Scattering Functions for Gaussian Molecules

B. E. EICHINGER

Department of Chemistry, University of Washington, Seattle, Washington 98195. Received November 29, 1977

Scattering functions for Gaussian molecules which are linear,[1] circular,[2] or branched[3-7] have been known for some time. It is also known that combinatorial problems encountered in the calculation of intramolecular interference factors for molecules containing many circuits are formidable. The general solution to this problem is presented here. The scattering function for a Gaussian molecule with connectivity specified by a Kirchhoff matrix is shown to be given in terms of the generalized inverse of this matrix. The result is specialized for illustrative purposes to linear and circular chains. For more complicated molecules, the scattering functions can be obtained by numerical computations.

The intramolecular interference factor $P(\theta)$ is the Fourier transform[8] of the pair distribution function $p(\mathbf{r})$, where

$$p(\mathbf{r}) = [n(n-1)/2]^{-1} \sum_{i<j} p_{ij}(\mathbf{r}) \qquad (1)$$

Here, n is the number of scattering elements, and $p_{ij}(\mathbf{r})$ is the pair correlation function for elements i and j. The latter function is evaluated from

$$p_{ij}(\mathbf{r}) = Z^{-1} \int \delta[\mathbf{r} - (\mathbf{r}_i - \mathbf{r}_j)] \times \exp[-(1/kT)V(\mathbf{r}_1, \ldots, \mathbf{r}_n)] \prod_{l=1}^{n} d\mathbf{r}_l \qquad (2)$$

in which Z is the configuration integral. The integral must be constrained, as will be seen later, to eliminate the divergent contribution from the center of mass motion.

The potential of mean force, $V(\mathbf{r}_1, \ldots, \mathbf{r}_n)$, in the Gaussian approximation is given by

$$V(\mathbf{r}_1, \ldots, \mathbf{r}_n) = (3kT/2\langle l^2\rangle)\mathbf{R}(\mathbf{K} \otimes \mathbf{1}_3)\mathbf{R}' \qquad (3)$$

where $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$, $\mathbf{R}'$ is the transpose of $\mathbf{R}$, $\mathbf{K}$ is the Kirchhoff matrix[9,10] of the graph that represents the molecular structure regardless of complexity, and $\langle l^2\rangle$ is the mean-square displacement of one link of the Gaussian molecule. (In first approximation, it may be assumed that volume exclusion expands $\langle l^2\rangle$ uniformly, so that $\langle l^2\rangle = \alpha^2\langle l^2\rangle_0$. If this approximation is deemed unsatisfactory, the results obtained here will nonetheless apply to the unperturbed state.) Matrix direct multiplication with the identity of rank three in eq 3 expands $\mathbf{K}$ to conform with $\mathbf{R}$.

Use of the Fourier representation of the delta function, and of a coordinate system comoving with the center of mass of the molecule, gives

$$p_{ij}(\mathbf{r}) = (2\pi)^{-3}Z^{-1} \int \exp[i\mathbf{k}\mathbf{r}' - i\mathbf{k}(c_{ij} \otimes \mathbf{1}_3)\mathbf{R}'] \times \exp[-\gamma\mathbf{R}(\mathbf{K} \otimes \mathbf{1}_3)\mathbf{R}']\delta\left(\sum_{1}^{n} \mathbf{r}_l\right) d\mathbf{R}\, d\mathbf{k} \qquad (4)$$

where $\gamma = 3/2\langle l^2\rangle$, and where $c_{ij} = (0, 0, \ldots, 0, 1, 0, \ldots, 0, -1, 0, \ldots, 0)$ is a $1 \times n$ matrix containing $+1$ in the ith column and -1 in the jth column. A normal coordinate transformation on $\mathbf{R}$ diagonalizes the symmetric matrix $\mathbf{K}$ and allows integration of eq 4 in the usual way[10] to give

$$p_{ij}(\mathbf{r}) = (\gamma/\pi g_{ij})^{3/2} \exp(-\gamma\mathbf{r}^2/g_{ij}) \qquad (5)$$

where

$$g_{ij} = c_{ij}\mathbf{T}_0\mathbf{\Lambda}_0^{-1}\mathbf{T}_0'c_{ij}' = c_{ij}\mathbf{K}^{(-1)}c_{ij}' \qquad (6)$$

