experiment. Besides the substantial reduction in computational time, we have found that the ability to display and calculate properties of models almost instantly has given us insights into the geometric and energetic properties of the molecules, and enables us to survey and compare more quickly the possible solutions and choose the most likely ones for further study. There are many intramolecular relationships which are immediately obvious when visually displayed but which are obscure or invisible when expressed on paper as numerical coordinates.[14]

The most pressing application is in solution of the structures of crystalline polynucleotides, such as tRNA. Yeast tRNA$^{\mathrm{Phe}}$ has been shown to crystallize in a conformation containing two helical regions orientated at right angles to each other. The solution reported by Rich *et al.*[2] is at 3-Å resolution, which does not enable precise definition of atomic coordinates. Further refinement against higher angle X-ray data, essential for comparison with monomer or dimer structures, requires a very good atomic model for a trial structure. The graphical method presented here would be ideal for developing such models, using the helicity parameters and phosphorus atom positions in the helical regions of the 3-Å structure as constraints. This possibility is now being explored with crystallographic data for tRNA available in our laboratory.

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Singularities of the Kirkwood–Riseman Equations of Polymer Hydrodynamics

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ABSTRACT: The equations of polymer hydrodynamics formulated by Kirkwood and Riseman utilize a collection of point forces which act as centers of frictional resistance. This model has been shown by Zwanzig, Kiefer, and Weiss to possess unphysical singularities when the segmental friction constant is high. Here, it is shown that, for the rigid rod molecule, the singularities are artifacts of the model. The singularities disappear if the segment represented by the point force is small, and if the segment has a finite cross section.

The methods of macroscopic hydrodynamics have been applied with considerable success to particles of molecular size. A procedure developed by Kirkwood and Riseman[1] (KR) from earlier work of Burgers[2] and Oseen[3] has been applied widely to polymer solutions, and a variety of results by different workers attest to the success of the procedure.[1]

One of the steps in the KR calculation is based on the solution of a set of simultaneous equations. In an important critical paper, Zwanzig, Kiefer, and Weiss[4] (ZKW) showed, that for both rigid rod and coiling macromolecules, the equations become singular for certain values of the segmental friction constant. In such a case there is no solution of the equations, and serious doubt is thrown on the logical structure of the Kirkwood–Riseman method.

It is our objective here to show, for the particular case of the rigid rod molecule, that the singularities disappear if the finite cross section of the macromolecule is introduced in the model, and if the segmental unit of the rod is sufficiently small.

In the KR equations for the translational diffusion problem, the mean force exerted on the fluid by segment number l is

$$\langle \mathbf{F}_l \rangle = -\zeta \mathbf{e}_x - (\zeta / 6\pi\eta_0) \sum_{s=0}^{N}{}' \langle 1/R_{ls} \rangle \langle \mathbf{F}_s \rangle \qquad l = 0 \text{ to } N \quad (1)$$

ζ is the segmental friction constant, η_0 is the viscosity of the solvent, $\mathbf{e}_x$ is a unit vector in the x direction, R_{ls} is the distance between segments l and s, angular brackets signify an average value taken over all possible orientations and internal configurations of the molecule, Σ' signifies a sum over all segments $s \neq l$. It is understood that the system is subject to overwhelming Brownian motion, and therefore the molecules are not preferentially oriented. Equation 1 may be written in matrix form

$$\mathbf{M}\mathbf{x} = \mathbf{y} \qquad (2a)$$

$$\mathbf{M} = \{M_{ls}\} \qquad (2b)$$

$$M_{ls} = \delta_{ls} + (1 - \delta_{ls})(\zeta / 6\pi\eta_0)\langle 1/R_{ls} \rangle \qquad (2c)$$

A similar set of equations apply to intrinsic viscosity. The vectors $\mathbf{x}$ and $\mathbf{y}$ differ from those of the diffusion problem. However, the point of crucial significance is that the matrix $\mathbf{M}$ remains the same. The existence of a solution of eq 2a depends on **M**, and the structure of solutions of the intrinsic viscosity problem mimics the translational diffusion problem faithfully. Accordingly, it is sufficient to consider eq 1 above in resolving the ZKW singularity problem.

