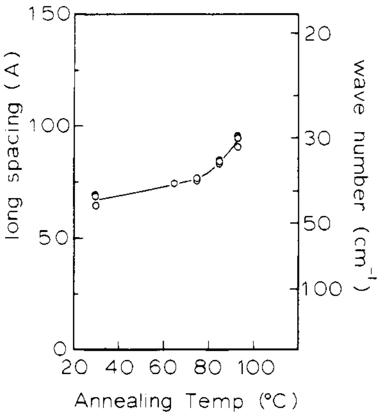

Figure 3. Plot of the band position and the derived long spacing against annealing temperature for the sodium salt of ethylene–methacrylic acid copolymer (4.0 mol % methacrylic acid).

its salts is about 30–40%.[22] The exact value depends on sample preparation. For the as-prepared sample, we would predict, using the E and ρ values applicable to polyethylene, a chain length distribution centered at 70 Å. This value is consistent with the value derived from SAXS measurements.[23] For the annealed samples, the chain lengths calculated from the Raman frequency are also shown in Figure 3. Since the frequency and the intensity of the LAM can be disrupted by conformational and configurational disorder,[23,24] the existence of this mode in a random copolymer is interesting.

In summary, although we have found three bands which are sensitive to the salt group on ion content in ethylene–methacrylic copolymers and their salts, they are characteristic of the lamellar structure associated with the polyethylene component and the conformational defects present. None can be associated unambiguously with structures such as ion "clusters" or "multiplets".

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Light Scattering from Hollow Finite Cylinders†

J. M. DEUTCH

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
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The advent of laser techniques has stimulated wide interest in employing light scattering to study both structural and dynamical properties of macromolecules in solution.[1] For example, Pecora and Aragon[2] have developed the theory of the light scattering spectrum from hollow spheres and discuss how this system may be employed as a model for dispersions of phospholipid vesicles. In order to obtain useful information on particle structure, it is necessary to have available theoretical expressions for the intramolecular scattering function for a variety of molecular shapes. These theoretical expressions are employed to compare and interpret intensity measurements. Prior interest[3] in the frictional properties of multisubunit microtubule assemblies has led us to note the absence of an explicit theoretical expression for the structure factor of finite-length hollow cylinders, a potentially useful model shape for some rigid molecular aggregates. The purpose of this note is to present an expression for $P(\mathbf{q})$, the dilute-solution structure factor for this case.

For a monodisperse system, the intramolecular interference structure factor is[1,4,5]

$$P(\mathbf{q}) = \frac{1}{N^2}\sum_{j,k}\langle \exp[i\mathbf{q}\cdot(\mathbf{r}_j - \mathbf{r}_k)]\rangle = \frac{1}{v^2}\int \mathrm{d}R\,\mathrm{d}R'\langle \exp[i\mathbf{q}\cdot(\mathbf{R} - \mathbf{R}')]\rangle \qquad (1)$$

where the double sum extends over all N optically isotropic scattering elements of the structure located at positions $\mathbf{r}_j$ and $|\mathbf{q}| = (4\pi/\lambda)\sin(\theta/2)$ is the scattering wave vector, with λ the incident wavelength and θ the scattering angle. In the second equality of eq 1, the sum over scattering elements has been replaced by an integral, with R denoting a position in the hollow cylinder of outer radius b, inner radius a, length L, and volume $v = [\pi L(b^2 - a^2)]$.

The angular brackets denote an isotropic orientational average between the axis of the hollow cylinder and the fixed scattering direction $\mathbf{q}$. The average is evaluated in cylindrical coordinates by decomposing $\mathbf{q}$ into components parallel ($q\cos\theta$) and perpendicular ($q\sin\theta$) to the cylinder axis. The terms involving the perpendicular component are best evaluated by expanding the exponential in a Bessel function, $J_n(x)$, series and then integrating over polar angles. The resulting radial integrals can be accomplished to yield

$$P(q) = \frac{1}{2}\int_0^\pi \mathrm{d}\theta\,\sin\theta\left\{\left[\frac{2}{b^2 - a^2}\right]\left[\frac{\sin[(qL/2)\cos\theta]}{[(qL/2)\cos\theta]}\right]\times\left[\frac{bJ_1(bq\sin\theta) - aJ_1(aq\sin\theta)}{q\sin\theta}\right]\right\}^2 \qquad (2)$$

This is the theoretical expression for the intramolecular structure factor for hollow cylinders. The result is only valid in the Rayleigh–Gans–Debye limit of small refractive index difference between the hollow cylinder and the medium in which it is placed. The result should be compared to the many related results for infinite cylinders that

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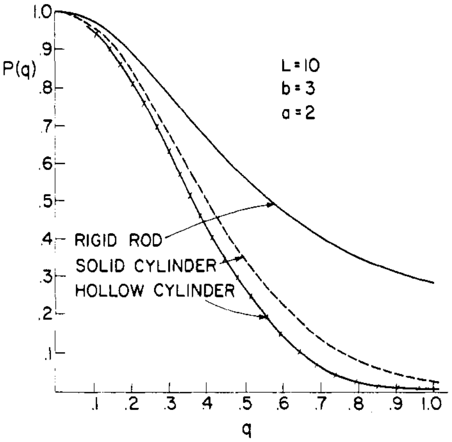

Figure 1. Intramolecular structure factor for cylindrical shapes. Numerical evaluation of eq 2 for $L = 10$: (——) rigid rods, $b = a = 0$; (- - -) $a = 0$, $b = 3$; crossed line, hollow cylinder, $a = 2$, $b = 3$.

may be found in ref 4, especially the case of a radially stratified cylinder. It is important to recognize that this expression has the proper limiting behavior.

