Calculations of the free conformation energy of a polymer chain on a diamond-type lattice within wide ranges of chain lengths, elongations and temperatures

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A method is proposed for calculating the partition function $Z(r)$ of a chain on a diamond-type lattice on the basis of the Monte Carlo algorithm for simulating a chain 'from point to point' with allowance made for the statistical weight factor of the conformation. The free energy is calculated for chains with the parameters of polyethylene, polytetrafluoroethylene, polyoxymethylene and poly(ethylene oxide), within a wide range of elongations for various chain lengths and temperatures. Allowance is made for the effect of the limiting planes on the free energy, which is characteristic for chains in amorphous regions of semicrystalline polymers. The accuracy of the proposed method is shown to rise with increasing elongations and decreasing chain lengths. A simple analytical approximation of the free chain energy is proposed for all the polymers examined.

(Keywords: Monte Carlo calculation; polymer chain; free conformation energy; end-to-end vector distribution; drawn semicrystalline polymer)

INTRODUCTION

The free conformation energy of chain molecules within wide ranges of lengths and elongations needs to be calculated in various fields of theoretical physics of polymers[1–3]. The free conformation energy of chains governs, to a substantial extent, the process of deformation and drawing of polymers[4,5], the thermokinetics of stress-induced crystallization, and the parameters of semicrystalline polymer structure[6,7].

The free energy of an elongated chain can be found if the end-to-end vector distribution $W(r)$ is known[1]. The function $W(r)$ has been studied theoretically in numerous works[1,8–16], but the applicability of the expressions obtained for $W(r)$ is restricted to high values of chain length and/or to low elongations. In two publications[1,8] the value of $W(r)$ is expressed as a series containing its even moments. The expression for the density of the distribution $W(r)$ obtained in ref. 9 contains both even and odd moments. This fact appears to reduce somewhat the number of highest moments necessary for calculating $W(r)$ within acceptable accuracy. However, the matrix method cannot be used as yet to calculate moments higher than the fourth moment, while the Monte Carlo method[9,14] cannot be used in practice if the number of chain units exceeds a few dozens.

In calculating the free energy of a polymer chain in amorphous regions of semicrystalline polymers account must be taken of the effect of the limiting surfaces of crystallites. In refs. 17–19 attempts have been made to take these limitations into account when calculating the chain entropy on a cubic lattice. However, no functional relationship between the entropy and the chain elongation have been obtained there and, in addition, the model used bore too remote resemblance to a real macromolecule.

The aim of the present work is to calculate and analytically approximate the free conformation energy of polymer chains within wide ranges of their lengths and elongations with allowance made for the effect of the limiting surfaces.

METHOD OF CALCULATION

The free conformation energy of a macromolecule with fixed ends has been calculated using the algorithm for simulating a chain 'from point to point' by the Monte Carlo method[20] with allowance made for the statistical weight of the conformation[21]. A polymer molecule has been simulated as a series of random walks within a body-centred cubic (b.c.c.) lattice, where each time, out of eight feasible directions of a step, the three directions corresponding to the *trans* and *gauche* conformers of the chain molecule and having the statistical weights:

$$P_l = \exp(-E^l/RT)$$

have been allowed. In the above-mentioned formula E^l are energies of the conformers of a given polymer[1,22] (see *Table 1*).

In the case where all directions on a b.c.c. lattice are allowed, according to ref. 20 the probability of selecting a step with vector $\boldsymbol{\delta}^l$ on condition of arriving after n steps at a prescribed point spaced $\Delta\mathbf{r}$ from the current point is equal to:

$$w_n(\boldsymbol{\delta}^l) = \prod_{j=1}^{3} \frac{n - \Delta r_j \delta_j^l}{2n}$$

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Considering the above-mentioned restrictions on the allowed conformations, this probability is equal to[23]:

$$\tilde{w}_n(\delta^l)=\frac{w_n(\delta^l)P_l}{q_n} \tag{1}$$

where

$$q_n=\sum_{l=1}^{3} w_n(\delta^l)P_l \tag{2}$$

is the Rosenbluth factor of a chain unit. The probability W_i of occurrence of the ith chain conformation with the given simulation method and its statistical weight Q_i are equal to[21,23]:

$$W_i=\prod_{n=1}^{N}\tilde{w}_n^i \quad \text{and} \quad Q_i=\prod_{n=1}^{N} q_n^i \tag{3}$$

