Monte Carlo Simulation of Tetrahedral Chains. 1. Very Long (Athermal) Chains by Pivot Algorithm

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ABSTRACT: By use of a dynamic Monte Carlo method, known as wiggle or pivot algorithm, chains of chain length N up to 10 000 segments are generated on a tetrahedral lattice. A new chain is obtained by rotating one part of a chain around a randomly selected bond by ±120°. If segments of the transformed subchain overlap with segments of the second (unmoved) part, the new chain is rejected and the old one retained. The starting configurations usually were prepared from an all-trans configuration by equilibrating except for short chains where they were generated using a simple step-by-step procedure. The most important results are as follows: The exponent α in the power law describing the decrease of the acceptance fraction f with increasing number of bonds $n = (N - 1)$, $f \sim n^{-\alpha}$, equals 0.1146. The position-dependent acceptance fraction, $f(x)$, roughly may be approximated by $f(x) = [x(1 - x)n]^{-\alpha}$, x being the length of the shorter subchain divided by n. By use of a simple double-logarithmic plot (in the range $100 \leq N \leq 10\,000$), the critical exponent in the scaling relation of the mean-square end-to-end distance $\langle h^2 \rangle \sim n^{\nu'}$ was estimated as $\nu' = 1.1802$, and for the mean-square radius of gyration $\langle s^2 \rangle \sim n^{\nu''}$ a value $\nu'' = 1.1832$ was found. These values are not equal and slightly exceed those predicted by renormalization group theory ($\nu' = \nu'' = \nu = 1.176$). This is in full accordance with other recent Monte Carlo results. However, taking into account a correction ($C_0 + C_1 n^{-\Delta}$) to n^ν and using $\nu = 1.176$ and $\Delta = 0.47$ as proposed by renormalization group theory, $\langle h^2 \rangle$ and $\langle s^2 \rangle$ may be very well described by $\langle h^2 \rangle = n^\nu(4.367 - 0.982n^{-\Delta})$ and $\langle s^2 \rangle = n^\nu(0.698 - 0.242n^{-\Delta})$.

1. Introduction

Among the various Monte Carlo methods available to produce self-avoiding walks (for a review see, for instance, ref 1) a very efficient procedure is the so-called pivot[2] or wiggle[3] algorithm, originally invented by Lal.[4] Concerned with chains on a two-choice, plane hexagonal lattice he described the following dynamic Monte Carlo method: (1) Divide any chain randomly into two parts. (2) Form the mirror image (across the line passing through the bond between the two parts) of the first part. (3) Build a new chain from the mirror image and the second part. (4) Perform a Metropolis–Rosenbluth test,[5] which in the athermal case degenerates to the simple rule: Accept the new chain if the excluded-volume condition is not violated; otherwise, discard it and retain the old one. An analogous mechanism for off-lattice chains was developed by Stellman and Gans,[6] for tetrahedral chains by Clark and Lal,[7] and for chains embedded in the square and cubic lattice by MacDonald et al.[3] Madras and Sokal,[2] in a very careful and thorough paper, gave an analytic analysis of the pivot algorithm for ordinary (non-self-avoiding) walks and a detailed discussion of numeric results on self-avoiding walks in square and cubic lattice, including a rigorous proof of the ergodicity of the pivot algorithm. In this paper the pivot algorithm is applied to the tetrahedral lattice. First of all, computational details are briefly described, and the acceptance fraction as a function of chain length and pivot position is discussed. Then, the autocorrelation functions of several properties characteristic of global and local structure are presented and the resulting (integral) autocorrelation times are compared with those obtained by block averaging. Finally, estimates for the critical exponents in the scaling relations of mean-square dimensions are given for chains of a chain length up to 10 000 segments.

It should be mentioned that, for many years,[8] ensembles of self-avoiding chains—to be used by our group in the study of the pair distribution functions and related properties—are generated by pivot algorithm, both for cubic and for tetrahedral[9] lattice chains.

2. Simulation Method

The procedure closely follows Lal's schema[4] outlined in the previous section, apart from the fact that the transformation adopted is rotation[7,9] of the subchain instead of mirroring. The coordinates of the segments—covering N lattice points (numbered from 1 to N and connected by $n = (N - 1)$ bonds), the length of one bond being $3^{1/2}$ lattice units in the tetrahedral lattice—and a code specifying the direction to the next segment are stored. A random number ξ, ranging from 2 to $n - 1$, determines the bond between segment ξ and segment $\xi + 1$ as an axis of rotation.[10] The shorter[11] part of the chain (the subchain containing segments 1 to ξ or $\xi + 1$ to N, respectively) is rotated by ±120°, the sign being chosen at random. Actually, the rotated subchain is built up step-by-step using a code derived from the old one with the aid of a transformation map. If an overlap occurs with a segment of the fixed part of the chain (only those segments are checked, which from purely geometric considerations actually can be subject to potential overlap), the trial is immediately stopped and the old configuration retained. Otherwise, the new chain is accepted. Then the procedure is started again, either using the new chain or the old one if the transformation had failed.

