Effects of Chain Stiffness on Equivalent Segment Length

James M. Bailey

School of Medicine and Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901.

Received July 17, 1978

ABSTRACT: A theory for the calculation of effective segment lengths of stiff polymers is developed. The theory is applicable to polymers modeled as space curves and characterized by a potential energy of the form $\int_0^L \mathrm{d}s\ [\beta\dot{\mathbf{u}}(s)^2 + \gamma\ddot{\mathbf{u}}(s)^2]$ ($\mathbf{u}(s)$ is the tangent vector of the space curve). To achieve a simple solution the constraints of differential geometry are relaxed and the calculation is restricted to chains of large contour length L. It is found numerically that the effective segment length, when normalized by the unperturbed segment length (for $\gamma = 0$), is a monotonically increasing function of γ/β^3 for all values of γ and β. The implications of this for polyelectrolytes is discussed.

It is well known that relatively stiff or short polymers cannot be accurately described as freely jointed chains.[1] This observation led some time ago to the development of the wormlike chain model.[2] Interest in the ramifications of this method of polymer characterization has persisted and has been especially notable in recent years. The original Kratky–Porod model has been extensively analyzed and also modified by the inclusion of stretching and torsional energies.[3-7] It is now generally accepted that this type of approach can adequately describe stiff chains.

In addition to serving as a model for short or stiff polymers, the wormlike chain representation also provides a means of relating the bending energy of the chain to its equivalent statistical segment length, in the limit of increasing contour length. This can be quite useful for chain molecules whose potential energy can be represented by an analytic function of $|\mathbf{r}(s) - \mathbf{r}(s')|$ (the distance between two points on the chain contour). The potential energy can then be expanded in a series, with the tangent vector $\mathbf{u}(s)$ and its derivatives serving as expansion variables. The lowest order term of this expansion should be proportional to $\dot{\mathbf{u}}(s)^2$. The coefficient of this term is the bending energy constant, which is simply related to the equivalent statistical segment length of the chain, in the limit of infinite length. This approach is exemplified by two recent studies of the electrostatic contribution to the persistence lengths of polyelectrolytes.[8,9]

While the approach to calculation of the persistence length of polyelectrolytes seems promising, it is valid only if the potential energy is well approximated by a bending energy alone. It is likely that in some cases one should include a more refined energy representation which includes terms not only in $\dot{\mathbf{u}}(s)^2$ but also in the next higher order derivative of the tangent vector. The purpose of this note is to provide the theoretical framework for relating the segment length to this next higher order term.

Theory

We consider a continuous space curve of length L described by $\mathbf{r}(s)$, $\mathbf{u}(s)$, and $\mathbf{a}(s)$ where s measures the contour length along the chain, $\mathbf{r}(s)$ is the radius vector from the origin to the point of contour length s, $\mathbf{u}(s)$ is the tangent vector

$$\mathbf{u}(s) \equiv \frac{\mathrm{d}\mathbf{r}(s)}{\mathrm{d}s} \equiv \dot{\mathbf{r}}(s)$$

and $\mathbf{a}(s)$ is the derivative of the tangent vector

$$\mathbf{a}(s) = \frac{\mathrm{d}\mathbf{u}(s)}{\mathrm{d}s} \equiv \dot{\mathbf{u}}(s)$$

We assume that the potential energy of the chain is given by

$$\int_0^L \mathrm{d}s[\alpha\mathbf{u}(s)^2 + \beta\mathbf{a}(s)^2 + \gamma\dot{\mathbf{a}}(s)^2] \tag{1}$$

where α is a stretching force constant, β is a bending force constant, and γ is a torsion force constant.[10] Note that the inclusion of a stretching energy, $\alpha\mathbf{u}(s)^2$, is not strictly consistent with the differentiable space curve model. It is well known that the tangent, $\mathbf{u}(s)$, of a continuous curve is constrained to be a unit vector.[4] Hence the term in $\alpha\mathbf{u}(s)^2$ should be a constant. This constraint, however, greatly complicates consideration of the statistical mechanics of this system.[7,10] Therefore in order to derive closed form expressions for $\langle R^2\rangle$, the mean-square end-to-end vector, we will relax the constraint on $\mathbf{u}(s)$, in the manner described by Freed. That is, we will not require that $\mathbf{u}(s)^2 = 1$. Instead we will employ α as an adjustable parameter to insure that the *average* value of $\mathbf{u}(L)^2$ for large L is equal to 1. This approach has been discussed at length by Freed.[10]