It can readily be seen from (1)–(3) that:

$$W_iQ_i=(1/\Gamma)\exp(-E^i/RT)$$

where E^i is the energy of the ith conformation of the entire chain; and Γ is the total number of conformations on a b.c.c. lattice for a chain with ends space r apart, which is known to be:

$$\Gamma=\prod_{j=1}^{3}\frac{N!}{[\frac{1}{2}(N-r_j)]![\frac{1}{2}(N+r_j)]!}$$

Assume that there are Γ_m conformations of statistical weight Q_m. Obviously, the probability of occurrence of any of the conformations is:

$$P_m=\sum_{i=1}^{\Gamma_m} W_i=\frac{1}{\Gamma Q_m}\sum_{i=1}^{\Gamma_m}\exp\left(-\frac{E^i}{RT}\right)$$

Then:

$$\bar{Q}=\sum_m Q_mP_m=\frac{1}{\Gamma}\sum_m\sum_{i=1}^{\Gamma_m}\exp\left(-\frac{E^i}{RT}\right)=\frac{Z(r)}{\Gamma}$$

where $Z(r)$ is the partition function of the chain with fixed ends. The free conformation energy of such a chain is:

$$F=-RT\ln(\Gamma\bar{Q}) \tag{4}$$

Chains of lengths N ranging from 6 to 5000 units have been examined. An ensemble of S chains of the same length with a preset distance between its ends has been simulated. In the case of short chains $S=(3\text{–}5)\times 10^3$, while in the case of long chains ($N=1000\text{–}5000$), $S=200$. The mean statistical weight of the conformation has been estimated to be equal to:

$$\bar{Q}=S^{-1}\sum_{i=1}^{S} Q_i$$

with the mean-square error of the estimate being equal to:

$$\sigma(\bar{Q})=[S^{-1}D(Q)]^{1/2} \tag{5}$$

where $D(Q)$ is the statistical weight variance:

$$D(Q)\approx S^{-1}\sum_{i=1}^{S} Q_i^2-\left(S^{-1}\sum_{i=1}^{S} Q_i\right)^2$$

The absolute error in finding the free energy is, considering (4) and (5), equal to:

$$\Delta F\approx RT\bar{Q}^{-1}[S^{-1}D(Q)]^{1/2}$$

The reliability of estimating the error in the free energy depends on the accuracy with which $D(Q)$ has been found. The spread of the Q_i values within the ensemble is very large. For example, $-36\leqslant\lg Q_i\leqslant -18$ for zero end-to-end distance r in a 30-unit chain and $-675\leqslant\lg Q_i\leqslant -648$ in a 1000-unit chain. As the elongation increases, the spread of the values of Q_i decreases sharply. However, in any case several peak values of Q_i make a significant contribution in the estimation of $\bar{Q}$ and $D(Q)$. It is evident that, the greater the ratio:

$$N_{\mathrm{eff}}=Q_{\max}^{-1}\sum_{i=1}^{S} Q_i$$

the greater is the reliability of the estimates. Since:

$$Q_{\max}^{-2}\sum_{i=1}^{S} Q_i^2<Q_{\max}^{-1}\sum_{i=1}^{S} Q_i$$

it can be written that:

$$D(Q)<Q_{\max}^2N_{\mathrm{eff}}S^{-1}(1-S^{-1}N_{\mathrm{eff}})<Q_{\max}^2N_{\mathrm{eff}}S^{-1}$$

Hence:

$$\Delta F<RTN_{\mathrm{eff}}^{-1/2} \tag{6}$$

In the present calculations the value of N_{eff} has been varied from a few units in the case of long chains to a few dozens and hundreds in the case of medium and short chains. The value of N_{eff} increases with increasing degree of chain elongation, i.e. the reliability of the calculation increases with increasing elongation and decreasing chain length. This fact offers a fundamental advantage of the present calculation method as compared with the analytical and numerical techniques used elsewhere[1,8–19].

As is normally assumed[24], the large spread of the statistical weights Q_i in the Rosenbluth method[21] does not allow an ensemble-averaged value of one or another physical parameter:

$$\bar{X}=\left(\sum_{i=1}^{S} Q_i\right)^{-1}\sum_{i=1}^{S} Q_iX_i$$

to be estimated with low error. Indeed, it can be easily shown that the relative mean-square error is:

$$\sigma(\bar{X})/\bar{X}\sim N_{\mathrm{eff}}^{-1/2}\gg S^{-1/2}$$

However, the free energy is proportional to the logarithm of Q, which means that, according to (6), its absolute error is approximately equal to $N_{\mathrm{eff}}^{-1/2}$ and the resultant relative error proves to be quite satisfactory.

The computer simulation has been made for chains with ends fixed at two sites (a segment in a network), fixed on two parallel planes (tie chains in the amorphous interlayer of a fibril) and fixed on a single plane (loops in an amorphous region) (see *Figure 1*).

