

Implications of using the entropy spring model for an ideal polymer chain

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When allowance for the finite orientational fluctuations in the end-to-end separation vector of an ideal Gaussian chain is made, while using a constant-length ensemble, the equation of state is no longer the simple Hooke's-law expression but contains, in addition, a repulsive force which opposes the tendency of the chain to collapse. The implications of this new equation of state are examined.

INTRODUCTION

Trying to account for the unique elastic properties of bulk rubber in terms of the properties of individual polymer molecules has provided a theoretical challenge for over 40 years.¹⁻⁴ Rubberlike elasticity manifests itself in a host of synthetic materials as well as in coals,⁵ swollen from solvent absorption. The macroscopic behavior of the bulk material is viewed as arising from the cumulative effect of the properties of the individual polymer chains, whose ends are bonded (crosslinked) to one another to form a continuous macromolecular network. Each chain is viewed, traditionally, as behaving as a microscopic "entropy spring;" a restoring force f proportional to the end-to-end separation, r , acts along the displacement direction. An equation of state for an ideal Gaussian chain can be established with the use of either a constant force or a constant displacement ensemble. By ideal Gaussian, we mean a chain which is located in a heat bath and which consists of a large but finite number of freely orienting volumeless segments which do not interact with one another. In a previous publication,⁶ we showed that in the weak-stretching regime, the equations of state from the two ensembles are fundamentally different. The Hooke's-law equation

$$f = -2k_B T b^2 r, \tag{1a}$$

$$f = 2k_B T b^2 r \tag{1b}$$

is derivable only from the constant displacement (r) ensemble.⁶ $f = |\mathbf{f}|$ and $r = |\mathbf{r}|$. \mathbf{f} is the average retractive force exerted by the chain on its end points, k_B is Boltzmann's constant, T is the absolute temperature, and $b^2 = 3/2Na^2$ where N is the number of links, each of length a . The weak-stretching regime implies $r \ll Na$. In the constant-force ensemble approach, the magnitude of the force in the weak-stretching regime is proportional to the averaged projection of r onto the line collinear with the force; it is not proportional to $\langle r \rangle$. Proportionality between this force and $\langle r \rangle$ would be expected if the ensembles were equivalent.

Equation (1) provides the traditional basis for viewing rubberlike elasticity; a single chain is considered to have a well-defined displacement whose magnitude r determines the magnitude of the average force tending to drive the

ends together. In the present work, it is shown that the fixed- r stipulation, used in deriving Eq. (1), is not consistent with r being a microscopic moment and hence subject to thermal fluctuation. The finite orientational fluctuation in r gives rise to two additional r -dependent terms in the chain's free energy and resulting equation of state, namely, a repulsive force proportional to $k_B T/r$ and a repulsive force derived from a specific interaction used to orient r . For these reasons, the analogy of a polymer chain with a Hookean mechanical spring becomes untenable. The implications of this result for the behavior of an ideal network and for the Rouse model of polymer chain dynamics are examined.

CONSTANT-LENGTH (r) ENSEMBLE

Figure 1 shows a Gaussian chain, one end of which is fixed at point A ; the free end carries a charge of $+Z$. The ends are connected by a rigid rod of length r , which

