Use of $S = k \log p$ for Stretched Polymers

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ABSTRACT: The entropy–probability relation $S(r) = k \log p(r)$ has been long used for the computation of the force required to maintain a given end-to-end displacement **r** in a long-chain molecule, with the probability density $p(r)$ computed on the basis of a random walk appropriate to the model. Recent work has distinguished two types of polymer models: rigid models, in which strong covalent bonds are represented by geometric constraints, and flexible models, in which they are represented by strong harmonic potentials. It is shown here that the use of $S = k \log p$, with p computed on the basis of the usual random walk, leads to the correct result for chains of arbitrary length only for flexible models. This is in accord with previous work on the two-bond, freely jointed chain for which the two models give radically different results.

I. Introduction

The entropic approach, frequently employed for the computation of the force **f** necessary to maintain a given end-to-end displacement **r** in a long-chain molecule, may be described as follows: (1) Find the probability density $p_{rw}(r)$ for the displacement **r** in a random walk which is defined so that it corresponds to the molecular model under study. The subscript rw emphasizes that the probability density is computed on the basis of a random walk. In the absence of initial anisotropic constraints, or for sufficiently long chains, $p_{rw}(\mathbf{r})$ will be spherically symmetric, $p_{rw}(\mathbf{r}) = p_{rw}(r)$, where $r = |\mathbf{r}|$. For notational simplicity, we assume that this is the case although it will be seen that the discussion applies as well to the general situation. (2) Compute the chain's entropy $S(r)$ by means of the relation

$$S(r) = k \log p_{rw}(r) \tag{1}$$

where k is Boltzmann's constant. (3) The force **f**, collinear with **r**, has magnitude

$$f = -T \frac{\partial S}{\partial r} \tag{2}$$

or

$$f = -kT \frac{\partial}{\partial r} \log p_{rw} \tag{3}$$

An alternate expression for the probability density, as a quotient of partition functions, has been given by Volkenstein:[1]

$$p_{sm}(r,T) = Z(r,T)/Z'(T) \tag{4}$$

where $Z(r,T)$ is the partition function of the chain with its end-to-end vector constrained to be **r**, $Z'(T)$ is the partition function of the same chain without this constraint, and the subscript sm emphasizes that this probability density is computed on the basis of statistical mechanics. From the principles of statistical mechanics

$$f = -kT \frac{\partial}{\partial r} \log Z(r,T) \tag{5}$$

or

$$f = -kT \frac{\partial}{\partial r} \log p_{sm} \tag{6}$$

since $Z'(T)$ is independent of r.

Of the two force–probability relations, eq 6 is the more fundamental since it is based directly on statistical mechanics, but eq 3 is more convenient computationally since well-developed random walk techniques can be employed.

Rigid and Flexible Models. In recent years, two distinct approaches to the modeling of the strong covalent bonds in chain molecules have been distinguished and studied.[2-9] They lead to what are generally referred to as rigid and flexible models, and the terminology describes two methods for the computation of the model partition function.

For a rigid model, strong covalent bonds are modeled by geometric constraints (such as fixed bond lengths and fixed valence angles) in the Hamiltonian H_r of the model, which must therefore be written in terms of suitable generalized coordinates. The partition function for the rigid model, Z_r, is then computed on the basis of H_r.

In a flexible model, the strong covalent bonds are modeled first by stiff linear springs whose spring constant is scaled by a parameter κ. Since there are no geometric constraints, the Hamiltonian H_f can be expressed either in terms of rectangular Cartesian coordinates or in terms of a set of convenient curvilinear coordinates. The partition function for the flexible model, Z_f, is then computed on the basis of H_f. Finally, the spring-constant scaling factor is regarded as arbitrarily large.

As shown in a recent note,[10] the two procedures give radically different results for the force–length relation in the two-bond, freely jointed chain. This raises the following questions: To which of these two classes of polymer models does Volkenstein's relation, eq 4, apply, and what is the relation between p_{sm} and p_{rw} in this case?

Intuitively it might appear that the random walk probability is naturally associated with rigid models and that therefore eq 4 applies only to those. The contrary turns out to be the case. In this paper we reexamine the derivation of eq 4 and show that its validity requires the use of flexible models. Furthermore, we show that for these models with arbitrarily large κ, $p_{sm} = p_{rw}$ and eq 3 and 6 give the same result.

