

Nonequivalence of the stress and strain ensembles in describing polymer-chain elasticity

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An equation of state for a single polymer chain can be established with use of either a constant force or a constant length ensemble. These two equations of state, often regarded as equivalent, are shown here to be fundamentally different in the weak-stretching (Hooke's law) regime. In this limit, the equation derived from the force ensemble is unrelated to Hooke's law. Various calculations of the influence of the excluded volume interaction on the equation of state are discussed.

I. INTRODUCTION

The so-called Hooke's-law equation of state for a single ideal Gaussian chain has been known for over 40 years.¹ By ideal Gaussian, we mean a chain which is located in a good solvent (heat bath) and which consists of a large but finite number of freely orienting volumeless segments which do not interact with one another. In the weak-stretching regime the dependence of the vector force, \mathbf{f} , required to maintain a fixed vector end-to-end separation, \mathbf{r} , on \mathbf{r} is determined with use of a constant length ensemble,^{2,3} henceforth to be called a strain⁴ ensemble. $\mathbf{f}_{\text{strain}}$ (abbreviated \mathbf{f}_{sn}) is obtained from $\mathbf{f}_{\text{sn}} = -T(\partial S/\partial \mathbf{r})$ where the entropy S is $S = k \ln P(\mathbf{r})$. $P(\mathbf{r})$, the normalized field-free end-to-end vector distribution function, is

$$b^3 \pi^{-3/2} \exp(-b^2 r^2), \text{ for } |\mathbf{r}| = r \ll Na.$$

N is the number of links each of length (a) and $b^2 = (3/2Na^2)$. It follows that

$$\mathbf{f}_{\text{sn}} = 2kTb^2 \mathbf{r}, \quad (1a)$$

$$f_{\text{sn}} = 2kTb^2 r, \quad (1b)$$

where $f_{\text{sn}} = |\mathbf{f}_{\text{sn}}|$. The chain behaves as an entropy spring of zero unstretched length. \mathbf{f}_{sn} is the force required to maintain an end-to-end separation of \mathbf{r} .

An equation of state regarded as being equivalent to Eq. (1) can be derived from the constant force ensemble.⁵⁻⁹ In the present work, the two approaches are shown to be quite different; moreover, the constant-force-derived equation of state is found to be incapable of describing the elastic properties of a chain in the weak-stretching region. Recent theoretical work on the chain with an excluded volume interaction is discussed from the viewpoint developed in this paper.

II. STRESS ENSEMBLE

In the constant force ensemble, henceforth to be called the stress⁴ ensemble, the chain ends are subject to a fixed force couple, denoted by \mathbf{f}_{ss} .⁵⁻⁹ The average properties of any variable, Q , can be calculated from

$$\begin{aligned} \langle Q \rangle &= \frac{\int Q P(\mathbf{r}) \exp(\beta \mathbf{f}_{\text{ss}} \cdot \mathbf{r}) dW}{\int P(\mathbf{r}) \exp(\beta \mathbf{f}_{\text{ss}} \cdot \mathbf{r}) dW} \\ &= \exp(-v^2/4) \int Q P(\mathbf{r}) \exp(\beta \mathbf{f}_{\text{ss}} \cdot \mathbf{r}) dW, \end{aligned} \quad (2)$$

where $\beta = (kT)^{-1}$, $v = \beta f_{\text{ss}}/b$, and $dW = r^2 \sin\theta d\theta d\phi dr$. x is defined to be the component of \mathbf{r} in the direction of \mathbf{f}_{ss} ;

$$x = (\mathbf{r} \cdot \mathbf{f}_{\text{ss}}/f_{\text{ss}}) = r \cos\theta,$$

where θ is the angle between \mathbf{f}_{ss} and \mathbf{r} . The following expressions can be derived from Eq. (2) by expanding $\exp(\beta f_{\text{ss}} r \cos\theta)$ in a power series:

$$\langle x \rangle = \frac{v}{2b}, \quad (3)$$

$$\langle r \rangle = \langle r \rangle_0 \left[1 + \frac{v^2}{12} + O(v^4) \right], \quad (4)$$

and

$$\langle \cos\theta \rangle = \frac{f_{\text{ss}} \langle r \rangle_0}{3kT} \left[1 - \frac{v^2}{20} + O(v^4) \right]. \quad (5)$$

$\langle r \rangle_0$ is the averaged scalar end-to-end separation in the absence of an external force. $\langle r \rangle_0 = (2/b\sqrt{\pi})$. Equation (3) can be written as

$$f_{\text{ss}} = 2kTb^2 \langle x \rangle, \quad (6)$$

which is the stress-ensemble-derived equation of state. Equation (6) describes the projection onto the \mathbf{f}_{ss} axis of the averaged end-to-end separation that results from the application of a force couple. Because of its resemblance to Eq. (1), Eq. (6) is stated to provide an equivalent description of an elastic chain obeying Hooke's law. $\langle x \rangle$ is identified with the averaged end-to-end separation. In the weak-stretching region ($v < 1$), however, Eq. (4) predicts that $\langle r \rangle \approx \langle r \rangle_0$. The chain's average end-to-end separation remains nearly constant as f_{ss} increases from zero to a finite value consistent with $v < 1$.

