

Effects of Bond Stretching on Polymer Statistics

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A probability distribution for polymer chain end-to-end separation is derived that incorporates the effects of bond stretching and bending. Each bond is represented by a spring with an equilibrium length that can stretch and contract according to a harmonic force law. Such a model is expected to be important for the description of polymeric materials under large deformations. Methods for computing the distribution and related quantities are derived and are shown to be robust and realistic. Computed distributions show noticeable differences from more commonly used models that do not have a dependence on the bond strengths.

I. Introduction

One property of rubber-like polymeric materials that sets them apart is their high degree of elasticity. Such materials can be stretched to many times their natural size under relatively weak external forces. This property, of course, can be directly related to the nature of the material at the molecular level. These materials consist of interconnected networks of polymer chains distributed randomly throughout. The randomness of the distribution is not only in terms of the orientation of the chain but also in how much they are extended from end to end. For an unstrained material, the distribution of end-to-end separations of these chains is reliably modeled, perhaps with some minor modifications, by the equilibrium distribution of end-to-end separations of an isolated chain. This equilibrium distribution function is therefore an important ingredient in the theoretical treatment of rubber-like polymeric materials.

When a polymeric material is deformed, the distribution of end-to-end chain separations is deformed along with it. By assuming affine motions of the junctions, it is possible to relate the deformed-state distribution directly to the equilibrium distribution.¹ Nonaffine motion would modify this relationship, but it is reasonable to assume that the actual distribution still bears some connection with the equilibrium distribution. With the deformed-state distribution, it is possible to determine the stress in the material.² So, even for deformed systems, the equilibrium distribution of end-to-end separations of the polymer chain plays an important role in the theoretical study of polymeric materials. In the classical statistical mechanical treatment of rubber elasticity, this distribution function, in fact, plays the central role.

Work is currently underway to study the behavior of polymeric materials when subjected to large deformations, including deformations large enough to cause failure. In such circumstances, the polymer chains are stretched and either breakage may occur or the restoring forces may become strong enough to cause the chains to disengage and slip past each other. The behavior of such chains is qualitatively different from that of chains at equilibrium in an unstrained material. The theoretical study of such systems requires a probability distribution of end-to-end separations that can reliably model both the unstrained

and highly strained systems. This paper presents the development leading to the construction of such a distribution function.

If the polymer chain is treated in full detail, the distribution of end-to-end separations of a polymer chain can become a complicated quantity. Issues involving self-avoidance, allowed bond angles, and successive torsional angles can impose mathematical difficulties in the analysis. However, the nature of the polymer chain itself and the medium in which it is placed allows the introduction of simplifications.

In an unstrained system, most of the longer polymer chains coil up and have small end-to-end separations. This justifies the use of what is known as the Gaussian chain model. The easiest way to develop the model is to view the polymer molecule as a chain of beads connected by freely jointed massless rods—the so-called Kramers chain.³ Although this model completely ignores the restrictions in bond angles found in real polymer chains, it still contains some very important features. In particular, the Kramers chain correctly represents the large number of ways that a polymer chain with small to moderate end-to-end separations can be oriented, extended, and deformed. Representing the polymer by a Kramers chain and assuming most of the chains to be long with small end-to-end separations, the distribution that results is given by a gaussian function of the chain extension. It can be shown⁴ that this model becomes exact in the limit of infinite polymer chain length. That is, even if the details of the individual bonds are taken into account, the distribution looks just like a Gaussian when the limit of infinite chain length is taken.

One issue that may be mentioned is that this model ignores self-avoidance of the chain. The loss in accuracy is amply offset by the simplification in the mathematics. One may point to the fact that, in θ -solutions and polymer melts, the mean-square end-to-end separation of the polymer chains is better described by a Gaussian chain distribution than the self-avoiding chain distribution.⁵ Although it is not firmly established, it will be assumed that self-avoidance is not important under large deformations and so will be ignored in this paper.

When a system becomes strained, longer chain end-to-end separations become more probable and the assumptions that go into the Gaussian chain model are no longer valid. In particular, the Gaussian chain model allows the polymer chains to stretch without limit. The associated probability distribution attaches too much weight to the probabilities at larger end-to-end

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separations, and a statistical analysis based on this distribution would unrealistically overemphasize the contributions of these longer chains. The natural improvement is to retain the Kramers chain description but to remove the assumption of small extension and impose a finite length for the polymer chains. This leads to what is referred to as a non-Gaussian model. It is possible to derive the exact probability distribution for the Kramers chain,⁶ although an approximation involving the inverse Langevin function⁷ is more commonly used for computational work. The non-Gaussian model has the desirable feature that the probability goes to zero when the chain reaches its maximum extension. The chain is prevented from stretching any further, resulting in a stiffening of the bulk material.

For large deformations, this model should be modified further. The resistance to extension in the non-Gaussian model is due solely to a reduction in number of configurations as the chain is lengthened. At some point, the polymer chain can extend no more. A real polymer chain does not reach an absolute limit of extension, but rather, starts stretching and bending bonds away from their equilibrium values when the extension gets large enough. There will be an increase in resistance relative to the Gaussian chain model, but not as rapid an increase as in the non-Gaussian model. Further, the increase in resistance is directly related to the molecular nature of the polymer chain. Polymers with weaker bonds will exhibit a weaker resistance to extension while those with stronger bonds will exhibit a stronger resistance. It would be useful to be able to incorporate this correlation into the theoretical model of the material.

