Chains between Two Parallel Walls: Distribution Functions and Force−Deformation Relations

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ABSTRACT: Force−deformation relations for finite chains between two parallel walls are studied. First, the force−deformation relation for a single finite chain between two walls is derived from a second-order tensorial Chebychev distribution function of the end-to-end vector. Second, the case of several chains between two parallel walls is studied. The chains bridging the gap between the two walls are assumed to exert forces only at their ends at the walls. The model is constructed by assuming a very long chain to bridge the gap between two parallel walls. At contact points, the chain is assumed to adsorb to the walls by an adsorption energy of ΔH_c per contact point. Thus the chain is divided into N_s strands, each extending from one wall to the other and $N_s + 1$ contact points. The contact points at the walls are assumed as "hinges" over which the chain passes. The most probable distribution of strand lengths is obtained, from which mechanical variables such as the force−extension relations, maximum extensibility, ductility, and toughness of the chain−wall system are calculated.

Introduction

The elastic activity of chains adsorbed between two walls plays an important role in determining the properties of a large body of inhomogeneous polymeric systems, ranging from micellar structures to rubbers filled with carbon black or silica. Determination of the structure−property relations for these systems beginning from the microscopic or mesoscopic scales is a challenging problem of surface rheology and has been treated by numerous authors at different levels of sophistication and approximation.[1] Compared to these references and to several others cited in them, the present paper is a very approximate evaluation of the force deformation relations for systems of chains between two parallel walls. The specific aim of the present work is to derive relations for maximum extensibility, ductility, and toughness of chain−wall systems, which are not studied in detail in the references cited in ref 1. It should be noted, however, that reference 1a is closest in spirit to the system treated in the present work. Reference 1i is a good review to which the reader is directed for further references.

In the first part of the paper, the effect of a single finite chain fixed to the walls at its two ends is studied. For finite chains with one end fixed, the strong spatial anisotropy and the abrupt cutoff of the end-to-end vector distribution cannot satisfactorily be represented by the simple Gaussian distribution function. The anisotropy of the distribution function of finite chains with fixed end had been investigated some years ago in terms of Hermite polynomials.[2,3] In the present study, we adopt a tensorial Chebychev polynomial for representing the end-to-end distribution function. The determination of the form of these polynomials is similar to that of the Hermite polynomials[2] and is presented in a concise form in the Appendix. A comparison[4] of the force−deformation relations obtained from Hermite[6] and Chebychev[4] polynomials with that obtained from Monte Carlo simulations shows that a second-order Chebychev polynomial gives a much closer agreement with Monte Carlo results than a second-order Hermite polynomial does.

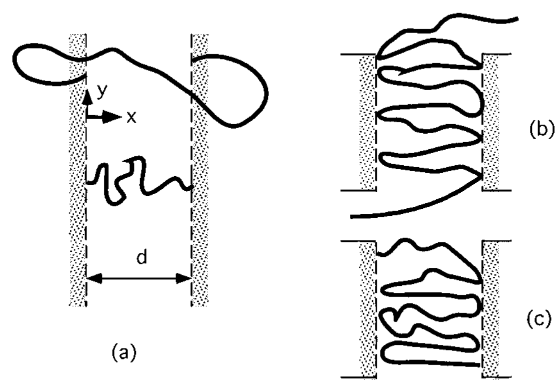

Figure 1. (a) Two parallel walls at a fixed distance *d* from each other. The first bond of the chain is affixed to the left wall, and the other end terminates at a point on the right wall. The chain shown in the upper part of the figure can penetrate either of the walls in obtaining its random configuration. The chain shown in the lower part is constrained to remain always between the two walls. (b) Part of the long chain shown is between the two parallel walls and its two ends are dangling. (c) The two ends of the long chain shown are fixed, one at each wall.

In the second part we study the effect of several chains between two parallel walls. We adopt simplified statistical models to represent the action of several chains between two parallel walls. The chains are assumed to be phantom chains, not interacting with each other but only with the two walls at their ends. Each of the chains is represented by a second-order Chebychev polynomial given in the first part of the paper.

Part I. A Single Chain between Two Parallel Walls

i. Distribution of the End-to-End Vector and Force−Deformation Relation for the Chain be-

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tween Two Parallel Walls. We consider two parallel walls at a fixed distance d from each other as shown in Figure 1a. We assume that the first bond of the chain is affixed to one of the walls and the other end terminates at a point on the other wall. The x-axis is affixed to the left wall and is perpendicular to it. The $y-z$ plane coincides with the plane of the left wall. We define the reduced coordinate variables as

$\rho_i = r_i/r_{max}$, where r_i stands for x, y, and z for $i = 1$, 2, and 3, respectively, and r_{max} denotes the maximum end-to-end separation. The chain shown in the upper part of Figure 1a can penetrate either of the walls in obtaining its random configuration. The chain shown in the lower part is constrained to remain always between the walls. We call these walls "penetrable" and "impenetrable", respectively.

For penetrable walls the probability $W(a)$ of having the ends of the chain at each wall is given, within the second-order Chebychev approximation, by eq A-21 of the Appendix as

$$W(a) = \frac{8}{3\pi}(1 - a^2)^{3/2}\Big[1 + 3\langle\Phi_1{}^{(1)}\rangle a + \frac{8}{5}\Big(\langle\Phi_{11}{}^{(2)}\rangle - \frac{1}{2}\overline{\langle\Phi^{(2)}\rangle}\Big)(6a^2 - 1)\Big] \quad (1)$$

Here, $W(a)$ represents the probability of having $\rho_1 \equiv a = d/r_{max}$ irrespective of the values of ρ_2 and ρ_3. The latter two variables have been integrated out over the total area of the wall. The remaining terms in eq 1 shown by angular brackets are averages of powers of chain dimensions as defined in the Appendix. Although not explicitly indicated, these averages depend on the number j of bonds of a given chain.

