# Static scattering function for randomly broken chains[a)]

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To analyze small angle neutron, x-ray, or static light scattering data from stiff macromolecules in dilute solutions, semiflexible chain models are needed. The randomly broken chain model is used to calculate by numerical simulation the static scattering function. It is then compared to other models.

## INTRODUCTION

Many models have been proposed to describe macromolecular chain stiffness. Some of them, such as the worm-like chain model,[1,2] describe the chain as a continuous object rather than a linked series of discrete monomeric units. An advantage of this continuous chain approach (large number of monomeric units $N\to\infty$, small statistical segment length $b\to 0$ with the requirement that the chain contour length Nb remains finite) is that some of the calculations are tractable analytically. Even though the intramolecular pair distribution function of worm-like chains is not known, equilibrium averages such as the one involved in the static structure factor:

$$S(q) = (1/N^2) \sum_{i,j=1}^{N} \langle \exp(\mathbf{iq}\cdot\mathbf{R}_{ij})\rangle \qquad (1)$$

have been estimated. In this definition, $q = (4\pi/\lambda)\sin(\theta/2)$ is the scattering wave number, $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ is the interdistance between two monomers $i$ and $j$ (that belong to the same chain) and all monomers have been assumed to scatter identically. Some models are based on expansions close to the rigid rod limit[3] or to the random flexible coil limit[4] whereas one model[5] is based on an extrapolation between these two stiffness limits.

The randomly broken chain model introduced by Garcia Molina and de la Torre[6] assumes that the chain is made of $\nu$ straight segments, each comprising a random number of monomeric units. These authors[6] calculated single-chain characteristic quantities such as the radius of gyration or the end-to-end distance by generating (on a digital computer) a sampling of randomly broken chains. It seems useful (for the analysis of small angle neutron, x-ray, or static light scattering data from macromolecules in dilute solutions) to calculate the static structure factor $S(q)$ for this model and compare it with a very simple model, the sliding rod model.[7] This last model assumes that the chain behaves as a rigid rod for lengths smaller than a characteristic length $a = (n-1)b$ (used as a stiffness parameter reminiscent of the statistical Kuhn length) whereas longer chain portions follow Gaussian statistics (flexible coils). The randomly broken chain model is also compared to three other models valid in the light scattering (small $q$) region: Norisuye–Murakama–Fujita model[3] based on an expansion of the distribution function near the rod limit, Yamakawa–Fujii[8] (Hermite polynomial expansion of the distribution function), and Sharp–Bloomfield[9] (expansion of the distribution function close to the Gaussian coil limit).

Only finite size chains at the infinite dilution limit are considered. Since scattering experiments are performed at finite concentrations (dilute solutions) concentration corrections would have to be included to analyze scattering data. Such corrections are not discussed here. Also excluded volume effects are neglected, i.e., solutions are assumed to be at the theta condition.

## THE RANDOMLY BROKEN CHAIN AND THE SLIDING ROD MODELS

Randomly broken chains are easily generated (Garcia Molina and de la Torre[6]) by assuming a probability $p$ that a bond be "rigid" and $1-p$ that it be "flexible." A rigid bond links two colinear statistical segments whereas a flexible one is an unhindered universal joint. The two limits in flexibility for a rigid rod and a freely jointed chain are obtained with $p = 1$ and $p = 0$, respectively. A persistence length $c = b/(1-p)$ and a statistical Kuhn length $a = 2c$ can be defined.

A statistical set of chains is generated by assuming random orientations (two angles for each step) if the bond is flexible. The static structure factor is then calculated by forming the following ensemble average over conformations:

$$S(qa) = (1/N^2) \sum_{i,j=1}^{N} \langle \sin(qR_{ij})/qR_{ij}\rangle, \qquad (2)$$

where an average over the random orientation of the scattering wave vector $\mathbf{q}$ has already been performed.