A rough idea of the potential importance of this modification of the distribution can be gained through consideration of a 200-bond chain of polyethylene. At a temperature of 298 K, the Gaussian chain model would predict a free energy change upon extension from zero to full end-to-end separation equal to 750 kJ/mol. On the basis of the analysis presented in section IV, the extension by only 1% more is calculated to be equal to 25 kJ/mol. Roughly, then, it takes about 4 times more energy to extend the chain per unit distance beyond the limit of full extension than it does below this limit. This is a considerable increase in energy expenditure but would not prohibitively hinder the extension of the chain past full extension. It is important to keep in mind that the concern here is a proper statistical description of the distribution of polymer chains under large average deformations. While most polymer chains are expected to remain below the limit of full extension, a noticeable fraction should stretch beyond this limit. The absolute limit of extension presented by the non-Gaussian limit is, in this regard, viewed as inadequate.

This paper presents an improvement of the non-Gaussian model which takes into account the stretching and bending of bonds. The advantages of the Kramers chain representation are retained, the polymer molecule being viewed as a chain of beads connected by freely jointed massless rods. However, to correctly model the behavior at large extensions, the rods are allowed to stretch and contract as needed. To retain some simplicity, a harmonic force law is assumed. For small extensions, the large number of equal-energy configurations available will be the dominating factor in the probability distribution, which is the same as that occurring in both the Gaussian and non-Gaussian chain models. For large extensions, though, the effects of bond stretching are more important. The increased resistance to stretching then becomes the dominating factor in the probability distribution. Even for small extensions, there may be a noticeable effect, since allowing the bonds to stretch and contract effectively increases the number of allowed configurations for

the polymer chain. The size of this increase may vary with end-to-end separation and so affect the dependence of the probability distribution on this variable. This is actually observed in the calculations.

Although bond angles are unrestricted in this model, the effects of equilibrium bond angles can still be incorporated by a judicious choice of the parameters. That is, the equilibrium length of a bond might not be taken as the actual bond length between beads but rather as the distance along an extended chain from one bead to the next. The chain will most likely zigzag when it is extended, so that this distance will be less than the actual bond length. Further, the force constant for the harmonic force law may be a mixing of bond stretching and bond bending forces. While bond bending is expected to occur more readily, both should occur to some extent as the chain is extended and they should be mixed in an appropriate way. Even though these effects are incorporated into the parameters in a rather contrived way, changes in molecular structure, either through changes in bond strengths, bond lengths, or bond angles, should be realistically modeled. The advantage of ignoring the equilibrium bond angles, of course, is that the computations are considerably simplified. It may be desirable, at a later stage, to consider refinements of the model that take these issues into account.

It should be mentioned that the proposed model has some similarities to some other models. First, Kuhn and Kuhn⁸ suggested a model which assumed a non-Gaussian chain for smaller extensions and a simple harmonic spring for larger extensions. An attempt to join the two models at intermediate extensions was then made. The present work has the advantage of using the same model for all extensions and is found to exhibit noticeable differences from the distribution of Kuhn and Kuhn. Second, the present model has some similarities to the Fraenkel spring⁹ force law used in the elastic dumbbell model for polymer solutions. A dumbbell model views a polymer chain as a single bond, so the present model may be viewed as an extension of the Fraenkel spring model to a chain. The Fraenkel spring model has advantages^{9,10} over the rigid dumbbell model and the Hookean elastic dumbbell model. It seems reasonable, then, to suppose that the chain of Fraenkel springs should have similar advantages over the chain of rigid rods or Hookean springs. It is finally worth mentioning that the proposed model is the same as that used in several molecular dynamics simulations of polymer systems.¹¹

The proposed model should not be confused with the popular Rouse¹² and Rouse-Zimm¹³ chain models. These models also assume a chain of flexible springs, but these springs are Hookean. That is, the equilibrium separation of each spring is zero. The rationale behind these models is that each bead represents not a single monomer, but rather a chain of monomers whose end-to-end separation should be reasonably described by a Gaussian distribution. This effectively results in a harmonic force law with an equilibrium separation of zero and a force constant that reflects the entropic nature of the restoring force. As with the Gaussian model, such a spring can be stretched without limit and so is inappropriate for the study of materials at large deformations.

This paper will present some of the mathematical details necessary for working with this model. Section II presents the model itself and some of its associated properties. Means for computing the distribution function are presented in section III. The details involved with determining the molecular parameters for a typical polymer chain are presented in section IV. Section V presents an application to the treatment of rubber-like materials using moments of the distribution, which can be

computed here in closed form. The final section will present a discussion of the model and present some suggestions for improvements.

II. The Model

The proposed model assumes that each polymer molecule behaves as a chain of beads connected by freely rotating springs. These springs are assumed to have a finite equilibrium length and to extend and contract according to a harmonic force law. While this model does not restrict the angles between successive bonds in any way, the restrictions encountered in real polymer chains may still be incorporated into the model's parameters. This will be discussed later in section IV.

