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STATISTICAL MECHANICS OF WORMLIKE CHAINS

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Abstract—Recent advances in the statistical-mechanical theory of wormlike chains are summarized. The basic physical assumptions in the Kratky–Porod model and some other modifications for stiff chain molecules are discussed, based on the "Lagrangian" of the chain by analogy with quantal motion of a particle. In the belief that among these the Kratky–Porod wormlike chain affords the best approximation, a statistical-mechanical analysis of its distribution functions and moments is then made rather in detail. It is shown that the analysis is facilitated by an application of operational and diagrammatic techniques with the use of a digital computer. A brief summary of some aspects of the application of the model to various observables is also given.

INTRODUCTION

There have been so far proposed a number of models for chain molecules. What model should be used depends on what property or behavior of a system is studied, and also on what molecular level it is treated. Among these, rotational-isomeric models[1] take an important place in the study of various configuration-dependent properties, because they take account of the details of the molecular structure. However, such details are often unnecessary to consider in the treatment of the equilibrium and dynamic properties of, for instance, dilute solutions of flexible chain polymers. Thus, rotational-isomeric models have long been replaced by random flight models.[2] On about the same molecular level, there are also a wide variety of models, such as wormlike chains,[2,3] for semiflexible or stiff chain molecules. However, there has been much less investigation of them.

The main purposes of this paper are twofold: (1) to make a comparison of various continuous models for stiff chains from a statistical-mechanical point of view, and (2) to make an analysis of the fundamental statistical properties of the Kratky–Porod wormlike chain.[4] Although the Kratky–Porod model cannot mimic exactly the dimensional behavior of real chains, it does often afford a rather good approximation, and it has therefore retained a valid place for many years. On the other hand, however, there have been various modifications of this model because of difficulties in its rigorous mathematical treatment. In order to clarify the mutual relations among these models, we first discuss the basic physical assumptions in them, based on the "Lagrangian" of the chain by analogy with quantal motion of a particle. In the belief that the Kratky–Porod model is the most satisfactory, we then study the distribution functions and moments for this model chain by an application of operational and diagrammatic techniques together with a path-integral formulation. It is pointed out that necessary diagrams may be generated effectively on a digital computer. Finally, a brief summary of some aspects of the application of the model to various observables is given.

COMPARISON OF VARIOUS STIFF CHAIN MODELS

The Kratky–Porod wormlike chain

Consider a freely rotating chain composed of n bonds of length l jointed with bond angle $\pi - \theta$. The Kratky–Porod wormlike chain is defined as a limiting continuous chain formed from this discrete chain by letting $n \to \infty$, $l \to 0$, and $\theta \to 0$ under the restriction that $nl \equiv L$, the total contour length, and $l/(1-\cos\theta) \equiv (2\lambda)^{-1}$, the persistence length, remain constant. The Kuhn segment length is equal to λ^{-1}. For this model, the mean-square end-to-end distance $\langle R^2 \rangle$ becomes proportional to L as λL approaches infinity, and becomes equal to L^2 as λL decreases to zero. The ratio $\langle R^2 \rangle / L$ increases monotonically with increasing L. Thus, the Kratky–Porod chain enables one to interpolate to any degree of stiffness or flexibility from the two extremes, random coil and rigid rod. In what follows, this chain is simply referred to as the wormlike chain.

The statistical mechanics of the wormlike chain may be developed by regarding it as a differentiable space curve of fixed length. Let $\mathbf{r}(s)$ be the radius vector of an arbitrary point of the curve as a function of the contour distance s from one end to that point. The unit vector $\mathbf{u}(s)$ tangential to the curve at the point s is given by

$$\mathbf{u}(s) = \mathrm{d}\mathbf{r}/\mathrm{d}s \tag{1}$$

with

$$\mathbf{u}^2 = 1. \tag{2}$$

The above definition of the wormlike chain yields the relation, $\langle (\Delta u)^2 \rangle = 4\lambda \Delta s$. This implies that the generation of the curve may be described by a simple Markov process, and therefore that there is a Fokker–Planck equation for the distribution function. Indeed, such a differential equation was derived first by Daniels[5] and subsequently by Hermans and Ullman.[6] It is convenient to introduce the Green's function $G(\mathbf{R}, \mathbf{u}|\mathbf{u}_0; t)$; it is the conditional distribution function of $\mathbf{r}(t) = \mathbf{R}$ and $\mathbf{u}(t) = \mathbf{u}$ when $\mathbf{r}(0) = 0$ and $\mathbf{u}(0) = \mathbf{u}_0$ (with $G = 0$ for $t < 0$). The Fokker–Planck equation then reads

$$(\partial/\partial t - \lambda \nabla_u^2 + \mathbf{u} \cdot \nabla_R) G(\mathbf{R}, \mathbf{u}|\mathbf{u}_0; t) = \delta(t)\delta(\mathbf{R})\delta(\mathbf{u} - \mathbf{u}_0). \tag{3}$$

The characteristic function $I(\mathbf{k}, \mathbf{u}|\mathbf{u}_0; t)$, which is the Fourier transform of G and also the Green's function, therefore satisfies

$$(\partial/\partial t - \lambda \nabla_u^2 - i\mathbf{k} \cdot \mathbf{u}) I(\mathbf{k}, \mathbf{u}|\mathbf{u}_0; t) = \delta(t)\, \delta(\mathbf{u} - \mathbf{u}_0) \tag{4}$$

with i the imaginary unit. Note that eqns 3 and 4 are subject to the condition given by eqn 2.

