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Comparative Study of Distribution Functions for the Excluded Volume Problem

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ABSTRACT

A comparative study of five distribution functions for excluded volume problem has been made. The function of Domb et al., Mazur, Gray et al., Reiss, and Kumbar have been compared with themselves and with the Gaussian function. All functions except the Gray et al. function assume the bell shape or a shape similar to it. All five functions shift the maximum point toward greater r. The shift is small for Domb et al., Mazur, Reiss, and Kumbar functions, and is large for Gray et al. function. It is indicated that the excluded volume function probably has the bell shape. The curves become much steeper with a shift in the maximum point toward lower r when local chain stiffness is included. The mean square end-to-end distance is represented in a three-parameter equation for the inclusion of local chain stiffness"

$$\langle r_n^2 \rangle = A + Bn^{1+\epsilon}$$

The curves are much sharper when the influence of stiffness is considered in the presence of high excluded volume,

indicating the greater role of chain stiffness when the chain is in the state of high expansion.

INTRODUCTION

The problem of configurational statistics of single polymer or polymer solution is a complicated subject. If we are talking of a polymer molecule, the configuration is usually characterized by two-dimensional properties, namely, the mean square end-to-end distance and the mean square radius (mean square radius of gyration). Similarly the polymer solution can be characterized on the basis of the characterization of a single polymer molecule. The problem of studying the polymer molecule in a Gaussian status has been thoroughly explored, and has led to a better understanding of polymer statistics. The success involved is mainly due to the mathematical ease of treating the Gaussian problem. However, the Gaussian status of the polymer molecule is the most simplified version of the real status. In reality, the polymer molecule deviates from the Gaussian status and is situated in a non-Gaussian status for a variety of reasons. Even though a great deal of progress has been achieved over the last decade in understanding the non-Gaussian status, the knowledge accumulated is still not complete. The reason for this is simply the mathematical difficulties or numerical difficulties involved in treating the non-Gaussian status.

In the present work we have concentrated on one aspect of the non-Gaussian status, the excluded volume effect. In dealing with the non-Gaussian problem, two kinds of approaches have been used. The studies based on an analytical treatment have used an expansion type of parameter to represent the non-Gaussian status:

$$\alpha^2 = \langle x^2 \rangle / \langle x_0^2 \rangle \qquad (1)$$

where x is either the end-to-end distance or the mean square radius. The term in the numerator describes the property in the non-Gaussian status, while the term in the denominator describes the same property in the Gaussian status. This kind of approach is more general and certainly is not restricted to the excluded volume problem only. The other approach has been used in numerical studies where only the intramolecular excluded volume has been accounted for. These studies have proposed that the configurational property be represented as

$$\langle x^2 \rangle \propto n^{1+\epsilon} \qquad (2)$$

where ϵ is the excluded volume parameter and n is the number of bonds in a given polymer molecule.

The distribution function for the Gaussian or non-Gaussian status plays an important role in polymer statistics. It has been well established that the polymer molecule in the Gaussian status obeys the Gaussian distribution in the limit of large n. For the entire range of n, one may use the exact formula developed by Treloar [1]. Kuhn and Grün [2], and James and Guth [3] also have proposed a formula for this study. A comparative study of these Gaussian status functions has been made by Treloar and by Jernigan and Flory [4]. As for the non-Gaussian function, there is no general rule such as exists for Gaussian polymer molecule. In recent years, few distribution functions for the excluded volume problem have been proposed or used. Therefore, we thought it might be worthwhile to make a comparative study of these functions. The comparison is made between the functions and with the Gaussian function. Further, we have examined the effect of local chain stiffness on the behavior of these functions.