Like any other dynamic Monte Carlo method, a pivot algorithm transforms one chain into another chain. Thus, an initial configuration is necessary; e.g., this might be an unbiased self-avoiding walk obtained by an appropriate static method. Alternatively, one can start with an arbitrary configuration (e.g., an all-trans chain) and discard a "sufficiently large" number of initial relaxations.[4] In order to get an idea of what is to be understood by sufficiently large, the mean-square radius of gyration $\langle s^2 \rangle$, a property characteristic of global (macro) structure, and the average fraction of trans units $\langle T \rangle$, a simple quantity characteristic of the local (micro) structure, were com-

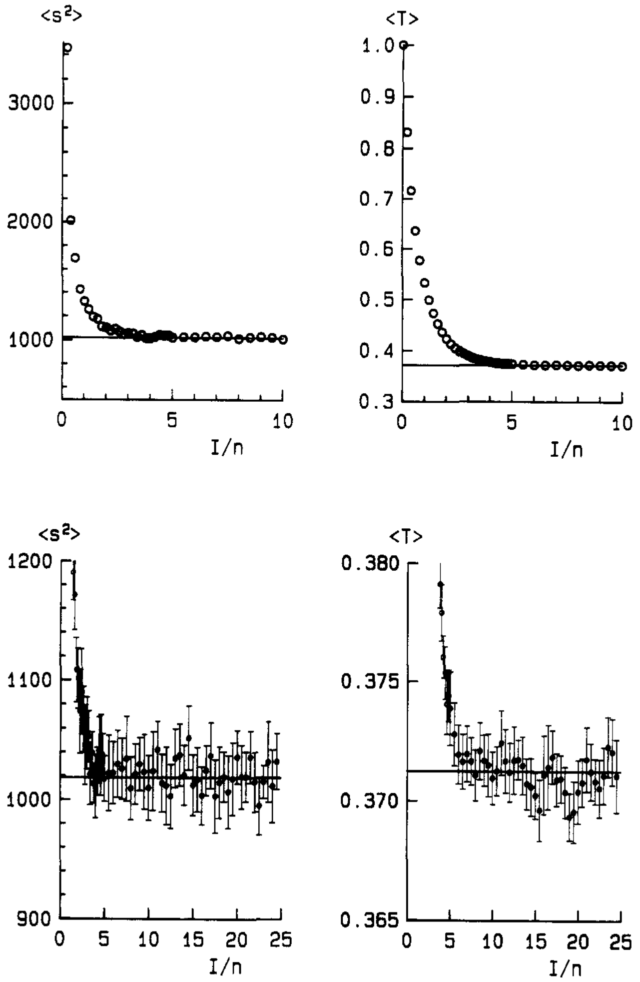

Figure 1. Mean-square radius of gyration, $\langle s^2 \rangle$, and average fraction of trans units, $\langle T \rangle$, as a function of relaxation trials I starting from the all-trans configuration of length $N = 500$. $\langle s^2 \rangle_{I=0} = 41\,666.75$. Top figures: normal scale. Bottom figures: extended scale (error bars for 95% confidence limits).

puted as a function of relaxation trials I. In Figure 1 $\langle s^2 \rangle$ and $\langle T \rangle$ for $N = 500$ obtained from ca. 1000 independent runs starting from the all-trans chain are shown. $\langle s^2 \rangle$ very rapidly decreases from its initial value (41 666.75; not shown in Figure 1) and reaches its average equilibrium value after approximately 2–3 attempted moves per bond. Clearly, more relaxations are needed to attain trans/gauche equilibrium. According to Figure 1 6–8 trials per bond, which is still a reasonable small number, should be sufficient. However, in order to be absolutely sure that the starting configuration is free of possible initial correlations, a much larger number of accepted moves, usually at least $20N$, were performed prior to data sampling.

3. Results and Discussion

(Average) Acceptance Fraction, *f*. Using a step-by-step procedure, the number of successful walks decreases exponentially with chain length. On the contrary, by use of a pivot algorithm, the average number of accepted chains per trial, i.e., acceptance fraction f, decreases only slightly with increasing chain length (see Table I) and is still fairly large for the longest chains examined. Figure 2a shows a double-logarithmic plot of the acceptance fraction versus the number of bonds $n = N - 1$. The data lie on a straight line, apart from a slight curvature in the range of short chains ($N < 200$). Therefore, as stated by Madras and Sokal,[2] the acceptance fraction may be expressed by the scaling law

$$f = An^{-\alpha} \qquad n \gg 1 \tag{1}$$

From a linear fit (in the range $200 \le N \le 10\,000$) $A = 1.296$ and $\alpha = 0.1146$ (a little larger than 0.1069, the value reported for cubic lattice chains[2]) are obtained. From the value of A alone, it is clear that the power law (eq 1) is only valid for large chains because the acceptance fraction cannot exceed unity. Replacing A in eq 1 by $A_0 + A_1/n + A_2/n^2$ yields an expression that is also appropriate for short chains[12]