Now, there is a close analogy between the wormlike chain and a quantal trajectory of a particle, the chain contour length being regarded as "time". Such an approach was first introduced by Saito, Takahashi and Yunoki,[7] and subsequently elaborated by Freed.[8,9] In this formalism, the Green's functions may be represented in terms of the Feynman path integrals.[10] For example, the "quantum-mechanical amplitude" $I(\mathbf{k}, \mathbf{u}|\mathbf{u}_0; t)$ may be written in the form,

$$I(\mathbf{k}, \mathbf{u}|\mathbf{u}_0; t) = \int_{\mathbf{u}(0)=\mathbf{u}_0}^{\mathbf{u}(t)=\mathbf{u}} \exp\left(i\int_0^t \mathscr{L}\,ds\right)\mathscr{D}[\mathbf{u}(s)], \quad (5)$$

where $\mathscr{L}$ is the "Langrangian" (in units of $\hbar$),

$$\mathscr{L} = \frac{i}{4\lambda}\left(\frac{d\mathbf{u}}{ds}\right)^2 + \mathbf{k}\cdot\mathbf{u}, \quad (6)$$

subject to the condition given by eqn 2. The first term on the right of eqn 6 is the free-particle Lagrangian or "kinetic energy", and the second term is the negative of the "potential energy" of the "particle," which in this case is a rigid dipole in an electric field $\mathbf{k}$. The true potential energy of the wormlike chain arises from its bending elastic energy, the first term of $\mathscr{L}$ divided by i being this energy per unit length. If the energy is measured in units of kT with k the Boltzmann constant and T the absolute temperature, the bending force constant α of the wormlike chain is related to the Kuhn segment length by

$$\alpha = (2\lambda)^{-1}. \quad (7)$$

The path integral form of eqn 5 may be transformed to the "Schrödinger" eqn 4 in a well-established manner.[10]

Modified wormlike chains

Since it is impossible to find the exact solution of eqn 3 or 4 in a closed form, various attempts have been made to relax the constraint of eqn 2. For these modified wormlike chains, the unnormalized and unconditional characteristic function $I(\mathbf{k}, \mathbf{u}, \mathbf{u}_0; t)$ may be written in the path integral form of eqn 5 with the Lagrangian,

$$\mathscr{L} = \frac{i\alpha}{2}\left(\frac{d\mathbf{u}}{ds}\right)^2 + iU + \mathbf{k}\cdot\mathbf{u}, \quad (8)$$

where U is an additional true potential energy (in units of kT) of the chain associated with the relaxation of the constraint, so that $-(iU + \mathbf{k}\cdot\mathbf{u})$ is the "potential energy" of the "particle." Then, the Schrödinger equation is of the form,

$$[\partial/\partial t - (2\alpha)^{-1}\nabla_u^2 + V - i\mathbf{k}\cdot\mathbf{u}]I(\mathbf{k}, \mathbf{u}, \mathbf{u}_0; t) = \delta(t)\delta(\mathbf{u} - \mathbf{u}_0), \quad (9)$$

where V is determinable from U. Note that eqns 8 and 9 are no longer subject to the condition of eqn 2.

Harris and Hearst (HH)[11] have permitted Rouse-type stretching as well as bending of the chain, so that their U and V are given by

$$U^{(\mathrm{HH})} = V^{(\mathrm{HH})} = \frac{1}{2}\beta\mathbf{u}^2 \quad (10)$$

with β the stretching force constant. For this model, α is equated to $3/4\,\lambda$, and β is determined as a function of t and λ; and t should be regarded as the contour length in the *unstretched* state. The differential eqn 9 with $V = V^{(\mathrm{HH})}$ was first derived by Freed,[8] and his model is therefore the same as that of Harris and Hearst except the equations determining α and β. This model becomes invalid for high stiffness; near the rod limit, it cannot give the correct wormlike moments except $\langle R^2\rangle$. In particular, the contour length increases indefinitely if an external force is applied and increased. Noda and Hearst[12] have attempted to remedy this defect by forcing β to depend on, for instance, rate of shear.

