above, but first, a somewhat simpler method will be employed. Kearsley and Zapas[37] have shown that for uniaxial deformation, the limiting value of W_2 in terms of the V–L function is

$$\lim_{\lambda\to 1} W_2 = \frac{1}{16}\left\{\frac{\partial w(\lambda)}{\partial\lambda} - \frac{\partial^2 w(\lambda)}{\partial\lambda^2} - \frac{\partial^3 w(\lambda)}{\partial\lambda^3}\right\}_{\lambda=1} \qquad \text{(C3)}$$

From the second column in Table I we find

$$\frac{1}{G_0}\frac{\partial w}{\partial\lambda} = A\lambda + (1 - A)(1 + \eta)^2(1 + 2\eta + \eta^2\lambda^2)\lambda(1 + \eta\lambda^2)^{-2} \qquad \text{(C4)}$$

Inserting the derivatives of eq C4 into eq C3, we obtain

$$\lim_{\lambda\to 1}\frac{W_2}{G_0} = (1 - A)\left\{(1 + \eta)\eta - 2\eta^2 + \frac{\eta^3}{1 + \eta}\right\} = (1 - A)\eta/(1 + \eta) \qquad \text{(C5)}$$

Thus for $A \leqslant 1$ and $\eta \geqslant 0$ the limiting value of W_2/G_0 is positive.

Using the procedure employed for the Gaylord model calculation, it is possible to show, after tedious algebraic manipulation, that

$$\frac{W_2}{G_0} = -\frac{1}{2}\,\frac{(1 - A)(1 + \eta)^2\eta}{(1 + \eta\lambda^{-1})^3(1 + \eta\lambda^2)^2(\lambda^2 - \lambda^{-1})^2}\{2(-\lambda^4 + 2\lambda - \lambda^{-2}) + \eta(-\lambda^6 - 3\lambda^4 + 2\lambda^3 + 6\lambda - 1 - 3\lambda^{-2}) + \eta^2(-2\lambda^6 + \lambda^5 + 3\lambda^3 - 2\lambda^2 + \lambda^{-1} - \lambda^{-3})\} \qquad \text{(C6)}$$

and thus $W_2/G_0 > 0$ when $\eta > \lambda/(1 - 2\lambda)$. Hence, in the case of uniaxial extension ($\lambda > 1$), W_2/G_0 is positive at all strains for any $A < 1$ and $\eta > 0$. The value of W_2 can become negative at high compressions ($\lambda < {}^1/_2$) for certain choices of η.

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Translational Diffusion of Poly(methyl methacrylate) in Acetone: Wormlike vs. Freely Jointed Chain Model

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ABSTRACT: The translational diffusion coefficients of poly(methyl methacrylate) standards with molecular weights 7.67×10^3, 2.7×10^4, 4.9×10^4, and 6.39×10^4 in acetone at infinite dilution were determined with the extended Taylor dispersion technique at temperatures from 274.2 to 313.2 K. Both wormlike and freely jointed chain models were found to represent quite well the experimental results, suggesting that the excluded volume effects on the hydrodynamic radii are virtually absent. The scaling relationship between diffusivity and molecular weight was verified, and a proportionality of D to $TM^{-0.49}/\mu_0$ was also established.

Introduction

Translational diffusioin coefficients of chainlike polymers in extremely dilute solution carry significant information on the hydrodynamic behavior of isolated macromolecules. Although a variety of macromolecular models have been advanced over the years, understanding of conformational characteristics at the molecular level relies on relevant experimental observation to which analytical models[1,2] are compared. From the practical point of view, such diffusion data are needed for the analysis of the diffusion-controlled casting of "asymmetric" membrane[3]

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for reverse osmosis and of composite membrane[4] for gas separation. In addition, the diffusion of polymers in dilute solution is an integral part of the resist development in microelectronic device processing.[5] The translational diffusion data will also yield quantitative information on the chain stiffness in terms of a characteristic ratio or Kuhn's statistical length, which might be related to liquid crystal formation in polymer systems.[6]