Let the equilibrium length of each bond be a and the force constant be H . It is being assumed that all the bonds are identical in this chain. Extension to chains of more than one type of bond should be straightforward. Suppose that a chain consists of N bonds, the actual bond lengths and directions for a specific configuration being given by the set of bond vectors $\{\mathbf{Q}_j, j = 1, \dots, N\}$. Using the notation \mathbf{Q}^N to represent the full set of bond vectors, the energy of a chain is given by

$$E(\mathbf{Q}^N) = E_0 + \frac{1}{2}H \sum_{n=1}^N (Q_n - a)^2 \quad (1)$$

where E_0 is some reference energy for the relaxed chain. Consider, now, an ensemble of such chains at absolute temperature, T . The equilibrium probability associated with a given configuration is then

$$\psi_{\text{eq}}(\mathbf{Q}^N) = \frac{e^{-E(\mathbf{Q}^N)/kT}}{\int e^{-E(\mathbf{Q}^N)/kT} d\mathbf{Q}^N} \quad (2)$$

where k is Boltzmann's constant. The symbol $d\mathbf{Q}^N$ represents the measure associated with integration over all N bond vectors, the range of integration for each vector being the entire three-dimensional space. Note that, in this quantity, and in the quantities to come, the dependence on E_0 cancels out in the numerator and denominator, as it should. The probability of a given end-to-end separation, \mathbf{r} , is given by

$$P_{\text{eq}}^{(N)}(\mathbf{r}) = \int \delta(\mathbf{r} - \sum_{j=1}^N \mathbf{Q}_j) \psi_{\text{eq}}(\mathbf{Q}^N) d\mathbf{Q}^N \quad (3)$$

It is straightforward to show that this probability distribution depends only on the magnitude of the separation. This may be argued to be necessary on physical grounds. Because it is more sensitive to the behavior at large extensions, some attention will be focused on the related function

$$g^{(N)}(r) = -\ln P_{\text{eq}}^{(N)}(r) \quad (4)$$

The free energy of an ensemble of polymer chains is related to $g^{(N)}(r)$,⁴ so this function is an important quantity in its own right for the statistical mechanics of these systems.

It is convenient to express the probability distribution in reduced units. An energy ratio

$$\epsilon = \frac{Ha^2}{kT} \quad (5)$$

is introduced. If distances are expressed in units of a and the probability distribution is expressed in units of a^{-3} , (3) becomes

$$P_{\text{eq}}^{(N)}(\mathbf{r}) = \frac{1}{Z_1^N} \int \delta(\mathbf{r} - \sum_{j=1}^N \mathbf{Q}_j) \exp \left[-\frac{\epsilon}{2} \sum_{n=1}^N (Q_n - 1)^2 \right] d\mathbf{Q}^N \quad (6)$$

where

$$Z_1 \equiv \int e^{-\epsilon(Q-1)^2/2} d^3Q = \left(\frac{2\pi}{\epsilon} \right)^{3/2} \left\{ \left(\frac{2\epsilon}{\pi} \right)^{1/2} e^{-\epsilon/2} + (1 + \epsilon) \operatorname{erfc}(-\sqrt{\epsilon/2}) \right\} \quad (7)$$

It is straightforward to show that the angular dependence on \mathbf{r} cancels out completely in (6).

For $N = 1$, the probability distribution is worked out in a trivial way.

$$P_{\text{eq}}^{(1)}(r) = \frac{1}{Z_1} e^{-\epsilon(r-1)^2/2} \quad (8)$$

This leads to

$$g^{(1)}(r) = \ln Z_1 + \frac{\epsilon}{2}(r-1)^2 \quad (9)$$

This function is just a quadratic function in r , the minimum being at the equilibrium bond length. In order to achieve a particular extension, the one-bond polymer can only stretch or contract. Since this costs energy, any extension other than the equilibrium bond length will be less probable and the free energy contribution higher. For larger values of N , however, the polymer can achieve smaller extensions with no cost in energy by properly orienting the bonds. Since there may be many different configurations that can achieve a particular extension, the probability of a smaller extension may be relatively high. This is the type of behavior observed for the Kramers chain and as a result, we would expect the probability distribution to have similar behavior for small r . Specifically, this implies that

$$g^{(N)}(r) \underset{r \rightarrow 0}{\sim} C + \frac{3r^2}{2N} \quad (10)$$

The fact that the bonds can also change their length to achieve a given extension means that there are actually more configurations possible than with the Kramers chain. The very small- r behavior of the distribution turns out to be slightly different for this reason.

For larger extensions, the effects of bond stretching become more important. If the chain is extended beyond the fully extended length N , there is only one configuration associated with the minimum energy: a straight chain with every bond equally stretched. The chain is extended by $(r - N)$ so that each bond is stretched by $(r - N)/N$. The energy of this configuration is equal to $E_0 + H(r - N)^2/2N$, implying

$$g^{(N)}(r) \underset{r \rightarrow \infty}{\sim} \frac{\epsilon(r - N)^2}{2N} \quad (11)$$

The function $g^{(N)}(r)$ therefore varies quadratically with r for both small and large extensions. As a function of r^2 , it should be linear in these two regions with one slope for smaller r and a different one for larger r , a transition occurring around $r = N$. More quantitatively, it is expected that the function $g^{(N)}(r)$ should satisfy the relations

$$\frac{d^2 g^{(N)}(r)}{dr^2} \sim \begin{cases} 3/N & r \rightarrow 0 \\ \epsilon/N & r \rightarrow \infty \end{cases} \quad (12)$$

The nature of the distribution clearly changes between the small- and large- r regions. The small- r region reflects the mainly entropic effects on the chain's behavior, while the large- r region reflects mainly the energetic effects of bond stretching. The relative importance of the two types of effects is represented by the ratio $\epsilon/3$. A large ratio would imply a relative insignificance of the bond stretching on the distribution. The distribution would reflect essentially the entropic behavior for extensions below the full extension limit, with little possibility of extending beyond this limit. A smaller ratio would imply a stronger effect due to bond stretching. For $\epsilon = 3$, the model would be similar to the Gaussian chain model. Clearly, a realistic parameter should be larger than this. Specific values for this parameter will be considered later in section IV.