Fixman and Kovac (FK)[13] have considered a more general modification by introducing an external potential $-\mathbf{R}\cdot\mathbf{f}$ acting on the end-to-end vector, so that

$$U^{(\mathrm{FK})} = V^{(\mathrm{FK})} = \frac{1}{2}\beta\mathbf{u}^2 - \mathbf{f}\cdot\mathbf{u}. \quad (11)$$

For this model, α is again equated to $3/4\,\lambda$, and β is determined as a function of t, λ, and also the force f, so that t and $\langle\mathbf{R}\rangle$ do not increase indefinitely with f. When $f = 0$, this model reduces to the Harris–Hearst model. Now, eqn 9 with $V = V^{(\mathrm{FK})}$ is just the Schrödinger equation for a harmonic oscillator in an external force field $\mathbf{k} - i\mathbf{f}$, and its solution is well known.[10] Thus we have for the normalized but unconditional characteriestic function $I(\mathbf{k}, \mathbf{u}, \mathbf{u}_0; t)$ for finite $\mathbf{f}$

$$I(\mathbf{k}, \mathbf{u}, \mathbf{u}_0; \mathbf{f}, t) = P(\mathbf{u}, \mathbf{u}_0; \mathbf{f}, t)\exp\left\{-\frac{t\mathbf{k}^2}{2\beta}\left(1 - \frac{1}{a}\tanh a\right) + i\mathbf{k}\cdot\left[\frac{t}{\beta}\left(1 - \frac{1}{a}\tanh a\right)\mathbf{f} + \frac{t}{2a}(\tanh a)(\mathbf{u} + \mathbf{u}_0)\right]\right\}, \quad (12)$$

where

$$P(\mathbf{u}, \mathbf{u}_0; \mathbf{f}, t) = \left(\frac{b}{\pi}\right)^3\exp\left\{-\frac{b}{\sinh 2a}[(\cosh 2a)(\mathbf{u}^2 + \mathbf{u}_0^2) - 2\mathbf{u}\cdot\mathbf{u}_0] + \frac{t}{2a}(\tanh a)\mathbf{f}\cdot(\mathbf{u} + \mathbf{u}_0) - \frac{t}{2a\beta}(\tanh a)\mathbf{f}^2\right\}, \quad (13)$$

$$a = \frac{t}{2}\left(\frac{\beta}{\alpha}\right)^{1/2}, \qquad b = \frac{1}{2}(\alpha\beta)^{1/2}. \quad (14)$$

When $\mathbf{f} = 0$, the I given by eqn 12 is identical with that of Freed[8] except the normalization constant. By Fourier inversion of eqn 12, we obtain for the normalized trivariate distribution function $P(\mathbf{R}, \mathbf{u}, \mathbf{u}_0; \mathbf{f}, t)$

$$P(\mathbf{R}, \mathbf{u}, \mathbf{u}_0; \mathbf{f}, t) = P(\mathbf{u}, \mathbf{u}_0; \mathbf{f}, t)\left[\frac{\beta}{2\pi t(1 - a^{-1}\tanh a)}\right]^{3/2} \times \exp\left\{-\frac{\beta}{2t(1 - a^{-1}\tanh a)}\left[\mathbf{R} - \frac{t}{2a}(\tanh a) \times (\mathbf{u} + \mathbf{u}_0) - \frac{t}{\beta}\left(1 - \frac{1}{a}\tanh a\right)\mathbf{f}\right]^2\right\}. \quad (15)$$

The distribution function $P(\mathbf{R}, \mathbf{u}, \mathbf{u}_0; t)$ given by eqn 15 with $\mathbf{f} = 0$ may also be obtained from the formulation of Harris and Hearst. If the radius vector $\mathbf{r}(s)$ is expanded in terms of the eigenfunctions ψ_i for the equation of motion, and if ϵ_i are the expansion coefficients, then the

instantaneous distribution function for the entire free Harris–Hearst chain may be expressed as a product of Gaussian distributions of ϵ_i.[11] From this, we can therefore derive the trivariate Gaussian distribution $P(\mathbf{R}, \mathbf{u}, \mathbf{u}_0; t)$ by the use of the Wang–Uhlenbeck theorem.[2] Thus, it is explicitly recognized that the Freed model is exactly equivalent to the Harris–Hearst model. However, their expressions for the moments, e.g. $\langle R^2 \rangle$ as functions of α and β are different. This arises from the fact that Freed has regarded the above $P(\mathbf{R}, \mathbf{u}, \mathbf{u}_0; t)$ erroneously as the conditional distribution $P(\mathbf{R}, \mathbf{u}|\mathbf{u}_0; t)$, and evaluated averages with $P(\mathbf{R}, \mathbf{u}, \mathbf{u}_0; t)P(\mathbf{u}_0; t)$.

Further, we consider two other models. Tagami (T)[14] has assumed $G(\mathbf{R}, \mathbf{u}|\mathbf{u}_0; t)$ to be the same as the Green's function for a free Brownian particle with $\mathbf{R}$ the position and $\mathbf{u}$ the velocity. Then the Fokker–Planck equation satisfied by this G and also its closed-form solution are well known.[15] The Lagrangian of this system has already been given by Saito and co-workers,[16,17] and we have

$$U^{(T)} = \frac{1}{2}\beta \mathbf{u}^2 + (\alpha\beta)^{1/2}\mathbf{u} \cdot \left(\frac{d\mathbf{u}}{ds}\right),$$
$$V^{(T)} = -\left(\frac{\beta}{\alpha}\right)^{1/2} \nabla_u \cdot \mathbf{u}, \tag{16}$$

with $\alpha = 3/4\,\lambda$ and $\beta = 3\,\lambda$. It is seen that the stretching energy is still of the Rouse type, but that there is coupling between bending and stretching. However, it is not clear what physical property of the real chain this coupling reflects. Further, we note that this model gives the correct rod limits of the moments, but not the correct first-order corrections to these limits.

