COMMENT

A freely jointed polymer chain with bond vectors of fixed lengths

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Abstract. A treatment of a macromolecule's configurational partition function, with an additional factor $g^{1/2}$ resulting from the momentum partition is given.

An expression for $g^{1/2}$ is derived in the form of multipliers, each of them depending on some neighbouring bond angles. In the case of equal bond angles $g^{1/2}$ can be calculated exactly.

A freely jointed chain with fixed bond vectors was first studied by Kramers (1946). In his model the polymer chain is supposed to be a set of mass points with fixed lengths between nearest neighbours. The space position of the mass points can be described either by the position vectors r_i, or by the internal variables: the lengths of the bond vectors l_i, the bond angles θ_i and the bond rotation angles ϕ_i (figure 1).
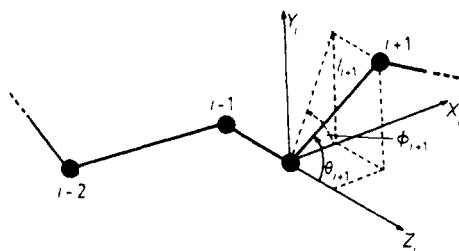
Figure 1. Part of the polymer chain. The internal variables $(l_{i+1}, \theta_{i+1}, \phi_{i+1})$ are shown.

Let F be a function of θ_i, ϕ_i. Then, within the framework of the Kramers model, the equilibrium average of F for a macromolecule in a particular state at temperature T is given by,

$$\bar{F} = \frac{1}{Z} \int F(\theta, \phi) \exp\left(-\frac{\frac{1}{2}\sum_{i,j} K_{ij} P_i P_j + U(\theta, \phi)}{kT} \right) d\theta \, d\phi \, dP \tag{1}$$

where the P's are the momenta conjugate to the angles ϕ_i, θ_i and Z is the partition function.

After integration over P_i, the expression for F takes the form

$$\bar{F} = \frac{1}{Z} \int F(\theta, \phi) g^{1/2} \, e^{-U(\theta,\phi)/kT} \, d\theta \, d\phi. \tag{2}$$

g, the determinant of the matrix inverse of K, is studied by Fixman (1974) who obtains a tractable expression for g.

In the present work, using δ-functions we shall obtain the same expression in another way. Thus, it is possible for g to be calculated exactly in the case of equal bond angles. The same method has already been used by the author (Svetogorsky 1973, 1974) to study the influence of g on the end-to-end distance of the polymer chain (in the framework of the rotational isometric state approximation). Earlier, Edwards and Goodyear (1972a, 1973), investigating the dynamics of the polymer chain, also treated bond vectors of fixed lengths by the help of δ functions.

We shall not discuss the physical meaning of the Kramers model which can be found in Gö and Scheraga (1969, 1976) and Flory (1974).

The proposed method is based on the fact that the fixed distances $l_i \equiv |r_i - r_{i-1}|$ imply the following constraints in the velocities:

$$(\dot{r}_i - \dot{r}_{i-1}) \cdot (r_i - r_{i-1}) = 0 \qquad i = 1, 2, \ldots, N. \tag{3}$$

We use these relations to write the expression

$$Z_g = \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} d\dot{r}_0 \ldots d\dot{r}_N \exp\left[-\left(\sum_{i=0}^{N} \frac{m_i \dot{r}_i^2}{2}\right)\right] \prod_{i=1}^{N} \delta[(\dot{r}_i - \dot{r}_{i-1}) \cdot (r_i - r_{i-1})]. \tag{4}$$

The approximation used by Edwards and Goodyear (1972a) in the calculation of Z_g is due to the specific nature of their problem, the real dependence of Z_g on the bond angles is lost. Thus, taking into account the problems of conformational statistical mechanics, we use a different method.

Introducing the variables l_i, $\dot{\theta}_i$, $\dot{\phi}_i$, we obtain

$$Z_g = \text{constant} \sin \theta_1 \ldots \sin \theta_N g^{-1/2}. \tag{5}$$

Where the constant is a factor which does not depend on θ_i, ϕ_i. On the other hand Z_g can be calculated using the Fourier representation of the δ functions:

$$\delta[(\dot{r}_i - \dot{r}_{i-1}) \cdot (r_i - r_{i-1})] = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\Omega_i \exp\{i\Omega_i[(\dot{r}_i - \dot{r}_{i-1}) \cdot (r_i - r_{i-1})]\}. \tag{6}$$