In the Introduction, it was mentioned that the rigid rod portion $[R_{ij} \leqslant (n-1)b]$ in the sliding rod model is reminiscent of the statistical Kuhn length $a$. A note of caution is in order at this point. For finite chain lengths, the rigid rod limit is obtained for $(n-1)b = L$ in the sliding rod model whereas this limit corresponds to an infinite Kuhn length for conventional worm-like chains (as well as for randomly broken chains). Even though the same symbol $a = (n-1)b$ is used (merely for the sake of comparison of the two models) to represent chain stiffness, it should be remembered

[a)] Dedicated to Professor R. K. Osborn, University of Michigan, on the occasion of his formal retirement.

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that $a$ and $(n-1)b$ are identical only for infinite chains and for finite chains close to the flexible coil limit. In the sliding rod model, the static structure factor is given by

$$S(qa) = 1/N + 2/N\left[\sum_{i=1}^{n-1}(1-i/N)\sin(qbi)/qbi + \sum_{i=n}^{N}(1-i/N)\exp(-q^2b^2ni/6)\right], \quad (3)$$

where we have kept the self-term ($i=j$) and used the fact that the equilibrium average depends on $|i-j|$ only. The remaining summations in Eq. (3) are performed numerically.

## OTHER SEMIFLEXIBLE CHAIN MODELS

Three semiflexible chain models useful for the analysis of small angle light (small $q$) scattering data are compared to the randomly broken chain model. Norisuye, Murakama, and Fujita[3] carried an expansion of the distribution function around the rigid rod limit (valid for $L/a \leqslant 1$) up to the fifth order in $L/a$ to obtain

$$S(qa) = P_0 + P_1(L/a) + P_2(L/a)^2 + P_3(L/a)^3 + P_4(L/a)^4 + P_5(L/a)^5, \quad (4)$$

where the coefficients $P_0$, $P_1$, $P_2$, $P_3$, $P_4$, and $P_5$ are given in Eq. (26) of Ref. (3). Note that there is a misprint in the expression of $P_3$ [Eq. (26)] which should read

$$P_3 = (1/63x^5)[-256x + (1512 - 500x^2 + 307x^4/15)\sin(x) - (1256x - 124x^3 + 31x^5/15)\cos(x)], \quad (5)$$

where $x = qL$. Yamakawa and Fujii[8] used a Hermite polynomial expansion of the distribution function and presented numerical variations of $S(qa)$ for different values of $L/a$ (valid for $1 < L/a \leqslant 10$). Sharp and Bloomfield,[9] on the other hand, used the first Daniels[4] distribution function (expansion around the Gaussian coil limit, i.e., valid for $L/a > 10$) to calculate

$$S(qa) = (2/y^2)[\exp(-y) - 1 + y] + 4a/15L + 7a/15yL - 11a\exp(-y)/15L - 7a\exp(-y)/15yL \quad (6)$$

with $y = q^2a^2L/6a$ as given by Eq. (B3) of Ref. 9. Note that the last term in this Eq. (B3) has been misprinted and was corrected in Eq. (27) of Ref. 8. Note also that lengths have been normalized in this paper with respect to the Kuhn length $a$, as done in Refs. 3, 8, and 9.

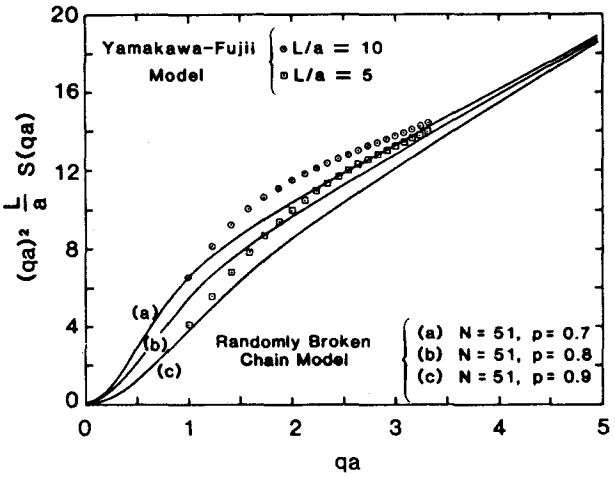


FIG. 2. Kratky plot $(qa)^2(L/a)S(qa)$ vs $qa$ for the randomly broken chain model with $N = 51$, $p = 0.7$, 0.8, and 0.9 and for the Yamakawa–Fujii model with $L/a = 5$ and 10.