In all of these modified wormlike chains, the minimum of the stretching energy is located $\mathbf{u} = 0$. Saito, Takahashi, and Yunoki (STY)[7] have instead introduced the stretching energy whose minimum is at $|\mathbf{u}| = 1$, so that

$$U^{(STY)} = V^{(STY)} = \frac{1}{2}\beta(|\mathbf{u}| - 1)^2. \tag{17}$$

Although the determination of α and β is not yet explicit, we must have $\alpha = (2\,\lambda)^{-1}$ for $\beta \to \infty$, since this model reduces to the wormlike chain in this limit. Its mathematical treatment is not always easier than that of the latter.

DISTRIBUTION FUNCTIONS AND MOMENTS

Having made a comparison of various stiff chain models, we still believe that the Kratky–Porod wormlike chain is the most satisfactory. In the present and next sections, therefore, it is further studied. In this section, we examine the mathematical structure of its distribution functions and moments. Two types of expansions of the characteristic function I, which are closely related to each other, are obtained from an integral equation[18] and the differential eqn 4[19] by operational methods. The former leads to operational expressions for the moments[18,20] and the moment-based distribution function $G(\mathbf{R}; t)$,[21] and the latter the Daniels-type distribution functions $G(\mathbf{R}, \mathbf{u}|\mathbf{u}_0; t)$.[19,21] Near the rod limit where these distributions become invalid, the "WKB" distribution functions[22] are useful. Throughout this section, the condition of eqn 2 is imposed, and all lengths are measured in units of λ^{-1}, for simplicity. Then, for example, the expression for $\langle R^2 \rangle$ is[4]

$$\langle R^2 \rangle = t - \frac{1}{2}(1 - e^{-2t}). \tag{18}$$

Even moments for the end-to-end distance

By analogy with quantum mechanics, an integral equation for I may readily be derived from the path integral form given by eqn 5,[10]

$$I(\mathbf{k}, \mathbf{u}|\mathbf{u}_0; t) = G(\mathbf{u}|\mathbf{u}_0; t) + i\mathbf{k} \cdot \int_0^t \int \mathbf{u}_1 G(\mathbf{u}|\mathbf{u}_1; t - s_1) \times I(\mathbf{k}, \mathbf{u}_1|\mathbf{u}_0; s_1)\, ds_1\, d\mathbf{u}_1, \tag{19}$$

where $G(\mathbf{u}|\mathbf{u}_0; t) = I(0, \mathbf{u}|\mathbf{u}_0; t)$ is identical with the well-known Green's function for a free rigid dipole (dumbbell rotor). Integrating both sides of eqn (19) over $\mathbf{u}_0$ and dividing by 4π, we have also an integral equation for $I(\mathbf{k}, \mathbf{u}; t)$, but the result is omitted.

We choose $\mathbf{u}_0$ in the direction of the z axis of a Cartesian coordinate system, and use spherical polar coordinates, $\mathbf{u} = (1, \theta, \phi)$ and $\mathbf{k} = (k, \chi, \omega)$. Both $I(\mathbf{k}, \mathbf{u}|\mathbf{u}_0; t)$ and $I(\mathbf{k}, \mathbf{u}; t)$, which we simply designate by $I(t)$, may then be expanded in terms of the normalized spherical harmonics $Y_l^m(\theta, \phi)$ such that Y_l^{-m} is equal to the complex conjugate of Y_l^m,

$$I(t) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} K_l^m(t) Y_l^m(\theta, \phi), \tag{20}$$

where $K_l^m(t)$ stands for $K_l^m(\mathbf{k}|\mathbf{u}_0; t)$ or $K_l^m(\mathbf{k}; t)$, as the case may be. The scalar product $\mathbf{k} \cdot \mathbf{u}_1$ may be expressed in terms of $Y_1^m(\chi, \omega)$. Thus, substitution of eqn 20 into eqn 19 and integration over $\mathbf{u}_1$ leads to the integral equations for $K_l^m(t)$,

$$K_l^m = f_l^m + i\bar{k} f_l * \mathcal{L} K_l^m, \tag{21}$$

where the asterisk indicates a convolution integration,

$$f * g = \int_0^t f(t - s) g(s)\, ds, \tag{22}$$

and

$$\bar{k} = (2\pi/3)^{1/2} k, \tag{23}$$

$$f_l = \exp[-l(l+1)t], \tag{24}$$

$$f_l^m = [(2l+1)/4\pi]^{1/2} \delta_{m0} f_l \quad \text{for} \quad K_l^m = K_l^m(\mathbf{k}|\mathbf{u}_0; t)$$
$$= (4\pi)^{-1/2} \delta_{l0} \delta_{m0} f_0 \quad \text{for} \quad K_l^m = K_l^m(\mathbf{k}; t) \tag{25}$$

with δ_{lm} the Kronecker delta. $\mathcal{L}$ is an operator (not Lagrangian) defined by

$$\mathcal{L} = 2^{1/2} Y_1^0 (a_1^0 + a_{-1}^0) + Y_1^1 (a_1^1 - a_{-1}^1) + Y_1^{-1} (a_1^{-1} - a_{-1}^{-1}), \tag{26}$$