This relaxation of the constraints of differential geometry immensely simplifies our problem. We must point out, however, that this approach has been criticized by Yamakawa. In particular, he notes that the model is invalid near the rod limit or if the polymer is subject to an external force.[7] We propose to employ this model, however, to investigate the equivalent statistical segment length of the chain in the limit of increasing contour length. In this limit the model is valid and provides useful information.

With these reservations we proceed to development of the model. For the potential energy described by eq 1 Freed has shown that the probability of the chain having a configuration for which $\mathbf{u}(0) = \mathbf{U}_0$, $\mathbf{a}(0) = \mathbf{A}_0$, $\mathbf{u}(L) = \mathbf{U}$, and $\mathbf{a}(L) = \mathbf{A}$ is given by the following path integral[10]

$$\int_{\mathbf{u}(0)=\mathbf{U}_0}^{\mathbf{u}(L)=\mathbf{U}} \mathbf{D}[\mathbf{u}(s)] \int_{\mathbf{a}(0)=\mathbf{A}_0}^{\mathbf{a}(L)=\mathbf{A}} \mathbf{D}[\mathbf{a}(s)] \int \mathbf{D}[\mathbf{q}(s)] \times \exp\left\{-\int_0^L \mathrm{d}s[\alpha\mathbf{u}(s)^2 + \beta\mathbf{a}(s)^2 + \gamma\dot{\mathbf{a}}(s)^2 + i\mathbf{q}(s)\cdot\mathbf{a}(s) - i\mathbf{q}(s)\cdot\dot{\mathbf{u}}(s)]\right\}$$

where $\mathbf{u}(s)$, $\mathbf{a}(s)$, and $\mathbf{q}(s)$ may be considered "independent" variables since a generalized delta function (in the variable $\mathbf{q}(s)$) has been introduced to insure that

$$\mathbf{a}(s) = \dot{\mathbf{u}}(s)$$

We now note that this path integral is equivalent to the following function

$$N \exp\left\{-\int_0^L \mathrm{d}s[\alpha\mathbf{u}(s)^2 + \beta\mathbf{a}(s)^2 + \gamma\dot{\mathbf{a}}(s)^2 + i\boldsymbol{q}(s)\cdot\mathbf{a}(s) - i\boldsymbol{q}(s)\cdot\dot{\mathbf{u}}(s)]\right\} \tag{2}$$

where the path of integration is that which causes the integral to be stationary [and N preserves normalization].[11] To determine this path we apply the equations of Euler to the integrand, deriving the following relationships

0024-9297/79/2212-0091$01.00/0

$$2\gamma\ddot{\mathbf{a}} - 2\beta\mathbf{a} - i\mathbf{q} = 0 \qquad (3)$$

$$-i\dot{\mathbf{q}} - 2\alpha\mathbf{u} = 0 \qquad (4)$$

$$-i\mathbf{a} + i\dot{\mathbf{u}} = 0 \qquad (5)$$

(Note that we must deal with three variables **a**, **u**, and **q**).

If one differentiates eq 3 twice with respect to s and then employs eq 4 (after differentiation with respect to s) and 5 one can derive the following formula[15]

$$\gamma\tilde{\mathbf{a}} - \beta\ddot{\mathbf{a}} + \alpha\mathbf{a} = 0 \qquad (6)$$