If a rigid rod polymer molecule is divided into N segments each of length b as was done by Kirkwood and collaborators,[5,6] the elements of **M** become

$$M_{ls} = \delta_{ls} + (1 - \delta_{ls})\lambda/|l - s| \tag{3a}$$

$$\lambda = \zeta/6\pi\eta_0 b \tag{3b}$$

ZKW showed that the determinant of **M** vanishes for certain critical values of λ, and in these instances, the matrix is singular. For N equals ten the lowest singularity, λ_1, is at 0.771 and as N approaches infinity $\lambda_1 = 0.722$. If the rigid rod molecule were composed of touching spherical beads which obey Stokes law, $\lambda = 0.5$. ZKW argued persuasively, that given the complexity of molecular shape, a value of λ larger than 0.5 is certainly feasible, and thus the Kirkwood–Riseman equations contain anomalies which require further analysis.

We agree with this conclusion. In what is to follow, we modify the model in two ways. First, the finite cross section of the chain molecule will be introduced into the problem. In this way, the crucial distance $\langle 1/R_{ls}\rangle$ never becomes infinite provided that the source of force acting on the fluid originates on the axis of the molecule and acts on the surface of the molecule.[7] Secondly, the segment length is redefined, and allowed to decrease while the number of segments increase so as to maintain the overall length of the molecule. These are desirable modifications since the segment is an artifact for a rigid rod model, while the molecular length and cross section are not.

Calculating $\langle 1/R_{ls}\rangle$ according to this model and substituting the result in eq 1 yields

$$\langle \mathbf{F}_l\rangle = -\zeta \mathbf{e}_x - \lambda {\sum_{s=0}^{N}}' \frac{\langle \mathbf{F}_s\rangle}{\left[(l - s)^2 + \left(\frac{r}{b}\right)^2\right]^{1/2}} \tag{4}$$

where r is radius of the cross section of the molecule.

If the force on a fluid is composed of a sum of forces originating from N small segments, division of each of these segments into a number of smaller units, requires that the force per segment be proportional to the segment length in order that the total force remain the same. Since the segmental friction constant is defined as the force per segment per unit velocity difference,[8] the segmental friction constant is proportional to segment length as well. This is the basis for the concept of friction constant per unit length utilized in continuous chain models.

We modify eq 4, by defining $b' = b/x$ and $N' = Nx$, where x is any integer greater than unity. Equation 4 becomes

$$\langle \mathbf{F}_l\rangle = -\zeta \mathbf{e}_x - \lambda {\sum_{s=0}^{Nx}}' \frac{\langle \mathbf{F}_s\rangle}{\left[(l - s)^2 + \left(\frac{rx}{b}\right)^2\right]^{1/2}} \tag{5}$$

Equation 5 follows from the fact that $\langle \mathbf{F}_l\rangle$ is proportional to ζ, and λ is a constant independent of segment length.

Equation 5 contains terms which are not present in eq 4. The hydrodynamic interaction is taken between all pairs of segments, the sum on the right side of eq 4 includes all $s \neq l$. As the segments become more numerous, hydrodynamic interaction between new segments which were part of the same segment is added. This has an appreciable effect on the singularities of the matrix **M** for the segmented rod.

The form of **M** corresponding to eq 5 is

$$M_{ls} = \delta_{ls} + (1 - \delta_{ls})\lambda[(l - s)^2 + p^2]^{-1/2} \tag{6}$$

$$p = rx/b$$

If **M** has a zero eigenvalue, the set of eq 6, does not possess a solution. We now show that for any segmental friction constant ζ, b' can be chosen to be sufficiently short that the lowest eigenvalue of M is greater than zero.

According to the theory of Toeplitz forms developed in Grenander and Szego,[9] upper and lower bounds on the eigenvalues of **M** can be found by considering the function $F(x)$ defined by

$$F(x) = \sum_{n=-\infty}^{\infty} \varphi_n e^{inx} \tag{7a}$$

$$\varphi_{l-s} = M_{ls} \tag{7b}$$

It is easily shown that the function $F(x)$ corresponding to M_{ls} of eq 5 is

$$F(x) = 1 + 2\lambda \sum_{n=1}^{\infty} \frac{\cos nx}{(n^2 + p^2)^{1/2}} \tag{8}$$

There are N eigenvalues of **M** which can be arranged in increasing order. If the greatest lower bound of $F(x)$ is b and the least upper bound[10] of $F(x)$ is B, then all eigenvalues lie between b and B. As the dimensions of **M** approach infinity, the lowest eigenvalue approaches b, and the highest eigenvalue approaches B. These upper and lower bounds can be infinite.