where the arguments of the spherical harmonics are χ and ω; and a_μ^ν ($\mu = \pm 1$; $\nu = 0, \pm 1$) are creation and annihilation operators which operate on f_l as

$$a_\mu^\nu f_l = f_{l+\mu}, \tag{27}$$

and on K_l^m and f_l^m as

$$a_\mu^0 f_l^m = A_{l+(1/2)(\mu-1)}^{|m|} f_{l+\mu}^m,$$
$$a_\mu^\nu f_l^m = [2h(\nu m) - 1] E_{l+(1/2)(\mu-1)}^{\frac{1}{2}\mu\nu[m-(\nu/2)(\mu-1)]} f_{l+\mu}^{m+\nu} \quad (\nu \neq 0) \tag{28}$$

with h the unit step function such that $h(x) = 1$ or 0 for $x \geq 0$ or < 0, and

$$A_l^m = [(l+m+1)(l-m+1)/(2l+1)(2l+3)]^{1/2},$$
$$E_l^m = [(l-m+1)(l-m+2)/(2l+1)(2l+3)]^{1/2}. \tag{29}$$

The solution for K_l^m may then be expressed as

$$K_l^m = \sum_{n=0}^{\infty} (i\bar{k})^n (f_l * \mathscr{L})^n f_l^m. \tag{30}$$

In particular, integration of eqn 20 over **u** leads to

$$I(\mathbf{k}|\mathbf{u}_0; t) = (4\pi)^{1/2} \sum_{n=0}^{\infty} (i\bar{k})^n (f_0 * \mathscr{L})^n f_0^0, \tag{31}$$

$$\mathrm{I}(\mathbf{k}; t) = (4\pi)^{1/2} \sum_{m=0}^{\infty} (-1)^m \bar{k}^{2m} (f_0 * \mathscr{L})^{2m} f_0^0, \tag{32}$$

where f_0^0 in eqns 31 and 32 are given by the first and second lines of eqn 25, respectively.

Now we expand $(f_0 * \mathscr{L})^n f_0^0$ in eqn 31 to obtain

$$I(\mathbf{k}|\mathbf{u}_0; t) = \sum_{n=0}^{\infty} (ik)^n \sum_{p \leq n} (2p+1)^{1/2} \sum_{\substack{\text{paths} \\ (0 \to p)}} \Gamma_{0\ldots p}(t) \sum (-1)^x \times 2^{-(n-n^0)} C_\mu^{\ \nu} \cos^{n^0}\chi \sin^{(n-n^0)}\chi, \tag{33}$$

where

$$C_\mu^{\ \nu} = (f_p^0)^{-1} a_{\mu_n}^{\nu_n} a_{\mu_{n-1}}^{\nu_{n-1}} \ldots a_{\mu_2}^{\nu_2} a_1^{\nu_1} f_0^0, \tag{34}$$

$$\Gamma_{0\ldots p}(t) = \sum_i z_i(t) \tag{35}$$

with $z_i(t)$ the residue of the function $Q(z)$,

$$Q(z) = \mathrm{e}^{tz} / z \prod_{j=1}^{n} [z + l_j(l_j+1)], \tag{36}$$

and

$$l_j = \sum_{i=j}^{j} \mu_i \geq 0 \quad (l_0 = 0, l_1 = \mu_1 = 1, l_n = p), \tag{37}$$

$$\sum_{i=1}^{n} \nu_i = 0. \tag{38}$$

Equation 38 must hold because of the first line of eqn 25, and $C_\mu^{\ \nu}$ is a constant independent of t. In eqn 33, n^0 and x are the numbers of $a_\mu^{\ 0}$ and $a_{-1}^{\ \nu}$ $(\nu \neq 0)$ in $C_\mu^{\ \nu}$, respectively, the third sum is taken over all possible paths $(01\, l_2 \ldots l_{n-1} p)$ from 0 to p, and the fourth sum is taken over $\nu_1, \ldots, \nu_n$ compatible with eqn 38. The paths $(01\, l_2 \ldots l_{n-1} p)$ may be conveniently represented by "stone-fence" diagrams in an (i, l_i)-plane, as shown in Fig. 1, where two paths I (0101212) and II (0123434) for $n = 6$ are depicted as examples. The figure is equivalent to the two-dimensional representation of one-dimensional random walks with a reflecting barrier at the origin.[15]

If we choose **k** in the direction of $\mathbf{u}_0$, i.e. $\chi = 0$, we obtain the expansion of $I(\mathbf{k}|\mathbf{u}_0; t)$ in terms of $\langle(\mathbf{R} \cdot \mathbf{u}_0)^n\rangle$ with

$$\langle(\mathbf{R} \cdot \mathbf{u}_0)^n\rangle = n! \sum_{p \leq n} (2p+1)^{1/2} \sum_{\substack{\text{paths} \\ (0 \to p)}} \Gamma_{0\ldots p}(t) C_\mu^{\ 0}, \tag{39}$$