It should be emphasized that eq 5 and 6 apply to chains of arbitrary length and it follows, therefore, that the same is true, for flexible models, of eq 3. It is not necessary in a discussion of the force–length–temperature relation for a flexible model utilizing eq 3–6 to introduce any of the functions of macroscopic thermodynamics. In this sense, we can regard eq 1 and 2 as serving only to provide a heuristic basis for eq 3; its rigorous justification comes from eq 4–6 and the identification of p_{rw} with p_{sm} for flexible models. Therefore eq 3 remains valid in the presence of rotational potentials even though in this case $p_{rw} = p_{rw}(r,T)$ and the entropy S should be replaced in eq 2 by the Helmholtz free energy F, as has been emphasized by Flory.[11]

The plan of the paper is as follows: Notation, particularly as it relates to the system of curvilinear coordinates, is summarized in section II. In section III, we rederive Volkenstein's relation and show that its derivation pre-

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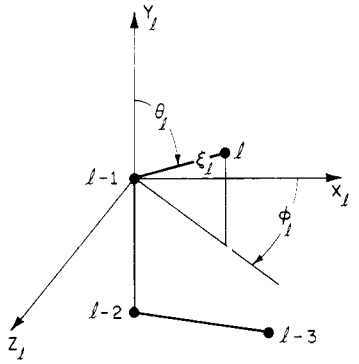

Figure 1. Curvilinear coordinate system. Atoms $l-1$, $l-2$, and $l-3$ lie in the X_l,Y_l plane.

supposes the use of a flexible model. It is then shown in section IV that the probability distributions $p_{sm} = p_{rw}$ for flexible models with arbitrarily large κ. Concluding remarks are contained in section V.

II. Notation

Consider a chain of atoms $l = 0, 1, ..., N$, all of the same mass which, for simplicity in notation, we take as unity. Let $\mathbf{x}_l$ denote the position of the lth atom with respect to a fixed rectangular Cartesian coordinate system with $\mathbf{x}_0 = 0$. In order to introduce the curvilinear coordinate system used, it is first convenient to refer the position of the lth atom, $l = 1, ..., N$, to a local rectangular Cartesian coordinate system (X_l, Y_l, Z_l) which is defined as follows: For $l = 3, ..., N$ (Figure 1), (a) atom $l-1$ is at the origin, (b) the vector $\mathbf{x}_{l-1} - \mathbf{x}_{l-2}$ defines the Y_l direction, and (c) atoms $l-1$, $l-2$, and $l-3$ define the X_l,Y_l plane. The coordinate system (X_1,Y_1,Z_1) coincides with the fixed reference frame and the (X_2, Y_2, Z_2) coordinate system is defined by properties a and b, with the X_2,Y_2 plane taken to coincide with the Y_1,Y_2 plane. We then introduce spherical coordinates ξ_l, θ_l, and ϕ_l in place of the local rectangular Cartesian coordinates X_l, Y_l, and Z_l, where ξ_l is the radial distance, θ_l is the polar angle (or valence angle supplement), and ϕ_l is the dihedral angle (Figure 1).

We therefore have two coordinate systems for the $3N$-dimensional configuration space of the chain: the rectangular Cartesian system, $\mathbf{x}_1, ..., \mathbf{x}_N$, and the curvilinear coordinate system, ξ_l, θ_l, ϕ_l, $l = 1, ..., N$. The $3N$-dimensional volume element $d\upsilon$ corresponding to differential displacements $d\xi_l$, $d\theta_l$, $d\phi_l$ is[12]

$$d\upsilon = \prod_{l=1}^{N} \xi_l^2 \sin\theta_l \, d\xi_l \, d\theta_l \, d\phi_l \tag{7}$$

As a more compact notation, let q^i, $i = 1, ..., 3N$, denote the curvilinear coordinates ξ_l, θ_l, ϕ_l, $l = 1, ..., N$, and let $g_{ij}(q)$ denote the covariant metric tensor for this system. It follows from eq 7 that

$$|g_{ij}|^{1/2} = \prod_{l=1}^{N} \xi_l^2 \sin\theta_l \tag{8}$$

where $|g_{ij}|$ is the determinant of g_{ij}.

We will also partition the coordinates q^i into two groups: q^α, $\alpha = 1, ..., f$, and q^A, $A = f+1, ..., 3N$, the first referred to as soft variables and the second as hard variables. For freely jointed chains, the soft variables are θ_l, ϕ_l and the hard variables are ξ_l; for freely rotating chains or for chains with hindered rotation, the soft variables are ϕ_l and the hard variables are ξ_l, θ_l. It is convenient to redefine the hard variables by subtraction of suitable constants so that $q^A = 0$ for the equilibrium values of these quantities. The Hamiltonian H_f of a flexible model can be written in this notation in the form

$$H_f(q^i,p_i;\kappa) = \tfrac{1}{2}g^{ij}p_ip_j + \tfrac{1}{2}\kappa a_{AB}q^Aq^B + V(q^\alpha) \tag{9}$$