Figure 1 shows such a chain where the constant force on the ends is maintained by placing electric charges, $\pm q$, on the ends and subjecting the entire chain to a constant external electric field \mathbf{E} . $\mathbf{f}_{\text{ss}} = q\mathbf{E}$. For simplicity, \mathbf{E} is taken to be collinear with the x axis. The end-to-end separation is depicted as being a vector of length $\langle r \rangle_0$, which is free to "rotate" by means of Brownian motion in the heat bath. In the weak-force region, $\langle \cos\theta \rangle = f_{\text{ss}} \langle r \rangle_0 / 3kT$ according to Eq. (5). Since $f_{\text{ss}} = qE$, and μ , the average "dipole moment" of the chain, is $\langle qr \rangle = q \langle r \rangle_0$, it follows that

$$\langle \cos\theta \rangle = \frac{\mu E}{3kT}. \quad (7)$$

This is the classical expression for the average orientation of

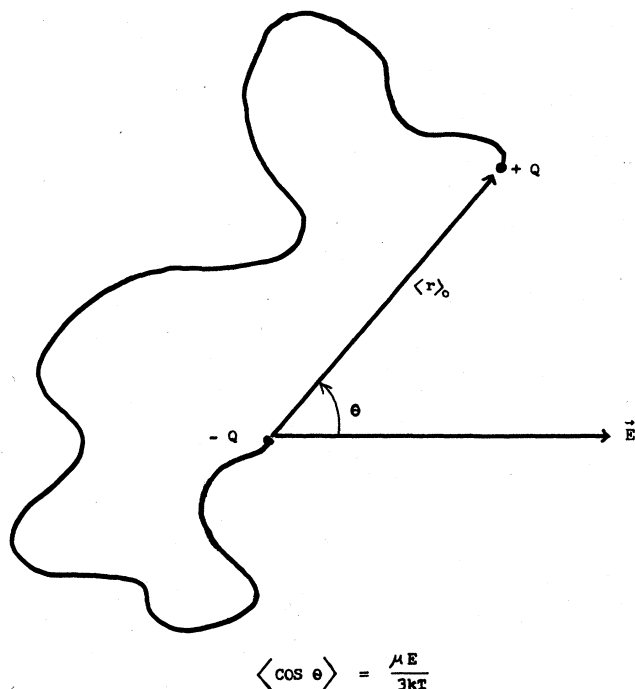


FIG. 1. Dipole analog of the stress-ensemble chain is depicted.

a thermally tumbling dipole in an electric field.⁹ The stress-ensemble chain can be represented by an electric dipole which "rotates" in response to an external force. Since $\langle x \rangle$ is the average value of the projection of r on the x axis, it can increase linearly with the force even though $\langle r \rangle$ remains essentially constant. While the stress ensemble correctly describes the physical picture for the single chain in a good solvent, it cannot describe a rubber network chain which undergoes a change in $\langle |r| \rangle$ in response to a macroscopic deformation caused by an external force acting on the bulk network.

One should recognize that when the force is strong enough to extend the chain fully, the two ensembles approach the same limit: $\langle r \rangle \rightarrow r \rightarrow x \rightarrow \langle x \rangle$.

III. CHAIN WITH AN EXCLUDED VOLUME INTERACTION (EVI)

The conclusions reached by those studying the polymer chain with an EVI can be reinterpreted in light of the present results. Using renormalization methods to study the effect of an EVI on the elasticity of a polymer chain described by a stress ensemble, Oono, Ohta, and Freed⁷ concluded that such a chain obeys Eq. (6) for $\nu < 0.7$; for

$\nu > 0.7$, a deviation from a linear stress-strain relation occurs. Our ν is related to their η by $\nu = \eta/1.2$. Webman, Lebowitz, and Kalos⁸ reached a similar conclusion in their Monte Carlo study of the polymer chain with an EVI. From Eq. (4), however, it is apparent that the ideal chain elongates by only 4% when $\nu = 0.7$. One would, therefore, expect that the chain with an EVI would also behave as a rotating dipole in the weak-stretching region and that the EVI would not affect the dependence of $\langle x \rangle$ of f_{ss} until $\langle r \rangle$ had increased significantly, as observed above.

A combined Monte Carlo-molecular dynamics calculation on the polymer chain with an EVI was recently undertaken by Berman and Weiner using a strain ensemble.¹⁰ They found a nonzero end-to-end separation r_e , where $f_{sn} = 0$. For $r > r_e$, f_{sn} is tensile ($f_{sn} > 0$), and for $r < r_e$, f_{sn} is compressive ($f_{sn} < 0$). For $\sigma/a = 0.8$ and $N = 10$, $r_e/Na \approx 0.2$, where σ defines the magnitude of the EVI. This result contrasts sharply with the stress-ensemble determinations, mentioned above, where a tensile force is present for all $r > 0$ and "Hooke's law" is obeyed for small forces until $f_{ss} = 0$ for $\langle x \rangle = 0$. Berman *et al.* concluded that the strain- and stress-ensemble approaches are fundamentally different when an EVI is present.

IV. CONCLUSION

Using an ideal polymer chain, we have shown that the stress ensemble describes a chain which is incapable of deforming in the weak-stretching region. $\langle r \rangle$ remains nearly constant at $\langle r \rangle_0$; the chain responds to an increasing force by "rotating" as if it were a permanent electric dipole of moment $\mu = q \langle r \rangle_0$. Because $\langle x \rangle$, in Eq. (6), is identified with the chain's elongation, the stress ensemble has been used incorrectly as a basis for describing polymer chain elasticity.

Excluded volume interactions can affect an equation of state only if the chain elongates in response to an increasing force. The real chain maintains its integrity as a "blob" until a force is able to pull it apart. Thus, the chain described by a stress ensemble^{7,8} has a region where Eq. (6) is obeyed because the chain behaves as a dipolar "blob" and orients itself with respect to the external field. When the force becomes sufficiently strong ($\nu > 0.7$), the chain will elongate ($\langle r \rangle$ will increase), thereby permitting the EVI to destroy the proportionality between f_{ss} and $\langle x \rangle$.

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