## DISCUSSION

As for the Kratky–Porod worm-like chain, the pair distribution function $P(R_{ij})$ for a randomly broken chain is not known analytically. Garcia Molina and de la Torre[6] plotted $P(R_{ij})$ (numerically) for $N = 200$ and $p = 0.98$. We are re-

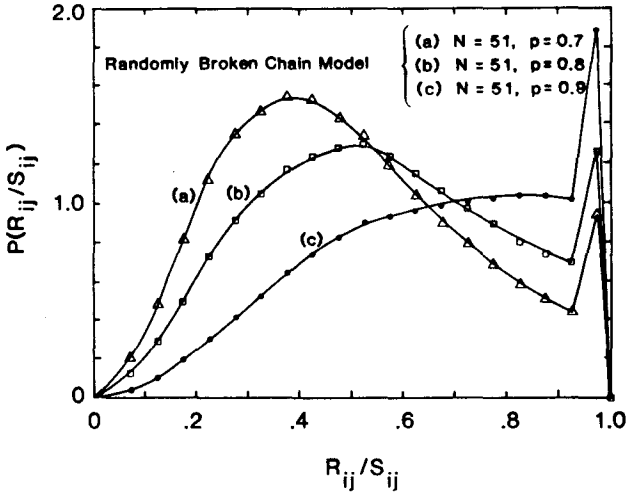


FIG. 1. Single chain pair distribution function $P(R_{ij}/S_{ij})$ for increasing normalized monomer–monomer interdistance $R_{ij}/S_{ij}$ ($S_{ij}$ is the contour length between monomers $i$ and $j$) for the randomly broken chain model ($p = 0.7$, 0.8, and 0.9).

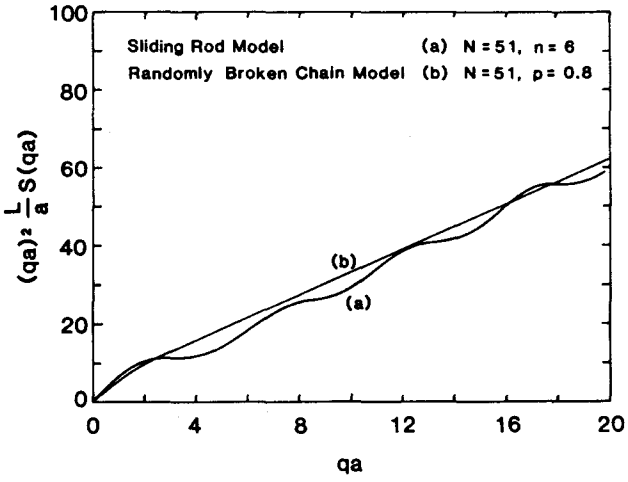


FIG. 3. Comparison of the Kratky plots $(qa)^2(L/a)S(qa)$ vs $qa$ for (a) the randomly broken chain model ($N = 51$, $p = 0.7$) and (b) the sliding rod model ($N = 51$, $n = 6$).

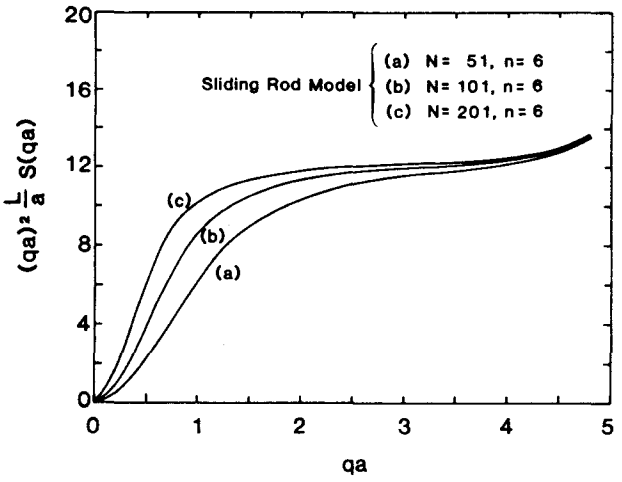


FIG. 4. Kratky plot $(qa)^2(L/a)S(qa)$ vs $qa$ for the sliding rod model with $n = 6$, $N = 51$, 101, and 201.