III. Computation of the Probability Distribution

Equation 6 can be evaluated in closed form for $N = 1$ and $N = 2$. The integrations become too difficult for larger values of N . Alternatively, the Fourier transform of the delta function can be introduced and all but one integration evaluated in closed form. The final integral, however, contains an oscillatory integrand that makes numerical evaluation difficult in the general case. To avoid these problems, a recursive scheme has been developed and will be presented here.

If (6) is evaluated for $N + 1$, it can be manipulated to

$$P_{\text{eq}}^{(N+1)}(r) = \frac{1}{Z_1} \int e^{-\epsilon(Q-1)^2/2} P_{\text{eq}}^{(N)}(|\mathbf{Q} - \mathbf{r}|) d^3 Q \quad (13)$$

By a translation of the integration variables and noting that the probability distribution depends only on the magnitude of its argument, two of the integrations can be evaluated in closed form and there results

$$P_{\text{eq}}^{(N+1)}(r) = \frac{2\pi}{Z_1} \int_0^\infty z P_{\text{eq}}^{(N)}(z) F(z, r, \epsilon) dz \quad (14)$$

where

$$F(z, r, \epsilon) = \frac{1}{r} \left\{ \frac{1}{\epsilon} \left(e^{-\epsilon(|z-r|-1)^2/2} - e^{-\epsilon(z+r-1)^2/2} \right) + \left(\frac{\pi}{2\epsilon} \right)^{1/2} [\text{erf}(\sqrt{\epsilon/2}(z+r-1)) - \text{erf}(\sqrt{\epsilon/2}(|z-r|-1))] \right\} \quad (15)$$

Starting with the distribution for $N = 1$ (8), it is possible to evaluate probability distributions for successively larger values of N .

Calculations were performed for values of ϵ ranging from 10 to 2500 and for N up to 200. The integrations were performed using 8193-point Romberg integration and double precision, allowing the evaluation of the distribution for values as small as 10^{-740} . This proved to be important for the generation of $g^{(N)}(r)$ for larger values of r . The recursive scheme proved to be quite stable. No special techniques were needed nor were there special situations to consider. It may be that use of fewer points in the Romberg integration could still yield accurate results and would clearly take less time.

Plots of $g^{(N)}(r)$ for the representative values $\epsilon = 10, 100, 1000$ and $N = 50$ are shown in Figure 1. Also shown, for comparison, are the corresponding functions from the Gaussian model, the non-Gaussian model (use of the exact⁶ and inverse Langevin

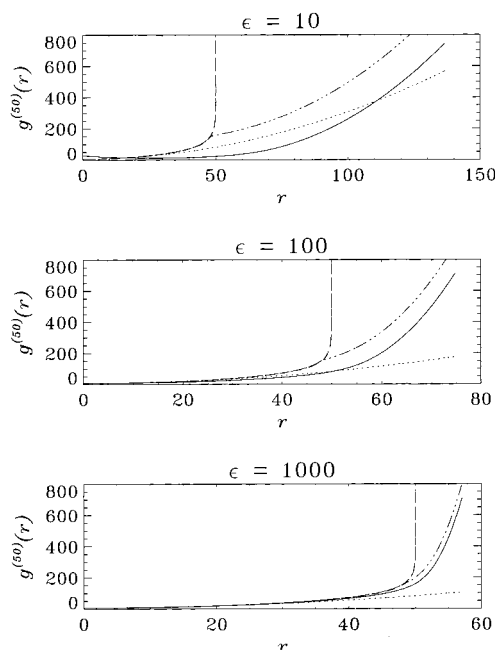


Figure 1. A comparison of the function $g^{(N)}(r)$ for a chain of Fraenkel springs (solid line) with the gaussian (dotted line) and non-gaussian (dashed line) model approximations. Also shown is the model of Kuhn and Kuhn⁸ (dotted-dashed line). Comparisons are for $N = 50$ and the three values $\epsilon = 10, 100, 1000$.

function approximation⁷ for this produce curves that are indistinguishable from each other), and the model of Kuhn and Kuhn.⁸ In every case, the Gaussian model yields a poor description for larger values of r . For $\epsilon = 10$, the Gaussian model is a poor approximation for all values of r . The non-Gaussian model, in all cases, shoots up too quickly near $r = N$. The approximation of Kuhn and Kuhn agrees best with the model proposed here, but is still poor for smaller values of ϵ . Further, Kuhn and Kuhn's approximation has a kink in it where the small and large r regimes are joined. This kink is small for $\epsilon = 1000$, but there is still a noticeable difference with the model proposed here. In all cases, the function for the chain of Fraenkel springs rises more slowly and at higher values of r than any of the other models.