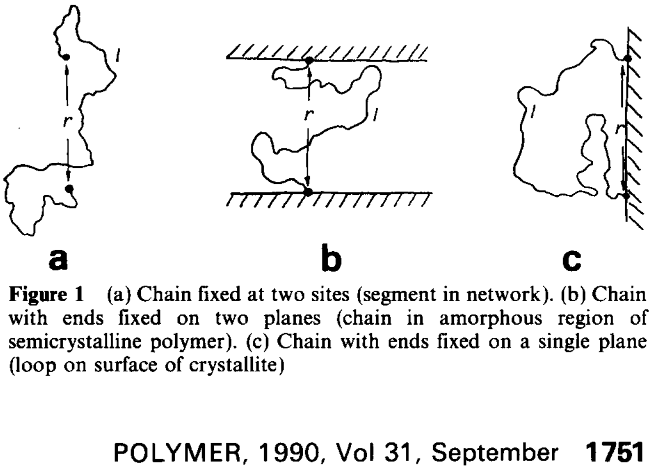

Figure 1 (a) Chain fixed at two sites (segment in network). (b) Chain with ends fixed on two planes (chain in amorphous region of semicrystalline polymer). (c) Chain with ends fixed on a single plane (loop on surface of crystallite)

Table 1 Parameters of investigated polymers

	Polymer	T_m^{25} (K)	T_g^{26} (K)	E_G^{1} (J/mol CH$_2$)	E^{*1} (J/mol CH$_2$)	$C_\infty^{1,22}$ ($C_n = r^2/nl^2$)
PE	$-CH_2-CH_2-$	414	203	2100	8380	6.87 at 413 K
PTFE	$-CF_2-CF_2-$	600	123	4620	∞	11.00 at 600 K[a]
POM	$-O-CH_2-$	470	213	−6300	7650	7.50 at 363 K
PEO	$-O-CH_2-CH_2-$	342	213	−1800 (3800)	1500 (∞)	4.50 at 313 K

[a] Ref. 22 presents the results of calculation of C_∞ for PTFE chains for models with three and four rotational isomers. For the first model $C = 11 \pm 2$, for the second model $C = 30 \pm 15$. Only the model with three rotational isomers is consistent with the diamond-type lattice

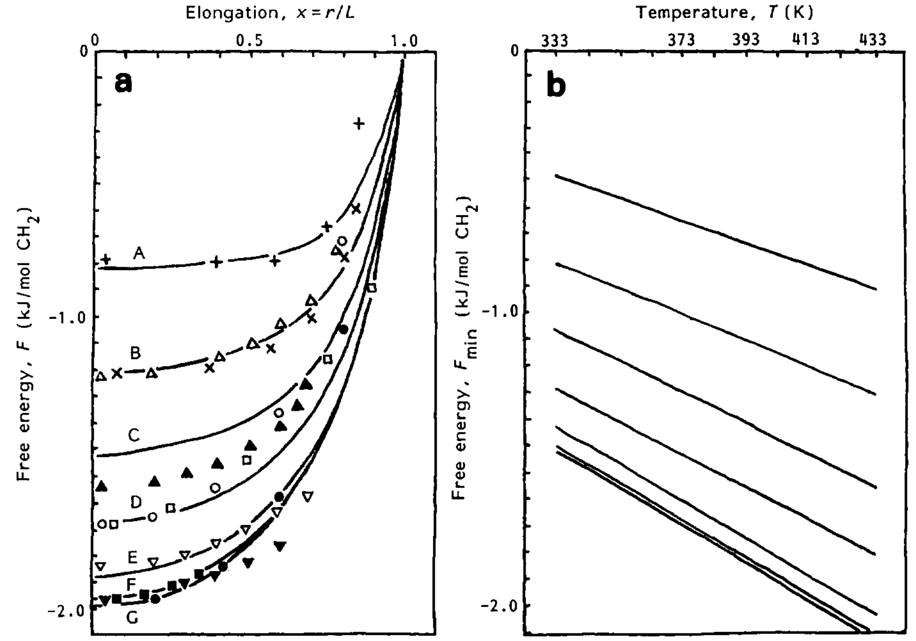

Figure 2 Free conformation energy of chains fixed at sites as a function of the elongation $x = r/L$, at $T = 413$ K. The number of chain units $N = 20$ (A), 30 (B), 50 (C), 100 (D), 300 (E), 1000 (F) and 5000 (G). For comparison, the figure also presents other results: ref. 1 for $N = 50$ (△), 100 (▲), 300 (▽) and 1000 (▼); ref. 10 for $N = 100$ (○) and 5000 (●); ref. 11 for $N = 100$ (□) and 1000 (■); ref. 12 for $N = 20$ (+) and 30 (×). (b) Variations of minimum free energies $F_{\min}$ with temperature for the same chains as in (a)