From eq 8, it is apparent that the range $0 \leq x \leq \pi$ is sufficient to characterize $F(x)$. $F(0)$ is infinite, and therefore the eigenvalues of **M** do not possess an upper bound. $F(x)$ is a continuous function, is not a constant, and therefore must reach an absolute minimum somewhere on the internal $0 \leq x \leq \pi$. In Appendix A it is shown that this minimum, in fact, occurs at $x = \pi$. We have then

$$F(\pi) = 1 + 2\lambda \sum_{n=1}^{\infty} \frac{(-1)^n}{(n^2 + p^2)^{1/2}} \tag{9}$$

The lowest eigenvalue of eq 5 is equal to or greater than $F(\pi)$.

Denote the sum in eq 9 by $S(p)$. The series is alternating, the terms are monotonically decreasing and approach zero as n becomes large. $S(p)$ is convergent. Rewriting $S(p)$ we have

$$S(p) = -\sum_{k=1}^{\infty}\left[\frac{1}{[(2k - 1)^2 + p^2]^{1/2}} - \frac{1}{[(2k)^2 + p^2]^{1/2}}\right] \tag{10}$$

Combining the two terms under the sum on the right of eq 9 and rationalizing the numerator yields

$$S(p) = \frac{1}{p^2}\sum_{k=1}^{\infty}\frac{(1 - 4k)}{D} \tag{11a}$$

$$D = \left\{1 + \frac{(2k - 1)^2}{p}\right\}^{1/2}\left\{1 + \frac{(2k)^2}{p}\right\}^{1/2}\left[\left\{1 + \frac{(2k)^2}{p}\right\} + \left\{1 + \frac{(2k - 1)^2}{p}\right\}^{1/2}\right] \tag{11b}$$

$S(p)$ is evaluated for large p by setting $2k/p = \tan\theta$, $1/p = \mathrm{d}\theta$, and discarding terms of the order of $(\mathrm{d}\theta)^2$. The result is

$$S(p) \approx -\frac{1}{2p}\int_0^{\pi/2} \sin\theta \, \mathrm{d}\theta = -\frac{1}{2p} \tag{12a}$$

Accordingly

$$F(\pi) \approx 1 - \lambda/p \tag{12b}$$

Table I
Some Values of p and $S(p)$

p	$S(p)$
0.5	−0.599262
1.0	−0.440917
2.0	−0.248167
3.0	−0.166602
5.0	−0.100000
7.0	−0.071429
10.0	−0.050000

If the segment length becomes small, p becomes large. For any given value of λ, an appropriate choice of p makes $F(\pi)$ greater than zero, and the lowest eigenvalue of $\mathbf{M}$ greater than zero as well. Therefore, by allowing the segment length of the rod-like molecule to approach zero in the real polymer chain of finite cross section, the singularities of the rod-like molecule vanish.

The correspondence between the approximate result of eq 12a and the series

$$S(p) = \sum_{n=1}^{\infty} \frac{(-1)^n}{(n^2 + p^2)^{1/2}} \tag{13}$$

is shown by summing a finite number of terms of eq 13. Utilizing Euler's transformation to speed convergence,[11] we write

$$S_N(p) = \sum_{n=1}^{N} \frac{(-1)^n}{(n^2 + p^2)^{1/2}} + T \tag{14a}$$

$$v_k = \frac{(-1)^n}{(k^2 + p^2)^{1/2}} \tag{14b}$$

$$T = \sum_{q=1}^{Q} \frac{1}{2^q} D^q v_{N+1} \tag{14c}$$

$$Dv_k = v_k - v_{k+1} \tag{14d}$$

$$D^2 v_k = Dv_k - Dv_{k+1} \tag{14e}$$

$$D^n v_k = D^{n-1} v_k - D^{n-1} v_{k+1} \tag{14f}$$

The upper limit, Q, of the sum in eq 14c was taken to be seven as a matter of convenience. Calculations were carried out on a DEC-10 computer, setting N of eq 14a equal to 2000 and to 2001. Double precision arithmetic was used.