The solutions of these equation are

$$\mathbf{a}(s) = \mathbf{C}_1 \exp(\epsilon_1 s) + \mathbf{C}_{-1} \exp(-\epsilon_1 s) + \mathbf{C}_2 \exp(\epsilon_2 s) + \mathbf{C}_{-2} \exp(-\epsilon_2 s) \qquad (7)$$

$$\mathbf{u}(s) = \frac{\mathbf{C}_1}{\epsilon_1} \exp(\epsilon_1 s) - \frac{\mathbf{C}_{-1}}{\epsilon_1} \exp(-\epsilon_1 s) + \frac{\mathbf{C}_2}{\epsilon_2} \exp(\epsilon_2 s) - \frac{\mathbf{C}_{-2}}{\epsilon_2} \exp(-\epsilon_2 s) \qquad (8)$$

where

$$\epsilon_1 = +\left\{\frac{\beta + [\beta^2 - 4\alpha\gamma]^{1/2}}{2\gamma}\right\}^{1/2} \qquad (9)$$

$$\epsilon_2 = +\left\{\frac{\beta - [\beta^2 - 4\alpha\gamma]^{1/2}}{2\gamma}\right\}^{1/2} \qquad (10)$$

(we take ϵ_1 and ϵ_2 to be the positive roots) and boundary conditions require that

$$\mathbf{u}(0) = \mathbf{U}_0 = \frac{\mathbf{C}_1}{\epsilon_1} - \frac{\mathbf{C}_{-1}}{\epsilon_1} + \frac{\mathbf{C}_2}{\epsilon_2} - \frac{\mathbf{C}_{-2}}{\epsilon_2} \qquad (11)$$

$$\mathbf{u}(L) = \mathbf{U} = \frac{\mathbf{C}_1}{\epsilon_1} \exp(\epsilon_1 L) - \frac{\mathbf{C}_{-1}}{\epsilon_1} \exp(-\epsilon_1 L) + \frac{\mathbf{C}_2}{\epsilon_2} \exp(\epsilon_2 L) - \frac{\mathbf{C}_{-2}}{\epsilon_2} \exp(-\epsilon_2 L) \qquad (12)$$

$$\mathbf{a}(0) = \mathbf{A}_0 = \mathbf{C}_1 + \mathbf{C}_{-1} + \mathbf{C}_2 + \mathbf{C}_2 \qquad (13)$$

$$\mathbf{a}(L) = \mathbf{A}_0 = \mathbf{C}_1 \exp(\epsilon_1 L) + \mathbf{C}_{-1} \exp(-\epsilon_1 L) + \mathbf{C}_2 \exp(\epsilon_2 L) + \mathbf{C}_{-2} \exp(-\epsilon_2 L) \qquad (14)$$

To proceed further we consider the above equations as L becomes large. If ϵ_1 and ϵ_2 have real parts the terms in $\exp(-\epsilon_1 L)$ and $\exp(-\epsilon_2 L)$ are negligible. Equations 12 and 14 become

$$\mathbf{U} \approx \frac{\mathbf{C}_1}{e_1} \exp(\epsilon_1 L) + \frac{\mathbf{C}_2}{\epsilon_2} \exp(\epsilon_2 L) \qquad (15)$$

$$\mathbf{A} \approx \mathbf{C}_1 \exp(\epsilon_1 L) + \mathbf{C}_2 \exp(\epsilon_2 L) \qquad (16)$$

It is now easy to derive simple expressions for $\mathbf{C}_1$, $\mathbf{C}_{-1}$, $\mathbf{C}_2$, and $\mathbf{C}_{-2}$

$$\mathbf{C}_1 = (\mathbf{A} - \epsilon_2\mathbf{U}) \exp(-\epsilon_1 L)\frac{\epsilon_1}{\epsilon_1 - \epsilon_2} \qquad (17)$$

$$\mathbf{C}_2 = (\mathbf{A} - \epsilon_1\mathbf{U}) \exp(-\epsilon_2 L)\frac{\epsilon_2}{\epsilon_2 - \epsilon_1} \qquad (18)$$

$$\mathbf{C}_{-2} = \frac{\epsilon_2}{\epsilon_2 - \epsilon_1}[\mathbf{A}_0 + \epsilon_1\mathbf{U}_0] \qquad (19)$$

$$\mathbf{C}_{-1} = \frac{\epsilon_1}{\epsilon_1 - \epsilon_2}[\mathbf{A}_0 + \epsilon_2\mathbf{U}_0] \qquad (20)$$

(Note that these expressions are consistent with the approximations used to derive eq 15 and 16.)