Several polymers with different conformation properties, namely polyethylene (PE), polytetrafluoroethylene (PTFE), polyoxymethylene (POM) and poly(ethylene oxide) (PEO), have been selected for examination. The chains of these polymers may be simulated, with minor distortions, by random walks in a diamond-type lattice. *Table 1* shows the energies E_G of *gauche* '±' conformers relative to the *trans* conformer energies, as well as the additional energies E^* of crossed sequence of *gauche* conformers $\cdots G^+G^- \cdots$ of various polymers. The infinite values of E^* correspond to forbidden crossed sequences of the $\cdots G^+G^- \cdots$ type. The difference in the conformation properties appears to be caused by differences in the polymer energies E_G and E^*.

RESULTS OF MONTE CARLO CALCULATIONS

Figure 2a shows the variation of the free energy for PE chains with ends fixed at sites as a function of the elongation $x = r/L$ at a temperature of 413 K (r = end-to-end distance, L = contour length of the chain). Within the region of small elongations the results shown in *Figure 2a* may be compared with the results obtained elsewhere[1,10–12]. The results presented in ref. 1 by Flory permit approximate calculations of the absolute value of the free conformation energy of a PE chain allowing for the fourth moment of the distribution density $W(r)$. The values of the free energies at $x = 0$ obtained in the present paper differ from those calculated with formula (8.76) of ref. 1 by about 20% in the case of a chain with $N = 50$, whereas both calculations yield the same results in the case of a chain with $N = 1000$. It should be noted that the accuracy with which the free energy is calculated with formula (8.76) of ref. 1 appears to fall rapidly with decreasing number of chain units because of a greater contribution from unaccounted higher moments of the distribution density. The results obtained[10–12] enable the calculation of only the relative values of the free energy. In *Figure 2a* these values are calculated from the absolute values of the free energy obtained by us at $x = 0$.

Thus, within the region of long chains and small elongations, which is least favourable for our method, the results obtained in refs. 1, 10–12 are in good agreement with our results. This offers good reason to expect that within the region of large elongations and short chains, where, as noted above, the calculation accuracy is higher, the results obtained by us are quite reliable.

The results of the calculations have shown that the values:

$$\varepsilon(x, N) = F(x; N, T)|F_{\min}(N, T)|^{-1}$$

are practically independent of temperature in the examined interval of 333 to 433 K for chains having more than 20 chain units. Here, $F(x; N, T)$ is the free energy of the chain as a function of elongation $x = r/L$, number of chain units N and temperature T, and $F_{\min}(N, T)$ is the minimum value of $F(x; N, T)$ at constant N and T. Within a wider temperature interval, ε is found to be affected weakly by temperature (see *Figure 5*). In such a case the following approximation, accurate within about 3% at all $N \geqslant 20$ and $0 \leqslant x < 1$, may be suggested:

$$\varepsilon(x, N) = \alpha + \beta \exp(\gamma x^2) \tag{7}$$

where $\gamma = 2.348 + 83.5N^{-1.363}$, and α and β are obtained from the conditions $\varepsilon(0, N) = -1$, $\varepsilon(1, N) = 0$ and are equal to:

$$\beta^{-1} = \exp(\gamma) - 1, \qquad \alpha = -1 - \beta$$

The variation of $F_{\min}$ with N and T (see *Figure 2b*) can be described by the following empirical formula:

$$F_{\min}(N, T) = 1192 - (7.1625 - 40N^{-0.89})(T + 50) \quad (\mathrm{J/mol\ CH_2})$$

Of course, the values of $F_{\min}(N, T)$ can be calculated using the expressions for the end-to-end vector distribution $W(r)$ and for the unrestricted partition function Z of the chain presented in ref. 1. As is noted above, however, the error in calculating $F_{\min}(N, T)$ increases greatly in the case of short chains, and at elongations $r\langle r^2\rangle_0^{-1/2} \geqslant 1.6$ the expression for $W(r)$ is completely incorrect, thereby certainly affecting the value of $W(r = \mathbf{0})$ through the normalization $1 = \int_0^1 4\pi r^2 W(r)\,\mathrm{d}r$ and, consequently, the value of the minimum free energy $F_{\min}(N, T)$.