Equation 1 may be written in a concise form as

$$W(a) = (1 - \rho^2)^{3/2}[C_{0j} + C_{1j}\rho + C_{2j}\rho^2] \quad (2)$$

where quantities dependent on the number of bonds are written with the subscript j. The coefficients C_{ij}, (i = 0, 1, 2), are

$$C_{0j} = \frac{8}{3\pi}\Big[1 - \frac{8}{5}\Big(\langle\Phi_{11}{}^{(2)}\rangle - \frac{1}{2}\overline{\langle\Phi^{(2)}\rangle}\Big)\Big]$$
$$C_{1j} = \frac{8}{\pi}\langle\Phi_1{}^{(1)}\rangle \quad (3)$$
$$C_{2j} = \frac{8}{3\pi}\Big(\frac{48}{5}\Big)\Big(\langle\Phi_{11}{}^{(2)}\rangle - \frac{1}{2}\overline{\langle\Phi^{(2)}\rangle}\Big)$$

For a chain confined between two impenetrable walls, the probability that one end is at $\rho = 0$ and the other end is at d is represented by the function $W(\rho_j = \rho; 0 \le \rho_k \le a, k = 2, ..., j - 1)$. However, the conditional distribution represented in this manner is too general, and simplifying assumptions are required for a mathematically tractable form. In the present study, we adopt a simple expression for this distribution by assuming that only the midpoint of the chain is confined to the region between the two parallel walls. The probability for the chain between impenetrable walls may then be expressed as $W(\rho_j = a; 0 \le \rho_{j/2} \le a)$ and written as

$$W(\rho_j = a; 0 \le \rho_{j/2} \le a) = C(1 - a^2)^{3/2}[C_{0j} + C_{1j}a + C_{2j}a^2][C_{0j/2}\phi_0(2a) + C_{1j/2}\phi_1(2a) + C_{2j/2}\phi_2(2a)] \quad (4)$$

where C normalizes the distribution over the interval $0 \le \rho \le 1$ and the functions $\phi_k(a)$ are

$$\phi_k(a) = \int_0^a \xi^k (1 - \xi^2)^{3/2}\, d\xi \quad (5)$$

ii. Sample Calculations for a Chain Between Two Parallel Walls. The tensorial components of the first and the second moments of the end-to-end vector are required for the evaluation of the distribution function presented in the preceding section. For chains with bond torsional energies subject to rotational isomerization, these moments may be evaluated either by matrix multiplication techniques[2] or by the Monte Carlo scheme.[5,6] We adopt the latter in the present study.

The chain is assumed to have three rotational isomeric states, trans (t), gauche$^+$ (g$^+$), and gauche$^-$ (g$^-$). The t, g$^+$, and g$^-$ states are assigned the torsional angles of 0, 120, and −120°, respectively. We take the bond length to be equal to 1.54 Å and the complement of the bond angle as 68°. The torsional state of each bond is assumed to be independent of the state of the neighboring bonds. Each configuration of the chain is obtained according to the Monte Carlo (MC) scheme of chain generation. The number of MC runs to yield reproducible values for the first and second tensorial moments of the end-to-end vector is seen to be on the order of 5000. The trans, gauche$^+$, and gauche$^-$ probabilities are chosen as $p_t = 0.8$ and $p_{g^+} = p_{g^-} = 0.1$. The relatively high value of 0.8 is assumed for the probability of the trans state in order to impart a high persistence to the chain in the direction perpendicular to the wall as obtained in brushes, i.e., chains densely attached to a wall.

For chains attached to penetrable walls, the coefficients C_{in} of eq 3 were evaluated by MC for $10 \le j \le 100$. The j dependence of the coefficients C_{in} were then determined by least-squares curve fitting in the following functional forms:

$$C_{0j} = 1.3896 - 26.7022j^{-1} + 103.2288j^{-2}$$
$$C_{1j} = 2.1052 - 88.2867j^{-1} + 409.5789j^{-2} \quad (6)$$
$$C_{2j} = -3.2425 + 160.1181j^{-1} + 618.5088j^{-2}$$

The functions given by eq 5 were integrated numerically and expressed as third order polynomials in the form

$$\phi_0(\rho) = 1.056\rho - 0.239\rho^2 - 0.228\rho^3$$
$$\phi_1(\rho) = -0.028\rho + 0.704\rho^2 - 0.477\rho^3 \quad (7)$$
$$\phi_2(\rho) = -0.0899\rho + 0.4339\rho^2 - 0.246\rho^3$$

The form of the expressions given by eq 7 were preferred to the functional forms obtained by closed form integration of eqs 5 because the latter were more complicated than those of eq 7.

The distribution functions obtained by using eqs 6 and 7 in eq 4 for chains between impenetrable walls are presented in Figure 2 for j = 20, 40, 60, and 100. The solid curve in each figure is the result obtained by using eq 3. The circles represent results of Monte Carlo calculations obtained over an ensemble of 10 000 chains subject to the condition that each atom is confined to the region between the two parallel walls. In all of the four figures as well as those for other values of j not shown here, a good agreement is observed between the results of eq 4 and Monte Carlo calculations. Thus, the assumption of confining only the midpoint of the chain between the walls seems plausible. For better agreement, higher order terms should be used in the expan-

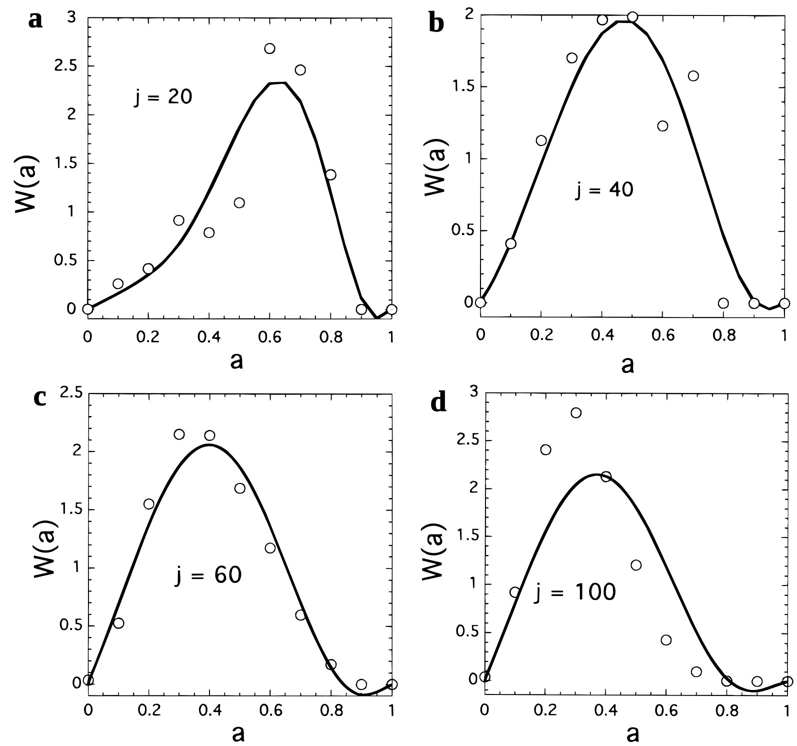

Figure 2. Distribution functions obtained by using eqs 6 and 7 in eq 4 for chains between impenetrable walls for (a) $j = 20$, (b) $j = 40$, (c) $j = 60$, and (d) $j = 100$. The solid curve in each figure is obtained by using eq 3. The circles represent results of Monte Carlo calculations obtained over an ensemble of 10 000 chains subject to the condition that each atom is confined to the region between the two parallel walls.