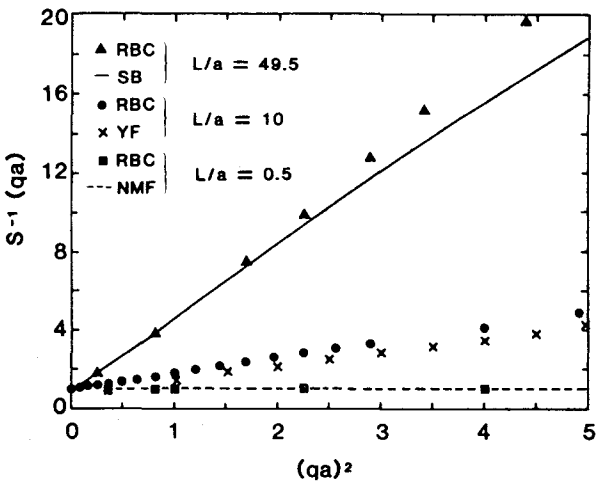


FIG. 5. Infinite dilution Zimm plot $S^{-1}(qa)$ vs $(qa)^2$ for the randomly broken chain model (RBC), for the Norisuye–Murakama–Fujita (NMF) model, for the Yamakawa–Fujii (YF) model, and for the Sharp–Bloomfield (SB) model.

producing their result (with a normalized variable $R_{ij}/S_{ij}$) in Fig. 1 for $p = 0.7$, 0.8, and 0.9 to show the effect of varying chain stiffness. As the stiffness parameter $p$ increases, the broad peak of $P(R_{ij}/S_{ij})$ is seen to move to higher values of $R_{ij}/S_{ij}$, its height decreases whereas the height of the sharp peak (at $R_{ij}/S_{ij} = 1$) increases. This sharp peak close to $R_{ij}/S_{ij} = 1$ corresponds to the relative number of chains that turned out to be single rods. Note that for the sliding rod model $P(R_{ij}/S_{ij})$ is given by

$$P(R_{ij}/S_{ij}) = 1; \quad R_{ij} \leqslant a,$$
$$P(R_{ij}/S_{ij}) = 4\pi R_{ij}^2 (1/2\pi S_{ij}^2)^{3/2} \times \exp(-3R_{ij}^2/2S_{ij}^2); \quad R_{ij} > a, \qquad (7)$$

where $S_{ij}$ is the contour length between monomers $i$ and $j$. Because of this sudden change from a rod-like to a flexible coil-like distribution at $R_{ij} = a$, the sliding rod model is not realistic physically and therefore gives an overall oscillatory behavior of the static scattering function[10] as shown in Figs. 3 and 4. Figure 2 represents the effect of changing chain stiffness (the parameter $p$) on the product $(qa)^2(L/a)S(qa)$ (Kratky plot). Recall that this product saturates to a constant value for Gaussian flexible chains but grows linearly (at high $qa$) for rigid rods and semiflexible chains.

The three solid curves of Fig. 2 correspond to $L/a = 5$, 10, and 15. On the same figure, $S(qa)$ given by Yamakawa and Fujii (taken from Table I of Ref. 8 for $L/a = 5$ and 10) is plotted for the sake of comparison. Figure 5 shows the variation of $S^{-1}(qa)$ vs $(qa)^2$ (Zimm plot at the infinite dilution limit) for the randomly broken chain model and for the three other expansion based models (Norisuye–Murakama–Fujita for $L/a = 0.5$, Yamakawa–Fujii for $L/a = 10$ and Sharp–Bloomfield for $L/a = 49.5$).

This paper dealt with the static structure factor (equilibrium single chain property) of semiflexible chains at infinite dilution. The sliding rod model has been applied successfully to investigate dynamical properties[7,10] as well (the initial slope of the dynamic scattering function also called first cumulant). Such dynamical properties could also be investigated for randomly broken chains.

## ACKNOWLEDGMENTS

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