There exist several techniques for the determination of translational diffusivity of polymer in solution such as NMR spin-echo,[7] ultracentrifuge,[8] interferometry,[9] and light scattering.[10,11] Questions as to the accuracy of the by far most frequently used light scattering technique, as first raised by Shepherd,[12] have been addressed in recent years in terms of the assessment of intramolecular motions vs. translational motion.[13,14] Although the contributions from intramodes could be diminished by lowering the scattering angle, problems remain at high dilution where the scattering spectrum is known[15] to be dominated by the presence of a slight amount of dust particles in solution and by background scattering at low angles for all the elaborate analyses of light scattering data given in the literature.[16] Furthermore, the light scattering diffusion data, namely, $\bar{D}_z$,[17] published thus far are mostly for $\bar{M}_w$ on the order of 10^5 or higher. There is a paucity of data for $\bar{M}_w < 10^5$ for which deviations from the classical Gaussian statistics may become more pronounced, an observation that has prompted one theoretical[18] and several experimental[19-22] investigations on relatively short chain polymers. A new alternative technique for determining translational diffusion coefficients in infinite dilute solution has recently been developed[20-22] based on the dispersion of polymer solutes in capillary flow at low Reynold's number. The unique feature of the extended Taylor dispersion technique is that the concentration distribution in space as a result of dispersion is followed without complications arising from the presence of traces of dust particles in solution or intra- and intermolecular interactions.

The main objective of the present work is to use the translational diffusivities of a series of nearly monodisperse poly(methyl methacrylates) (PMMA) in acetone (a good solvent), determined with the extended Taylor dispersion method, to test the performance of the wormlike[23] and freely jointed chain[18] models in the context of Kirkwood's theory.[24] Of particular interest is the excluded volume effect on the unperturbed dimension as the chain length of PMMA increases. One of the reasons for examining PMMA in this study is that it is commonly used as positive photoresist in microelectronic device fabricatioin.[25-28] The other reason is that PMMA represents a class of polymer different from the polystyrene previously studied.[20,21] in terms of chain flexibility, which should subject theoretical models and/or Monte Carlo simulations of chainlike polymers to a more extensive test.

Experimental Section

The analysis of the extended Taylor dispersion method and experimental procedures have been presented previously[20] with the exception that a variable wavelength UV absorbance detector (Model V,[4] Isco) was used to monitor polymer concentration distribution at the end of the dispersion tube. The wavelength was set at λ_{max} = 213.5 nm for the absorbance of PMMA in acetone determined with a UV spectrophotometer (Model Lambda 9, Perkin-Elmer). Solvent acetone (99.6%, Mallinckrodt) was filtered through a 0.5-μm Teflon membrane (Millipore) on an all-glass filtration apparatus (Millipore) before usage. The PMMA standard as listed in Table I were used as received from Pressure Chemical Co. According to a previous analysis,[20] the peak molecular weight is the quantity relevant to the extraction of translational diffusion coefficient from the observed dispersion curve for nearly monodisperse polymer solute.

Table I
Peak Molecular Weight (M) and Polydispersity Index ($\bar{M}_w/\bar{M}_n$) of the Poly(methyl methacrylate) Standards under Investigation

M	$\bar{M}_w/\bar{M}_n$	notation
7670	1.15	M-1
27000	1.10	M-2
49000	1.07	M-3
63900	1.08	M-4

Table II
Translational Diffusion Coefficients (10^6D, cm²/s) and Hydrodynamic Radii (R_h, nm) of PMMA Standards in Acetone at Infinite Dilution and at Temperatures from 274.2 to 313.2 K[a]