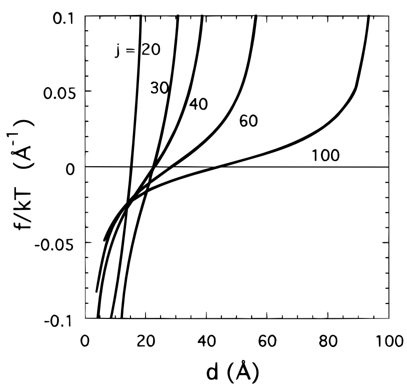

Figure 3. Relationship of force on a chain to wall separation. Results for j =20, 30, 40, 60, and 100 are shown. The ordinate values are given as f/kT in $Å^{-1}$ units. The abscissa values are given in ångstrom units.

sion, and more points along the chain should be forced to lie between the walls. Also, when the separation between the two walls gets smaller, the assumption of confining only the midpoint between the walls fails. A better assumption in this case would be to confine a larger number of points of the chain between the walls. This, however, complicates the problem and therefore is not considered in the present work.

The average force f to be applied along the a direction to keep the two impenetrable walls at a given separation was calculated numerically from the distribution functions obtained from eq A-22. Results for $j = 20$, 30, 40, 60, and 100 are shown in Figure 3. The ordinate values are given as f/kT in $Å^{-1}$ units. The abscissa values are given in ångstrom units rather than reduced units. Several obvious but interesting and important features are observed in the figure: (i) The force−extension relations exhibit a wide linear range followed by a strongly nonlinear region both in the tension and compression regions. The extent of the linear region diminishes as j becomes smaller. For $j = 20$, the linear and the nonlinear regions have merged into a single straight line. (ii) The $f = 0$ intercept of each curve, or the "equilibrium distance" d_0 at which the two parallel walls may be kept fixed with zero average force, depends strongly on chain length. (iii) The "spring constant" of the linear part of the chains depends on chain length. That the dependence is strong especially for shorter chains follows from the expressions given by eq A-22.

For a chain of j bonds, the equilibrium distance d_{0j} has a linear j dependence:

$$d_{0j} = 7.95 + 0.36j \tag{8}$$

where d_{0j} is expressed in Å units.

In the remaining part of the paper we assume a linear relation for the force−displacement relations of the chains. Although not necessary, we assume linearity in the interest of simplifying the presentation. The formulation may easily be extended to chains with nonlinear force−deformation relations. The linearized force−displacement relation is expressed as

$$\frac{f}{kT} = \frac{k_j}{kT}(d - d_{0j}) \tag{9}$$

where f represents the average force per chain. k_j is the spring constant for a chain of j bonds, and d_{0j} is given by eq 8. Equation 9 represents the first term of the Taylor series expansion of eq A-22 about $f = 0$ from which the value of k_j may be obtained. In the present paper, we prefer to use the values of k_j as obtained from Figure 3. Due to the approximations involved in the curve fits to the distribution functions, the accuracy of the k_j values lies within 20%. For further accuracy, one should use higher order terms in the Chebychev expansion.

The dependence of k_j/kT on chain length is obtained from the curves of Figure 3 by least-squares methods as

$$\frac{k_j}{kT} = 0.03j^{-1} + 160.66j^{-3} \tag{10}$$

where the right-hand side of eq 10 has units of $Å^{-2}$.

Part II. Dense System of Chains between Two Parallel Walls

In the preceding section the case of a single chain, extending from one wall to a second parallel wall, is investigated. Force−extension relations are obtained when the chain is assumed to take all configurations subject to the condition that once one of its ends is attached to one of the walls, its second end may attach to any point on the other wall. In the present section, we investigate the case where an infinitely long polymer chain is placed between two parallel walls. In this case, the infinite chain will go from one wall to the other, until the whole available space is occupied by the segments of the chain. When a chain reaches one of the walls, its segments in contact with the wall will attach to the wall with an enthalpy of adsorption per contact equal to ΔH_c. A loop is formed when the two successive contact points are on the same wall. A train is formed when consecutive bonds along the chain become contact points at one of the walls. For simplicity we assume that there are no loops and no trains and two successive contact points are never on the same wall. Each sequence of bonds or chain segment extending from a contact point on one wall to the other on the other wall is referred to as a "strand". There will be N_s strands between the walls and $N_s + 1$ contact points made by the chain and the two parallel walls. The number of bonds, j, in a strand will not be fixed and will depend on the manner the system is constrained and will vary with the separation of the two parallel walls. The number of strands having j bonds is denoted by n_j.

The energy of a strand with j repeat units when the two walls are at a distance d from each other is

$$\frac{E_j}{kT} = \frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2 + \frac{\Delta H_c}{kT} \tag{11}$$

The chain is assumed to be linear in writing eq 11. The adsorption energy at each of the two contact points is taken as $^1/_2\Delta H_c$, and the expression has been rendered dimensionless by dividing into kT. For $j = 30$ for example, k_j/kT is on the order of 10^{-3} $Å^{-2}$ as may be obtained from eq 9. If $\Delta H_c/kT$ is taken to be on the order of unity, one sees that a stretch, $d - d_{0j}$, on the order of 30 Å makes the elastically stored energy compete with the adsorption energy responsible for attaching the ends of the strand to the walls.

The following three cases will be considered:

Case 1. This case is shown in Figure 1b, where a part of the chain is between the two parallel walls and its two ends are dangling. The contact points may be imagined as "hooks" rigidly attached to the two walls through which the chain passes. This picture conserves the number of contacts or the number of strands between the contact points, but the number of bonds between the two walls is not conserved. Upon stretching, the bonds at the two tails outside the walls are pulled in. Under compression, bonds are transferred from between the walls to the tails. Thus, at a given separation d of the two walls, the most probable distribution $\{n_j\}$ of the strands will be obtained subject to the constraints that (i) the number of contact points between the walls, and (ii) the total energy E_t of the wall−strand system will remain constant, i.e.

$$\sum_j n_j = N_s \tag{12}$$

$$\sum_j n_j E_j = E_t \tag{13}$$

This assumption implies that the number n_j of strands with a given number j of bonds and the total number of bonds between the two walls may change as the separation of the walls is changed. This is accompanied simultaneously by transfer of bonds from the neighboring longer strands to a given shorter strand without breaking contacts. This implies that the wall−strand system will take up segments from the surroundings when tension is applied to the two walls and will exude segments under compression. However, the number of contact points will remain constant during this process. The system defined in this manner corresponds to a canonical ensemble with d, N_s, and E_t fixed.[7] A lower and an upper cutoff value should be adopted for all summations over j. The lower cutoff value of j should be adopted for strands behaving approximately as rigid rods, and the upper cutoff should be related to the entanglement length of the strands. In most of the following, the respective cutoff values are chosen as 20 and 100. Other values do change the quantitative aspect of the problem but the qualitative aspect remains the same.