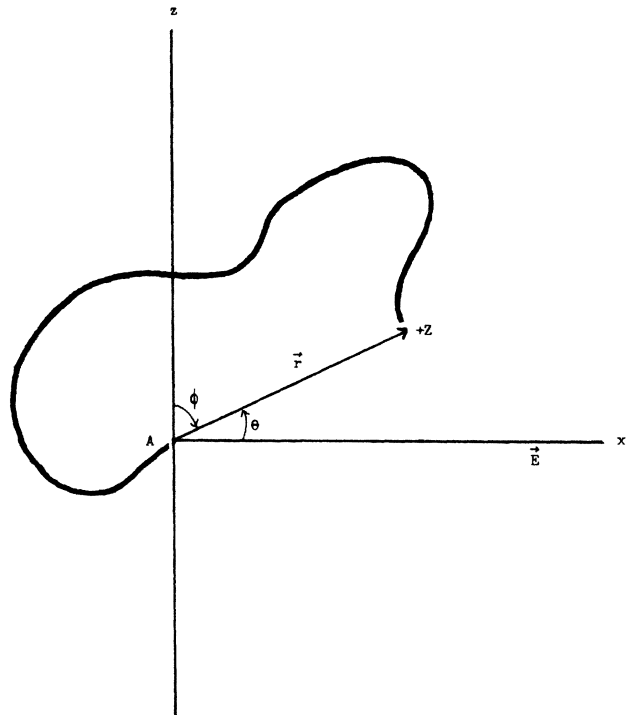


FIG. 1. The constant-length-ensemble chain is depicted.

is free to rotate about A and which makes an angle θ with the external electric field \mathbf{E} . The choice of external interaction is arbitrary;⁷ the field provides a convenient means for fixing the direction of \mathbf{r} . The constant-length ensemble becomes a constant-displacement ensemble in the limit $E \rightarrow \infty$. The equation of state we wish to calculate will determine the tension in the rod as a function of r . A negative f indicates a compressive force and a positive f indicates a tensile force in the rod.

The partition function Q for the chain depicted in Fig. 1 is given by

$$Q = \int d\mathbf{L} P(\mathbf{L}) \exp(\beta \mathbf{F} \cdot \mathbf{L}) \delta(L - r), \quad (2)$$

where $\mathbf{F} = Z\mathbf{E}$, $\beta = (k_B T)^{-1}$, and $d\mathbf{L} = L^2 \sin(\theta) d\theta d\phi dL$. $P(\mathbf{L})$, the normalized field-free end-to-end vector distribution function, gives the relative number of chain conformations associated with a particular orientation \mathbf{L} . For $L \ll Na$, $P(\mathbf{L}) = b^3 \pi^{-3/2} \exp(-b^2 L^2)$. Thus, Q is proportional to $r^2 \exp(-b^2 r^2) [\sinh(cr)/cr]$ where $c = Z\beta E$. The average tension between the chain ends is $f = k_B T (\partial \ln Q / \partial r)$ or

$$f = 2k_B T / r - 2k_B T b^2 r + Z E \mathcal{L}(cr), \quad (3)$$

where $\mathcal{L}(cr)$ is the Langevin function $\coth(cr) - 1/cr$. We note that $\mathcal{L}(cr) = \langle \cos\theta \rangle$. The middle term in the equation of state is the Hooke's-law "entropy spring" expression. The last term is the tension derived from the external force acting on the charge. In the limit $E \rightarrow \infty$, $\mathcal{L}(cr) = \langle \cos\theta \rangle \rightarrow 1$, and the resulting contribution of the field is ZE . The first term can be viewed as arising from the "centrifugal" force imparted to \mathbf{r} from the thermal motion in the heat bath.^{7,8} Alternately, it can be viewed as a form of the ideal gas law where a repulsive force, instead of pressure, exists between any pair of particles separated by a distance r in a heat bath.⁸

Equation (3) implies that an ideal polymer chain has a well-defined displacement only when an external interaction is sufficiently strong so as to fix \mathbf{r} . Thus, the correct constant-displacement-ensemble result would be

$$\mathbf{f} = \frac{2k_B T}{r^2} \mathbf{r} - 2k_B T b^2 \mathbf{r} + Z\mathbf{E}. \quad (4)$$

Here, "constant" implies an \mathbf{r} with vanishingly small (yet nonzero) orientational fluctuations. The third term, of course, depends on the chosen interaction. In the absence of an external interaction ($E = 0$, above), the equation of state, derived from the constant-length ensemble, is

$$f = 2k_B T \left[\frac{1}{r} - b^2 r \right]. \quad (5)$$

Equation (5) describes a chain whose ends are a length r apart. When $r = 1/b$, which is the most probable end-to-end separation for a freely orienting chain (ends not fixed at r by a rod), $f = 0$.

