, deserves special consideration. It is not difficult to show that

$$P(\mathbf{S}) \, d\mathbf{S} = (9\gamma)^2 |S_1 - S_2| (S_1S_2)^{-1/2} \exp(-9\gamma s^2) \, dS_1 \, dS_2 \quad (43)$$

in agreement with the Šolc and Gobush result.[3]

V. Ellipsoids of Revolution in Three Dimensions

The simplest route to information on the subspace diag $(S_1,S_2,S_3) = \text{diag}(S_\perp,S_\perp,S_\parallel) = \mathbf{S}^*$ of ellipsoids of revolution is to inquire into the form that $\mathbf{Y}$ must take when $\mathbf{S}$ is as specified. First, let $\mathbf{S} = h_1\mathbf{S}^*h_1'$, and choose a parametrization of h_1 as

$$h_1 = A(\alpha_1)B(\beta_1)A(\gamma_1)$$

$$\mathbf{A}(\alpha) = \begin{bmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$\mathbf{B}(\beta) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\beta & \sin\beta \\ 0 & -\sin\beta & \cos\beta \end{bmatrix} \quad (44)$$

The angles α_1, β_1, and γ_1 are not the Euler angles, but they are simply related to the latter. Note that $A(\gamma_1)$ commutes with $\mathbf{S}^*$, so that

$$\mathbf{S} = A(\alpha_1)B(\beta_1)\mathbf{S}^*B(\beta_1)'A(\alpha_1)' \quad (45)$$

depends upon four parameters (α_1, β_1, $S_\perp$, $S_\parallel$) only. To fix $\mathbf{S}$ on the appropriate subspace of $\mathbf{Q}_0$ it is necessary for $\mathbf{Y}$ in eq 7 to depend upon only four parameters. That is, $\mathbf{Y} = h_2'\mathbf{y}^*h_2$ with $\mathbf{y}^* = \text{diag}(y_\perp,y_\perp,y_\parallel)$, and $h_2 = A(\gamma_2)B(\beta_2)A(\alpha_2)$; hence

$$\mathbf{Y} = A'(\alpha_2)B'(\beta_2)\mathbf{y}^*B(\beta_2)A(\alpha_2) = x_2'\mathbf{y}^*x_2 \quad (46)$$

since $A(\gamma)$ commutes with $\mathbf{y}^*$.

Use will now be made of some notions from the theory of coset spaces.[18] Write $h_1 = x_1A(\gamma_1)$, with $x_1 = A(\alpha_1)B(\beta_1)$. Then x_1 is in the left coset SO(3)/SO(2). Conversely, $h_2 = A(\gamma_2)x_2$, and $x_2 = B(\beta_2)A(\alpha_2)$ is in the right coset SO(2)\SO(3). The product h_2h_1 is $A(\gamma_2)x_2x_1A(\gamma_1) = A(\gamma_2)xA(\gamma_1)$ and x is an element of the double coset SO(2)\SO(3)/SO(2). Since $h_2h_1 \in$ SO(3), it follows that x is parametrized simply as $B(\beta)$, and $\text{tr}(\mathbf{Y}^*\mathbf{S}^*) = \text{tr}(\mathbf{y}^*B(\beta)\mathbf{S}^*B(\beta)') = s^2y_+ + \Delta y_-(3\cos^2\beta - 1)$. Here $s^2 = 2S_\perp + S_\parallel$, $\Delta = S_\perp - S_\parallel$, $y_+ = (2y_\perp + y_\parallel)/3$, and $y_- = (y_\perp - y_\parallel)/3$. The volume elements $d\mathbf{S}$ and $d\mathbf{Y}$ are obtained by the standard procedure, with $\mathbf{S} = x_1\mathbf{S}^*x_1'$ and $\mathbf{Y}$ given by eq 46; one finds

$$d\mathbf{S} = (1/2)\Delta^2 dS_\parallel \, dS_\perp \, d\alpha_1 \sin\beta_1 \, d\beta_1$$

$$= 2\pi\Delta^2 \, dS_\parallel \, dS_\perp \text{ (in principal axes)}$$

$$d\mathbf{Y} = 27y_-^2 \, dy_+ \, dy_- \, d\alpha \sin\beta \, d\beta \quad (47)$$

where $d\mathbf{Y}$ depends on α and β, not α_2 and β_2, by the right invariance of the Haar measure on SO(2)\SO(3). Upon inserting the required matrix elements into eq 6 and 7, and then completing the $\mathbf{Q}_0$, α, and β integrations, one obtains

$$P(\mathbf{S}) \, d\mathbf{S} = \Delta^{3/2} \, dS_\parallel \, dS_\perp \, 3^{5/2}(2\pi)^{-3/2} \int \int_{-\infty}^{\infty} \exp(is^2y_+ - i\Delta y_-) y_-^{3/2} \{C[(6\Delta y_-/\pi)^{1/2}] + iS[(6\Delta y_-/\pi)^{1/2}]\} F(y_\perp)^2 F(y_\parallel) \, dy_+ \, dy_- \quad (48)$$

Macromolecules **1985**, *18*, 216–219

Here $C(\cdot)$ and $S(\cdot)$ are the standard Fresnel integrals,[20] and the F functions are defined as in eq 32b. The range of integration for $y_\perp$ and $y_\parallel$, or $y_\pm$, is $-\infty < y_\pm < \infty$; the essential reason for the difference between these ranges for this special case and the restricted ranges for the general case is the presence of y_-^2 in eq 47. Alternatively, both prolate ($S_\parallel > S_\perp$) and oblate ($S_\parallel < S_\perp$) ellipsoids of revolution are encompassed by eq 48, and the corresponding Fourier variables are likewise unrestricted.