DISTRIBUTION FUNCTIONS

Domb et al. [5] have proposed the following function based on a numerical study (exact enumeration technique) of lattice models:

$$P(r)\,dr = C_n r^l \exp\left[-(r/\sigma_n)^t\right] dr \tag{3}$$

where

$$C_n^{-1} = \sigma_n^{l+1}\,\Gamma\left(\frac{l+1}{t}\right)/t$$

$$\sigma_n^2 = \langle r_n^2 \rangle\,\Gamma\left(\frac{l+1}{t}\right)/\Gamma\left(\frac{l+3}{t}\right)$$

where $\langle r_n^2 \rangle$ is the mean square end-to-end distance. $t = 2.0$ for the Gaussian problem and 2.5 for the excluded volume problem, and $l = t$. Fisher [6] further suggested that $t = 2.0/(1 - \epsilon)$, where ϵ is the excluded volume parameter given in Eq. (2).

Mazur [7] proposed a very similar function, again based on the numerical study (Monte Carlo method) of lattice models:

$$P(r)\,dr = ak^{3/2} \exp\left(-b' k^{t/2} r^t\right) r^2\,dr \tag{4}$$

where

$$a = t/\Gamma(3/t)\,[\Gamma(5/t)/\Gamma(3/t)]^{3/2}$$

$$b' = \Gamma(5/t)/\Gamma(3/t)$$

and

$$k = \langle r_n^2 \rangle^{-1}$$

$t = 2.0$ for the Gaussian problem and 3.2 for the excluded volume problem. In Eqs. (3) and (4), $\Gamma(x)$ are the gamma functions.

Gray et al. [8] have used the following empirical function in treating the hydrodynamic properties of biological molecules:

$$P(r)\,dr = (2/\pi)^{1/2}(3/b^2 n^{1+\epsilon})^{3/2} \exp\,(-3r^2/2b^2 n^{1+\epsilon})r^2\,dr \qquad (5)$$

where b is the bond length. This function has been proposed assuming that the mean square length under excluded volume condition is given by

$$\langle r_n^2 \rangle = b^2 n^{1+\epsilon} \qquad (6)$$

Reiss [9], while applying the variational principle to the excluded volume problem, has derived the following distribution function:

$$P(r)\,dr = (3/2\pi b^2 n) \exp\,(-3r^2/2b^2 n) \exp\,(-k_1 n/r)\,4\pi r^2\,dr \qquad (7)$$

where k_1 is the constant which depends on the temperature. This equation assumes that only the repulsive potential is responsible for the excluded volume effect, and this kind of potential can be described by the Coulombic type.

Kumbar [10] modified the Reiss function while arguing that the excluded volume effect arises not only by repulsive forces but also to some extent by attractive forces, and the segments connected by bonds behave like dipoles rather than point charges. He proposed the following dipolar form:

$$P(r)\,dr = (3/2\pi b^2 n) \exp\,(-3r^2/2b^2 n) \exp\,(-k_2 n^2/r^3)\,4\pi r^2\,dr \qquad (8)$$

where k_2 is a constant which depends on the temperature.

EFFECT OF CHAIN STIFFNESS

To investigate the effect of the local chain stiffness, we assumed that the polymer chain under consideration can be represented by the Rouse [11], Bueche [12], and Zimm [13] spring bead model. We also assume that the above-mentioned distribution functions also apply to this model. The effect of chain stiffness on the behavior of the distribution function can be studied by relating the chain stiffness to mean square length. Previously [14] we derived an equation for the mean square radius of linear molecules by using the above model in terms of excluded volume and chain stiffness:

$$\langle S_n^2 \rangle \approx \frac{b^2}{(4\beta + 1)} \left[\frac{4\beta}{3} + \frac{n^{1+\epsilon}}{(2+\epsilon)(3+\epsilon)} \right] \tag{9}$$

where β measures the local chain stiffness. Then the mean square length can be obtained through the relation

$$\langle r_n^2 \rangle = (2+\epsilon)(3+\epsilon) \langle S_n^2 \rangle$$

which is

$$\langle r_n^2 \rangle \approx \frac{(2+\epsilon)(3+\epsilon)b^2}{4\beta + 1} (4\beta/3) + \frac{b^2 n^{1+\epsilon}}{(4\beta + 1} \tag{10}$$

