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Scattering Functions for Gaussian Molecules. 2. Intermolecular Correlations

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It is well known that radiation scattered from dense systems is dependent upon the radial distribution function for molecular centers.[1-4] If the system consists of Gaussian molecules the molecular structure factor makes an important contribution to the apparent intermolecular scattering function. The approach taken in the previous paper[5] is elaborated here, so as to include the effects of intermolecular interference; the calculation is based upon Gaussian statistics, but is otherwise general in respect to intermolecular correlations.

The pair correlation function, $p(\mathbf{r})$, for an array of m Gaussian molecules centered at $\sigma_1, \sigma_2, ..., \sigma_m$ may be written

$$p(\mathbf{r}) = [2/N(N-1)]Z^{-1}\sum_{i<j}\int \delta(\mathbf{r} - \mathbf{r}_i + \mathbf{r}_j) \times \exp[-\gamma \mathrm{Tr}(\mathbf{XKX}')] \prod_{j=1}^{m} \delta(\mathbf{X}J_l' - \sigma_l)\, \mathrm{d}\mathbf{X} \quad (1)$$

where $N = mn$, with n being the average number of beads in a molecule, and Z is the configuration integral or normalization constant. Here $\mathbf{X}$ is a $3 \times N$ dimensional matrix of coordinates, $\mathbf{K}$ is the Kirchhoff matrix for the molecular graph, which is the direct sum of m Kirchhoff matrices, each of dimension $n_l \times n_l$, and $J_l = (0, 0, ..., 1/n_l, 1/n_l, ..., 1/n_l, 0, ..., 0)$. The transpose of J_l is denoted by J_l'; the nonzero elements of this matrix are located at the n_l positions corresponding to the labels on the lth molecule. The product of δ functions fixes the centers of mass of the molecules at the respective σ_l. The parameter $\gamma = 3/2\langle l^2 \rangle$, which implies use of the uniform expansion approximation $\langle l^2 \rangle = \alpha^2 \langle l^2 \rangle_0$ away from the Θ temperature, or if you prefer the treatment is restricted to unperturbed molecules (this approximation is analogous to Albrecht's smoothed density models[2]).

The vector difference $\mathbf{r}_i - \mathbf{r}_j$ may be expressed as $\mathbf{X}c_{ij}'$, where $c_{ij} = (0, 0, ..., 0, 1, 0, ..., 0, -1, 0, ..., 0)$, with the +1 and −1 occurring at locations i and j, respectively. Use of the Fourier integral representation of the first δ function together with a normal coordinate analysis gives

$$p(\mathbf{r}) = [2/N(N-1)8\pi^3 Z]\sum_{i<j}\int \exp(i\mathbf{k}'\mathbf{r}) \times \exp[-\gamma \mathrm{Tr}(\mathbf{Q\Lambda Q}' + i\gamma^{-1}\mathbf{QT}'c_{ij}'\mathbf{k}')] \times \prod_{l=1}^{m} \delta(n_l^{-1/2}\mathbf{q}_l^{\circ} - \sigma_l)\, \mathrm{d}\mathbf{Q}\, \mathrm{d}\mathbf{k} \quad (2)$$

where $\mathbf{\Lambda}$ is the diagonal matrix of eigenvalues of $\mathbf{K}$, including the m zero eigenvalues, $\mathbf{k}' = (k_x, k_y, k_z)$ so that $\mathbf{k}'\mathbf{r} = \mathrm{Tr}(\mathbf{k}'\mathbf{r}) = \mathrm{Tr}(\mathbf{rk}')$, and the $\mathbf{q}_l^{\circ}$ are the center of mass coordinates of the normal coordinates $\mathbf{Q}$. Note that $\mathbf{T}'$, the matrix which diagonalizes $\mathbf{K}$ by a similarity transformation, is a direct sum of m matrices. The first row of each of those matrices is a constant vector $n_l^{-1/2}(1, 1, ..., 1)$. *Hence, upon performing the integrals over the* $\mathbf{q}_l^{0}$, the center of mass components of $\mathbf{QT}'$ are simply replaced by the appropriate σ_l, and $\mathbf{QT}'$ can be written as $\sigma + \mathbf{Q}_0\mathbf{T}_0'$, where

$$\sigma = (\sigma_1, \sigma_1, ..., \sigma_1, \sigma_2, ..., \sigma_2, ..., \sigma_m) \quad (3)$$

is a $3 \times N$ matrix, $\mathbf{Q}_0$ is a $3 \times (N - m)$ matrix obtained from $\mathbf{Q}$ by deletion of the $\mathbf{q}_l^{\circ}$, and $\mathbf{T}_0'$ is an $(N - m) \times N$ dimensional matrix obtained from $\mathbf{T}'$ by deletion of the $\mathbf{m}$ rows, one for each submatrix, that belong to the center of mass coordinates. Deletion of the zero eigenvalues from Λ yields the $(N - m) \times (N - m)$ matrix Λ_0.