	274.2 K	280.5 K	298.2 K	313.2 K
		M-1		
10^6D_{expt}	2.85 ± 0.05	3.21 ± 0.02	3.93 ± 0.06	4.59 ± 0.06
R_h	1.83	1.88	1.84	1.85
D_w/D_{expt}	1.00	1.02	1.00	1.01
D_{fj}/D_{expt}	1.00	1.02	1.01	1.01
		M-2		
10^6D_{expt}	1.54 ± 0.03	1.87 ± 0.02	2.16 ± 0.02	2.57 ± 0.04
R_h	3.39	3.22	3.34	3.31
D_w/D_{expt}	1.00	0.95	0.98	0.98
D_{fj}/D_{expt}	0.98	0.93	0.97	0.96
		M-3		
10^6D_{expt}	1.16 ± 0.01	1.32 ± 0.03	1.53 ± 0.01	1.82 ± 0.01
R_h	4.51	4.57	4.72	4.66
D_w/D_{expt}	0.99	1.00	1.03	1.02
D_{fj}/D_{expt}	0.96	0.97	1.00	0.99
		M-4		
10^6D_{expt}	1.06 ± 0.01	1.18 ± 0.01	1.37 ± 0.01	1.64 ± 0.02
R_h	4.94	5.09	5.27	5.17
D_w/D_{expt}	0.95	0.98	1.02	1.00
D_{fj}/D_{expt}	0.92	0.94	0.98	0.96

[a] D_w: wormlike chain model prediction with α = 0.77 nm. D_{fj}: freely jointed chain model prediction with h^* = 0.30.

Results and Discussion

Given in Table II are the measured values of the translational diffusion coefficients D for the four PMMA standards listed in Table I as a function of temperature. The concentrations of the injected pulse never exceeded 0.2 wt %, and each reported value of D is the mean of three or four measurements with a standard deviation of no more than ±2% of the mean. The hydrodynamic radii R_h calculated from D and solvent viscosity μ_0 collected from the literature[29] using the formula $R_h = kT/6\pi\mu_0D$, where k is Boltzmann's constant and T is the absolute temperature, are also presented in Table II. It is noted that the R_h values for the four PMMA standards stay constant to within ±2% across the temperature range, an indication that these polymer molecules are probably not perturbed by the excluded volume effect. This observation is partially substantiated by Norisuye and Fjuita's[30] work on the correlation between chain stiffness and the critical chain length below which the perturbation on the mean-square radius of gyration due to excluded volume effect is absent. Specifically, they showed that for PMMA of molecular weight less than 2 × 10^4 the molecules remain virtually unperturbed by the excluded volume effect. In what follows, both freely jointed chain[18] and wormlike chain[23] models with no excluded volume considerations will be employed to interpret the experimentally observed values of translational diffusion coefficients. Both schemes of data interpretation can yield information on the presence or absence of excluded volume effect on the hydrodynamic radius as chain length increases.

According to Yamakawa and Fujii's wormlike chain model,[23] the translational diffusion coefficient can be expressed as

$$D_{\mathrm{YF}} = \frac{kT}{6\pi\mu_0 L\alpha}\left(A_1 L^{0.5} + A_2 + \frac{A_3}{L^{0.5}} + \frac{A_4}{L} + \frac{A_5}{L^{1.5}}\right) \quad \text{for } L > 2.278 \quad (1)$$