The idea of a Gaussian model behavior for smaller r and a steepening due to bond stretching for larger r is borne out in the calculations for the larger values of ϵ . However, for $\epsilon = 10$, an additional feature becomes evident. A small value of ϵ corresponds to either weak bonds or high temperatures where stretched bonds are more probable. The enhanced contribution from stretched configurations will lead to larger numbers of available configurations than in the Gaussian model. If the number of configurations is increased by the same amount for all extensions, there would be no change in the distribution due to the fact that it is normalized. However, if the increase in available configurations varies with extension, this effect should be observed in the distribution and its logarithm. The effects of bond stretching seem to become more important as the extension moves away from zero so that there is a minimum in $g^{(N)}(r)$, and hence a maximum probability, for a nonzero value of r . This effect is also evident for $\epsilon = 100$. When calculations were performed for larger values of N at $\epsilon = 1000$, the effect again became evident.

Apparently, stretching of the bonds plays a more important role as either the bonds become weaker, the temperature is increased, or the length of the chain is increased. The first two effects are readily understood. The last effect can be rationalized

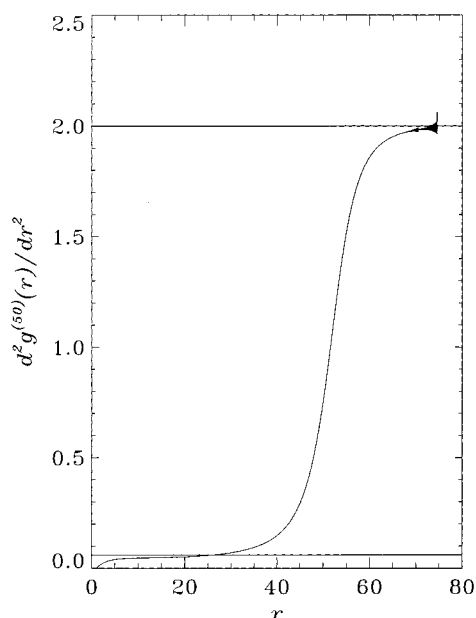


Figure 2. The second derivative of $g^{(N)}(r)$ for $\epsilon = 100$ and $N = 50$. Horizontal lines are drawn at values of $3/N$ and ϵ/N . See (12).

if one considers the behavior of the chain in this case. A long polymer chain can achieve a large number of configurations for a given extension. In addition, the stretching of individual bonds raises the energy only slightly relative to the total energy of the chain. In the ensemble averaging indicated in (3), then, it may be deduced that, for long polymer chains, orientations with slightly stretched bonds should have comparable probabilities to nearby orientations without stretched bonds. The contributions from such orientations should become more prominent as the chain becomes longer. Considering a real polymeric system, the thermal averaging of the chain orientations should come about through collisions with other molecular species in the system, be they other chains, solvent molecules, or other species. One can imagine a long chain being jostled about, either through its own thermal motions or through collisions with other molecules in the system, with the stretching of bonds being easier to achieve for a long chain than moving the entire chain to keep the energy at a minimum. One might expect the effects of bond stretching to become more important as the chain length is increased.

The second derivative of $g^{(N)}(r)$ was computed numerically for a number of values of N and ϵ . It was found that the properties (12) are satisfied except for one feature. For very small r , the second derivative seems to drop to zero. This is illustrated in Figure 2 for $\epsilon = 100$ and $N = 50$. This feature was observed for all the values of ϵ and $N > 1$ considered. Closer analysis indicated that the second derivative does not actually go to zero but becomes slightly negative in this region. Since the first derivative is zero for zero extension (this can be proved), this implies an initial decrease in $g^{(N)}(r)$ for extensions close to zero. This is consistent with the observations made above related to the enhancement in the number of available configurations due to bond stretching.

IV. Determination of the Parameters

Although this model ignores molecular details involved with restrictions on bond angles, it is still possible to incorporate them into the parameters. A procedure for doing this will be presented in this section by considering a specific type of polymer chain: one with N identical bonds that preferentially

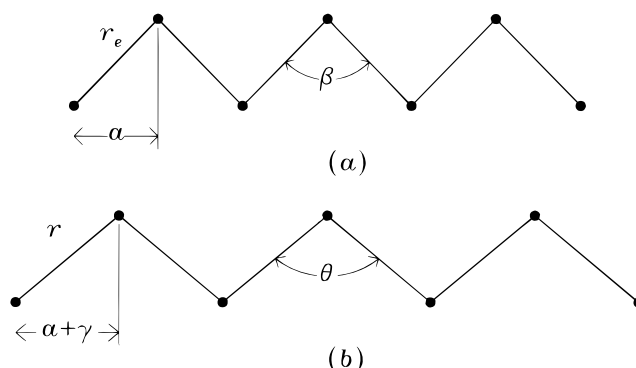


Figure 3. A segment of the extended polymer chain of identical bonds, both (a) when relaxed and (b) after stretching. When relaxed, each bond has equilibrium length r_e and each bond angle has equilibrium value β . After stretching, each bond has a modified length r and each bond angle has a modified angle θ . The length along the extended chain increases from a when relaxed to $a + \gamma$ after stretching.

achieves a *trans* arrangement of bonds in the stretched configuration. This is the situation, for instance, in polyethylene. Different types of situations can readily be accommodated within this model by a judicious choice of parameters. If there is more than one type of bond, for instance, one may break the chain up into identical segments, each composed of several bonds which in general may be different. The appropriate parameters may be obtained by considering the force law associated with stretching this segment as a whole rather than the individual bonds. To avoid extra complications, however, the simpler case of a chain with identical bonds will be considered here.