A distribution $\{n_j\}$ of strand lengths represents a state of the system. The most probable distribution $\{n_j^*\}$ will be obtained when the number of states $\Omega(n)$ is a maximum. The latter is given by the expression

$$\Omega(n) = \frac{(n_1 + n_2 + ...)!}{n_1!n_2! ...} = \frac{N_s!}{\Pi n_j!} \tag{14}$$

The number n_j^* of strands with j bonds in the most probable distribution subject to the constraints given by eq 12 and 13 is obtained as

$$n^*_j = N_s Q_1^{-1} e^{-E_j/kT} \tag{15}$$

where

$$Q_1 = \sum_j e^{-E_j/kT} = \sum_j \exp\left(-\frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2 - \frac{\Delta H_c}{kT}\right) \tag{16}$$

The probability P_j of observing a strand with j bonds is

$$P(n_j) = \frac{n^*_j}{N_s} \equiv \frac{e^{-E_j/kT}}{Q_1} \tag{17}$$

Substitution of eq 11 into eq 17 results in

$$P(n_j) = \frac{\exp\left\{-\frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2\right\}}{\sum_j \exp\left\{-\frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2\right\}} \tag{18}$$

Thus the probability of having a strand between the walls with j bonds is independent of the adsorption energy. This results from the assumption of constant number of contact points. Thus the number of bonds in strands will change by transfer of bonds from one strand to the neighboring strands by "sliding" through the contact point.

The energy of the system is

$$E_t = kT^2\left(\frac{\partial(\ln Q_1)}{\partial T}\right)_d \quad (19)$$

Substituting eq 11 into eq 19 leads to

$$E_t = \frac{kT}{Q_1}\sum_j\left(\frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2 + \frac{\Delta H_c}{kT}\right) \times \exp\left[-\left(\frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2 + \frac{\Delta H_c}{kT}\right)\right] \quad (20)$$

Negative values of E_t indicate that the strain energy stored into the system by deformation is less than the adsorption energy of the contact points. When the strain energy equates to the total adsorption energy, the system will be expected to reach an unstable state. This may be used to estimate the maximum degree of stretch that may be applied before instability. Thus, equating eq 20 to zero and solving for d gives the maximum distance d_{max} as

$$d_{max} = \frac{\eta_2 + \left(\eta_2{}^2 - \eta_1\eta_3 - 2\eta_1\frac{\Delta H_c}{kT}\right)^{1/2}}{\eta_1} \quad (21)$$

where

$$\eta_1 = \sum_j P(n_j)\frac{k_j}{kT} \quad (22)$$

$$\eta_2 = \sum_j P(n_j)\frac{k_j}{kT}d_{0j} \quad (23)$$

$$\eta_3 = \sum_j P(n_j)\frac{k_j}{kT}d_{0j}{}^2 \quad (24)$$

Inspection of the right hand side of eq 21 indicates that a minimum threshold energy is required for the stability of the system when the force applied on the walls is zero. This is obtained by equating the determinant of eq 21 to zero, as

$$\frac{\Delta H_{c,min}}{kT} = \frac{1}{2}\left[\left(\sum_j d_{0j}\frac{k_j}{kT}\right)^2 \Big/ \left(\sum_j \frac{k_j}{kT}\right) - \left(\sum_j d_{0j}{}^2\frac{k_j}{kT}\right)\right] \quad (25)$$

A reduced partition function Q_1' not involving the adsorption energy may be defined as

$$Q_1' = \sum_j \exp\left\{-\frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2\right\} \quad (26)$$

The total Helmholtz free energy A of the system is

$$A = -kT(\ln Q_1') \quad (27)$$

and the force required to keep the two walls at a distance d is

$$f = \left(\frac{\partial A}{\partial d}\right)_{T,j} = -kT\left(\frac{\partial(\ln Q_1')}{\partial d}\right)_{T,j} \quad (28)$$

Substituting eq 11 in eqs 26 and 28 and performing the differentiation leads to the following expression for the force

$$f = \frac{kT}{Q_1'}\sum_j\frac{k_j}{kT}(d - d_{0j})\exp\left[-\frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2\right] \quad (29)$$

The ratio of the total number of bonds, $N_b = \sum jnj$, to the number of strands varies with extension, and is obtained from the expression

$$\frac{N_b}{N_s} = \sum_j jP(n_j) \quad (30)$$

Case 2. We assume in this case that the two ends of the infinitely long strand are fixed, one at each wall, as shown in Figure 1c and therefore the total number N_b of bonds remain constant, i.e., $\sum_j jn_j = N_b$. Although N_b is constant, changing the distance between the two walls will cause a change in the number of bonds of the individual strands running from one wall to the other. This may happen either by transfer of bonds from one strand to the neighboring ones without breaking contacts as in case 1 or by creating new strands resulting from breaking of contacts. Introduction of junction breaking into the formulation requires the use of a grand-canonical partition function which we were not able to obtain rigorously. Instead we solved the problem in an approximate way as follows: The number of bonds $m_j = jn_j$ in a set of n_j strands each having j bonds will change when chain slippage takes place through the junctions and when junction points break. The state of the system may be described by the distribution of m_j for which equilibrium conditions are established when the distribution $\{m_j\}$ of the groups of bonds is such that the number of states $\Omega(m_j)$ of the system is a maximum, subject to the conditions

$$\sum_j m_j = N_b \quad (31)$$

$$\sum_j \frac{m_j}{j}E_j = E_t \quad (32)$$

Maximization of $\Omega(m_j)$ in a way similar to that of case 1 leads to the most probable distribution $\{m^*_j\}$ of the number of bonds in a set of strands each having j bonds as

$$m^*_j = N_b Q_2{}^{-1}e^{-E_j/jkT} \quad (33)$$

where

$$Q_2 = \sum_j e^{-E_j/jkT} = \sum_j \exp\left(-\frac{1}{2}\frac{k_j}{jkT}(d - d_{0j})^2 - \frac{\Delta H_c}{jkT}\right) \quad (34)$$