The $n \times (n-1)$ matrix $\mathbf{T}_0$ contains all but the constant vector of the $n \times n$ orthogonal matrix $\mathbf{T}$ that diagonalizes $\mathbf{K}$, and $\mathbf{\Lambda}_0$ is the $(n-1) \times (n-1)$ diagonal matrix of nonzero eigenvalues of $\mathbf{K}$. The generalized inverse[11] of $\mathbf{K}$ is denoted by $\mathbf{K}^{(-1)}$. The function $p_{ij}(\mathbf{r})$ in eq 5 is obviously normalized and signifies that the individual pair correlation function in a Gaussian molecule is Gaussian, regardless of the connectivity of the molecule. The Fourier transform of eq 6 gives, together with eq 1, the interference factor

$$P(\theta) = [n(n-1)/2]^{-1} \sum_{i<j} \exp(-g_{ij}\bar{u}) \qquad (7)$$

where

$$\bar{u} = (8\pi^2\langle l^2\rangle/3\lambda^2) \sin^2 \theta/2 \qquad (8)$$

Here, λ is the wavelength of radiation, and θ is the scattering angle. The parameter $\bar{u}$ is different by a factor of n from the quantity u occurring in the scattering function for a linear chain.[1]

Equation 7 is an exact result, within the context of the Gaussian chain, and is valid for molecules of arbitrary complexity. Its virtue lies in the fact that a formidable combinatorial problem is reduced to unequivocal matrix inversion to obtain $\mathbf{K}^{(-1)}$ and to subsequent trivial computation of

$$g_{ij} = k_{ii}^{(-1)} + k_{jj}^{(-1)} - 2k_{ij}^{(-1)} \qquad (9)$$

For simple cases, these computations can be done analytically, and for more complicated molecules they are easily programmable.

To illustrate the equivalence of eq 7 with standard approaches, the scattering functions for linear and circular chains will be considered. Three condition inverses $\mathbf{K}^{(-1)}$ for these molecules have been previously obtained, and these suffice for calculation of g_{ij} by eq 9. For the linear chain[12]

$$k_{ij}^{(-1)} = [i(i-1) + (n-j)(n-j+1)]/2n \qquad (i \leq j)$$

and hence $g_{ij} = j - i$. Conversion of the sum in eq 7 to an integral gives the Debye scattering function. For the circular chain[9] the three-condition inverse is

$$k_{ij}^{(-1)} = -(j-i)(n-j+i)/2n \qquad (i \leq j)$$

so that

$$g_{ij} = (j-i)(n-j+i)/n$$

Since this expression is symmetric on the interchange $j - i \rightarrow n - (j - i)$, one finds

$$P(\theta) = (2/n) \sum_{l=1}^{n/2} \exp[-\bar{u}l(n-l)]$$

where $n - 1 \approx n$ and the distinction between even and odd n for the upper limit of the sum is ignored. Conversion of this sum to an integral gives the scattering function calculated by Casassa.[2]

The fact that these two illustrative examples were previously solved by direct methods should not detract from the utility of this formulation in terms of the generalized inverse. The reduction of otherwise laborious calculations for complex molecules to algorithmic form should be of use in analysis of radiation scattering from gels and networks.

Note Added in Proof: The scattering function given in eq 7 is an explicit generalization of the integrated intensity obtained by Pecora[13,14] for the linear chain.

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Ultrasonic Studies on Monovalent and Divalent Cation Salts of Carrageenans in Aqueous Solution

G. PASS,* G. O. PHILLIPS, D. J. WEDLOCK, and E. WYN-JONES

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, Lancs, U.K.

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It has been demonstrated that activity coefficients and osmotic coefficients of polyelectrolytes are much lower than those of simple salts, in aqueous solution at equivalent concentrations. This phenomenon of ion binding or ion condensation has received a variety of treatments,[1–5] the most comprehensive recent treatment being that of Manning,[6] who showed that in solutions of polyelectrolytes with a linear charge parameter, ξ, greater than 1, a fraction of monovalent counterions $(1 - \xi^{-1})$ will condense on the polyion in order to reduce the charge parameter to an effective value of 1. In general, equilibrium studies of the factors affecting counterion condensation in polyelectrolytes have proved particularly valuable in the development of a fundamental understanding of bulk physical properties and biological functions. However, a complete understanding of the mechanistic details of such processes can only be gained through kinetic studies, which can be carried out on these systems using ultrasonic relaxation methods. We report here our preliminary measurements on some carrageenan salts, characterized[2] by values of $\xi > 1$.

Experimental Section

The carrageenan samples in the appropriate counterion salt forms were prepared and estimated as described previously.[2] Ultrasonic absorption was determined at 298 K by the resonance interferometric technique developed by Eggers.[7] The electronic system was a modified version of a standard sweep level measuring set produced by Wandel and Goltermann.[8] Before measurements were taken, solutions of carrageenans were clarified by briefly subjecting them to a vacuum, in order to remove air bubbles.