Let the equilibrium length of each bond be denoted by r_e and let the equilibrium bond angle between adjacent bonds be denoted by β . These quantities are illustrated in Figure 3. If it is assumed that the *trans* arrangement of successive bonds is stable, the chain can be fully extended into a zigzag arrangement without stretching or bending any bonds beyond their equilibrium values. The length of the extended, relaxed chain will be $Nr_e \sin(\beta/2)$, implying the identification

$$a = r_e \sin(\beta/2) \quad (16)$$

As the chain is extended further, the bonds will stretch and the bond angles bend. There will be a resistance to these effects that can be expressed in terms of force constants. Suppose that there is a stretching force constant, k_r , for each bond and that there is a bending force constant, k_θ , associated with each bond angle. For small deviations from equilibrium, the total energy associated with stretching the chain is given by

$$E = E_0 + \frac{1}{2}k_r \sum_{j=1}^N (r_j - r_e)^2 + \frac{1}{2}k_\theta \sum_{\alpha=1}^{N-1} (\theta_\alpha - \beta)^2 \quad (17)$$

where r_j is the actual bond length of bond j and θ_α is the actual bond angle of the α th angle.

Consider the extension of the chain beyond the equilibrium length by an amount $(X - Na)$. The minimum energy geometry of the chain in this case will occur when each bond is stretched equally and each bond angle is bent equally. Each bond length may be denoted by the common value r and each bond angle by the common value θ , so that the equilibrium energy is given by

$$E_m = E_0 + \frac{1}{2}Nk_r(r - r_e)^2 + \frac{1}{2}(N - 1)k_\theta(\theta - \beta)^2 \quad (18)$$

Before stretching, the length of each bond along the polymer chain is equal to a , as expressed in (16). After stretching, this extension is increased to $a + \gamma$, and simple geometric arguments lead to

$$a + \gamma = r \sin(\theta/2) \quad (19)$$

Alternatively, if each bond is assumed to be extended equally, γ can be associated with the overall extension of the chain by

$$\gamma = \frac{X - Na}{N} \quad (20)$$

If the bond length is expressed as $r_e + \epsilon$ and if it is assumed that both γ and ϵ are small, there results

$$\theta = \beta + \frac{2(\gamma - \epsilon \sin(\beta/2))}{r_e \cos(\beta/2)} + \dots \quad (21)$$

The extension, and hence γ , are viewed as given quantities. The energy may be minimized with respect to ϵ and the resulting energy at this minimum derived. Keeping only up to second order in the small quantities, there results

$$E_m = E_0 + \frac{2N(N-1)k_r k_\theta}{Nk_r r_e^2 \cos^2(\beta/2) + 4(N-1)k_\theta \sin^2(\beta/2)} \gamma^2 \quad (22)$$

Introducing (20) and comparing with the energy associated with stretching the chain of Fraenkel springs, the Fraenkel spring force constant comes out to be

$$H = \frac{4(N-1)k_r k_\theta}{Nk_r r_e^2 \cos^2(\beta/2) + 4(N-1)k_\theta \sin^2(\beta/2)} \quad (23)$$

If it is assumed that N is relatively large, the force constant becomes independent of the chain length, and the final result is

$$H = \frac{4k_r k_\theta}{k_r r_e^2 \cos^2(\beta/2) + 4k_\theta \sin^2(\beta/2)} \quad (24)$$

It should be noted that this is the same as the result derived by Kuhn and Kuhn,⁸ although a different approach was used to obtain it.

While an overall harmonic force law has been assumed, there are actually two force constants that are incorporated into H . An overall harmonic force law certainly applies for small enough extensions, in which case the bending force constant most likely predominates. As the extension grows, however, the stretching force constant should make an increasing contribution. A crossover must occur and it is not immediately clear where it will occur or whether it is important to take it into consideration. This may be worth investigating in future work.

To get an idea of a typical value for the parameters, consider a chain of polyethylene. The bonds all have the same bond length ($r_e = 1.541$ Å),¹⁴ and the angles between bonds should be close to the tetrahedral value of $\beta = 109.47^\circ$. This leads to the extended length of $a = 1.258$ Å. Stretching force constants for carbon-carbon bonds were the subject of investigation in a theoretical study reported in the literature.¹⁵ The value appropriate for polyethylene comes out to be $k_r = 4.379$ mdyne/Å. An estimate for the bending force constant was obtained from a value computed by Kuhn and Kuhn:⁸ $k_\theta = 9.0 \times 10^{-11}$ erg. Using these values, (24) gives $H = 270$ N/m. At a temperature of 298 K, this implies $\epsilon = 1000$. It is expected that this should be a good ballpark figure for polymer chains composed of a

carbon single-bond backbone at room temperature. It may be worth mentioning that molecular dynamics simulations on polymer melts have been performed¹⁶ using the model studied in this paper. In those simulations, a value of $\epsilon = 276$ was used, a value considerably smaller than computed here. As it turns out, the reasoning behind this choice was to allow longer time steps by artificially weakening the bonds.