We are able to integrate here over all Cartesian velocities $\dot{r}_i$ and Z_g takes the form

$$Z_g = \text{constant} \int_{-\infty}^{\infty} d\omega_1 \ldots \int_{-\infty}^{\infty} d\omega_N \, e^{-\omega_1^2}$$
$$\times \prod_{i=1}^{N-1} \exp[-(\mu_i^2 \omega_i^2 - 2\mu_{i+1} \cos \theta_{i+1} \omega_i \omega_{i+1} + \omega_{i+1}^2)] \, e^{-\mu_N^2 \omega_N^2} \tag{7}$$

where,

$$\omega_i = l_i \Omega_i / (2m_i)^{1/2}; \qquad \mu_i = (m_i/m_{i-1})^{1/2}.$$

Comparison of equations (5) and (7) leads to

$$g^{-1/2} = \text{constant} \prod_{i=1}^{N} (\sin \theta_i)^{-1} \int d\omega \, e^{-\omega_1^2}$$
$$\times \prod_{i=1}^{N-1} \exp[-(\mu_i^2 \omega_i^2 - 2\mu_{i+1} \cos \theta_{i+1} \omega_i \omega_{i+1} + \omega_{i+1}^2)] \, e^{-\mu_N^2 \omega_N^2}. \tag{8}$$

Let us first discuss the case of equal masses ($\mu_i = 1$) and bond angles ($\theta_i = \theta$). In this case

using the well known method of the maximal eigenvalue for cyclic boundary conditions we have

$$\int d\omega \prod_{i=1}^{N} \exp[-(\omega_i^2 - 2 \cos \theta_i \omega_i \omega_{i+1} + \omega_{i+1}^2)] = \lambda_0^N, \qquad N \to \infty \qquad (9)$$

where λ_0 is the maximum eigenvalue of the equation

$$\lambda \psi(x) = \int_{-\infty}^{\infty} K(x, y) \psi(y) \, dy \qquad (10)$$

where

$$K(x, y) = \exp[-(x^2 - 2 \cos \theta xy + y^2)]$$

Equation (10) can be solved exactly, its eigenfunctions and the corresponding eigenvalues are

$$\psi_n(x) = \left(\frac{2\alpha}{\pi}\right)^{1/4} \frac{1}{(2^n n!)^{1/2}} e^{-\alpha x^2} H_n(x(2\alpha)^{1/2}), \qquad n = 0, 1, \ldots$$

$$\lambda_n = [\pi/(1+\alpha)]^{1/2} [\cos \theta/(1+\alpha)]^n, \qquad \alpha = |\sin \theta| \qquad (11)$$

where H_n are the hermite polynomials. Therefore, up to a constant we have

$$g^{1/2N} = \sin \theta (1 + |\sin \theta|)^{1/2}. \qquad (12)$$

In the general case for unequal θ_i equation (9) allows us to integrate over $\omega_1, \omega_2, \ldots$ consecutively and to obtain the following expression:

$$g^{1/2} = \text{constant} \prod_{i=1}^{N} \sin \theta_i V_i^{1/2}. \qquad (13)$$

For the quantities V_i we have the following recurrence relation:

$$V_i = 1 + \mu_i^2 - \mu_i^2 \cos^2 \theta_i / V_{i-1}; \qquad V_1 = 1 + \mu_1^2. \qquad (14)$$

For $N \to \infty$ and ignoring the effect of the boundary conditions, V_i is a continued fraction. Our exact solution in the case of equal θ and equal masses allows us to evaluate its convergence. Indeed, we have, comparing (12) and (14),

$$1 + |\sin \theta| = V_i(\theta) = 2 - \cfrac{\cos^2 \theta}{2 - \cfrac{\cos^2 \theta}{2 - \ldots}}. \qquad (15)$$

If we want to obtain $V_i(\theta)$ with a given accuracy then for different values of θ we should take different numbers of terms (n) in the continued fraction. In table 1 we show the calculated n for some values of θ when the required accuracy of $V_i(\theta)$ is 10^{-2}.

In the general case (14) V_i depends on $\theta_i, \theta_{i-1}, \ldots$ and it is intuitively clear that, as far as not all of the θ's are near zero, it would suffice to take a few terms in V_i to obtain a good accuracy.

Table 1. The calculated values of n with accuracy of $V_i(\theta)$ 0·01 for some values of θ.

θ (deg)	0	10	20	45	60	80	90
n	23	9	5	3	2	1	0

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