This equation can be put into a general form:

$$\langle r_n^2 \rangle \approx A(\epsilon, \beta) + B(b,\beta)n^{1+\epsilon} \tag{11}$$

If $\epsilon = 0$,

$$\langle r_n^2 \rangle \approx A(\beta) + B(b,\beta)n \tag{12}$$

and if $\beta = 0$,

$$\langle r_n^2 \rangle \approx B(\beta)n^{1+\epsilon} \tag{13}$$

Thus $\langle r_n^2 \rangle$ can be described by the three-parameter Eq. (11) if the chain stiffness is nonzero. This type of representation for $\langle r_n^2 \rangle$ was previously suggested by Domb [15] who based his derivation on an exact enumeration study of lattice models. In Ref. 14 we have also proposed the three-parameter equation for the mean square radius. If either excluded volume or chain stiffness is zero, the three-parameter equation reduces to the two-parameter equation (Eq. 12

or 13). If the experimental equation is available in the three-parameter representation (Eq. 11), β and ϵ are easily evaluated by comparison.

COMPUTATION

The distribution functions given in Eqs. (3), (4), (5), (7), and (8) have been computed for the range $0 \leqslant r \leqslant 50$, where r is in arbitrary units. We have chosen n = 500, b = 1, and ϵ = 0, 0.2, and 0.5. While studying the chain stiffness, we have selected β = 0, 0.2, and 0.5. In computation of Eqs. (7) and (8), k_1 and k_2 are assigned the values 10^{-2} and 10^{-4}, respectively. The above selection of various parameters are somewhat personal.

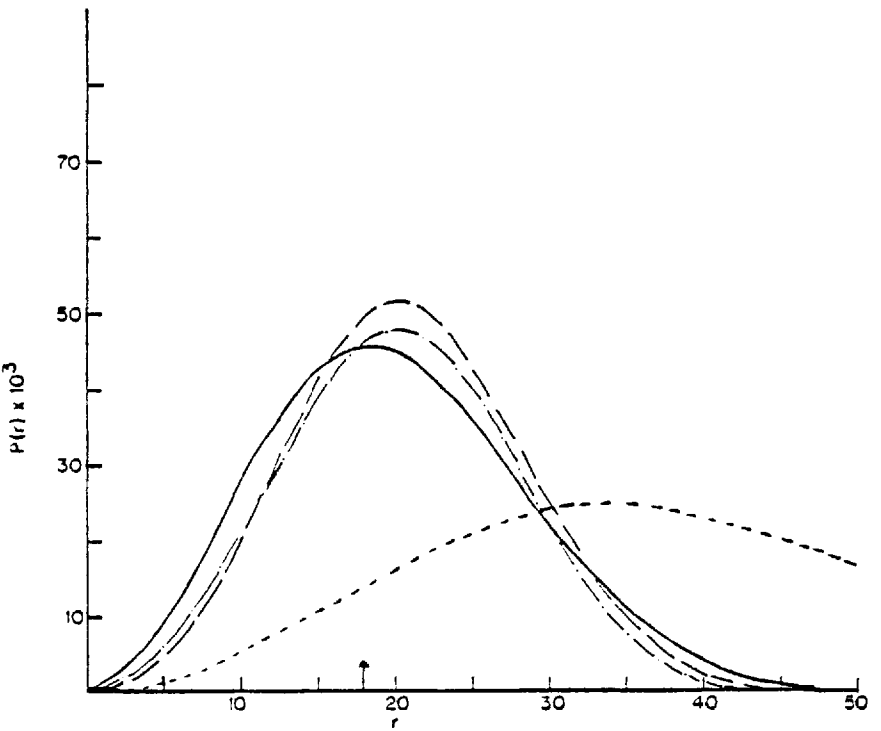

FIG. 1. Plot of radial distribution functions vs r (——) Gaussian, (— —) Domb et al., (- - -) Mazur, and (- -) Gray et al. functions. The arrow indicates the maximum point of the Gaussian function.