The integrals over the $\mathbf{Q}_0$ may now be performed to give

$$p(\mathbf{r}) = [2/N(N-1)]\sum_{i<j}(\gamma/\pi g_{ij})^{3/2} \times \exp[-(\gamma/g_{ij})(\mathbf{r}' - \sigma c_{ij}')(\mathbf{r} - c_{ij}\sigma')] \quad (4)$$

where

$$g_{ij} = c_{ij}\mathbf{T}_0\mathbf{\Lambda}_0^{-1}\mathbf{T}_0'c_{ij}' = c_{ij}\mathbf{K}^{(-1)}c_{ij}' \quad (5)$$

The generalized inverse of $\mathbf{K}$ is $\mathbf{K}^{(-1)}$. It is now appropriate to elaborate the counting somewhat. Let $i(k)$ be the ith node on the kth chain. It is easy to compute eq 5 to show that

$$\mathrm{g}_{\mathrm{i(k),j}(l)} = k^{-1}{}_{i(k),i(k)} + k^{-1}{}_{j(k),j(k)} - 2k^{-1}{}_{i(k),j(k)} \qquad \text{for } k = l \quad (6a)$$

$$g_{i(k),j(l)} = k^{-1}{}_{i(k),i(k)} + k^{-1}{}_{j(l),j(l)} \qquad \text{for } k \neq l \quad (6b)$$

and from the definition of σ, one obtains

$$\sigma c'_{\mathrm{i(k),j(l)}} = 0 \qquad \text{for } k = l \quad (7a)$$

$$\sigma c'_{i(k),j(l)} = \sigma_k - \sigma_l \qquad \text{for } k \neq l \quad (7b)$$

The scattering function $P(\Theta)$ is defined as the Fourier transform of eq 4. A straightforward integration gives

$$P(\Theta) = [2/N(N-1)]\{\sum_{l=1}^{m}\sum_{i(l)<j(l)} \exp[-(g_{i(l),j(l)}/4\gamma)\mu^2] + \sum_{k<l}\sum_{i(k)}\sum_{j(l)} \exp[-(g_{i(k),j(l)}/4\gamma)\mu^2 + i(\sigma_k - \sigma_l)\cdot\mu]\} \quad (8)$$

where vector notation is now used. The sums are over all pairs of beads, with the elements of g_{ij} given by eq 6. The magnitude of the scattering vector is $\mu = (4\pi/\lambda) \sin \Theta/2$.

Equation 8 is general with respect to dispersity and connectivity, and therein lies its virtue. What has not been accounted for is the statistical mechanical average of $\Pi(\mathbf{X}J_l' - \sigma_l)$ in eq 1. The average of this quantity commutes with all the operations that have been carried out so long as the chain statistics are independent of intermolecular interactions.[2] In such a case, the sum over pairs of chains in eq 8 can be written in terms of a probability function, and that equation becomes

$$P(\Theta) = (n-1)/(mn-1)\langle P_1(\Theta)\rangle + n(m-1)/(mn-1)\langle F^2(\Theta)\rangle V^{-1}\int \rho(\mathbf{r})e^{i\mu\cdot\mathbf{r}}\, \mathrm{d}\mathbf{r} \quad (9)$$

where $\langle P_1(\Theta)\rangle$ is the average single chain scattering function,[5] and $\langle F^2(\Theta)\rangle$ is the average square of the molecular structure factor, one term of which is given by

$$F_k(\Theta) = n_k^{-1}\sum_{i(k)} \exp(-k^{-1}{}_{i(k),i(k)}\mu^2/4\gamma) \quad (10)$$

on account of eq 6. In eq 9, the spatial distribution function $\rho(\mathbf{r})$ is the fraction of pairs of molecules separated by the vector $\mathbf{r}$. This function need not be taken to be spherically symmetric, and will not be so for anisotropic media. If the molecules are anisotropic, the treatment of molecular statistics must be modified.[6,7] The integral is taken over the scattering volume V. It may be noted that $P(0) = 1$, since

$$V^{-1}\int \rho(\mathbf{r})\, \mathrm{d}\mathbf{r} = 1$$

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The function $\rho(\mathbf{r})$ is related to the Ursell-Mayer cluster functions used by Albrecht[2] and Yamakawa,[3] but the present formulation leaves off here in the treatment of intermolecular interactions. The coefficient of the first term in eq 9 is $[2/mn(mn-1)]mn(n-1)/2$, whereas that of the second term is $[2/mn(mn-1)]n^2m(m-1)/2$; for a polydisperse system $\langle P_1(\Theta)\rangle$ and $\langle F^2(\Theta)\rangle$ must be defined so as to be compatible with these coefficients.