Results

In the use of the ultrasonic method to study the chemical relaxation of the very fast reactions, it is necessary to interpret macroscopic measurements in terms of the microscopic behavior of the systems being investigated. Previous work has shown that the relaxation spectra of polyelectrolytes are characterized by a distribution of relaxation times resulting from the perturbation of equilibria involving counterion condensation as well as fast processes associated with the polymer chain.[9] In an attempt to resolve the relaxation effects, it has been suggested[10] that the contribution to the excess sound absorption arising from counterion condensation equilibria, $\Delta\alpha$, in any particular salt of a polyanion, can be obtained from expression 1, f being ultrasonic frequency.

$$\frac{\Delta\alpha}{f^2} = \left(\frac{\alpha}{f^2}\right)_s - \left(\frac{\alpha}{f^2}\right)_t \qquad (1)$$

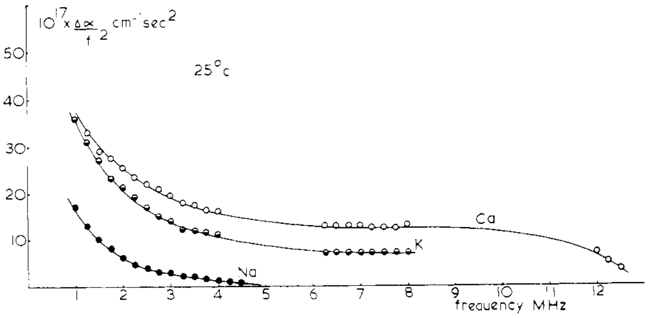

Figure 1. Plots of ultrasonic absorption ($\Delta\alpha/f^2$) vs. f for 0.04 N aqueous solutions of calcium, potassium, and sodium salts of κ-carrageenan.

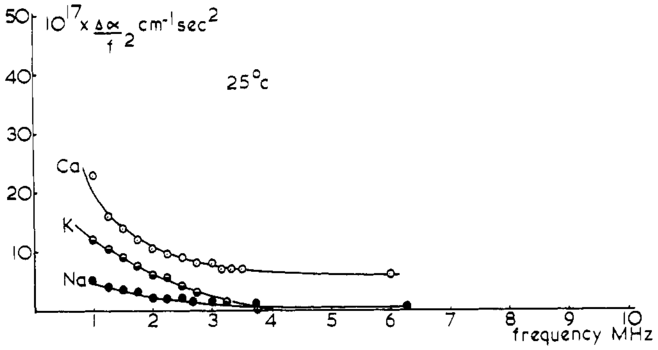

Figure 2. Plots of ultrasonic absorption ($\Delta\alpha/f^2$) vs. f for 0.04 N aqueous solutions of calcium, potassium, and salts of λ-carrageenan.

Where $(\alpha/f^2)_s$ is the measured sound absorption in a solution of a particular metal ion salt of the polyanion and $(\alpha/f^2)_t$ is the corresponding sound absorption measured in a solution having the same concentration of the tetramethylammonium salt of the polyanion. This equation is based on the assumptions that the volume changes associated with the counterion condensation process in the TMA salts are zero,[10] and that the other relaxation processes associated with the polymer chain are not affected by the counterion. The relaxation data for all the solutions have been determined on this basis.

The measurements were carried out over the frequency range 1–12 MHz. In all cases, $\Delta\alpha/f^2$ was found to decrease with increasing frequency as shown in Figures 1 and 2, indicating the presence of a relaxation. Due to the high viscosities of the solutions, concentrations were limited to 4×10^{-2} N. One consequence of being limited to such low concentrations of polyions is that the observed variations of $\Delta\alpha/f^2$ with frequency are extremely small. In addition, since $\Delta\alpha/f^2$ is apparently proportional to concentration, as shown in Figures 3 and 4, the effect becomes weaker as the concentration is lowered. In all cases, the observed relaxations are characterized by more than one relaxation time and the variation of $\Delta\alpha/f^2$ with frequency can be described by an equation[11] involving a distribution of relaxation times and which contains four adjustable parameters. However, as a result of our narrow frequency range and the limitations imposed by the low concentrations of polyions which result in a weak relaxation amplitude, we are not justified in using the detailed results obtained from the analysis of the data. However, for the purpose of the following discussion, several noteworthy features of the relaxation data are summarized below.

(i) For the two concentrations studied, $\Delta\alpha/f^2$ was found to be proportional to polyion concentration, as shown in Figures 3 and 4.

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