Figure 3 presents the results of the calculations performed for PE chains with ends fixed on two parallel planes (*Figure 1b*). Chains of lengths varying within $30 \leqslant N \leqslant 2000$ have been examined in the temperature interval of 333 to 413 K. Except for the region of weak elongations, where the chain is subjected to strong compression by the limiting planes, the curves representing the free energy $F(x; N, T)$ as a function of elongation x, number of chain units N and temperature T coincide with similar curves for the chains fixed at sites. It is not difficult to indicate the region where this approximation is valid: the distance between the planes should be greater than the mean-square end-to-end distance for unperturbed chain $r > \langle r^2\rangle_0^{1/2}$; equality of the distances corresponds to the minimum of the free energy (see *Figure 3*).

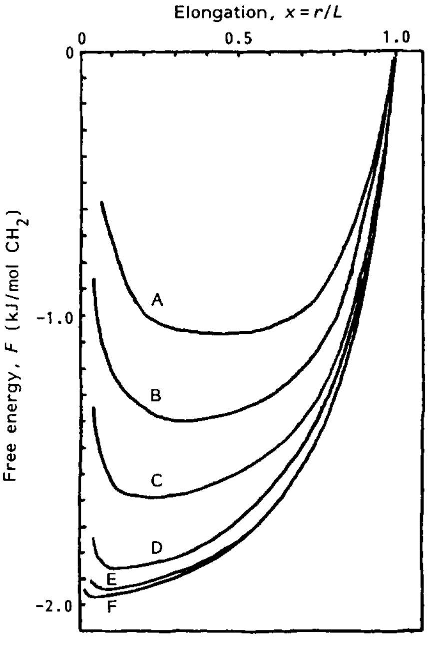

Figure 3 Free conformation energy of chains fixed on two planes as a function of elongation $x = r/L$, at $T = 413$ K. The number of chain units $N = 30$ (A), 50 (B), 100 (C), 300 (D), 1000 (E) and 2000 (F)

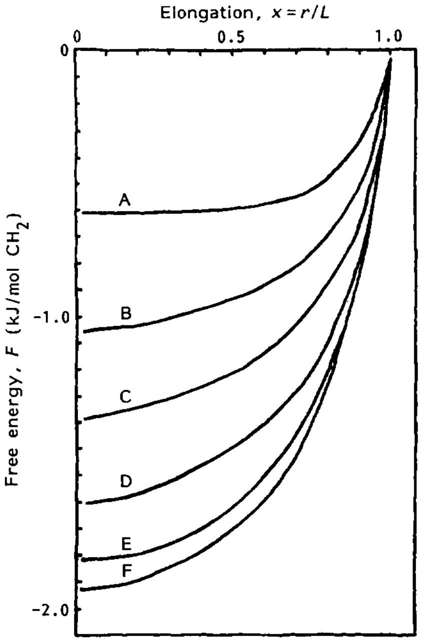

Figure 4 Free conformation energy of chains fixed to a single plane as a function of elongation $x = r/L$, at $T = 413$ K. (Curves A–F are the same as in *Figure 2a*.)

The results presented correspond to the case where the projections of the points in which the chain ends are fixed onto the plane of crystallites coincide, i.e. the end-to-end vector of the chain is perpendicular to the planes. Additional examination has show that at inclination angles of up to 40° the effect of the angle of end-to-end vector inclination to the planes on the free energy may be neglected.

Figure 4 shows the results obtained for chains fixed on one plane at $T = 413$ K. PE chains of $20 \leqslant N \leqslant 1000$ have been examined within the interval 333 to 413 K. In this case the function:

$$\varepsilon(x, N) = F(x; N, T)|F_{\min}(N, T)|^{-1}$$

can also be approximated by expression (7), but the least free energies here are higher than in the case of chains fixed at sites. For $F_{\min}$ the following empirical formula may be proposed:

$$F_{\min}(N, T) = 1035 - (7.1625 - 36N^{-0.79})(T + 28)$$

From *Figure 5* it is seen that the reduced free energies $\varepsilon(x, N)$ for various types of chains with N varying from 30 to 5000 differ from one another by not more than 6–7%. If we limit ourselves to such an accuracy, the expression (7) approximating $\varepsilon(x, N)$ may be simplified if the effect of N can be neglected:

$$\varepsilon(x) = \alpha + \beta \exp(\gamma_0 x^2) \tag{8}$$

$$\gamma_0 = 2.354, \qquad \beta^{-1} = \exp(\gamma_0) - 1, \qquad \alpha = -1 - \beta$$