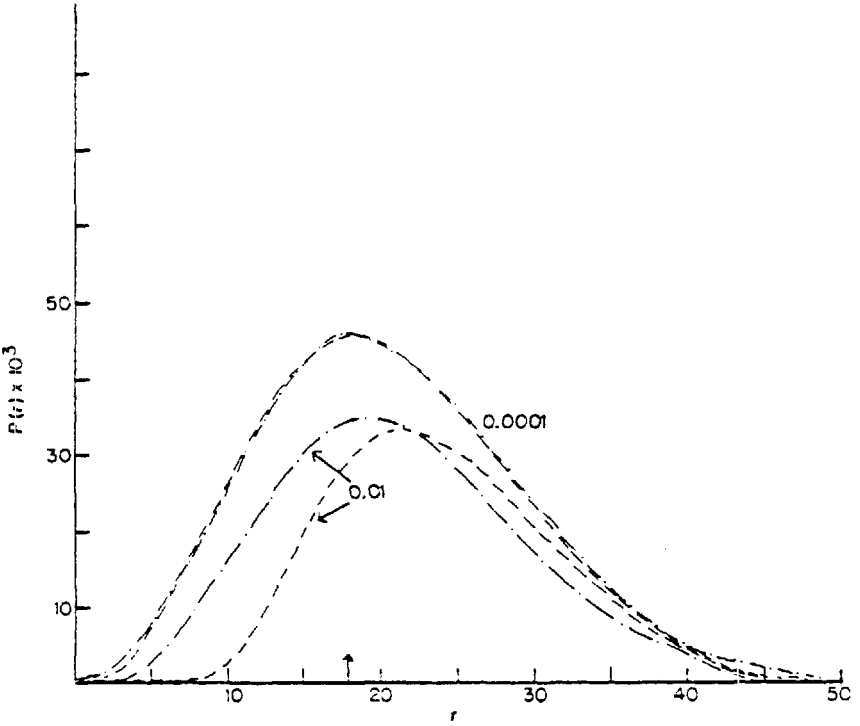

FIG. 2. Plot of distribution functions given in Eqs. (7) and (8) vs r for two values of k_1 and k_2 for (-·-) Reiss and (--) Kumbar functions. The arrow indicates the maximum point of the Gaussian function.

DISCUSSION

Figure 1 shows the radial distribution functions given in Eqs. (3), (4), and (5) for the same excluded volume parameter, $\epsilon = 0.2$. The Gaussian function has also been included in the same figure. The effect of excluded volume as described by these functions is clearly displayed. The Gaussian function has a bell shape and has the distribution maximum at the point indicated by the arrow on the abscissa. Domb et al. and Mazur functions retain the bell shape while shifting the distribution maximum toward greater r. The Domb et al. function is steeper than Mazur's function. However, both functions have their function maximum at the same point. The shift in the maximum point can be calculated by the difference between the function maximum