The molecular structure factor for the linear chain will be calculated for illustration. (It should be recalled that the power of the generalized inverse is in its application to molecules with circuits, for which it is not easy to do calculations by other methods.) The four-condition inverse is required, and has elements given by

$$k_{ii}^{-1} = [i(i-1) + (n-i)(n-i+1) - n^2/3 + \tfrac{1}{3}]/2n \qquad (11)$$

which can be obtained from the three-condition inverse[5,8,9] by adding the constant term $-(n^2-1)/6n$, so that

$$\sum_{j=1}^{n} k_{ij}^{-1} = 0$$

Upon replacing the sum in eq 10 by an integral and dropping terms of $0(1/n)$ from eq 11, one obtains

$$F_k(\Theta) = \pi^{1/2}\exp(-u/12)\,\mathrm{erf}(u^{1/2}/2)/u^{1/2} \qquad (12)$$

where

$$u = (8\pi^2\langle r_k^2\rangle/3\lambda^2)\sin^2\Theta/2 = \mu^2\langle s_k^2\rangle \qquad (13)$$

is the Debye variable, and $\mathrm{erf}(x)$ is the error function. Here, $\langle r_k^2\rangle = n_k\langle l^2\rangle = 6\langle s_k^2\rangle$, as usual. [If the chain is labeled with atoms of various cross sections, group structure factors f_i will multiply the exponential function in eq 10.] It may be noted that eq 12 defines a monotonic function which decreases from 1.0 at $u = 0.0$ to 0.535 at $u = 4.0$. It was first obtained in a different context by Benoit and Goldstein[10] and has also been encountered in dynamic scattering theory.[11,12] It is slightly different from the corresponding function calculated by Flory and Bueche.[13] Equation 9 with eq 12 might be useful for analysis of radiation scattered by concentrated polymer solutions.[14]

Equation 8 may be applied to a pair of linear chains separated by a distance r. This illustration might find application to scattering from denatured duplex DNA prior to diffusive strand separation,[15] provided that the molecules are not correlated and hence adopt Gaussian statistics within times short compared with the rate of strand separation. An alternative application could be made to flash photolytic scission of a long polymer chain at its midpoint. For these cases, $m = 2$, $n - 1 \approx n$, $P_1(\Theta)$ is the Debye function, $F(\Theta)$ is given by eq 12, and $\exp(i\mathbf{r}\cdot\mu)$ is rotationally averaged to give

$$P(\Theta) = P_1(\Theta)/2 + (\pi/2u)\exp(-u/6)[\mathrm{erf}(u^{1/2}/2)]^2 \sin(u^{1/2}\xi)/u^{1/2}\xi \qquad (14)$$

where u is defined by eq 13, and $\xi = r/\langle s^2\rangle^{1/2}$. If the scattered radiation is observed at an angle Θ_1 such that $u = 1$, for example, eq 14 gives

$$P(\Theta_1) = 0.368 + 0.360(\sin\xi)/\xi$$

the derivative $\mathrm{d}P(\Theta_1)/\mathrm{d}t$ will give the rate of strand separation.

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Evidence Specifying the Origin of the NMR Doublet of Water in Oriented Macromolecular Systems

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A doublet has been consistently observed as part of the NMR spectrum of water absorbed by a variety of macromolecular systems.[1-6] The usual explanation is that the splitting arises due to the dipole-dipole interaction, but it has been suggested that such a splitting may be due to a diamagnetic susceptibility effect.[7,8]

If the splitting is dipolar in origin, its magnitude should be independent of the strength of the magnetic field in which the NMR experiment is performed.[9,10] On the other hand, splitting due to a diamagnetic susceptibility effect should be proportional to the field strength.[11,12] We obtained room temperature ^{1}H NMR spectra for samples of oriented (parallel to H_0) Fortisan (a highly oriented and highly crystalline rayon formed by the saponification of acetate), equilibrated at 65% relative humidity (about 9% moisture content), at two frequencies (and correspondingly, different field strengths): 15.1 and 56.4 MHz. In each case

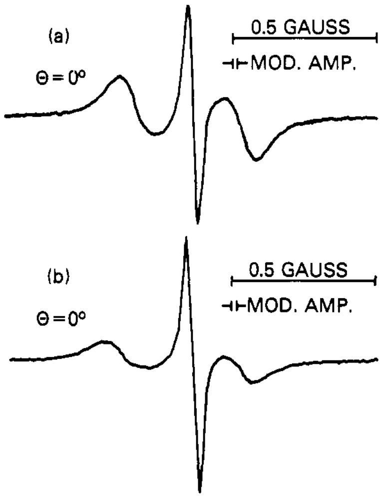

Figure 1. ^{1}H NMR spectra obtained using oriented Fortisan rayon fiber equilibrated at 65% relative humidity. Spectra were made at 15.1 MHz (a) and 56.4 MHz (b) with the fiber parallel to the magnetic field. The temperature was about 28 °C; the sweep frequency was 80 Hz, and the modulation amplitude was 17 mg.

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