What stands out about this calculation is the large value for ϵ . On the basis of the plots in figure 1, the natural conclusion to draw is that bond stretching should not be terribly important for polymer chain statistics. However, this conclusion is worth investigating further. For $\epsilon = 1000$, the present model distribution deviates noticeably from the Gaussian chain model for extensions of about 70% of full extension. It deviates from the non-Gaussian chain model for extensions of about 85% of full extension. Theoretical studies¹⁷ indicate that deviations from the Gaussian chain model are necessary to reasonably describe the ultimate properties of elastomeric materials. The ultimate stiffening in such materials under large deformations shows up when the non-Gaussian chain model is used, but not the Gaussian chain model. This implies that, under such conditions, enough polymer chains are close to the full extension limit in their end-to-end separations that their effect on the bulk properties is noticeable. If so, it is possible that the differences between the model of Fraenkel springs studied here and the non-Gaussian model may also be noticeable in the bulk properties.

V. Moment Expansion

It is possible to develop a formalism¹⁷ for the bulk level stress-strain behavior of an elastomeric material that is based on the information contained in the distribution function of polymer chain end-to-end separations. The formalism was originally used with the non-Gaussian chain model, and it would be interesting to consider how the results are changed if the distribution developed here were used instead.

Even though the distribution must be evaluated numerically, closed form expressions can be derived for its moments. The general procedure is presented elsewhere¹⁸ and the results are similar to those for the non-Gaussian chain distribution.⁴ The first two even moments are given by

$$\begin{aligned} \langle r^2 \rangle_0 &= N \langle Q^2 \rangle_Q \\ \langle r^4 \rangle_0 &= \frac{5}{3} N(N-1) \langle Q^2 \rangle_Q^2 + N \langle Q^4 \rangle_Q \end{aligned} \quad (25)$$

where

$$\langle Q^{2j} \rangle_Q = \frac{(2j+2)!}{2e^j} \frac{D_{-(2j+3)}(-\sqrt{\epsilon})}{D_{-3}(-\sqrt{\epsilon})} \quad (26)$$

and $D_\nu(z)$ is a parabolic cylinder function.¹⁹ Recall that distances have been assumed to be in units of a . More generally, the right hand side of (26) would contain a factor of a^{2j} . It has been shown^{17,20} that, if it is assumed that the distribution is dominated by a Gaussian function, the distribution and related functions can be expanded in terms of these moments.

The stress tensor for an incompressible, isotropic, hyperelastic material under a strain is given by²

$$\boldsymbol{\pi} = \beta_1 \mathbf{B} + \beta_{-1} \mathbf{B}^{-1} + p \boldsymbol{\delta} \quad (27)$$

where \mathbf{B} is the Finger strain tensor, p plays the role of a

hydrostatic pressure, δ is the unit tensor, and the coefficients, β_1 and β_{-1} , are given in the moment expansion by

$$\begin{aligned}\beta_1 &= G + 2[c_{11} + 6I_1c_{12}] + \dots \\ \beta_{-1} &= 8c_{12} + \dots\end{aligned}\quad (28)$$

In these equations,

$$I_1 = \text{tr } \mathbf{B} \quad (29)$$

is the first principal scalar invariant of the strain tensor and the coefficients are averages over the polymer chains in the network. If $\rho^{(N)}$ represents the density of chains containing N bonds, and the notation

$$\|f\| \equiv kT \sum_N \rho^{(N)} f(N) \quad (30)$$

is defined for the average over chain lengths, the coefficients are given by

$$\begin{aligned}G &= \left\| \frac{\langle r^2 \rangle_0}{\langle r^2 \rangle_*} \right\| \\ c_{11} &= \frac{10}{3} \left\| d_2 \frac{\langle r^2 \rangle_0}{\langle r^2 \rangle_*} \right\| \\ c_{12} &= -\frac{1}{5} \left\| d_2 \frac{\langle r^4 \rangle_0}{\langle r^2 \rangle_*^2} \right\|\end{aligned}\quad (31)$$

where $\langle r^2 \rangle_*$ is that portion of the second moment that is directly proportional to N and

$$d_2 = \frac{9}{40\langle r^2 \rangle_*^2} \left\{ \langle r^4 \rangle_0 - \frac{10}{3} \langle r^2 \rangle_0 \langle r^2 \rangle_* + \frac{5}{3} \langle r^2 \rangle_*^2 \right\} \quad (32)$$

All terms up to order N^{-1} have been included in these expressions.

If the Gaussian chain model is assumed, the coefficients c_{ij} are zero and the stress-strain relation becomes

$$\pi = G\mathbf{B} \quad (33)$$

The quantity G is computed to be equal to $\rho_c kT$, ρ_c being the total number density of cross-linking chains. This constant can be identified with the elastic modulus of the material. The ability of this equation to model the behavior of rubber-like materials for small deformations is well known,²¹ as is its inability to model the behavior for large deformations.