IMPLICATIONS OF EQ. (4) FOR RUBBER NETWORKS AND THE ROUSE MODEL

An ideal or phantom rubber network is perceived as having a Hooke's law force, given by Eq. (1), acting along the average chain displacement vector connecting each

pair of junction points.² As a result, the network has a tendency to collapse as these entropy springs connecting the junction points have an unstretched length of zero. Eichinger⁹ believes network collapse to be a serious conceptual problem in the theory of rubber elasticity. According to Eq. (4), however, a network chain is not prone to collapse, but rather, will experience a repulsive force proportional to $1/r$. Here, we avoid the question of which ensemble is appropriate for a network chain and follow convention by assuming the applicability of a constant-displacement ensemble.

The Rouse model of ideal polymer chain dynamics provides a vivid example of the theoretical collapse of a single chain in a heat bath.¹⁰ The chain is regarded as consisting of n identical subchains, each of which obeys Gaussian statistics. The assembly is treated as a series of n mechanical springs whose force-versus-displacement behavior is defined by Eq. (1). The ends of the subchains are beads which move in a viscous medium. The time dependence of the end-to-end separation vector for the whole chain takes the form¹⁰

$$\mathbf{r}_p(t) = \mathbf{R} \exp(-t/\tau_p), \quad (6)$$

where τ_p is the time constant for the p th mode. It is assumed that the chain is released from some initial configuration; Eq. (6) describes the subsequent time evolution of \mathbf{r} . We note the counterintuitive result for $t \rightarrow \infty$, namely, $\mathbf{r} \rightarrow 0$; the collapse of the ideal chain is a consequence of using "springs" of zero unstretched length. This same result is obtained if the entire chain is viewed as a super Gaussian chain with a bead at each end. The ends are then driven together by a force law described by Eq. (1).

Equation (5), however, suggests that the chain, once released from a fixed position, will relax into a state where $r = a(2nN/3)^{1/2}$, the most probable end-to-end separation for the chain. This is consistent with the result for $\langle r^2 \rangle^{1/2}$ calculated from elementary statistics, $a(nN)^{1/2}$.

CONCLUSION

These results along with those from Ref. 6 indicate that a single ideal Gaussian chain cannot be treated as a thermodynamic system (no matter how large N is) in the weak-stretching regime. The chain's equation of state depends on whether the force, displacement, or length is fixed; different ensembles result in different equations of state. Here we demonstrated that if a constant-displacement (\mathbf{r}) ensemble is viewed as the limiting case of a constant-length (r) ensemble, a repulsive force of magnitude $2k_B T/r$ is present. Because \mathbf{r} can be fixed, in the macroscopic sense, only by means of an external interaction, some fluctuation must always be present, making Eqs. (3) or (4) the physically correct ones. The conventional constant-displacement description assumes no orientational fluctuation in \mathbf{r} ; the volume element is $d\mathbf{L}$ and the external interaction required to fix the position of \mathbf{r} is ignored. Hence $Q = P(\mathbf{r})$ and $\mathbf{f} = -2k_B T b^2 \mathbf{r}$, as in Eq. (1).

We have deliberately ignored the question of when the constant-displacement ensemble should or should not be

used to describe a polymer chain. Rather, we have suggested that if such an ensemble is appropriate for the ideal chain, then Eq. (4) (with an appropriate external interaction) is the correct equation of state. Furthermore, there is no simple Hooke's-law dependence of force on displacement in the weak-stretching regime no matter which ensemble is used to calculate the equation of state.

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Here one considers a given link, of length a in a polymer chain, to be the "rod." The ends of the chain are fixed at a displacement \mathbf{R} from one another. The average force in the rod is $\langle f_a \rangle = 2k_B T/a + (k_B T/N)[\partial P(\mathbf{R})/\partial a]$. The first term is the "centrifugal" term and the second term is the "external interaction" tending to orient \mathbf{a} .

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