where p_i are the momenta conjugate to q^i, g^{ij} is the contravariant metric tensor, a_{AB} is a positive definite matrix, $V(q^\alpha)$ describes any rotational potentials which are present, and the summation conventions $i, j = 1, ..., 3N$ and $A, B = f+1, ..., 3N$ are employed. The same Hamiltonian can also be written in terms of the rectangular Cartesian coordinate system $\mathbf{x}_l$ in the form

$$H_f(\mathbf{x}_1,...,\mathbf{x}_N,\mathbf{p}_1,...,\mathbf{p}_N;\kappa) = \tfrac{1}{2}\sum_{l=1}^{N}|\mathbf{p}_l|^2 + \bar{V}(\mathbf{x}_1,...,\mathbf{x}_N;\kappa) \tag{10}$$

where $\mathbf{p}_l = \dot{\mathbf{x}}_l$ are the momenta and $\bar{V}$ is the sum of the harmonic constraining potential $^1/_2\kappa a_{AB}q^Aq^B$ and the rotational potentials $V(q^\alpha)$, both expressed in terms of $\mathbf{x}_1$, ..., $\mathbf{x}_N$.

III. Volkenstein's Relation

The canonical distribution function for the flexible model may be expressed in terms of rectangular Cartesian coordinates as

$$\rho(\mathbf{x}_1,...,\mathbf{x}_N,\mathbf{p}_1,...,\mathbf{p}_N,T;\kappa) = \frac{1}{Z'}e^{-H_f/kT} \tag{11}$$

with H_f given by eq 10 and

$$Z'(T) = \int_\Gamma e^{-H_f/kT}\prod_{l=1}^{N} d\mathbf{x}_l \, d\mathbf{p}_l \tag{12}$$

The function ρ is the probability density (probability per unit volume) of finding the N chain atoms which are in thermal motion at a given point of the phase space Γ. Therefore, the probability density $p(r,T;\kappa)$ of finding the Nth atom at $\mathbf{r}$ without regard to the position of the other atoms or to the values of any of the momenta is obtained from ρ by integration over the remaining atomic positions and over all of the momenta:

$$\begin{aligned} p(r,T;\kappa) &= \int \rho(\mathbf{x}_1,...,\mathbf{x}_{N-1},\mathbf{r},\mathbf{p}_1,...,\mathbf{p}_N,T;\kappa)\prod_{l=1}^{N-1} d\mathbf{x}_l \prod_{l'=1}^{N} d\mathbf{p}_{l'} \\ &= \frac{1}{Z'(T)}(2\pi kT)^{3N/2}\int e^{-\bar{V}(\mathbf{x}_1,...,\mathbf{x}_{N-1},\mathbf{r};\kappa)/kT}\prod_{l=1}^{N-1} d\mathbf{x}_l \end{aligned} \tag{13}$$

On the other hand, the Hamiltonian for the flexible model, with $\mathbf{r}$ as the imposed end-to-end vector, is obtained from that of eq 10 by setting $\mathbf{x}_N = \mathbf{r}$ and $\mathbf{p}_N = 0$. The corresponding partition function is

$$\begin{aligned} Z(r,T;\kappa) &= \int e^{-H_f(\mathbf{x}_1,...,\mathbf{x}_{N-1},\mathbf{r},\mathbf{p}_1,...,\mathbf{p}_{N-1},0;\kappa)/kT}\prod_{l=1}^{N-1} d\mathbf{x}_l \, d\mathbf{p}_l = \\ &\quad (2\pi kT)^{3(N-1)/2}\int e^{-\bar{V}(\mathbf{x}_1,...,\mathbf{x}_{N-1},\mathbf{r};\kappa)/kT}\prod_{l=1}^{N-1} d\mathbf{x}_l \end{aligned} \tag{14}$$

By comparison of eq 13 and 14 we see that

$$p(r,T;\kappa) = \frac{(2\pi kT)^{1/2}}{Z'(T)}Z(r,T;\kappa) \tag{15}$$

This is the same as Volkenstein's relation, eq 4, except for the factor of $(2\pi kT)^{1/2}$, which, since it is independent of $\mathbf{r}$, is irrelevant in the present context. As discussed in the Introduction, Volkenstein's relation is significant in the present context because it provides a link between the partition function $Z(r,T;\kappa)$, which is needed in the computation of the force–length relation on the basis of statistical mechanics as in eq 5, and the probability distribution $p(r,T;\kappa)$, which can be used for this purpose as in eq 6.

Note that this derivation procedure is restricted to flexible models since it requires the presence of $\mathbf{x}_N$ as an independent variable in the Hamiltonian of the model, eq 10, and therefore in the canonical distribution, eq 11. This

is not the case for rigid models, where the Hamiltonian H_r must be written in terms of the generalized coordinates q^α.