In Table I, we show some values of $S(p)$ obtained from the sum as a function of p. The correspondence between the sum and limiting value of eq 12a is already close when p is greater than 2.

Zwanzig, Kiefer, and Weiss also found singularities of the Gaussian coil polymer molecule which were similar to those encountered for the rigid rod. In trying to resolve the difficulty by the same method used for the rigid model, some new elements are encountered. These arise in the following way.

The extended chain length L and mean-square end-to-end distance R of a Gaussian coil obey the relations

$$L = Nb \tag{15a}$$

$$R^2 = Nb^2 \tag{15b}$$

In carrying out the transformation $b' = b/x$ and $N' = Nx$, and requiring that neither L nor R be changed, we find

$$L = N'b' \tag{16a}$$

$$R^2 = N'b'^2 x \tag{16b}$$

In the primed system, R^2 is a function of x. Obviously the bond length b which yields the usual result (eq 15b) for mean end-to-end distances is not arbitrary in the Gaussian chain model, while as we have seen earlier, b is arbitrary for the rigid rod. In Appendix B we show that the ZKW singularities disappear for the Gaussian coil if x is sufficiently large. The meaning of this is unclear. It depends on the inclusion of hydrodynamic interaction between subsegments in the primed system which were part of the same segment in the unprimed system. It is also a reflection of the fact that Gaussian statistics for segments on a polymer chain make little sense if terms arising from near neighbors become important. This had been pointed out in a scattering problem by Luzzati and Benoit[12] a number of years ago. It had not appeared to be important in the hydrodynamic calculation until the ZKW report of singularities.

The Kratky–Porod model of a polymer chain[13] is rodlike at short intrachain distances and coil like at long intrachain distances. It would be desirable, for completeness, to demonstrate that singularities arising from a segmented Kratky–Porod-type model also disappear if the segment is sufficiently small. We have not succeeded in doing this. It is likely, however, that those singularities will disappear since the Kratky–Porod molecule is rodlike at short intrachain distances which are crucial to the problem.

Discussion

In analyzing the nature of singularities in the Kirkwood–Riseman equations found by Zwanzig *et al.*, we have made use of the fact that a segment of a rigid rod molecule is an artifact, and a segmental model approaches reality as the segment length approaches zero. A satisfactory resolution of the problem need only remove the singularities as the segment length becomes small. This, we have done.

Another fundamental difficulty does remain. It is perfectly proper to imagine a collection of resisting particles connected by strings which have a negligible effect on the flow. This may not be a good model for a polymer, but is a conceivable model for some real body of either macroscopic or molecular dimensions, and for such a system, the singularities will exist. We have not been able to pinpoint in a formal way where the trouble lies, but there is one aspect which deserves special mention.

The singularities only occur when the segmental friction constant is high, of the order of three halves that obtained by Stokes law. That this is possible, given the irregularity of a molecular surface and the cavalier way of treating Brownian motion of the KR method, is evident. Yet there may be a natural upper bound on frictional drag which comes from the hydrodynamic equations themselves, the friction constant being a parametric form of a result obtainable in principle from a complete detailed analysis. In order to show that the singularities are real, it is necessary to prove that the friction constant can reach the high values required. We wish to emphasize that the probable existence of a natural upper bound on the friction constant has been discussed in earlier work. A complete discussion with particular reference to rod-like molecules has been presented by Yamakawa and Tanaka.[14]

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Appendix A

Here we wish to demonstrate that the function

$$F(x,p) = \sum_{n=1}^{\infty} \frac{\cos nx}{(n^2 + p^2)^{1/2}} \qquad 0 < x \leq \pi \tag{A1}$$

possesses a minimum at $x = \pi$. It is well known that

$$\frac{1}{(n^2 + p^2)^{1/2}} = \frac{2}{\pi}\int_0^\infty \frac{\mathrm{d}y}{n^2 + p^2 + y^2} \qquad \text{(A2)}$$

Substitution of eq A2 in eq A1 and reversal of the order of integration and summation leads to

$$F(x, p) = \frac{2}{\pi}\int_0^\infty \mathrm{d}y\left(\sum_{n=1}^\infty \frac{\cos nx}{n^2 + p^2 + y^2}\right) \qquad \text{(A3)}$$

