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On Frenkel's Governor Model for Stretched Polymers

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The usual discussion of the force required to maintain a long-chain molecule at a fixed length is based on the concept of entropy, an approach in which the fundamental basis for the resulting force is not easily accessible to one's physical intuition. In an attempt to provide an explanation of what he termed the kinetic origin of the force, Frenkel[1] introduced the atomistic analogue of a centrifugal governor. The model consists of a chain of three atoms with fixed bond length a and the two end atoms fixed at a distance $2l$ apart, Figure 1. If it is assumed that the central atom is in thermal motion with a velocity corresponding to its mean kinetic energy of $^1/_2kT$, then it is easily derived by elementary mechanics[1,2] that the required force f is

$$f = \frac{l}{2(a^2 - l^2)}kT \qquad (1)$$

a result which shows the dependence upon temperature and upon end-to-end length which is typical of a long-chain molecule under tension. The same force–length–temperature relation can be derived more formally on the basis of classical equilibrium statistical mechanics. The Hamiltonian of the model in terms of the angle coordinate θ (Figure 1) and corresponding momentum p_θ is

$$H_r(\theta,p_\theta) = \frac{1}{2}\frac{p_\theta^2}{mr^2} \qquad (2)$$

where

$$r = (a^2 - l^2)^{1/2} \qquad (3)$$

and the corresponding partition function is, with $\beta = (kT)^{-1}$

$$Z_r(l,T) = \int_0^{2\pi} d\theta \int_{-\infty}^{\infty} e^{-\beta p_\theta^2/2mr^2}\, dp_\theta = 2\pi(2\pi mkT)^{1/2}(a^2 - l^2)^{1/2} \qquad (4)$$

Therefore the required force is

$$f_r = -\frac{\partial}{\partial(2l)}kT \log Z_r(l,T) = \frac{l}{2(a^2 - l^2)}kT \qquad (5)$$

as before.

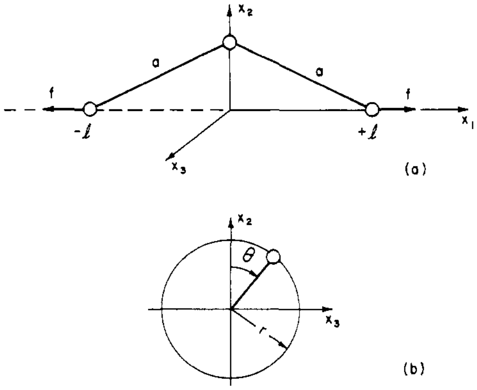

Figure 1. Two-bond model of stretched polymer. (a) End atoms are maintained at fixed positions $x_1 = \pm l$ by axial force f while the central atom is in thermal motion. In the rigid model, bond lengths are fixed at a and the central atom moves on a circle of radius $r = (a^2 - l^2)^{1/2}$ in the x_2–x_3 plane as shown in (b). The position of the central atom is then described in terms of the angle coordinate θ.

Frenkel's model is, in present terminology, a rigid polymer model in the sense that the fixed bond length a is imposed first in the Hamiltonian of the model and the partition function is computed subsequently; the subscript r on H, Z, and f has been added in order to emphasize that these quantities apply to the rigid case. The corresponding flexible model is obtained if in the model Hamiltonian H_f the bond lengths are held approximately constant by means of stiff linear springs with spring constant κ, the partition function Z_f is computed on the basis of H_f, and κ is allowed to become arbitrarily large in the resulting expression.

There have been a number of recent studies devoted to the comparison of the statistical behavior of rigid and flexible models,[3-7] and for some cases, striking differences have been demonstrated by computer simulation.[8-10] These works have been directed primarily at free molecules in solution. It is the purpose of this note to consider the flexible version of Frenkel's model and to compare its force–length–temperature relation with that for the corresponding rigid model.

The Hamiltonian for the flexible model may be described in terms of a rectangular Cartesian coordinate system, with $\mathbf{x}$ the position and $\mathbf{p}$ the momentum of the moving atom, as

$$H_f(\mathbf{x},\mathbf{p}) = \frac{1}{2m}|\mathbf{p}|^2 + V(\mathbf{x}) \qquad (6)$$

where

$$V(\mathbf{x}) = {}^1/_2\kappa[(|\mathbf{x} - \mathbf{l}| - a)^2 + (|\mathbf{x} + \mathbf{l}| - a)^2] \qquad (7)$$