IV. Random Walk Interpretation

The probability distribution function $p(r,T;\kappa)$ of eq 15 is valid for any value of κ, the spring-constant scaling factor. For a chain in thermal motion with one end fixed at the origin, it is the probability density for finding the free end at position $\mathbf{r}$. We show next that if κ is arbitrarily large, then the appropriate random walk interpretation can be given to this probability distribution. For this purpose we first introduce the three-dimensional Dirac delta function $\delta(\mathbf{x})$ by the operational property that

$$\int_{R_3} g(\mathbf{x})\delta(\mathbf{x} - \mathbf{r})\, d\mathbf{x} = g(\mathbf{r}) \tag{16}$$

for an arbitrary function $g(\mathbf{x})$ and rewrite eq 13 in terms of an integral over the $3N$-dimensional configuration space as

$$p(r,T;\kappa) = C(T) \int e^{-\bar{V}(\mathbf{x}_1,\ldots,\mathbf{x}_N;\kappa)/kT}\delta(\mathbf{x}_N - \mathbf{r}) \prod_{l=1}^{N} d\mathbf{x}_l \tag{17}$$

where $C(T)$ is independent of r. We now rewrite this integral in terms of the curvilinear coordinate system $q^i = (q^\alpha, q^A)$ defined in section II. Then

$$p(r,T;\kappa) = C(T) \int e^{-[(\kappa/2)a_{AB}q^Aq^B + V(q^\alpha)]/kT}\delta(\mathbf{x}_N(q^\alpha,q^A) - \mathbf{r}) \times |g_{ij}|^{1/2} \prod_{\alpha=1}^{f} dq^\alpha \prod_{A=f+1}^{3N} dq^A \tag{18}$$

where $\mathbf{x}_N(q^\alpha,q^A)$ is the position of the Nth atom expressed as a function of the curvilinear coordinates (q^α,q^A).

The limiting form of $p(r,T;\kappa)$ for arbitrarily large κ is obtained by carrying out the integration with respect to the q^A variables in the exponential while setting $q^A = 0$ everywhere else in the integrand. This yields what corresponds to the first term in the asymptotic expansion of $p(r,T;\kappa)$ as obtained by Laplace's method.[13] This result is

$$p(r,T) = C(T)\left(\frac{2\pi kT}{\kappa}\right)^{c/2} |a_{AB}|^{-1/2} \times \int e^{-V(q^\alpha)/kT}\delta(\mathbf{x}_N{}^0(q^\alpha) - \mathbf{r})|g_{ij}|_0{}^{1/2} \prod_{\alpha=1}^{f} dq^\alpha \tag{19}$$

where $\mathbf{x}_N{}^0(q^\alpha)$ and $|g_{ij}|_0$ are the functions $\mathbf{x}_N(q^\alpha,q^A)$ and $|g_{ij}|(q^\alpha,q^A)$, with $q^A = 0$, $A = f + 1, \ldots, 3N$, and $c = 3N - f$. Note that the presence of κ in eq 19 is of no concern since only $\log p$ is of interest.

Equation 19 lends itself directly to a random walk intepretation. Consider, for example, the case of a model in which the bond lengths and valence angles are hard variables with equilibrium values a and θ_0, respectively, with the dihedral angles ϕ_l, $l = 1, \ldots, N$, as soft variables and with no rotational barriers. Then, from eq 8, $|g_{ij}|_0 = (a^2 \sin \theta_0)^N$, and eq 19 takes the form

$$p(r,T) = C'(T)(a^2 \sin \theta_0)^{N/2} \int_0^{2\pi} \cdots \int_0^{2\pi} \delta(\mathbf{x}_N{}^0(\phi_l) - \mathbf{r})\, d\phi_1 \ldots d\phi_N \tag{20}$$

The integral is proportional to the probability of choosing a set of dihedral angles, $\phi_1, \ldots, \phi_N$, with uniform probability on $0 \le \phi_l \le 2\pi$ for each angle, such that $\mathbf{x}_N = \mathbf{r}$ when these angles are applied to a chain with bond length a and valence angle θ_0.

Similar random walk interpretations can be given for other chain models. This completes the demonstration that $p_{sm} = p_{rw}$ (in the terminology used in section I) for flexible models with arbitrarily large κ.

V. Concluding Remarks

As an example, we can consider the two-bond, freely jointed chain. For this case[14] $p_{rw} = C/r$ for $0 \le r < 2a$ and $p_{rw} = 0$ for $r > 2a$. This is the same r dependence as found in ref 10 by the evaluation of the partition function for the flexible model for arbitrarily large κ and leads to the anomalous force–length relationship noted there, a relationship verified by computer simulation.

Further examples of the use of eq 3 are given in the following paper.[15]

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