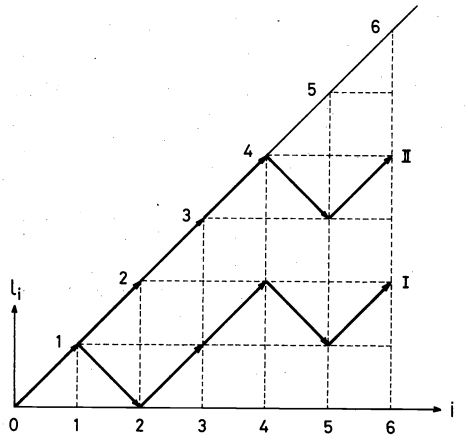

Fig. 1. Stone-fence diagram for the paths $(0 \to p)$. Two paths I(0101212) and II (0123434) for $n = 6$ are depicted as examples.

where only the paths from 0 to p with $\nu_1 = \nu_2 = \cdots = \nu_n = 0$ contribute.

Similarly, eqn 32 is reduced to the expansion in terms of $\langle R^{2m}\rangle$. The result is

$$I(\mathbf{k}; t) = \sum_{m=0}^{\infty} (-1)^m k^{2m} \langle R^{2m}\rangle / (2m+1)! \tag{40}$$

with

$$\langle R^{2m}\rangle = (2m+1)! \sum_{\substack{\text{paths} \\ (0 \to 0)}} \Gamma_{0\ldots 0}(t) C_\mu^{\ 0}. \tag{41}$$

In this case, only the paths from 0 to 0 with $\nu_i = 0$ contribute because of the second line of eqn 25, and $C_\mu^{\ 0}$ is explicitly given by

$$C_\mu^{\ 0} = \prod_{j=1}^{2m} A_{l_{j-1}}^0 + (1/2)(\mu j - 1) \tag{42}$$

with $\mu_1 = 1$ and $\mu_{2m} = -1$. If p_j is the number of the factors with $l_i = j$ in the denominator of eqn 36, the formula for residues gives

$$\Gamma_{0\ldots 0}(t) = \sum_{\substack{j=0 \\ p_j \neq 0}}^{m} \frac{1}{(p_j - 1)!} \left\{ \frac{\mathrm{d}^{p_j - 1}}{\mathrm{d}z^{p_j - 1}} \frac{[z + j(j+1)]^{p_j} \mathrm{e}^{tz}}{\prod_{i=0}^{m} [z + i(i+1)]^{p_i}} \right\}_{z = -j(j+1)}. \tag{43}$$

Thus, the final expression for $\langle R^{2m}\rangle$ is

$$\langle R^{2m}\rangle = \sum_{j=0}^{m} \sum_{i=j}^{m} A_{ij}^{(m)} t^{i-j} \mathrm{e}^{-j(j+1)t}, \tag{44}$$

where $A_{ij}^{(m)}$ are numerical constants independent of t, and may be expressed in terms of $C_\mu^{\ 0}$ and p_j, the result being omitted. For $m = 1$, 2, and 3, eqn 44 gives the well-known results.[4,6,23,24]

The coefficients $A_{ij}^{(m)}$ may be evaluated effectively by the use of a digital computer; it consists of generating all possible $(0 \to 0)$ paths and counting the number p_j. Thus, their values for $m \leq 11$ have already been obtained.[20] The whole calculation from $m = 1$ to $m = 6$ has been finished in less than 2 min, and the case of $m = 11$ has taken about 8 min. We note that the analytical expressions for $\langle R^{2m}\rangle$ may also be obtained from the recurrence formula of Hermans and Ullman,[6] but that the evaluation becomes

extremely laborious as m is increased. Thus, Nagai[25] has obtained numerical values of $\langle R^{2m}\rangle$ as a function of t for $m \leq 20$ from their formula by the use of a computer. His results for $m \leq 6$ are in good agreement with ours (to order 10^{-5}) for all values of t, but for higher m are much less accurate, especially at small t.

In general, the correction to the Gaussian distribution $G(\mathbf{R};\ t)$ for $t \to \infty$ may be expanded in terms of the moments $\langle R^{2m}\rangle$,[26] or of the Hermite polynomials,[1,27] it giving the so-called moment-based distribution function of $\mathbf{R}$. The successive approximations to this distribution have been obtained by taking account of $\langle R^{2m}\rangle$ with $m \leq 1$ to 11 successively.[21]

Daniels-type distribution functions

The correction to the Gaussian distribution may also be expanded in inverse powers of t to give the so-called Daniels-type distribution functions. Daniels[5] first solved the differential eqn 3 to derive the asymptotic expansion of $G(\mathbf{R}|\mathbf{u}_0; t)$ of this kind to terms of order $t^{-3/2}$. Many years later, Gobush *et al.*[19] attempted to solve the differential equation for the Laplace transform $\tilde{I}(\mathbf{k}, \mathbf{u}|\mathbf{u}_0; p)$ of I with respect to t by an application of operational techniques developed by Prigogine and co-workers[28,29] in attacking the Liouville equation, and obtained the expansion of $G(\mathbf{R}, \mathbf{u}|\mathbf{u}_0; t)$ to terms of order t^{-2}.