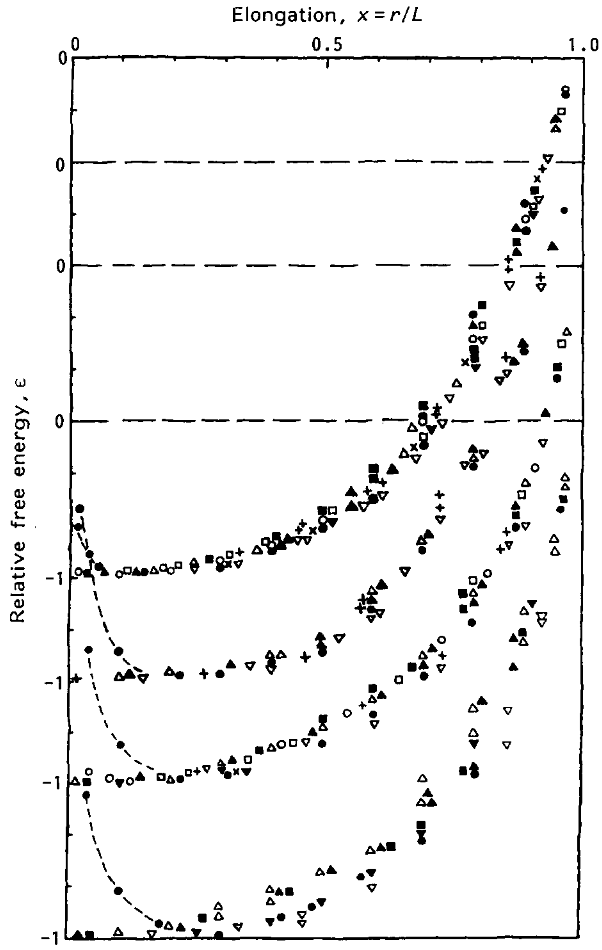

Figure 5 Reduced free energy of chains $\varepsilon(x, N)$ as a function of elongation (at various N and T) for four investigated model chains with the parameters of PE, PTFE, POM and PEO. Chains with ends fixed on two planes: $N=1000$ (○) and 100 (●). Chains with ends fixed to a single plane: $N=1000$ (□), 100 (■), 30 (+) and 20 (×). Chains fixed at sites: $N=1000$ (△), 100 (▲), 30 (▽) and 20 (▼). The temperature intervals are 273–470 K (POM), 273–342 K (PEO), 333–413 K (PE) and 273–600 K (PTFE). In the cases where curves $\varepsilon(x, N)$ do not coincide at different temperatures, the higher values of $\varepsilon(x, N)$ correspond to lower temperatures

In finding the value of γ_0 ensuring the best approximation the chains with $N \geqslant 1000$ have been examined.

This approximation possesses one remarkable property: at small values of x it coincides with the reduced free conformation energy of a long equivalent Gaussian chain. For the Gaussian chain[1-3]:

$$F(r) = F(0) + \frac{3}{2}\frac{r^2}{Nl_n^2}$$

where l_n is the length and n is the number of equivalent segments. Considering that:

$$nl_n = Na \sin\theta$$

$$nl_n^2 = C_N Na^2$$

where 2θ is the valence angle of PE carbon chain, C_N is the characteristic ratio for an N-unit chain and having in mind that for a long chain:

$$F_0 = -RT \ln Z_0$$

where Z_0 is the partition function of the unperturbed rotational isomeric model of the chain (formula (3.40) from ref. 1), we shall obtain for the long Gaussian equivalent chain:

$$E_G = -1 + \frac{3}{2}\frac{N \sin^2\theta}{C_\infty \ln Z_0} x^2 \tag{9}$$

For small values of x expression (9) shall be valid for a sufficiently long chain of any polymer. Equating (8) and (9) and expanding the exponent in (8) into a series to a second-order infinitesimal gives:

$$\frac{\gamma_0}{\exp(\gamma_0) - 1} = \frac{3}{2}\frac{N \sin^2\theta}{C_\infty \ln Z_0} \tag{10}$$

If we take the values of θ, C_∞ and Z_0 for the rotational isomeric model of the PE chain with correlated rotation (formula (3.40) from ref. 1) it is not difficult to check that the solution of this equation is $\gamma_0 = 2.38$, i.e. a value nearly equal to that obtained from the approximate Monte Carlo calculation results.

Figure 5 represents the results of Monte Carlo calculations for chains on a diamond lattice with the parameters of POM, PEO and PTFE for various N and T and under various constraints. Just as in the case with PE the type of constraint imposed on the chain (fixed end-to-end distance, fixing the ends of the chain on a plane or on two parallel planes spaced $r \geqslant \langle r^2 \rangle_0^{1/2}$ apart) has no noticeable effect on the reduced free energy $\varepsilon(x, N)$. In the case of loops (see *Figure 1*) the minimum free energies are somewhat higher than in the case of chains with fixed ends. Limiting ourselves to the accuracy of 6–7%, within the intervals of temperature of 400 to 600 K for PTFE, 370 to 470 K for POM and 273 to 342 K for PEO, the effect of N and T on the reduced free energy can be neglected and the latter can be considered to be a function of elongation x alone.