where $A_1 = 1.843$, $A_2 = -(1 - 0.01412d^2 + 0.00592d^4) \ln d - 1.0561 - 0.1667d - 0.1900d^2 - 0.0224d^3 + 0.0190d^4$, $A_3 = 0.1382 + 0.6910d^2$, $A_4 = -(0.04167d^2 + 0.00567d^4) \ln d - 0.3301 + 0.5d - 0.5854d^2 - 0.094d^3 - 0.0421d^4$, and $A_5 = -0.0300 + 0.1209d^2 + 0.0259d^4$ In eq 1 and the expressions for coefficients A_1–A_5, both contour length L and cross-sectional diameter d have been reduced with twice the persistence length α. Note that in the relatively short-chain PMMA the ratio of the Kuhn statistical length to persistence length (l_s/α) becomes less than the commonly accepted value of 2 for relatively long chains, which is exactly the reason for the length scales L and d to be reduced with 2α rather than l_s, a point to be further addressed later in the paper. This observation is also important in the interpretation of diffusion data using the freely jointed chain model also to be pursued in this study. Using the conformational characteristics of PMMA as recently reported[31,32] and compared to the characteristics of polystyrene,[33] we established for PMMA that the cross-sectional diameter is 0.65 nm, on the basis of the value of 0.94 nm for polystyrene determined by Wang,[34] and that the length l for a repeating unit is 0.27 nm. One is then left with a single adjustable parameter, α. In view of the fact that the Oseen tensor has been preaveraged in the Yamakawa–Fujii theory[23] leading to eq 1, it seems imperative that the errors involved in such a procedure be corrected for. To this effect Zimm's[35] Monte Carlo calculation results were used to reduce the D_{YF} value predicted with eq 1 by a factor of 1.11 in the process of backing out the value for persistence length from experimental D values. It turned out that with $\alpha = 0.77$ nm eq 1 corrected for the preaveraging error is capable of representing the observed values for D to within ±2%, as demonstrated in Table II in terms of $D_{\mathrm{w}}/D_{\mathrm{expt}}$, where $D_{\mathrm{w}} = D_{\mathrm{YF}}/1.11$. The success of the wormlike chain model is further justified by the observation that the so-determined value for the single adjustable parameter is fairly close to that fitted from the intrinsic viscosity of PMMA in 4-heptanone and acetonitrile (cf. $\alpha = 0.68 \pm 0.03$ nm) at Θ temperatures.[36] The fact that the wormlike chain model with no consideration for excluded volume effect predicts D for M-2, M-3 and M-4 with an error comparable to that for M-1, for which the excluded volume effect is known to be absent,[30] suggests that none of the PMMA standards under the present investigation are subject to excluded volume effect. This observation will be further verified in the following in terms of the freely jointed chain model with no consideration for excluded volume effect. A test of the performance of the freely jointed chain model should also permit the two distinctly different models to be compared to each other.

The interpretation of translation diffusivity in terms of the freely jointed chain model should start with Kirkwood's theory[24] expressed as

$$D_{\mathrm{K}} = \frac{kT}{6\pi\mu_0}\left[\frac{(3/\pi)^{1/2}}{n_s l_s h^*} + \left\langle\frac{1}{R}\right\rangle\right] \quad (2)$$

in which n_s and l_s are the number of statistical segments and length per segment, respectively, $\langle 1/R\rangle$ is the mean reciprocal segment-to-segment distance, and h^* is the hydrodynamic interaction parameter. Note that in eq 2 the Oseen tensor has been preaveraged, which results in consistent overestimation of D. According to the Monte Carlo computation results,[37] the error introduced by the preaveraging procedure can be corrected for via

$$D_{\mathrm{fj}} = D_{\mathrm{K}}\left[1 - \frac{\delta_{\mathrm{K}}}{100}\right] \quad (3)$$

where

$$\delta_{\mathrm{K}} = 20.3 - \frac{35.2}{(n_s + 1)^{1/2}} \quad \text{for } \frac{\sigma}{l_s} = 0.39 \quad (4a)$$

$$= 18.5 - \frac{35.0}{(n_s + 1)^{1/2}} \quad \text{for } \frac{\sigma}{l_s} = 0.32 \quad (4b)$$

In eq 4a $\langle 1/R\rangle$ or 4b, σ is Stoke's radius. The term $\langle 1/R\rangle$ in eq 2 can be evaluated numerically for a freely jointed chain by using eq 5 deduced from ref 18

$$\left\langle\frac{1}{R}\right\rangle = \frac{4}{\pi l_s (n_s + 1)^2}\sum_{m=1}^{n_s}\left[(n_s + 1 - m)\int_0^{\infty}\left(\frac{\sin x}{x}\right)^m \mathrm{d}x\right] \quad (5)$$

in which $n_s = Ml/M_0 l_s$ with $M_0 = 101$ g/mol for a repeating unit. Equations 2–5 then constitute the basis for treating experimentally observed D values in terms of the freely jointed chain model.