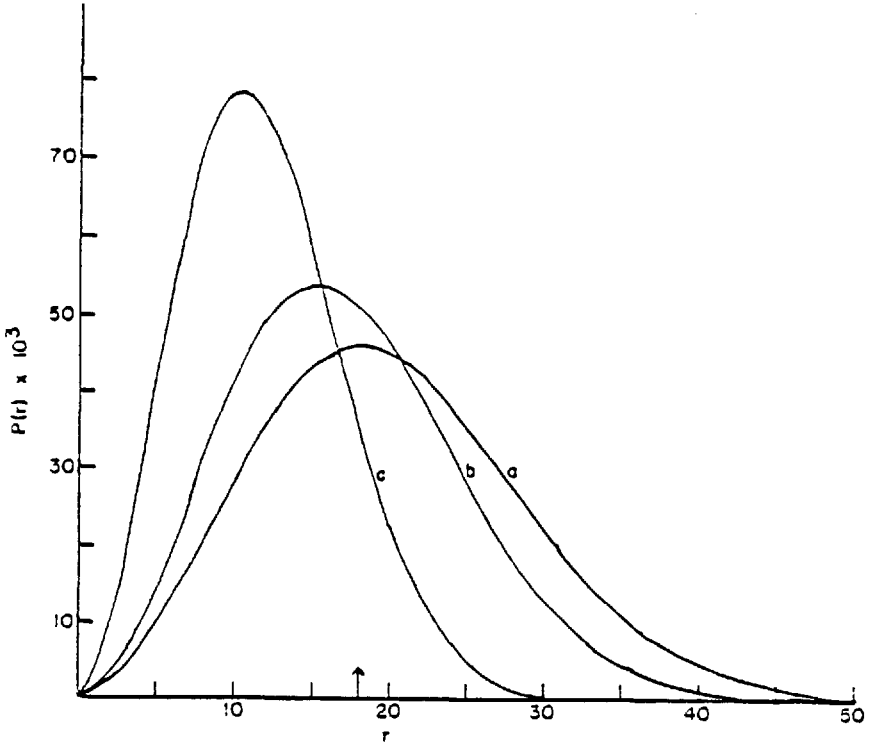

FIG. 3. Plot of Gaussian function ($\epsilon = 0$) vs r for various β values. (a) $\beta = 0$, (b) $\beta = 0.1$, and (c) $\beta = 0.5$. The arrow indicates the maximum point of the Gaussian function.

point and the Gaussian maximum point. For these functions the shift is very small. A further increase in ϵ has a similar effect on the distribution function. We have examined this effect on the Domb et al. function (Fig. 5a) for $\epsilon = 0.5$. The function is much sharper and the shift in the maximum is larger. The function of Gray et al. behaves much differently in the same range of r. First, this function is much flatter, and second, the shift in maximum is too large. It certainly does not retain the bell shape of the two previous functions. A further increase in ϵ makes the curve much flatter and shifts the maximum toward greater r (see Fig. 7a). Figure 2 describes the distribution functions given by Reiss and Kumbar for two values of k_1 and k_2. It is evident that the shape and the maximum point depend on these constants. For k_1 and $k_2 = 10^{-4}$, both functions have the same behavior,

which is very close to that of the Gaussian, as they should be. For a higher value, for example, k_1 and $k_2 = 10^{-2}$, these functions still retain the bell shape and shift the maximum point toward the right-hand side. However, the Kumbar function has a larger shift than the Reiss function.