We now insert eq 7, 8, and 17–20 into eq 2 to derive the probability of a configuration having $\mathbf{a}(0) = \mathbf{A}_0$, $\mathbf{a}(L) = \mathbf{A}$, $\mathbf{u}(0) = \mathbf{U}_0$, and $\mathbf{u}(L) = \mathbf{U}$ (valid only at large L). Integrating by parts and using eq 3–5 we derive the following equation

$$P[\mathbf{U},\mathbf{A},\mathbf{U}_0\mathbf{A}_0] = N \exp\{-\gamma\epsilon_1\epsilon_2(\epsilon_1 + \epsilon_2)\,\mathbf{U}^2 + [\gamma(\epsilon_1 + \epsilon_2)^2 - \beta]\mathbf{A}\cdot\mathbf{U} - \gamma(\epsilon_1 + \epsilon_2)\mathbf{A}^2\} \qquad (21)$$

where $P[\mathbf{U},\mathbf{A},\mathbf{U}_0,\mathbf{A}_0]$ is the probability that the chain have $\mathbf{u}(L) = \mathbf{U}$, $\mathbf{a}(L) = \mathbf{A}$, $\mathbf{u}(0) = \mathbf{U}_0$, and $\mathbf{a}(0) = \mathbf{A}_0$. N is a function of $\mathbf{U}_0$ and $\mathbf{A}_0$. Note that there are no cross terms between **U** and $\mathbf{U}_0$, **U** and $\mathbf{A}_0$, etc., and that the distribution function is a product of independent factors describing the two ends of the molecule. This is to be expected in the limit of large contour length considered in this paper.

In deriving eq 21 we have, as discussed earlier, ignored the contraint imposed by differential geometry that $\mathbf{u}(s)$ is a unit vector. As pointed out by Freed we can thus expect our results to be physically realistic only if[10]

$$\lim_{L\to\infty} \langle \mathbf{U}^2 \rangle = 1 \qquad (22)$$

This condition is satisfied if α is determined by the following equation

$$\alpha\beta + \frac{\alpha^2\gamma}{\beta + 2(\alpha\gamma)^{1/2}} = \frac{9}{4} \qquad (23)$$

where the radical must be taken as positive.

Let us now consider evaluation of $\langle R^2 \rangle$, the mean-square end-to-end distance. Let $P[\mathbf{R},\mathbf{U},\mathbf{A},\mathbf{U}_0,\mathbf{A}_0]$ represent the distribution function of $\mathbf{R},\mathbf{U},\mathbf{A},\mathbf{U}_0,\mathbf{A}_0$ and let $I[\mathbf{k},\mathbf{U},\mathbf{A},\mathbf{U}_0,\mathbf{A}_0]$ denote the characteristic function (the Fourier transform of this distribution function). Using the techniques employed by Freed it is very easy to demonstrate that[10]

$$\mathbf{I}[\mathbf{k},\mathbf{U},\mathbf{A},\mathbf{U}_0,\mathbf{A}_0] = \exp\left[\frac{-\mathbf{k}^2 L}{4\alpha}\right] P\left[\left(\mathbf{U} - \frac{ik}{2\alpha}\right),\mathbf{A},\left(\mathbf{U}_0 - \frac{ik}{2\alpha}\right),\mathbf{A}_0\right] \qquad (24)$$

where $P[\mathbf{U},\mathbf{A},\mathbf{U}_0,\mathbf{A}_0]$ is given by eq 21 (in the limit of large L). With this expression one can easily demonstrate that the characteristic function in the limit of large L is identical to that derived by Freed. Thus Freed's expression for $\langle R^2 \rangle$ in this limit, $\langle R^2 \rangle = L(3/2\alpha)$, is applicable here. Hence we can identify the effective segment length with $(3/2\alpha)$.