Approximation (8) for $\varepsilon(x)$ can be applied as well to chains with the parameters of PTFE, POM and PEO, with the results of the approximation being closest to the results of the Monte Carlo calculations at γ_0, which are essentially the solution of equation (10) with corresponding parameters C_∞ and Z_0.

The values of γ_0 obtained for all the polymers that have been examined are tabulated in *Table 2*.

As is seen from *Figure 6*, expression (8) for $\varepsilon(x)$ yields results much closer to the results of the Monte Carlo calculations than formula (9) and the expression for the reduced conformational free energy $\varepsilon(x)$ of the equivalent freely jointed chains obtained on the basis of $\mathscr{L}^*$ distribution[1]:

$$\varepsilon_{\mathscr{L}^*}(x) = -1 + \frac{1}{RT \ln Z_0} \int_0^{xNl_n} f(r)\,\mathrm{d}r$$
$$f(r) = \left(\frac{RT}{l_n}\right) \int_0^r \mathscr{L}^*\left(\frac{r'}{Nl_n}\right) \mathrm{d}r' \tag{11}$$
$$x = \frac{r}{Nl_n}$$

Table 2 Parameters of approximations (8) and (9)

Polymer	γ_0	γ'_0	γ'_3
PE	2.354	0.589	1.011
PTFE	2.212	0.272	1.021
POM	1.728	0.098	0.581
PEO	2.092	5.005	−2.072

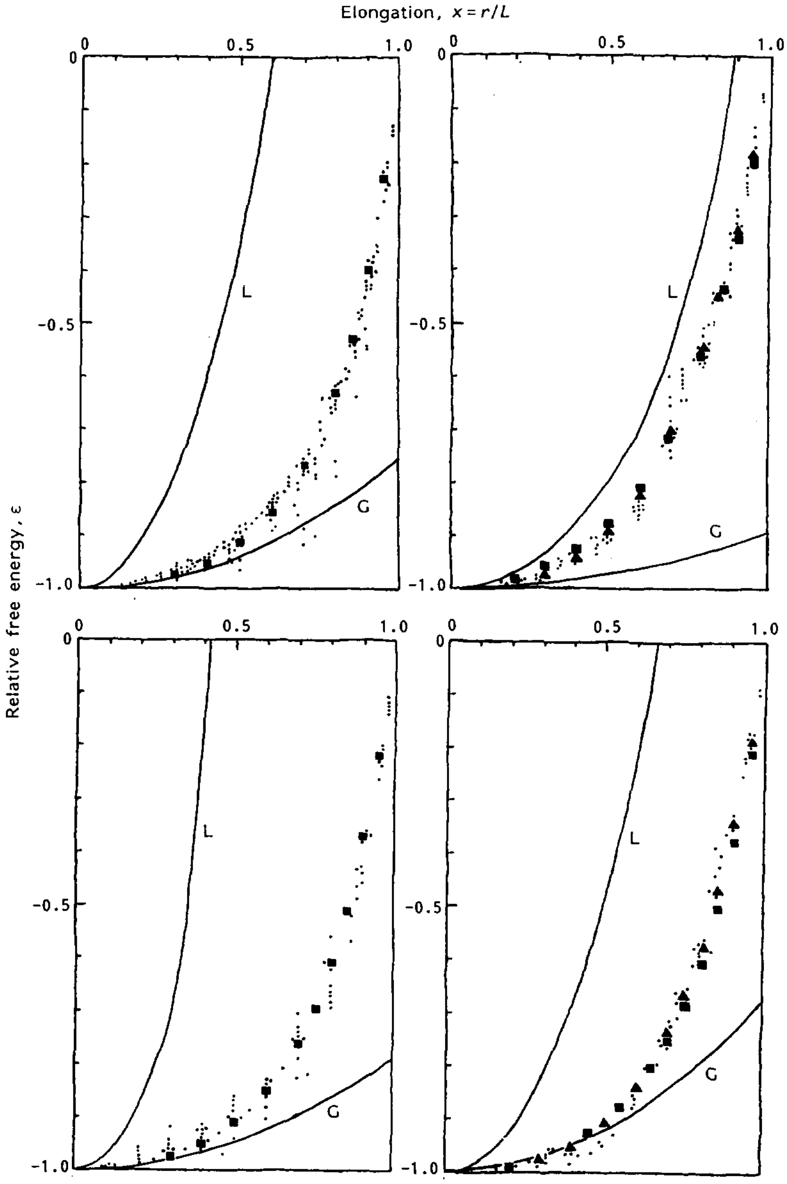

Figure 6 Reduced free energy $\varepsilon(x)$ as a function of elongation x: (●) obtained in simulation (correspond to *Figure 5*); (■) calculated from formula (8); (▲) calculated from formula (8a); curve G, calculated from formula (9); curve L, calculated from formula (11)

However, it should be noted that, whereas in the cases of PE and PTFE, approximation (8) may be regarded as quite satisfactory, in the case of PEO and particularly in the case of POM it shows systematic deviations from the results of the Monte Carlo calculations in the range of medium values of elongation x.