There are three parameters in the above treament: l_s, h^*, and σ. The value of l_s was found to be 1.43 ± 0.05 nm for the four PMMA standards by using eq 6

$$\frac{l_s(L + 2l_s)}{6(L + l_s)} = \frac{\alpha}{3}\left\{1 - \left(\frac{3\alpha}{L}\right)\left[1 - \frac{2\alpha}{L} + 2\left(\frac{\alpha}{L}\right)^2 - 2\left(\frac{\alpha}{L}\right)^2 \exp\left(-\frac{L}{\alpha}\right)\right]\right\} \quad (6)$$

which originates from equating the freely jointed[38] and wormlike[39] chain model expressions for $\langle S^2\rangle_0$, the unperturbed mean-square radius of gyration. The ratio l_s/α as a function of n_s resulting from eq 6 is illustrated in Figure 1 for the number of repeating units $n = 100$. It is quite clear that as chain stiffness increases (or n_s decreases) l_s/α decreases from the asymptotic value of 2. It has to be recognized that the two remaining parameters h^* and σ are related to each other via eq 7

$$h^* \equiv \frac{\zeta}{(12\pi^3)^{1/2}\mu_0 l_s} = 0.977\left[\frac{\sigma}{l_s}\right] \quad (7)$$

assuming that the friction coefficient ζ for a Stokesian resistance center is simply $6\pi\mu_0\sigma$. Hence, the success of the freely jointed chain model is justifiable in terms of the h^* value fitted from the diffusion data and compared to eq 4 and 7. Through the minimization of the sum of $(D_{\mathrm{fj}} - D_{\mathrm{expt}})^2$ over all the experimental data given in Table II, as was done for the parameter α in the wormlike chain model earlier in the text, h^* was found to be 0.30, a value consistent with eq 4b and 7. It is thus legitimate to claim that the PMMA standards presently under investigation are well represented by the freely jointed chain model with Stokes's radius being roughly one-third of the Kuhn statistical length. It is also noted that for PMMA real chains

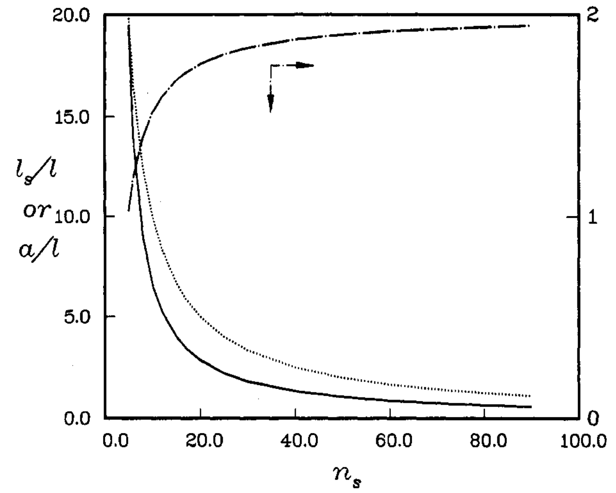

Figure 1. l_s/l (dotted curve), a/l (solid curve), and l_s/a (chain-dot curve) as a function of n_s for $n = 100$.