Deviations from the Gaussian model are contained in the coefficients c_{ij} . For the non-Gaussian model, these coefficients are worked out to be

$$\begin{aligned}c_{11} &= -\frac{1}{2} \left\| \frac{1}{N} \right\| \\ c_{12} &= \frac{1}{100} \left\| \frac{5N-2}{N^2} \right\|\end{aligned}\quad (34)$$

These coefficients can be shown to be proportional to $\rho_c kT$, so that the quantities $c_{ij}/\rho_c kT$ are independent of the temperature. For the model proposed here, the coefficients are slightly different

$$\begin{aligned}c_{11} &= -\frac{1}{4} \left\| \frac{5 - 3\langle Q^4 \rangle_Q \langle Q^2 \rangle_Q^2}{N} \right\| \\ c_{12} &= \frac{1}{200} \left\| \frac{(5 - 3\langle Q^4 \rangle_Q \langle Q^2 \rangle_Q^2)(5N - 5 + 3\langle Q^4 \rangle_Q \langle Q^2 \rangle_Q^2)}{N^2} \right\|\end{aligned}\quad (35)$$

Since the averages of Q^j depend on ϵ and ϵ varies with temperature, the quantities $c_{ij}/\rho_c kT$ will have a temperature dependence in this model. Further, modifications in the molecular structure of the polymer that change ϵ will also lead to a modification of the coefficients. Such modifications will change the coefficients in the non-Gaussian model only if they affect the overall chain lengths.

To get an idea of how the present model compares with the non-Gaussian model, calculations were done on a rough model of isoprene. In isoprene, cross-links occur only with 3, 7, 11, ..., bonds between them. To simplify matters, assume the bonds are identical and assume a most probable distribution²² of

$$\rho^{(N(j))} = \rho_j p(1-p)^{j-1} \quad (36)$$

where $N(j) = 4j - 1$, $j = 1, \dots$, and p is the fraction of monomers that are involved in cross-links. Calculations were performed for $p = 0.09$, and it was found that the coefficients differed by 0.6% for $\epsilon = 1000$, by 5% for $\epsilon = 100$, and by 33% for $\epsilon = 10$. For larger values of ϵ , predictions with the present model and the non-Gaussian model should be close. The agreement gets worse as ϵ gets smaller. However, the present model has the bond strengths incorporated directly into the model and the effects of structural modifications as well as temperature changes will be more realistically modeled here.

VI. Conclusions

A model for polymer chains has been proposed that not only contains the non-Gaussian nature of the distribution of end-to-end separations, but also incorporates the effects of bond stretching and bending. The model is similar to the Gaussian chain model for smaller extensions but becomes stiffer due to bond stretching at larger extensions. This stiffening is different from that observed in the non-Gaussian model. The non-Gaussian chain reaches an absolute limit of extension, while in the model proposed here, the chain can extend further by stretching the bonds. The resistance to further extension is weaker than that for the non-Gaussian chain and depends on the actual bond strengths. If a chain were modified to change the bond strengths without significantly modifying the extended length of the polymer chain, this model would provide a more realistic prediction of the effects on the properties of the polymeric material.

Means of computing the distribution function and its logarithm have been presented. Also, a method for estimating the necessary parameters from a knowledge of the molecular structure of the chain has been presented. These computational methods are not very difficult. This model should be a reasonable improvement over the more commonly used Gaussian and non-Gaussian models in the study of polymeric materials. Comparison of the distribution with those of other models shows noticeable differences, particularly at large extensions. This implies that systems where large chain extensions are important would be better represented with the proposed model.

The main advantage of this model is that it provides a closer connection with the chemical properties of the material at the molecular level. Effects due to changes in bond length and bond strength would be better described. Further, the dependence on the temperature would be reflected not only in the entropic effects, as is the case in the Gaussian and non-Gaussian models, but also in the energetics of the molecular bonds. Higher temperatures would result in more bond stretching and hence higher probabilities for moderate to large extensions. Lower temperatures would lead to a relative freezing of the bonds and a closer agreement with the non-Gaussian model.

This model is not expected to make much of a difference for systems where small extensions predominate. For instance, polymer solutions would be just as reliably, but more conveniently, described with the Gaussian model. The Rouse and Rouse–Zimm models are ideal in this case. The present model was originally developed for the study of amorphous polymeric materials under large deformations and is expected to provide a more realistic connection between the bulk and molecular properties.

A situation where such a description may prove valuable is in the study of the ultimate properties of elastomeric materials.²³ Large deformations in such materials typically lead to a stiffening²¹ that is commonly attributed to the limited extensibility of the networked chains. Under such conditions, it seems reasonable to suppose that a noticeable fraction of polymer chains are at least close to the limit of full extension. More recently, there has been some interest in the mechanical properties of bimodal network elastomers.^{24,25} It seems that the desirable properties of these materials is in part related to the limited extensibility of the shorter chains. Under large deformations, these shorter chains are expected to be close to their full extensions. In the theoretical investigation of ultimate properties, then, it may be important to allow the chains to stretch beyond their full extensions to get a proper description of their statistical behavior.

Various improvements to this model may be worth making in future work. There are two specific improvements that seem worth pursuing. First, the structure of the model polymer chain may be made to be closer to that of a real molecule. In particular, free rotation of the bonds should be restricted to the actual bond angles found in real polymers. Not only the angles between bonds, but also the dihedral angles might be incorporated. It is not suggested that these bond angles be frozen, but rather, that they vary by some harmonic force law about average values. A recursive scheme similar to the one presented in this paper may be developed to deal with these more complicated distributions.

The second improvement would be in the force law describing the bonding interactions. A harmonic force law will pull the

beads of the chain back together no matter how far apart they are pulled. In a real polymer chain, the bond will break at some point. Since a driving force for this work has been the study of the ultimate properties of polymeric materials and the points at which failure will occur, it may be useful to incorporate the possibility of bond-breaking into the energy function. A reasonable modification would be to replace the harmonic bond potential with a Morse oscillator potential. It seems that much of the foregoing development could be applied to this case with little modification.

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