In order to eliminate these deviations one more member has been added in formula (8):

$$\varepsilon(x) = \alpha' + \beta' \exp(\gamma_0' x^2 + \gamma_3' x^3)$$
$$(\beta')^{-1} = \exp(\gamma_0' + \gamma_3') - 1, \qquad \alpha' = -1 - \beta' \tag{8a}$$

The requirement of the correct asymptotic approach of $\varepsilon(x)$ for long chains at $x \to 0$ expression (9) gives the following equation:

$$\frac{\gamma_0'}{\exp(\gamma_0' + \gamma_3') - 1} = \frac{3}{2} \frac{N \sin^2 \theta}{C_\infty \ln Z_0} \tag{10a}$$

from which both of the parameters γ_0' and γ_3' can no longer be determined. The second equation necessary for this determination may be obtained from the requirement of a minimum of the sum of squares of the deviations of approximation (8a) for the results of the Monte Carlo calculation. The coefficients thus obtained (γ_0' and γ_3') are presented in *Table 2* and the corresponding curves $\varepsilon(x)$ are shown in *Figure 6*.

Thus, expressions (8) and (8a) well approximate the results of the Monte Carlo calculations within a wide range of elongations, chain lengths and temperatures. However, in the cases of very short chains and/or lower temperatures, function $\varepsilon(x)$ shows great changes in shape. *Figure 7* shows functions $\varepsilon(x, N)$ for certain short chains of various polymers. It is clearly seen that the free energy minimum shifts from the point $x = 0$ into the region of medium elongation. A similar result has been obtained for PE chains in ref. 12. This fact means actually that the best way for the subchain is to straighten out. This conclusion looks quite natural for PE, PTFE and PEO whose *gauche* conformer energy is higher than the *trans* conformer energy. The shorter the chain, the higher is

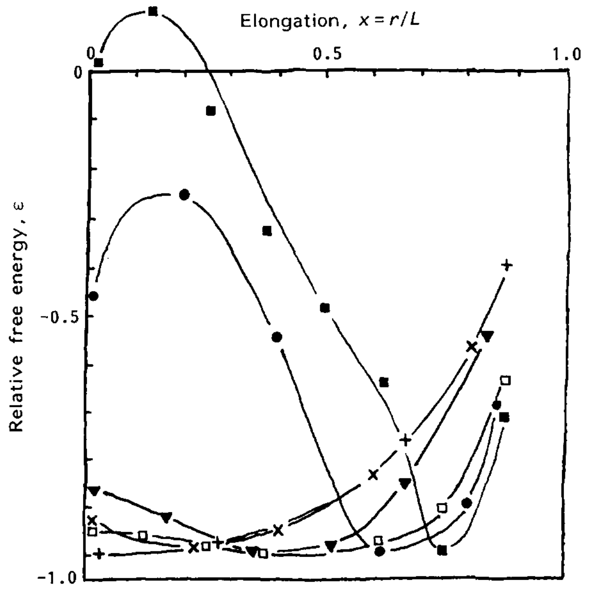

Figure 7 Reduced free energy $\varepsilon(x, N)$ of short chains as a function of elongation $x = r/L$: (■) PE, $N = 16$, $T = 203$ K; (□) PE, 16,413; (●) PTFE, 10,600; (▼) PEO, 12,342; (+) POM, 6,470; (×) POM, 10,213

the temperature at which the shift of a minimum of $\varepsilon(x, N)$ is observed. In chains longer than $N = 20$ units in PE and PEO and $N = 100$ units in PTFE this effect is not observed even at the glass temperature. In the case of POM, where the most advantageous is the *gauche* conformation (see *Table 1*), even at the glass temperature the minimum shifts only for very short chain with $N = 10$ chain units. At higher temperatures the approximation (8a) is valid for chains with $N \geqslant 6$.

The analytical expressions obtained for the free energies of subchains can be used for theoretical analysis of the processes of deformation, orientation and crystallization of polymers. The method proposed is applicable for calculating the free energy of polymer chains whose conformations are consistent with the diamond-type or b.c.c. lattice (higher polyoxyalkanes, vinyl polymers, etc.).

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