The sum in eq A3 is known and is given by[15]

$$\sum_{n=1}^\infty \frac{\cos nx}{n^2 + p^2 + y^2} = \frac{1}{2(y^2 + p^2)^{1/2}}\left[\frac{\pi \cosh [(\pi - x)(p^2 + y^2)^{1/2}]}{\sinh [\pi(p^2 + y^2)^{1/2}]} - \frac{1}{(p^2 + y^2)^{1/2}}\right] \quad 0 < x < 2\pi \qquad \text{(A4)}$$

Substitution of eq A4 in eq A3 leads to

$$F(x, p) = \int_0^\infty \frac{\cosh [(\pi - x)(p^2 + y^2)^{1/2}]\mathrm{d}y}{(p^2 + y^2)^{1/2} \sinh [\pi(p^2 + y^2)^{1/2}]} - \frac{1}{2p} \qquad \text{(A5)}$$

For any x, $0 < x < \pi$, the integrand in eq A5 decreases as $\exp [-x(p^2 + y^2)^{1/2}]$ for large y. Therefore the integral of eq A5 converges. The numerator of the integrand decreases monotonically as x goes from 0 to π, and $F(x,p)$ is a minimum at $x = \pi$, where the numerator of the integrand of eq A5 equals unity.

The inversion of order of summation and integration in arriving at eq A3 requires justification.[16] (1) The series

$$\sum_{n=1}^\infty \frac{\cos nx}{n^2 + p^2 + y^2}$$

converges uniformly for all y, $0 \le y \le \infty$. (2) The integral of eq A5 converges uniformly for $a \le x \le \pi$, $a > 0$, $p > p_0 > 0$. This is sufficient for

$$\int_0^\infty \mathrm{d}y \sum_{n=1}^\infty \frac{\cos nx}{n^2 + p^2 + y^2} = \sum_{n=1}^\infty \cos nx \int_0^\infty \frac{\mathrm{d}y}{n^2 + p^2 + y^2} \qquad \text{(A6)}$$

which justifies the steps leading to eq A3.

Appendix B

The force exerted by lth segment of a Gaussian coil on the fluid is in analogy with (eq 4)

$$\langle \mathbf{F}_l \rangle = -\zeta \mathbf{e}_x - \lambda^* \sum_{s=0}^{\infty}{}' \frac{\langle \mathbf{F}_s \rangle}{[|l - s| + q(r,b)]^{1/2}} \qquad \text{(B1)}$$

$$\lambda^* = \zeta/[(6\pi^3)^{1/2}\eta_0 b] \qquad \text{(B2)}$$

In this formulation, the segment length is b and the number of segments is N. The quantity $q(r,b)$ merely takes account of the finite thickness of the coil in computing the mean distance from one point on an axis to another on the surface. It is analogous to $(r/b)^2$ in eq 4.

In the primed system $N' = Nx$ and $b' = b/x$, the change in R^2, the mean end-to-end distance, shown in eq 15b and 16b has its counterpart in $\langle 1/R_{ls} \rangle$. This latter which in the unprimed system is given by

$$\left\langle \frac{1}{R_{ls}} \right\rangle = \left(\frac{6}{\pi}\right)^{1/2} \frac{\zeta}{\eta_0 b |l - s|^{1/2}} \qquad \text{(B3)}$$

becomes

$$\left\langle \frac{1}{R_{ls}} \right\rangle = \left(\frac{6}{\pi}\right)^{1/2} \frac{\zeta}{\eta_0 b x^{1/2} |l - s|^{1/2}} \qquad \text{(B4)}$$

The substitution of eq B4 in eq B1 yields

$$\mathbf{F}_l = -\zeta \mathbf{e}_x - (\lambda^*/x^{1/2}) \sum_{s=0}^{Nx}{}' \frac{\langle \mathbf{F}_s \rangle}{[|l - s| + q(r,b')]^{1/2}} \qquad \text{(B5)}$$

In the ZKW calculation for the Gaussian coil, the first singularity in eq B1 occurs when $\lambda^* = 0.827$. In that model of point segments, $q(r,b) = 0$. In our model of a polymer molecule of finite cross section, $\lambda^*/x^{1/2}$ in the primed system replaces λ^* in the unprimed system. By choosing x to be sufficiently large, $\lambda^*/x^{1/2} < 0.827$, and the singularities of the model vanish.

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