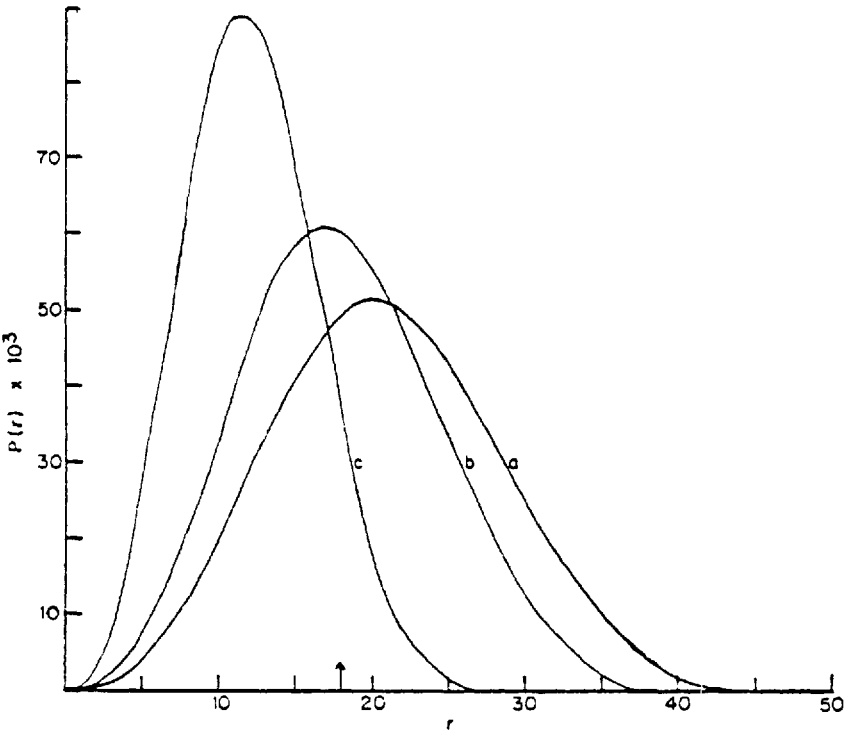

FIG. 4. Plot of Domb et al. function ($\epsilon = 0.2$) vs r for various values of β. (a) $\beta = 0$, (b) $\beta = 0.1$, and (c) $\beta = 0.5$. The arrow indicates the maximum point of the Gaussian function.

The effect of chain stiffness on the Gaussian function, the Domb et al. function, and the Gray et al. function has been investigated. Figure 3 describes the effect of chain stiffness on Gaussian function. As the stiffness increases, the function becomes much sharper and still retains the bell shape. Now the maximum point shifts toward lower r, which is just opposite to that of the excluded volume effect. Excluded volume functions in the presence of chain stiffness have

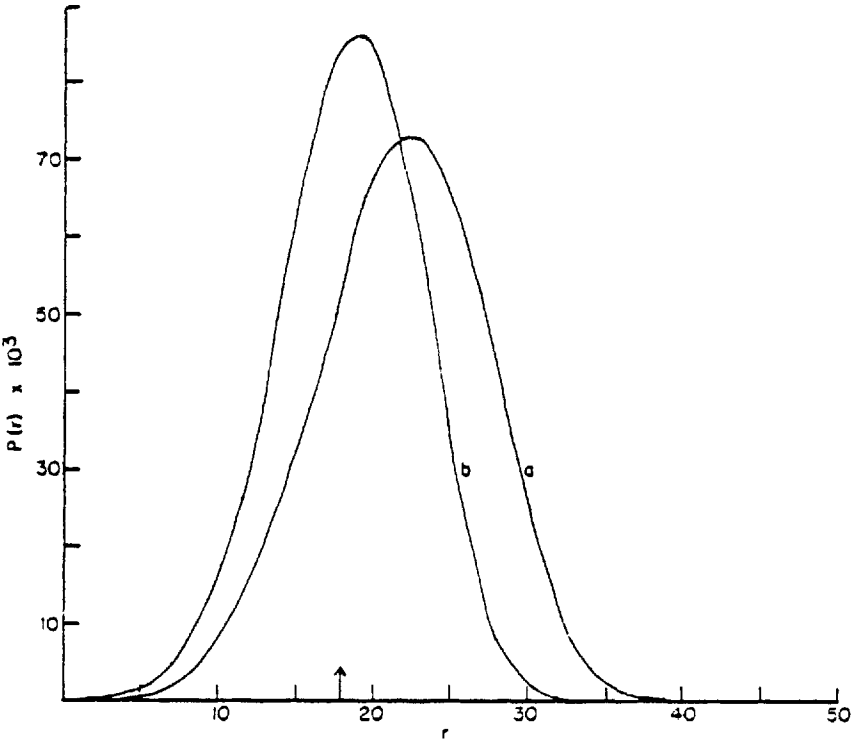

FIG. 5. Plot of Domb et al. function ($\epsilon = 0.5$) vs r for (a) $\beta = 0$ and (b) $\beta = 0.5$. The arrow indicates the maximum point of the Gaussian function.

the same behavior as has the Gaussian: Figs. 4 and 5 refer to the Domb et al. function while Figs. 6 and 7 refer to the Gray et al. function for two values of ϵ. We have not investigated the effect of chain stiffness on other functions. We assume that the behavior of these functions is very similar to that of the Domb et al. function.