Now we reformulate the Gobush expansion along our line of the preceding section. As before, we choose $\mathbf{u}_0$ in the direction of the z axis, and express $\mathbf{u}$ and $\mathbf{k}$ in spherical polar coordinates, the azimuthal angle of $\mathbf{k}$ being $\phi - \psi$ instead of ω. In our notation, the Gobush operator $\delta L \equiv ik\delta\bar{L}$ may be written as

$$\delta\bar{L} = (\cos\chi)(a_1{}^0 + a^0_{-1}) + \frac{1}{2}(\sin\chi)(a_1{}^1 - a^1_{-1}) + \frac{1}{2}(\sin\chi)(a_1{}^{-1} - a^{-1}_{1}). \tag{45}$$

$a_\mu{}^\nu$ operate on f_l and $g_l{}^m$ (instead of $f_l{}^m$) in the same way as in eqns 27 and 28, where $g_l{}^m$ is defined by

$$g_l{}^m = f_l Y_l{}^m(\theta, \psi). \tag{46}$$

By Laplace inversion of the Gobush solution for $\tilde{I}$, we then have

$$I(\mathbf{k}, \mathbf{u}|\mathbf{u}_0; t) = \sum_{n=0}^{\infty}\sum_{l=0}^{\infty}(ik)^n[(2l+1)/4\pi]^{1/2}(f_l * \delta\bar{L})^n g_l{}^0. \tag{47}$$

The structure of the cascade of the successive $a_\mu{}^\nu$ operations involved in eqn 47 seems different from that in eqn 20 with 30, but both are equivalent. This is observed more explicitly by considering $I(\mathbf{k}|\mathbf{u}_0; t)$. From eqn 47, we have

$$I(\mathbf{k}|\mathbf{u}_0; t) = \sum_{n=0}^{\infty}\sum_{l=0}^{\infty}(ik)^n(2l+1)^{1/2}\int g_0{}^0(f_l * \delta\bar{L})^n g_l{}^0\,\mathrm{d}\mathbf{u}. \tag{48}$$

It can be seen that if the integrand of eqn 48 is expanded, there is one-to-one correspondence between the terms in eqns 33 and 48; each path of the stone-fence diagram in the latter is just the reversal of the corresponding $(0 \to l)$ path in the former.

Similarly, the Gobush expansion gives

$$I(\mathbf{k}; t) = \sum_{m=0}^{\infty}(-1)^m k^{2m}(g_0{}^0)^{-1}(f_0 * \delta\bar{L})^{2m} g_0{}^0, \tag{49}$$

where only the $(0 \to 0)$ paths with $\nu_i = 0$ contribute as in eqn 40. Of course, eqns 40 and 49 equivalent.

By Fourier inversion of any of these $I(\mathbf{k}; t)$, we can obtain Daniels-type distribution function $G(\mathbf{R}; t)$. It includes no terms of order of inverse half-integer powers of t; the sth approximation retains terms to order t^{-s}. The first[5] and second[19] approximations have been derived analytically, and the expansion coefficients in the third to tenth approximations have been evaluated numerically from eqn 49 by generating all possible paths on a computer.[21] Although the convergence of both the moment-based and Daniels distributions is poor at small t, the convergence of the ring-closure probability $G(0; t)$ and the mean reciprocal distance $\langle R^{-1}\rangle$ from the latter is better than that from the former. In particular, the second Daniels approximation to $\langle R^{-1}\rangle$ is valid for $t \geq 3$.

WKB distribution functions

In order to obtain the distribution functions valid near the rod limit $(t \to 0)$, we must resort to a different method. The problem is to find the WKB solution of the Schrödinger eqn 4 in the "classical" limit $k \to \infty$ (corresponding to the limit $\hbar \to 0$). If we let k approach infinity and suppress the Laplacian operator in eqn 4, it gives the distribution function for the rod that is a delta function. If we adopt the path integral approach, this limit is obtained from the "classical" path $\bar{\mathbf{u}}(s)$ which satisfies the extremum condition,

$$\delta\int_0^t \mathscr{L}\,\mathrm{d}s = 0 \tag{50}$$

with $\mathscr{L}$ the Lagrangian given by eqn 6. Then, the WKB approximation consists of taking into account the deviation of the "potential energy" part $-\mathbf{k}\cdot\mathbf{u}$ of $\mathscr{L}$ from its classical value to second order.[10] Thus, eqn 5 is reduced to the form,

$$I(\mathbf{k}, \mathbf{u}|\mathbf{u}_0; t) = F(\mathbf{k}, t)\exp\left(i\int_0^t \bar{\mathscr{L}}\,\mathrm{d}s\right), \tag{51}$$

where $\bar{\mathscr{L}}$ is the classical value of $\mathscr{L}$ with $\mathbf{u} = \bar{\mathbf{u}}$, and $F(\mathbf{k}, t)$ is the normalization factor.