Results and Discussion

Segment lengths were calculated for various values of β and γ, employing eq 23 as a quartic equation for $\alpha^{1/2}$. Since the dimensionless variable γ/β^3 is a natural expansion parameter of eq 23 the data are plotted as l/l_0 vs. γ/β^3, where l is the segment length and l_0 is the segment length when $\gamma = 0$. This procedure reduces the solution of eq 23 for all values of β and γ to a single dimensionless plot. This is shown in Figure 1 for values of γ/β^3 ranging from 0 to 1 and in Figure 2 for values of 1 to 10. Qualitatively, the numerical calculations show that the segment length increases in a smooth monotonic manner as γ increases. It is clear that the higher order stiffness term has a significant effect on the segment length, even when γ/β^3 is small (0.1). Nevertheless, the plot of l/l_0 vs. γ/β^3 levels off somewhat at larger values of γ and when $\gamma/\beta^3 = 10$ (l/l_0) is only 2.34.

Unfortunately, these results cannot be directly applied to polyelectrolytes without further theoretical development. When the electrostatic potential energy is expanded,

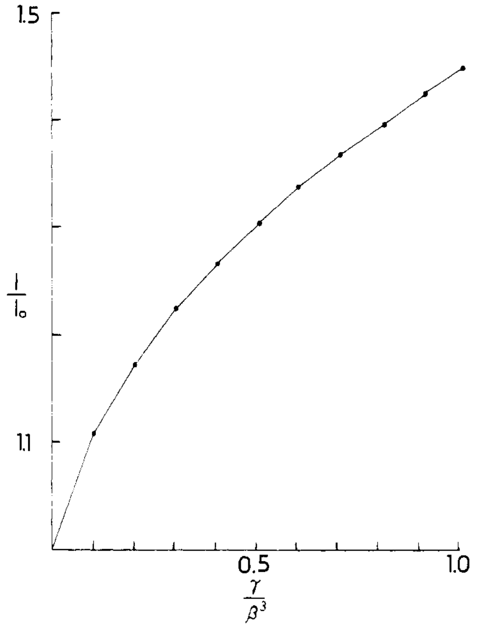

Figure 1. The reduced effective segment length l/l_0 is plotted as a function of γ/β^3 for values ranging from 0 to 1.0.

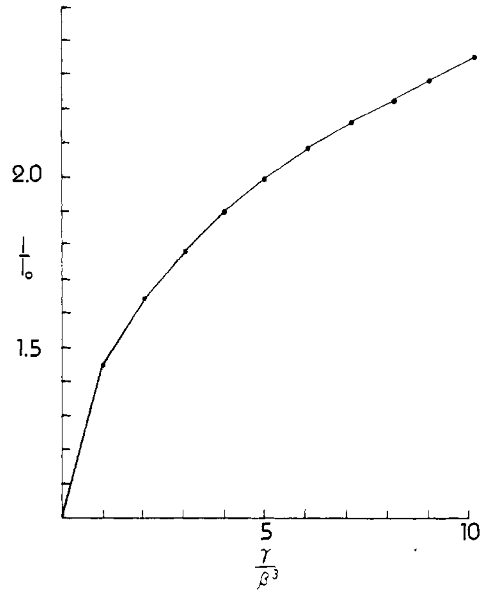

Figure 2. The reduced effective segment length l/l_0 is plotted as a function of γ/β^3 for values ranging from 0 to 10.0.

following Scolnick's and Fixman's method,[9] one finds terms in $|\mathbf{a}|^4$ and cross terms in the various derivatives of $\mathbf{u}(s)$ as well as the terms $\beta\mathbf{a}(s)^2$ and $\gamma\dot{\mathbf{a}}(s)^2$. Thus eq 27 is not directly applicable. However, it is possible to use the results obtained above to reach some qualitative conclusions about the procedures used by Scolnick and Fixman and Odijk for calculating the segment length of polyelectrolytes.[8,9] These investigators have shown that the electrostatic contribution to β is $[\sigma^2/8DkT\kappa^2]$ where σ is the charge per unit length, D is the dielectric constant, and κ is the Debye–Hückel screening variable. This allows calculation of the segment length (or persistence length) as a function of salt concentration by means of the relationship between β and the persistence length for wormlike chains. Clearly, however, this is valid only if the term identified here as $\gamma\dot{\mathbf{a}}^2$ has no significant effect on the segment length, which roughly implies that $\gamma/\beta^3 < 0.1$ (see Figure 1). It is not difficult to show that for polyelectrolytes γ is $[2\sigma^2/5DkT\kappa^4]$ (assuming no nonelectrostatic contributions). If we consider a 0.01 M univalent salt solution, one can then use the expressions for β and γ to determine that the unperturbed segment length (the segment length at infinite salt concentration) must be approximately 70 Å in order for $\gamma/\beta^3 < 0.1$. This is an underestimate since we have ignored several terms in the potential energy of polyelectrolytes. Nevertheless it provides a rough estimate. The calculations also suggest an intriguing possibility. The variable γ/β^3 is given by