One further integration, over $y_\perp$, can be accomplished in eq 48 for any spectrum since $F(y_\perp)^2$ has simple poles. It will prove useful to reduce the double integral to a sum and single integral for numerical evaluation of this equation in the case of linear chains or otherwise nondegenerate spectra. For a doubly degenerate spectrum eq 48 can be further reduced to a double sum by use of the methods described in the previous section. Since ellipsoids of revolution are not apt to be of interest apart from applications to rubber elasticity, where approximations to spectra are called for, the messy equations generated by the last one or two integrations of eq 48 are not given here.

Conclusion

The general solution to the shape distribution problem has been shown to reside within the theory of multivariate statistics. In practice much more needs to be done to reduce the three-dimensional equation to tractable form before numerical work is undertaken to evaluate it. The asymptotic distributions for linear chains in a space of any dimension has been given.

The distribution for two-dimensional rings has been rederived, whereas that for three-dimensional ellipsoids of revolution is new. The latter is much more easily evaluated than is the full three-dimensional distribution.

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References and Notes

(1) Šolc, K.; Stockmayer, W. H., *J. Chem. Phys.* **1971**, *54*, 2756.
(2) Šolc, K. *J. Chem. Phys.* **1971**, *55*, 335.
(3) Šolc, K.; Gobush, W. *Macromolecules* **1974**, *7*, 814.
(4) Eichinger, B. E. *Pure Appl. Chem.* **1975**, *43*, 97.
(5) Eichinger, B. E. *Macromolecules* **1977**, *10*, 671.
(6) Gobush, W.; Šolc, K.; Stockmayer, W. H. *J. Chem. Phys.* **1974**, *60*, 12.
(7) Olaj, O. F.; Lantschbauer, W.; Pelinka, K. H. *Macromolecules* **1980**, *13*, 299.
(8) Eichinger, B. E. *Macromolecules* **1980**, *13*, 1.
(9) Muirhead, R. J. "Aspects of Multivariate Statistical Theory"; Wiley: New York, 1982.
(10) Richards, D.; private communication of a paper submitted to *SIAM Rev.*
(11) Eichinger, B. E. *SIAM Rev.* **1984**, *26*, 117.
(12) Satake, I. *Notices Am. Math. Soc.* **1980**, *27*, 442.
(13) James, A. T. *Ann. Math. Stat.* **1964**, *35*, 475.
(14) Gupta, R. D.; Richards, D. *Ann. Inst. Stat. Math.* **1979**, *31*, 207.
(15) Eckart, C. *Phys. Rev.* **1934**, *46*, 383.
(16) Eckart, C. *Phys. Rev.* **1935**, *47*, 552.
(17) Ben-Israel, A.; Greville, T. N. E. "Generalized Inverses: Theory and Applications"; Wiley-Interscience: New York, 1974.
(18) Steenrod, N. "The Topology of Fibre Bundles"; Princeton University Press: Princeton, NJ, 1951.
(19) Gradshteyn, I. S.; Ryzhik, I. M. "Table of Integrals, Series, and Products"; Academic Press: New York, 1965; Entry 6.671.7, p 731.
(20) Abramowitz, M., Stegun, I. A., Eds. "Handbook of Mathematical Functions"; National Bureau of Standards, Applied Mathematics Section 55, U.S. Government Printing Office: Washington, DC, 1967; p 300.

Effect of Pressure on Polymer–Polymer Phase Separation Behavior

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ABSTRACT: An equation based on the equation-of-state theory of Flory and co-workers was used to describe the effect of pressures, up to 900 atm, on the phase separation behavior of various polymer mixtures. The mixtures under consideration were of an ethylene–vinyl acetate copolymer with chlorinated polyethylenes and of a polyether sulfone with poly(ethylene oxide). These had previously been shown to be miscible and to phase separate on heating. The theory was used to simulate the spinodal curves of mixtures at the operating pressures. For mixtures at compositions close to the critical compositions these were compared with the experimental values and were found to be consistent within the experimental uncertainties. Calculations of volume changes on mixing were also carried out by various methods based on experimental and theoretical results and were also self-consistent. For mixtures of polyether sulfone with poly(ethylene oxide) the state properties of the polymers are very diverse. These mixtures show a very large effect of pressure on phase separation temperatures and a very large volume change on mixing.

Introduction

The equation-of-state theory as developed by Flory and his collaborators[1–4] has many advantages over the classical Flory–Huggins theory in describing the properties of polymer mixtures. McMaster[5] examined the contribution of the state parameters to the miscibility of hypothetical mixtures and showed that the theory is capable of predicting both lower critical solution temperature (LCST) and upper critical solution temperature (UCST) behavior. Also, because it abandons a fixed lattice, it is capable of predicting volume changes on mixing and, hence, the effects of pressure on the phase diagram.

Olabisi[6] has applied McMasters' treatment to a real system of polycaprolactone and poly(vinyl chloride). We have also used a modified form of the above theory to simulate the spinodal curves for mixtures of poly(methyl methacrylate) with chlorinated polyethylene,[7] of poly(butyl acrylate) with chlorinated polyethylene,[8] of ethylene–vinyl acetate copolymers with chlorinated polyethylene,[9] and of poly(ethylene oxide) (PEO) with a polyether sulfone