The probability of finding a total of m_j bonds from a set of n_j bonds is

$$P(m_j) = \frac{m_j}{N_b} = \frac{\exp\left\{-\frac{1}{j}\left[\frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2 + \frac{\Delta H_c}{kT}\right]\right\}}{\sum_j \exp\left\{-\frac{1}{j}\left[\frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2 + \frac{\Delta H_c}{kT}\right]\right\}} \quad (35)$$

and the probability of finding a strand with j bonds is

$$P(n_j) = \frac{n_j}{N_c} = \frac{j^{-1}\exp\left\{-\frac{1}{j}\left[\frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2 + \frac{\Delta H_c}{kT}\right]\right\}}{\sum_j j^{-1}\exp\left\{-\frac{1}{j}\left[\frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2 + \frac{\Delta H_c}{kT}\right]\right\}} \quad (36)$$

The probability defined in this manner leads to the partition function Q as

$$Q = \sum_j j^{-1}\exp\left\{-\frac{1}{j}\left[\frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2 + \frac{\Delta H_c}{kT}\right]\right\} \quad (37)$$

The ratio of the number of strands to the total number of bonds varies by stretching because the number of contact points decrease by breaking. This ratio is obtained from eqs 35 by writing it in terms of $m_j = jn_j$, summing over j, and using eq 31:

$$\frac{N_s}{N_b} = \frac{\sum_j j^{-1}\exp\left(-\frac{E_j}{jkT}\right)}{\sum_j \exp\left(-\frac{E_j}{jkT}\right)} \quad (38)$$

The force to be applied to the walls to keep them at a separation of d is obtained by the weighted average of the force

$$f = \frac{kT}{Q_2}\sum_j \frac{1}{j}\frac{k_j}{kT}(d - d_{0j}) \times \exp\left\{-\frac{1}{j}\left[\frac{1}{2}\frac{k_j}{kT}(d - d_{0j})^2 + \frac{\Delta H_c}{kT}\right]\right\} \quad (39)$$

It is to be noted that the force in this case depends on the adsorption energy. The maximum stretch may be obtained from eqs 21−24 with $P(n_j)$ substituted from eq 37 which yields

$$d_{\max} = \frac{\eta_2 + \left(\eta_2^{\,2} - \eta_1\eta_3 - 2\eta_1\eta_4\frac{\Delta H_c}{kT}\right)^{1/2}}{\eta_1} \quad (40)$$

where

$$\eta_1 = \sum_j P(n_j)\frac{k_j}{jkT} \quad (41)$$

$$\eta_2 = \sum_j P(n_j)\frac{k_j}{jkT}d_{0j} \quad (42)$$

$$\eta_3 = \sum_j P(n_j)\frac{k_j}{jkT}d_{0j}^{\,2} \quad (43)$$

$$\eta_4 = \sum_j \frac{P(n_j)}{j} \quad (44)$$

Case 3. In this case we assume that once the most probable distribution P_j^0 is obtained in the state of zero force, the contact points and the distribution of strand lengths are frozen and do not change by further deformation. The total energy of the system is

$$E_t = N_s\sum_j P_j^{\,0}E_j \quad (45)$$

and the expression for the force is

$$f = \sum_j P_j^{\,0}f_j = kT\sum_j P_j^{\,0}\frac{k_j}{kT}(d - d_{0j}) \quad (46)$$

where f_j is the force for the strand of j bonds, obtained from the expression $f_j = \partial E_j/\partial d$. It should be noted that the force will be independent of ΔH_c if P_j^0 is chosen according to eq 17 whereas it will depend on ΔH_c if P_j^0 is chosen according to eq 36.

The maximum stretch may be obtained from eqs 21−24 where P_j^0 is used in place of $P(n_j)$.

The predictions based on the model of case 3 are expected to resemble those predicted by case 2. For this reason case 3 is not further considered in the remainder of this paper.

Calculations for a Dense System of Chains between Two Parallel Walls

i. Force Deformation Relations. The relationship of force to deformation for cases 1 and 2 are shown in Figure 4. The values of the force are determined from eqs 29 and 39 for cases 1 and 2, respectively. The values of d_0, corresponding to the separation of the two walls in the absence of an external force, are obtained by the numerical solution of eqs 29 and 39. In the summations in these equations, the lower and upper cutoff values of the number of bonds are assumed as 20 and 100, respectively. The value of ΔH_c is taken as 1.0 kcal/mol for both cases. The values of d_0 are obtained as 21.300 Å for case 1 and 18.725 Å for case 2. The force deformation relation for case 2 is approximately linear, while that for case 1 is sigmoidal and is significantly below the curve for case 2. The absorption and desorption of the tails under tension and compression for case 1 is the reason for the lower curve.

The two curves in Figure 4 are terminated when the maximum extensibility is reached. The maximum extensibility for case 1 is calculated from eq 21 as $\lambda_{\max} = 4.258$. The force corresponding to this deformation is $f_{\max}/kT = 0.0368$ Å^{-1}. The maximum extensibility for case 2 is calculated from eq 41 as $\lambda_{\max} = 1.812$ with the corresponding force $f_{\max}/kT = 0.074$ Å^{-1}. The area under the force−extension curve for positive values of the ordinate values is a measure of the toughness of the material indicating the amount of energy absorbed up

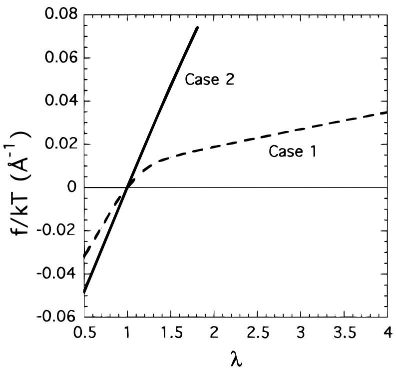

Figure 4. Force deformation relations for cases 1 and 2. The value of ΔH_c is taken as 1.0 kcal/mol for both cases. The lower and upper cutoff values of the number of bonds are taken as 20 and 100, respectively. The values of d_0 are 21.300 Å for case 1 and 18.725 Å for case 2.

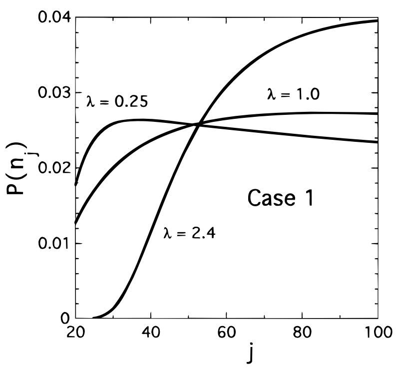

Figure 5. Transformation of number of bonds *j* of the individual chains upon deformation for case 1. Calculations are performed for $\Delta H_c = 1.0$ kcal/mol.