$$\frac{(2\sigma^2/5DkT\kappa^4)}{[\beta_{\text{ne}} + (\sigma^2/8DkT\kappa^2)]^3}$$

(β_{ne} is the nonelectrostatic contribution to β). This function will reach a maximum at some value of κ and then decrease as the ionic strength decreases. Thus the theories of Scolnick and Fixman and Odijk might actually improve at lower ionic strengths, despite the fact that γ increases. A more exact characterization of polyelectrolytes, which takes into account potential energy terms ignored in this paper, is currently being developed in order to more fully explore this possibility.

It is not clear how generally useful this approach will be for the calculation of segment lengths. It is of value only if one derives expressions for β and γ and this requires that the potential energy be given by a known function of $|\mathbf{r}(s) - \mathbf{r}(s')|$. (If such an expression is not known a Gaussian model parameterized to give correct second moments might be more useful. Such an approach has been described by Zwanzig.[12,13]) Such potential energies can be expanded in terms of $\mathbf{a}(s)$ and $\dot{\mathbf{a}}(s)$ to provide expressions for β and γ. Furthermore, these systems can not be analyzed by the helical wormlike chain model, elegantly developed by Yamakawa and co-workers.[6] The helical wormlike chain has a potential energy term in τ^2 where τ is the torsion as strictly defined in differential geometry. If the potential energy is a function of $|\mathbf{r}(s) - \mathbf{r}(s')|$ only, however, there will be no simple energy term proportional to τ^2. In fact it is easy to show, using the equations of Frenet, that the term in $\dot{\mathbf{a}}(s)^2$ used in this paper is equal to $\kappa^4 + \kappa'^2 + \kappa^2\tau^2$ where κ' is the derivative of κ with respect to s and where κ is the curvature and τ is the torsion.[12] In this limited sense the model employed here is more complex than the helical wormlike chain. However, since the constraints of differential geometry have been relaxed and since our equations have been solved only for large L this approach is useful only for consideration of the equivalent statistical segment length.

References and Notes

(1) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971.
(2) O. Kratky and G. Porod, *Recl. Trav. Chim. Pays-Bas*, **68**, 1106 (1949).
(3) H. Yamakawa, *Annu. Rev. Phys. Chem.*, **25**, 179 (1974).
(4) R. A. Harris and J. E. Hearst, *J. Chem. Phys.*, **44** 2595 (1966).
(5) N. Saito, K. Takahishi, and Y. Yunoki, *J. Phys. Soc. Jpn.*, **22**, 219 (1967).
(6) H. Yamakawa and M. Fujii, *J. Chem. Phys.*, **64**, 5222 (1976).
(7) H. Yamakawa, *Pure Appl. Chem.*, **46**, 135 (1976).
(8) T. Odijk, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 477 (1977).
(9) J. Skolnick and M. Fixman, *Macromolecules*, **10**, 944 (1977).
(10) K. F. Freed, *J. Chem. Phys.*, **54**, 1453 (1971).
(11) R. P. Feynmann and A. R. Hibbs, "Quantum Mechanics and Path Integrals", McGraw-Hill, New York, N.Y., 1965, Chapter 4.
(12) R. Zwanzig, *J. Chem. Phys.*, **60**, 2717 (1974).
(13) M. Bixon and R. Zwanzig, *J. Chem. Phys.*, **68**, 1896 (1978).
(14) D. J. Struik, "Differential Geometry", Addison-Wesley, Reading, Mass., 1950, Chapter 1.
(15) The tilde denotes the fourth derivative.