The distribution functions thus obtained[22] give the correct first-order corrections to the rod limits of all the moments,

$$\begin{aligned}\langle(\mathbf{R}\cdot\mathbf{u}_0)^n\rangle &= t^n[1 - nt + 0(t^2)],\\ \langle R^{2m}\rangle &= t^{2m}\left[1 - \frac{2}{3}mt + 0(t^2)\right],\\ \langle R^{-1}\rangle &= t^{-1}\left[1 + \frac{1}{3}t + 0(t^2)\right].\end{aligned} \tag{52}$$

However, we note that the ring-closure probability $G(0, \mathbf{u}|\mathbf{u}_0; t)$ for $t \to 0$ cannot be obtained from the WKB solution; it requires a more direct treatment.[30]

APPLICATION TO VARIOUS OBSERVABLES

Earlier work on the application of the wormlike chain has been reviewed elsewhere,[2,3] and in this section, we discuss only some aspects of the recent study. In general,

the excluded volume effect in stiff chains is rather small; when it is necessary to take it into account, the first-order perturbation theory will suffice. Indeed, the excluded-volume expansion factor and the second virial coefficient have been evaluated in this approximation for wormlike bead models.[30] Throughout the remainder of this section, however, we ignore this effect. All lengths are again reduced by λ^{-1}.

First, we consider the light-scattering form factor $P(\theta)$ for the chain of total contour length L. It is related to the characteristic function by

$$P(\theta) = 2L^{-2}\int_0^L (L-t)I(\mathbf{k};t)\,dt, \tag{53}$$

where $\mathbf{k}$ has just the meaning of the scattering vector. In this case, the $I(\mathbf{k};t)$ from the moment-based distribution function $G(\mathbf{R};t)$ gives a more rapid convergence of $P(\theta)$ than does that from the Daniels distribution. Indeed, values of $P(\theta)$ have been obtained for various values of L over the important range of $k^2 \lesssim 10$, taking account of $\langle R^{2m}\rangle$ with $m = 1$–11.[20] On the other hand, Peterlin[31] and Hearst and Harris[32] have adopted the Gaussian approximation; Benoit and Doty[33] have used the first three terms of eqn 40, including only $\langle R^2\rangle$ and $\langle R^4\rangle$; and Sharp and Bloomfield[34] have used the first Daniels approximation. Necessarily, all of these $P(\theta)$ break down at small L, or in the typical stiff chain region. However, we note that for $L \geq 10$ and $k^2 \leq 10$, the closed-form expression of Sharp and Bloomfield gives a good approximation.

The steady-state transport coefficients such as the sedimentation coefficient and the intrinsic viscosity may be evaluated using wormlike bead models[35–38] or wormlike cylinder models.[39–42] In any case, if the hydrodynamic interaction is taken into account through the Oseen formula,[2] we need the mean reciprocal distance $\langle R^{-1}\rangle$ between two contour points separated by contour distance t. However, we cannot derive an exact expression for it valid for all values of t, and an approximation is required. For example, Hearst and Stockmayer[37] have made an interpolation from the Daniels and WKB approximations. If the second Daniels approximation is adopted, it is given by

$$\begin{aligned}\langle R^{-1}\rangle &= \left(\frac{6}{\pi t}\right)^{1/2}\left(1-\frac{1}{40t}-\frac{73}{4480t^2}\right) \quad \text{for } t > \sigma \\ &= t^{-1}(1+\tfrac{1}{3}t + a_2t^2 + a_3t^3) \qquad \text{for } t \leq \sigma.\end{aligned} \tag{54}$$

The constants σ, a_2, and a_3 are determined in such a way that the two $\langle R^{-1}\rangle$ have the same first and second derivatives at their intersection $t = \sigma$; the results are $\sigma = 2.278$, $a_2 = 0.1130$, and $a_3 = -0.02447$.[41] The accuracy of eqn 54 has been verified by a Monte Carlo study[41] of freely rotating chains with such small complementary bond angles that they are nearly wormlike. As for the method of classical hydrodynamics, we believe that the Oseen–Burgers procedure[41,42] may be applied reasonably to cylinder models, in the sense that the final result may be expressed in terms of only the dimensional parameters L, λ, and the diameter d of the cylinder. Note that an additional phenomenological parameter appears if the Kirkwood–Riseman procedure[43] is applied to bead models, followed by taking the continuous limit.[39,40]

If the properties cited above are important, one of the experimental problems is to determine L, λ, and also d. The determination of L is equivalent to determining a shift factor M_L, or the molecular weight M per unit contour length,

$$M_L = M/L. \tag{55}$$

For chains having rigid local conformations, M_L is estimated from crystallographic data. For example, it is known that $M_L = 195$ daltons/Å for DNA; and analyses of light scattering, sedimentation, and viscosity data for DNA lead to good values of M_L on the assumption of the wormlike chain model.[20,42] For chains having no rigid local conformations, there arises an interesting question:[44] What value is to be assigned to M_L for a given chain in dilute solution? The analyses made so far[42,44] show that its best value is close to that obtained by taking L as the length of the real chain fully extended to the all *trans* conformation except for a few cases, but it requires further study. If there is not a unique value of M_L for a given chain, it cannot be represented by the wormlike chain model.

There have been very few investigations of the dynamic properties. For the Harris–Hearst model, for example, the storage and loss moduli have been evaluated,[45] and some analysis of its Brownian motion has been made.[7] However, the theory breaks down for typical stiff chains,[46] as expected. This field also requires further study.

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