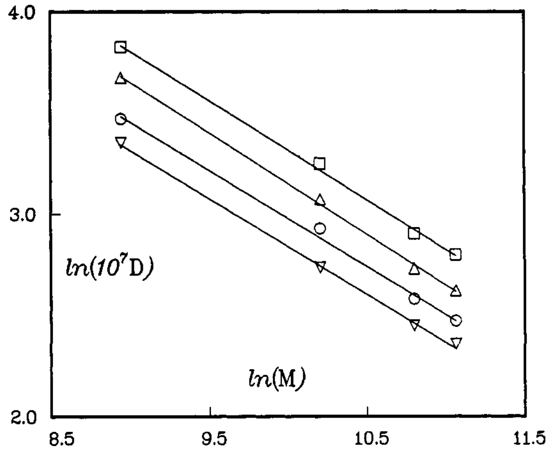

Figure 2. ln (10^7D) vs. ln M for the translational diffusion of PMMA in acetone at 273.2 (▽), 280.5 (○), 298.2 (△), and 313.2 K (□).

up to 117 statisitical segments (i.e., M-4) the excluded volume effects on R_h appear to be practically nil within the framework of either the freely jointed or the wormlike chain model. While the wormlike chain model prediction gives rise to relative errors (D_w/D_{expt} in Table II) that are more or less uniform for the four PMMA standards, the freely jointed chain prediction appears to lead to the largest relative error (D_{fj}/D_{expt} in Table II) at highest molecular weight. However, this numerical result cannot be interpreted as the consequence of possible excluded volume effect for M-4 within the framework of the freely jointed chain model; the model would have overpredicted the diffusivity had the excluded volume effect come into play. It is worth mentioning that the wormlike chain model performs consistently slightly better than the freely jointed version.

Finally, as a practical note we have established in Figure 2 the scaling relationship between D and M, namely, $D \propto M^{-\beta}$, in which the values of β were found to be reasonably constant at four temperatures: 0.49 ± 0.01. The four linear relationships can be collapsed into a single one expressed as

$$D = (3.21 \times 10^{-9})TM^{-0.49}/\mu_0 \qquad (8)$$

which was found to represent the experimentally observed D values to within ±2% on the average with maximum deviation of 4%. The exponent −0.49 on M is close to the limiting value of −0.5 for linear macromolecules in the context of the freely jointed chain model without excluded volume effects.[18]

Conclusions

In summary, the following points emerge from the present study:

1. The translational diffusivities for PMMA standards with molecular weights 7.67×10^3, 2.7×10^4, 4.9×10^4, and 6.39×10^4 were determined at temperatures from 274.2 to 313.2 K by using the extended Taylor dispersion method.

2. Both wormlike and freely jointed chain models corrected for the error due to the preaveraging of the Oseen tensor were found to perform satisfactorily in predicting the translational diffusivities for the PMMA standards studied here. The value of the single adjustable parameter, persistence length for the wormlike chain model or the hydrodynamic interation parameter for the freely jointed version, was shown to be physically significant. The implication of this observation is that virtually no excluded volume perturbations on the hydrodynamic radii R_h exist for PMMA chains of up to 632 repeating units (or 117 Kuhn's statistical segments).

3. The scaling relationship, $D \propto M^{-0.49\pm0.01}$, was also established for practical applications by using the observed values of translational diffusivity. Moreover, there exists a linear correlation between the proportionality constant and the ratio of absolute temperature to solvent viscosity. Numerical results are summerized by eq 8, which is capable of representing experimental observation to within ±2% on the average.

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Excluded-Volume Effects on Force–Length Relations of Long-Chain Molecules[1]

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ABSTRACT: The force–length relation $f(r)$ for a freely jointed chain with excluded volume has been determined by Monte Carlo techniques for chains with up to $N = 200$ bonds for the strain ensemble (r fixed and f fluctuates). As in the recent treatment for chains with $N = 10$ bonds, it is found that excluded-volume effects in this ensemble cause f to be compressive ($f < 0$) for small r, in contrast to the stress ensemble (f fixed and r fluctuates) that leads to $f \geqslant 0$ for all r. However, in contrast to the results for short chains, the force–length relation for longer chains varies smoothly and monotonically and shows all of the generally observed characteristics of experiments on rubber-like materials in uniaxial tension. The results are interpreted in terms of a statistical mechanics framework that computes, as a function of r, the fraction of the configuration space region that is accessible to the phantom chain, which becomes inaccessible due to excluded volume. It is found that this fraction, which is zero for the fully extended chain, becomes large quite rapidly as r decreases. The force–length relation for pairs of interacting chains with common end-to-end displacement vector $\mathbf{r}$ is also computed by a Monte Carlo technique. Chain-chain interaction is found to have little effect. Molecular dynamics calculations determine the separate contributions of the covalent and noncovalent potentials to the force and provide insight into the nature of the transmission of forces in the molecule.