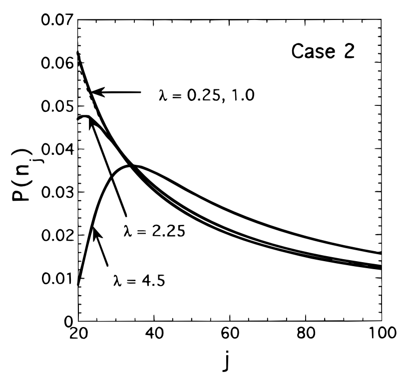

Figure 6. Transformation of the number of bonds *j* of the individual chains upon deformation for case 2. See legend for Figure 5.

to failure. For case 1 this area equates to 0.0748 Å^{-1} whereas for case 2 it is equal to 0.0307 Å^{-1}. The higher toughness of the system of case 1 results from the fact that new bonds are absorbed into the region between the two walls under a tensile force, which allows for the rearrangement of chain lengths and results in the relaxation of forces in the individual chains.

ii. Transformation of Distribution of Chain Lengths upon Deformation. The transformation of number of bonds *j* of the individual chains upon deformation is shown in Figures 5 and 6. Calculations are performed for $\Delta H_c = 1.0$ kcal/mol. Ordinate values in both figures indicate the fraction of chains having *j* bonds. For case 1, depicted in Figure 5, the effect of deformation on the distribution of chain lengths is significant. Under compression, the fraction of shorter chains is large. Under tension, the fraction of longer chains becomes significantly larger. For case 2, shown

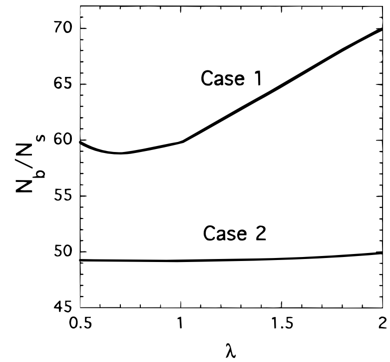

Figure 7. Average number of bonds per strand, N_b/N_s, presented as a function of deformation ratio for cases 1 and 2.

in Figure 6, however, the effect of deformation is not as significant. The distribution of chain lengths for chains having more than 30 bonds remain approximately the same. Under high degrees of compression, shown by the dotted curve in Figure 6 for $\lambda = 0.25$, there is a small decrease in the number of short chains relative to those in the unperturbed state, resulting from the fact that short chains are energetically unfavorable at high deformations. In order to accentuate the effect of extension, a fictitious stretch ratio of $\lambda = 4.5$ is shown in the same figure. It is to be noted, however, that this value of λ is above λ_{max} corresponding to a $\Delta H_c/kT$ of 1.0 (see Figure 4).

iii. Exchange of Bonds between the Tails and the Internal Chains and Change in Number of Contact Points by Deformation. In Figure 7, the average number of bonds per strand, N_b/N_s, is presented as a function of deformation ratio, based on the model represented by cases 1 and 2. According to the model, the number of contact points is constant in case 1. The significant increase in the ratio N_b/N_s is therefore a result of an increase of the number of bonds absorbed from the tails of the chain under tension. A small increase in N_b/N_s in the compression region results from the fact that the probability of having a small end-to-end distance increases if the number of bonds per strand increases, as can be seen from Figure 2a−d. Thus at high compression, it is more favorable to increase the number of bonds per strand. The curve for case 2 shows an insignificant increase in the ratio N_b/N_s. According to this model, the number of bonds of the chain between the two walls is constant and the number of strands decrease due to breaking of contact points. At $\lambda = 2$, only 2% of the contact points break, as seen from the figure.

iv. Relationship of Maximum Extensibility to Adsorption Energy. In Figure 8, the relationship of maximum extensibility to the adsorption energy per contact at the walls is shown. This energy is also equal to the maximum strain energy that may be applied by deformation. The curve for case 1 is significantly above that for case 2, indicating that the system represented by case 1 is much more "ductile", the ductility being defined as the strain at break. The reason for this behavior is that, in case 1 upon tension, segments of the tails are absorbed into the system and the distribution of strand lengths changes such that shorter strands decrease and longer strands increase in number. This seems to be an efficient mechanism of relaxation. For case 2, the average length of strands remains approximately constant, and therefore relaxation of internal forces due to redistribution of strand lengths is not as significant.

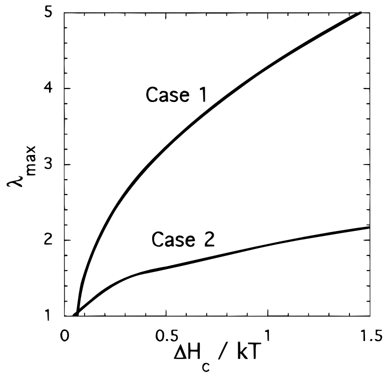

Figure 8. Relationship of maximum extensibility to the adsorption energy per contact (the maximum strain energy that may be applied by deformation) at the walls for cases 1 and 2.

v. Dependence of Force−Deformation Relation on the Upper Cutoff Value of *j*. The upper cutoff value of *j* is expected to depend on the degree of entanglement of the chains in the bulk state that obtains during the insertion of the chain between the walls. The above calculations were presented for a repeat unit of 100. Results of calculations performed for cases 1 and 2 with different values of the upper cutoff values show that a larger value results in a more ductile material, as expected.

Conclusion

In the present study, the force−deformation relations of a finite chain and an ensemble of finite chains between two parallel walls are investigated. The formulation of the problem is based essentially on the distribution of the end-to-end vector of a single finite chain. The use of a second-order Chebychev polynomial for this distribution may be considered as a good approximation for a qualitative description of the problem. Higher order terms may be required for a better and quantitatively more precise description. The present approach also allows for the determination of the effects of a shear force applied to the walls. The solution to this problem, which may be of interest in the field of tribology, follows directly from the present analysis by suitably modifying eq A-19 for the case of a shear force.

The two cases investigated for two parallel walls with several chains may find an analogy to the theoretical models treated in the literature on rubber−filler systems. More specifically, the model of Boonstra[9] has close resemblance to the system represented by case 1 in the present work. According to the model proposed by Boonstra, the nonhomogeneous distribution of stress in a filled rubber is improved by a relieving mechanism of the stresses by chains carrying the highest loads. This takes place by slippage of the chains at the chain−filler bonding sites. Both the chains and the chain-filler bonding sites are assumed not to break during the deformation. Similarly, case 2 of the present treatment shows parallelisms with the analysis of Bueche[10,11] according to which a chain may break at the chain−filler bonding site, resulting in stress relaxation.