The distribution function maximum for various functions can be calculated by using the formulas given in Table 1. It is clear that the maximum point depends on the excluded volume, chain stiffness, and bond length. The function shifts are also given in the same table. Table 2 shows the numerical values of shifts in the maximum for various functions.

From the above discussion it can be concluded that, among the five functions studied, only the Gray et al. function behaves

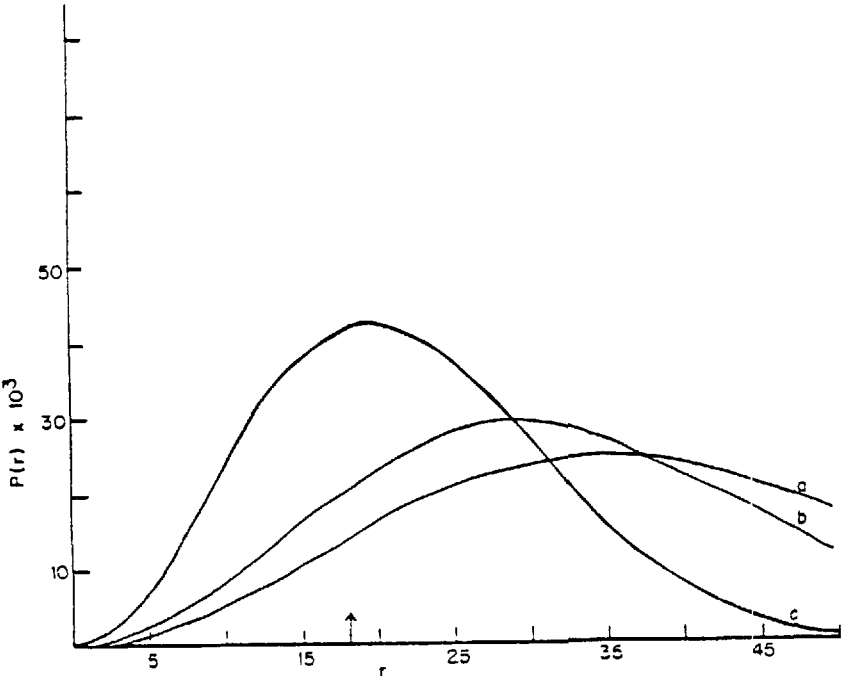

FIG. 6. Plot of Gray et al. function ($\epsilon = 0.2$) vs r for (a) $\beta = 0$, (b) $\beta = 0.1$, and (c) $\beta = 0.5$. The arrow indicates the maximum point of the Gaussian function.

differently. It does not retain the bell shape and has a relatively large shift in maximum point. The other four functions retain the bell shape and shift the maximum point relatively little. The maximum of the Domb et al. and Mazur functions lies above the Gaussian maximum, while that of Reiss, and Kumbar, and Gray et al. lies below the Gaussian maximum. It is not clear whether the bell shape is retained or not when the character is non-Gaussian. Except for the Gray et al. function, all other functions indicate that the bell shape is probably retained. Certainly all these functions agree that there is a shift in the maximum point toward greater r. The effect of chain stiffness makes the function much steeper and shifts the maximum toward lower r whether it is Gaussian or non-Gaussian. In the presence of high excluded volume, the stiffness has a greater effect as seen from

TABLE 1. The Distribution Function Maximum and the Shift in the Maximum Point for Various Functions