I. Introduction

This paper continues and extends earlier work[2,3] on excluded-volume effects on the force–displacement relation, $f(r)$, for a long-chain molecule whose atoms are in thermal motion with large amplitude consistent with the constraints imposed by the covalent bonds between neighboring atoms. In the notation we employ, $\mathbf{r}$ is the displacement between the end atoms of the chain; $\mathbf{f}$ and $-\mathbf{f}$ are the forces applied to these end atoms; and $r = |\mathbf{r}|$, $f = \mathbf{f}\cdot\mathbf{r}/r$. By the convention adopted, $f > 0$ corresponds to a tensile force, while $f < 0$ corresponds to a compressive force.

Although it also finds application to aspects of polymer solution and melt behavior, the importance of this relation lies mainly in the subject of rubber elasticity, which treats amorphous, cross-linked networks of such chains. In this context, we may think of the forces $\mathbf{f}$ and $-\mathbf{f}$ as applied to the chain through the cross-linking junctions. The mechanical behavior of such networks for different types of non-Gaussian models of polymer molecules is often studied on the basis of the three-chain model of rubber elasticity,[4] which makes direct application of the force–length relation.

From the viewpoint of equilibrium statistical mechanics, we can distinguish between two types of ensembles for the calculation of the force–displacement relation $f(r)$. In the first, the end atoms are fixed with displacement $\mathbf{r}$ between them, and the force $\mathbf{f}$ that must be applied to the end atoms fluctuates as the free atoms of the chain undergo thermal motion. We refer to this as a strain ensemble[5] in analogy to the term volume ensemble for a gas. For this case, the phase-average $\langle f\rangle = \langle\mathbf{f}\rangle\cdot\mathbf{r}/r$ is identified with f to obtain the $f(r)$ relation.

In the second statistical ensemble, one end of the chain is fixed at the origin, a fixed force $\mathbf{f}$ is applied to the other end, and the displacement $\mathbf{r}$ fluctuates. We refer to this as a stress ensemble,[5] in analogy to the term pressure ensemble for a gas. For this case, the phase-average $\langle r_f\rangle = \langle\mathbf{r}\rangle\cdot\mathbf{f}/|\mathbf{f}|$ is identified with r to obtain the $f(r)$ relation.

For a gas it is generally assumed and can be rigorously demonstrated for reasonable mathematical models[6] that the pressure and volume ensembles are equivalent in the macroscopic limit. This does not appear to be the case for the corresponding stress and strain ensembles for a single polymer chain.[3,7,8] Although both the stress and strain ensembles predict purely tensile relations ($f > 0$ for all r), if excluded volume effects are ignored, the situation is changed when the latter are treated in the model. In that case, the stress (constant $\mathbf{f}$) ensemble still leads to a purely tensile relation, but the strain (constant $\mathbf{r}$) ensemble yields $f < 0$ for sufficiently small r.

A further distinction between the $p(v,T)$ relation for a gas and the $f(r,T)$ relation for a long-chain molecule may be made in terms of fluctuations. For the gas, $\Delta p/p$, the relative fluctuations in pressure in the volume ensemble become vanishingly small for sufficiently large systems. For the polymer molecule, on the other hand, $\Delta f/f$, the relative fluctuations in the force in the strain ensemble, remain large, regardless of the length of the chain.[9]

The previous work of Berman and Weiner[3] on excluded-volume effects on the force–length relation relied on