Appendix: End-to-End Vector Distribution for a Finite Chain in Terms of Second-Order Chebychev Polynomials and Force−deformation Relations for a Single Chain

Distribution Function and Force−Deformation Relation for a Chain Affixed to a Wall at One End. The first bond of the chain is held fixed along the *x*-axis of a laboratory fixed coordinate system, O*xyz* and the second bond lies in the *xy*-plane. The notation and terminology of refs 5 and 6 are adopted.

We let $W_e(\mathbf{r})$ denote the exact density distribution, per unit volume, of the end-to-end vector $\mathbf{r}$. We minimize the functional *I* defined as

$$I = \int_V [W_e(\mathbf{r}) - \Psi(r) \sum_{\nu=0}^{\infty} \mathbf{A}^{(\nu)} \cdot \Phi^{(\nu)}(\mathbf{r})]^2 \Psi^{-1}(r)\, dV \quad \text{(A-1)}$$

Defined in this manner, *I* is a measure of the difference between the exact distribution function $W_e(\mathbf{r})$ and the approximating infinite sum given by the second term in the square brackets. This equation is the generalized form of the expression given in ref 5 for Hermite polynomials. In eq A-1, $\Psi(r)$ is the weight function, a scalar function of the scalar variable *r*. The integral is weighted by $\Psi^{-1}(r)$. $\Phi^{(\nu)}(\mathbf{r})$ is a tensor of rank ν whose components are polynomials of the form $x^k y^l z^m$, where *x*, *y*, and *z* are the components of $\mathbf{r}$ and $k + l + m \le \nu$. The components of $\Phi^{(\nu)}(\mathbf{r})$ may be obtained[5] from the members of the νth Cartesian product of $\mathbf{r}$ with itself, denoted as r^{xp}. $\mathbf{A}^{(\nu)}$'s are the tensors of coefficients. The dot indicates the inner product or the trace of the matrix product of $\mathbf{A}^{(\nu)}$ and $\Phi^{(\nu)}(\mathbf{r})$. The difference is weighted with $\Psi(\mathbf{r})^{-1}$, and the integration is carried over the volume *V* available to $\mathbf{r}$. The best approximating function is obtained by minimizing the functional *I* with respect to tensor coefficients $\mathbf{A}^{(\mu)}$

$$\frac{\partial I}{\partial A^{(\mu)}} = 2\int_V [W_e(\mathbf{r}) - \Psi(r) \sum_{\nu=0}^{\infty} \mathbf{A}^{(\nu)} \cdot \Phi^{(\nu)}(\mathbf{r})] \Phi^{(\mu)}(\mathbf{r})\, dV = 0 \quad \text{(A-2)}$$

The condition of orthogonality for the tensors $\Phi^{(\nu)}$ in V is written as

$$\int_V \Psi(r) \Phi^{(\nu)}(\mathbf{r}) \Phi^{(\mu)}(\mathbf{r})\, dV = 0 \qquad \text{for } \nu \neq \mu \quad \text{(A-3)}$$

Equation A-2 may now be written, subject to the restrictions imposed by eq A-3, as

$$\mathbf{A}^{(\nu)} \int_V \Psi(\mathrm{r}) \Phi^{(\nu)}(\mathbf{r}) \Phi^{(\nu)}(\mathbf{r})\, dV = \langle \Phi^{(\nu)}(\mathbf{r}) \rangle \quad \text{(A-4)}$$

where $\langle \Phi^{(\nu)}(\mathbf{r}) \rangle$ denotes the configurational average of the tensor $\Phi^{(\nu)}(\mathbf{r})$:

$$\langle \Phi^{(\nu)}(\mathbf{r}) \rangle = \int_V W_e(\mathbf{r}) \Phi^{(\nu)}(\mathbf{r})\, dV \quad \text{(A-5)}$$

The unknown coefficients $\mathbf{A}^{(\nu)}$ are to be evaluated from eq A-4 in terms of the configurational averages of the components of r and their higher products. If the $\mathbf{A}^{(\nu)}$'s, are known, the density distribution function, $W(\mathbf{r})$, can be calculated from

$$W(\mathbf{r}) = \Psi(r) \sum_{\nu=0}^{\infty} \mathbf{A}^{(\nu)} \cdot \Phi^{(\nu)}(\mathbf{r}) \quad \text{(A-6)}$$

The density distribution $w(r)$ of the magnitude of $\mathbf{r}$ may be obtained from eq A-6 by representing $\mathbf{r}$ in terms of spherical coordinates, *r*, θ, and ϕ as

$$x = r \cos\theta$$
$$y = r \sin\theta \cos\phi \qquad \text{(A-7)}$$
$$z = r \sin\theta \sin\phi$$
$$\mathrm{d}V = r^2 \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi \, \mathrm{d}r$$

and integrating over the variables θ and ϕ. The resulting expression for $w(r)$ takes the form

$$w(r) = \Psi(\mathbf{r})\sum_{\nu=0}^{\infty}\mathbf{A}^{(2\nu)}\cdot\varphi^{(2\nu)}(r) \qquad \text{(A-8)}$$

where

$$\varphi^{(2\nu)}(r) = \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\Phi^{(2\nu)}(r,\theta,\phi)\,\mathrm{d}\phi\,\mathrm{d}\theta \qquad \text{(A-9)}$$

The orthogonal functions $\Phi^{(\nu)}(\mathbf{r})$ appearing in eq A-6 may be derived from the Rodriguez formula[8] generalized to three dimensions as

$$\Phi^{(\nu)}(\mathbf{r}) = \frac{1}{c_\nu\Psi(\mathrm{r})}\nabla^{(\nu)}\{\Psi(r)[g(r)]^\nu\} \qquad \text{(A-10)}$$

where $\nabla^{x\nu}$ is the gradient operator of rank ν

$$\nabla^{x\nu} = \frac{\partial^\nu}{\partial x_{\mathrm{i}_1}\partial x_{\mathrm{i}_2}...\partial x_{\mathrm{i}_\nu}} \qquad \text{(A-11)}$$

x_{i_1}, x_{i_2}, ... being the indicial representations for the coordinates x, y, or z. In eq A-10, c_ν is the coefficient of the nth term, $\Psi(r)$ is the weighting function, defined in eq 1, and $g(r)$ is the generating function which is a function of the scalar r. Expressions for c_ν, $\Psi(r)$, and $g(r)$ are given in ref 7 for different orthogonal polynomials.