Here κ is the linear spring constant and $\pm\mathbf{l}$ are the positions of the fixed atoms. The corresponding partition function is

$$Z_f(l,T) = \int_{\Gamma_\mathbf{p}} e^{-\beta|\mathbf{p}|^2/2m}\, d\mathbf{p} \int_{\Gamma_\mathbf{x}} e^{-\beta V(\mathbf{x})}\, d\mathbf{x} = (2\pi mkT)^{3/2} \int_{\Gamma_\mathbf{x}} e^{-\beta V(\mathbf{x})}\, d\mathbf{x} \qquad (8)$$

where the integration over momentum space $\Gamma_\mathbf{p}$ has been performed. To evaluate the integral over the configuration space $\Gamma_\mathbf{x}$, we use the fact that for large κ, $V(\mathbf{x})$ is large except when $\mathbf{x}$ is in the neighborhood of a point on the circle of radius $r = (a^2 - l^2)^{1/2}$ at an arbitrary angle θ as in Figure 1. We introduce local rectangular Cartesian coordinates (ξ,η) with origin on this circle in the plane of $-\mathbf{l}, \mathbf{x}, \mathbf{l}$,

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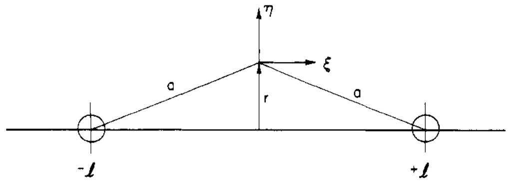

Figure 2. Local (ξ, η) coordinate system used for approximate analysis of the flexible model. Coordinate axes lie in the plane of the three atoms with origin at $r = (a^2 - l^2)^{1/2}$ as shown.

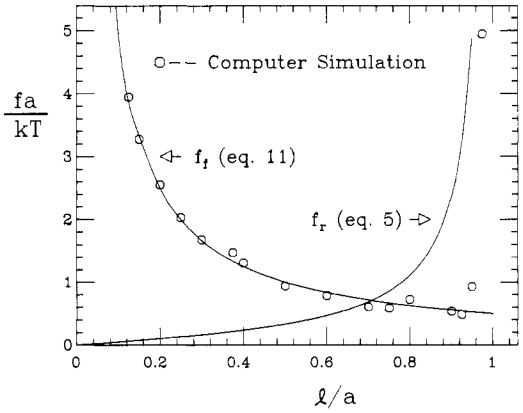

Figure 3. Comparison between end force required for the rigid model, f_r, and for the flexible model, f_f. Also shown are the results of the computer simulation of the flexible model by the method of Brownian dynamics, with spring constant $\kappa a^2/kT = 1.5 \times 10^3$.

as shown in Figure 2. A Taylor series expansion of $V(\mathbf{x})$ up to quadratic terms of ξ and η leads to the result

$$V(\mathbf{x}) \simeq V(\xi,\eta) = \frac{\kappa}{a^2}(l^2\xi^2 + r^2\eta^2) \tag{9}$$

so that for large κ

$$Z_f(l,T) \simeq (2\pi mkT)^{3/2} \int_0^{2\pi} r \, d\theta \int_{-\infty}^{\infty} d\xi \int_{-\infty}^{\infty} d\eta \; e^{(-\beta\kappa/a^2)(l^2\xi^2+r^2\eta^2)}$$

$$= (2\pi mkT)^{3/2} \frac{2\pi^2 kT}{\kappa} \frac{a^2}{l} \tag{10}$$

Therefore, f_f, the force required on the basis of the flexible model, is

$$f_f = -\frac{\partial}{\partial(2l)} kT \log Z_f = kT/2l \tag{11}$$

This result is independent of the spring constant κ, so long as the latter is sufficiently large to justify the approximation made in the evaluation of Z_f.

The results for the two models are compared in Figure 3. We see that their behavior is totally different, and, moreover, the dependence of f_f upon l is not at all like that of an entropic spring.

The behavior of the flexible model may be rationalized as due to the dependence of the curvature of the potential well upon the length l as seen in eq 9. Nevertheless, the resulting force-length relation of eq 11 is sufficiently counterintuitive to warrant a computer simulation of the model described by eq 6 and 7 in order to provide a test of the analysis.[11] This has been performed by the method of Brownian dynamics.[12] The results are shown in Figure 3 and are seen to agree quite well with the theoretical prediction for l/a not too large. When $l/a \to 1$, the approximate evaluation of Z_f is no longer valid. In this region, the computer simulation results show a rapid rise in f_f while the approximate theory indicates a monotonic decline.

This simple model, therefore, provides another example of the possible striking differences in behavior between rigid and flexible macromolecular models. It also suggests that the rigid version, the governor model, is a poor example for the demonstration of the kinetic origin of the force in stretched polymers since its closely related and, in a sense, more realistic flexible counterpart shows such anomalous behavior.

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(12) The general procedure employed is similar to that described in Appendix B of ref 10. Further details for this computation will be found in the forthcoming doctoral dissertation of D. Perchak.

Method for Gel Permeation Chromatography Calibration and the Evaluation of Mark-Houwink-Sakurada Constants

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The evaluation of the Mark-Houwink-Sakurada constants, K and α, for a particular polymer-solvent system normally requires the preparation of a series of samples having a wide range of molecular weights and their subsequent characterization by light scattering and dilute-solution viscometry. However, gel permeation chroma-

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