(1) In the limit $b \to 0$, $a \to 0$, one obtains the *rigid rod* result[6]

$$P(\mathbf{q}) = u^{-1}\int_0^u \mathrm{d}x \left(\frac{\sin x}{x}\right)^2 \tag{3}$$

with $u = (qL/2)$. The limit $a \to 0$ corresponds to the case of a right circular cylinder of finite thickness.

(2) In the limit $L \to 0$, $a \to 0$, one obtains the *solid disk* result[7]

$$P(\mathbf{q}) = \int_0^\pi \mathrm{d}(\cos\theta)\, F(z\sin\theta) = \left(\frac{2}{z^2}\right)[1 - F(2z)] \tag{4}$$

where $F(x) = 2J_1(x)/x$ and $z = bq$. The equality in eq 4 was originally correctly stated by Kratky and Porod[7] and is frequently repeated without proof.[4,5] A direct proof requires some ingenuity.[8]

(3) In the limit of an *infinitesimal shell* $a \to b$, one obtains

$$P(\mathbf{q}) = \frac{1}{2}\int_0^\pi \mathrm{d}\theta \sin\theta \left[\frac{\sin(u\cos\theta)}{u\cos\theta} J_0(z\sin\theta)\right]^2 \tag{5}$$

which is consistent with the result for rings given by Oster and Riley.[9]

(4) In the limit $q \to 0$, one obtains the *low* q result:

$$P(\mathbf{q}) = 1 - \frac{q^2S^2}{3} + \mathcal{O}(q^4) \tag{6}$$

where S^2 is, by necessity,[10] the radius of gyration of the hollow cylinder

$$S^2 = \frac{b^2 + a^2}{2} + \frac{L^2}{12} \tag{7}$$

(5) Limiting expressions in the *large* q limit depend upon the relative magnitude of the parameters. For example, in the limit $qL \to \infty$, qa, qb finite one obtains

$$P(\mathbf{q}) = \frac{\pi}{2qL}\left\{\frac{1}{b^2 - a^2}[b^2F(bq) - a^2F(aq)]\right\}^2 \tag{8}$$

The quadrature in eq 2 cannot be evaluated analytically but, of course, can be numerically evaluated for pertinent values of the parameters q, L, b, and a. In addition, useful expansions may be constructed in various regions of interest. For example, in the limit of a hollow "needle", where $a/L \ll 1$, $b/L \ll 1$, and $u = qL/2 \sim 1$, one may easily show, to order $(a/L)^2$ and $(b/L)^2$

$$P(\mathbf{q}) = \left[1 - \left(\frac{b^2 + a^2}{L^2}\right)u^2\right]P_{\mathrm{rod}}(\mathbf{q}) + \left(\frac{b^2 + a^2}{2L^2}\right)\left[1 - \frac{\sin(2u)}{2u}\right] \tag{9}$$

where $P_{\mathrm{rod}}(\mathbf{q})$ is given by eq 3.

Figure 1 presents results for $P(q)$ obtained from numerical evaluation of eq 2 for illustrative values of the parameters: $L = 10$, $b = 3$, and $a = 2$. The hollow cylinder results lie very close to the comparable solid cylinder result for $L = 10$, $b = 3$, and $a = 0$, although it is somewhat more sharply peaked in the forward direction. This suggests that intensity angular distribution measurements are not sensitive to the internal configuration of molecular multisubunit assemblies.

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CNDO/2 Charge Density Calculation for Large Molecules

OSAMU KIKUCHI

Department of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 305, Japan. *Received June 23, 1981*

Molecular mechanics calculation is a popular technique for investigating intramolecular and intermolecular properties of macromolecules.[1] It requires the evaluation of atomic charge densities so as to calculate the electrostatic interaction energy. The use of the semiempirical CNDO/2 and ab initio MO methods has become popular for this purpose,[2,3] although bond moments, electronegativities of atoms, and Del Re charges are still used for a simple estimation of the charge distribution. However, these MO methods cannot easily be applied to large molecules because of limited computer core memory; the charge densities of large molecules are usually estimated from those of the smaller model compounds. This note describes the direct calculation of charge densities of large molecules at the level of the CNDO/2 approximation.[4]

In the SCF CNDO method, the orthogonal **C** matrix which satisfies

$$\tilde{\mathbf{C}}\mathbf{F}\mathbf{C} = \mathbf{E} \tag{1}$$

must be found, where **F** is the Fock matrix and **E** is the diagonal orbital-energy matrix. The charge densities are calculated from the diagonal elements of the density matrix, **R**, which is constructed by the occupied part of the **C** matrix:

$$\mathbf{R} = \mathbf{C}_o\tilde{\mathbf{C}}_o \tag{2}$$

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