In this section we apply the general formulation of the preceding section and express the distribution function $W(\mathbf{r})$ in terms of three different orthogonal polynomials. The space variables ρ_i are used in the nondimensional form

$$\rho_i = \frac{r_i}{r_{\max}}$$
$$\rho^2 = \rho_1^{\,2} + \rho_2^{\,2} + \rho_3^{\,2} \qquad \text{(A-12)}$$

Expansion of $W(\mathbf{r})$ into tensorial Hermite polynomials has been given by Flory and Yoon.[5,6] In this section we present expansion into Chebychev polynomials of the second kind. The coefficient, weight function, and the generating functions for these polynomials are[8]

$$c_\nu = \frac{(-1)^\nu 2^{\nu+1}\Gamma(\nu + 3/2)}{(\nu+1)\sqrt{\pi}} \qquad \text{(A-13)}$$

$$\Psi(\rho) = (1-\rho^2)^{1/2} \qquad \text{(A-14)}$$

$$g(\rho) = (1-\rho^2) \qquad \text{(A-15)}$$

Applying the Rodriguez formula to eqs A-13–A15, the tensorial Chebychev polynomials are obtained. In this study we will be interested in expansions up to second order, which we give below. The polynomials are

$$\Phi^{(0)} = 1$$
$$\Phi_i^{\,(1)} = 2\rho_\mathrm{i} \qquad \text{(A-16)}$$
$$\Phi_{ij}^{\,(2)} = 3\rho_i\rho_j - (1-\rho^2)\delta_{ij}$$

The coefficients for the first two orders are

$$A^{(0)} = \frac{4}{\pi^2}$$
$$A_i^{\,(1)} = \frac{6}{4\pi}\langle\Phi_i^{\,(1)}\rangle \qquad \text{(A-17)}$$
$$A_{ij}^{\,(2)} = \frac{32}{3\pi^2}\left[\langle\Phi_{ij}^{\,(2)}\rangle - \frac{1}{6}\sum_k\langle\Phi_{kk}^{\,(2)}\rangle\delta_{ij}\right]$$

The second order form of tensorial Chebychev polynomials follows from eq A-6 as

$$W(\rho) = \frac{4}{\pi^2}(1-\rho^2)^{1/2}\left[1 + \frac{3}{2}\sum_{i=1}^{3}\langle\Phi_i^{\,(1)}\rangle\Phi_i^{\,(1)} + \frac{8}{3}\sum_{i=1}^{3}\sum_{j=1}^{3}\left(\langle\Phi_{ij}^{\,(2)}\rangle - \frac{1}{2}\,\overline{\langle\Phi^{(2)}\rangle}\delta_{ij}\right)\Phi_{ij}^{\,(2)}\right] \qquad \text{(A-18)}$$

where ρ^2 and ρ_i that appear in the functions $\Phi^{(1)}$ abd $\Phi^{(2)}$ are given by eq A-12.

The components of the force vector **f** to be applied to the end of the chain in order to keep it at **r** are obtained from the expressions of the distribution functions according to the relation

$$f_i = -kT\nabla_{\mathbf{r}_i}\ln[W(\mathbf{r})] = -\frac{kT}{r_{\max}}\nabla_{\rho i}\ln[W(\rho)] \qquad \text{(A-19)}$$

Applying eq A-19 to eq A-18 yields the second-order Chebychev polynomial expression for the Cartesian components of the force required to keep the end-to-end vector at a fixed value ρ:

$$f_i = \frac{kT}{r_{\max}}\left\{\frac{\rho_i}{1-\rho^2} - \frac{4}{\pi^2}\frac{(1-\rho^2)^{1/2}}{W(\rho)}\left[3\sum_{k=1}^{3}\langle\Phi_k^{\,(1)}\rangle\delta_{ik} + \frac{8}{3}\sum_{k=1}^{3}\sum_{j=1}^{3}\left(\langle\Phi_{jk}^{\,(2)}\rangle - \frac{1}{2}\overline{\langle\Phi^{(2)}\rangle}\delta_{jk}\right)(3\rho_j\delta_{ki} + 3\rho_k\delta_{ji} + 2\rho_i\delta_{kj})\right]\right\} \qquad \text{(A-20)}$$

Distribution Function and Force–Deformation Relation for a Chain between Two Parallel Walls. We now consider two parallel walls at a fixed distance d from each other. To facilitate the discussion, one may assume the two walls to be vertical, perpendicular to the plane of this paper, one at the left and the other at the right. We assume that the first two bonds of the chain are affixed to the left wall and the other end to terminate at a point on the right wall. The x-axis is affixed to the left wall and is perpendicular to it. The y–z plane coincides with the plane of the left wall. The probability of having one end of the chain fixed at the left wall in the manner stated and the other end to terminate at any point on the right wall is $W(a)$, where the latter represents the probability of having $\rho_1 \equiv a = d/r_{\max}$ irrespective of the values of ρ_2 and ρ_3. Letting $\xi^2 = \rho_2^{\,2} + \rho_3^{\,2}$, $\rho_2 = \xi\cos(\phi)$ and $\rho_3 = \xi\sin(\phi)$ in eq A-18, where ϕ is the angle in the yz-plane with $0 < \phi < 2\pi$, and integrating over the total area of the second wall with the area element being $\mathrm{d}A = \xi\,\mathrm{d}\phi\,\mathrm{d}\xi$, one obtains the expression

$$W(a) = \frac{8}{3\pi}(1 - a^2)^{3/2}\left[1 + 3\langle\Phi_1^{(1)}\rangle a + \frac{8}{5}\left(\langle\Phi_{11}^{(2)}\rangle - \frac{1}{2}\langle\overline{\Phi^{(2)}}\rangle\right)(6a^2 - 1)\right] \quad \text{(A-21)}$$

The average force exerted by the chain on the walls in the ρ_1 direction is obtained by substituting eq A-21 in eq A-19

$$f = \frac{kT}{r_{\max}}\left[\frac{3a}{(1 - a^2)^{1/2}} - \frac{8}{3\pi}\frac{(1 - a^2)^{3/2}}{W(a)}\left(3\langle\Phi_1^{(1)}\rangle + \frac{96}{5}\left(\langle\Phi_{11}^{(2)}\rangle - \frac{1}{2}\langle\overline{\Phi^{(2)}}\rangle\right)a\right)\right] \quad \text{(A-22)}$$

References and Notes

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