Function	Maximum point at	Shift in the maximum point $r_f - r_G$
Gaussian	$r_G = (2/3b^2 n)^{1/2}$	
Gray et al.	$r_f = (2/3b^2 n^{1+\epsilon})^{1/2}$	$(2/3b^2 n)^{1/2}\ (n^{\epsilon/2} - 1)$
Domb et al.	$r_f = (1/t)^{1/t}\left[b^2 n\,\Gamma\left(\frac{1+1}{t}\right)/\Gamma\left(\frac{1+3}{t}\right)\right]^{1/2}$	$(b^2 n)^{1/2}\left[(1/t)^{1/t}\left[\Gamma\left(\frac{1+1}{t}\right)/\Gamma\left(\frac{1+3}{t}\right)\right]^{1/2} - (2/3)^{1/2}\right]$
Mazur	$r_f = [2/tb^2 n\Gamma(3/t)/\Gamma(5/t)]$	$(b^2 n)^{1/2}\left\{\left[\frac{2}{t}\,\frac{\Gamma(3/t)}{\Gamma(5/t)}\right]^{1/2} - (2/3)^{1/2}\right\}$
Reiss	$r_f = 2(2b^2 n/9)^{1/2}\cos\left[\frac{1}{3}\cos^{-1}(k_1 n^{1/2}\,3^2/2^{5/2}b)\right]$	$(2b^2 n/3)^{1/2}\left\{\frac{2}{(3)^{1/2}}\cos\left[\frac{1}{3}\cos^{-1}\left(\frac{k_1 n^{1/2}\,3^2}{2^{5/2}b}\right)\right] - 1\right\}$

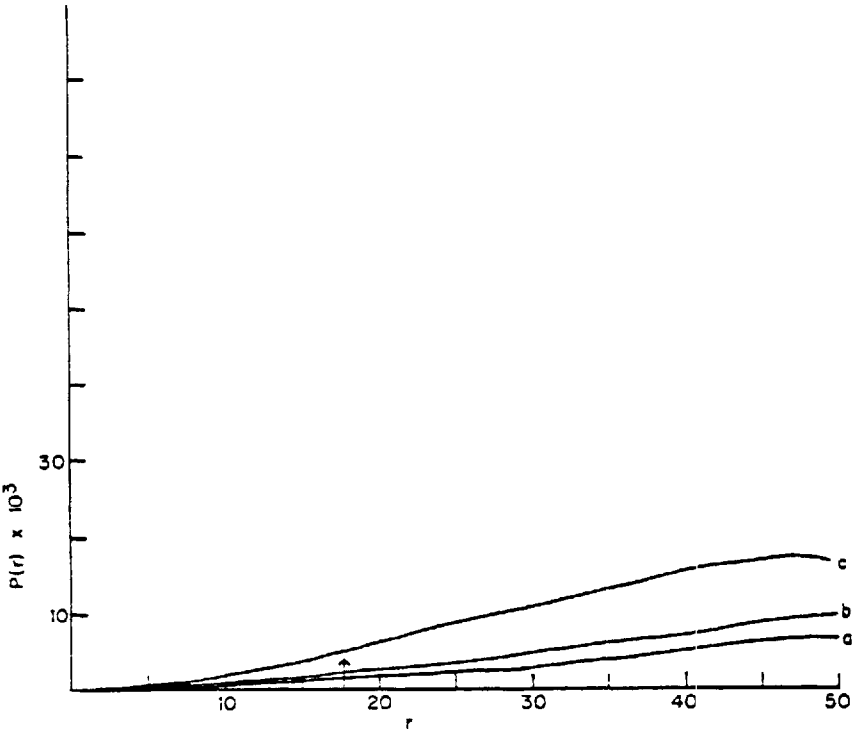

FIG. 7. Plot of Gray et al. function ($\epsilon = 0.5$) for (a) $\beta = 0$, (b) $\beta = 0.1$, and (c) $\beta = 0.5$. The arrow indicates the maximum point of the Gaussian function.

TABLE 2. Numerical Values of Shift in Maximum Points

Gaussian	ϵ		
β	0.0	0.2	0.5
0	0	12	68
0.1	-3	11	55
0.5	-7	2	22
Domb et al.			
0		2[a]	4
0.1		-1	1
0.5		-7	-

k	Reiss	Kumbar
10^{-2}	1	3
10^{-4}	0	0

[a]This shift also corresponds to that of Mazur when $t = 3.2$.

the sharpness of the curves which can be verified from Fig. 5. This can be viewed in terms of the greater role of stiffness when the chain is in a state of high expansion.

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