$$f = (A_0 + A_1/n + A_2/n^2)n^{-\alpha} \qquad \text{for } n > n_0 \tag{1a}$$

$$f = 1 \qquad \text{for } n \le n_0$$

n_0 being the number of bonds of the largest chain that forms self-avoiding conformations only ($n_0 = 5$ in tetrahedral lattice). The parameters A_0, A_1, and A_2 can be extracted from short-chain data by a polynomial regression of $f/n^{-\alpha}$ versus $1/n$. Such a fit was well suited for tetrahedral chains of length $6 \le N \le 100$, and using $\alpha = 0.1146$, see Figure 2b, yields $A_0 = 1.296$, $A_1 = -0.970$, and $A_2 = 2.526$. The deviation of f-values calculated using eq 1a from Monte Carlo data is not larger than $\approx 0.3\%$, which is comparable with the statistical error of the latter.

Position-Dependent Acceptance Fractions *f*(*x*). The question arises of whether the impressively large (average) acceptance fraction is realized by comparable contributions from all pivot positions or only from some pivot positions leading to movements of only a few segments. In this latter case nearly vanishing $f(x)$-values of one sort of pivot positions had to be compensated by acceptance fractions close to unity of another one in order to achieve the reasonable high overall acceptance rates observed. This is hard to imagine, but such a situation, of course, would degrade the pivot algorithm into a rather useless method. By direct enumeration, Madras and Sokal computed position-dependent acceptance fractions of short ($n \le 17$) self-avoiding chains on the square lattice (see Table VIII in ref 2). Their data give no evidence of a disadvantageous behavior; to get an ultimate picture of the situation, however, the acceptance fraction $f(x)$ as a function of (reduced) pivot position $x = j/n$, j being the number of bonds of the shorter part of the chain, was studied for n = 499, 999, 1999, and 4999, the number of trials on average being approximately 800 per pivot position. In Figure 3 for chains of length $n = 4999$ $f(x)$ is shown together with the expected acceptance fraction $f'(x)$ for combining two independent self-avoiding walks of length xn and $(1 - x)n$, respectively. As the number of different n-step self-avoding walks (in the limit $n \to \infty$) is given[13] by $Z_n = q_{\text{eff}}{}^n n^{\gamma-1}$, $\gamma - 1$ being 0.162 in three dimensions,[14] the latter quantity simply reads

$$f'(x) = \frac{Z_n}{Z_j Z_{n-j}} = [x(1-x)n]^{-0.162} \tag{2}$$

the effective coordination number q_{eff} dropping out. $f'(x)$ very rapidly decreases from ≈ 1 close to the chain ends to a very broad minimum reaching a value of 0.315 (for $n = 4999$) at $x = 0.5$. From an inspection of $f'(x)$ alone, it is clear that the suspicion that $f(x)$ could be very small for some regions lacks justification. Since the global dimensions of subchains being part of a (longer) chain are larger than those of isolated chains of the same chain length,[15,16] it is expected that a self-avoiding chain is formed with larger probability by splitting a chain of length n into two parts (xn and $(1 - x)n$, respectively) with consecu-

Table I
Simulation Results[a]

n	k	f	$\langle s^2\rangle$	$\langle h^2\rangle$	$\langle NN\rangle$	$\langle T\rangle$
49	1 000 000	0.817 81	64.294	409.72	2.648	0.366 89
69	1 000 000	0.788 85	96.274	612.75	3.898	0.369 24
99	1 000 000	0.760 31	149.101	946.86	5.758	0.369 72
199	1 000 000	0.704 88	342.681	2167.43	11.980	0.370 33
299	1 000 000	0.674 85	557.699	3515.77	18.246	0.371 73
499	1 100 000	0.635 99	1019.193	6436.32	30.551	0.371 72
699	1 200 000	0.612 34	1519.092	9561.09	43.061	0.371 00
999	1 300 000	0.586 10	2308.942	14529.08	62.116	0.371 31
1999	1 400 000	0.543 50	5285.576	33173.65	125.342	0.371 59
2999	1 514 000	0.517 23	8480.648	53175.81	187.221	0.371 95
4999	1 600 000	0.487 18	15503.593	97159.80	312.694	0.371 51
6999	1 802 000	0.470 06	23142.685	144969.56	434.161	0.372 79
9999	1 992 500	0.450 66	35229.687	220155.84	618.527	0.371 89

[a] The variance of the data was estimated from $\langle \sigma^2\rangle$ and $\tau_{x,\mathrm{int}}$-values, see Table III, using eqs 4 and 7. On the basis of 95% confidence limits, the statistical error is ca. 0.3–0.5% for $\langle s^2\rangle$ and $\langle h^2\rangle$, ca. 0.8% for $\langle NN\rangle$, and ca. 0.2–0.3% for $\langle T\rangle$.

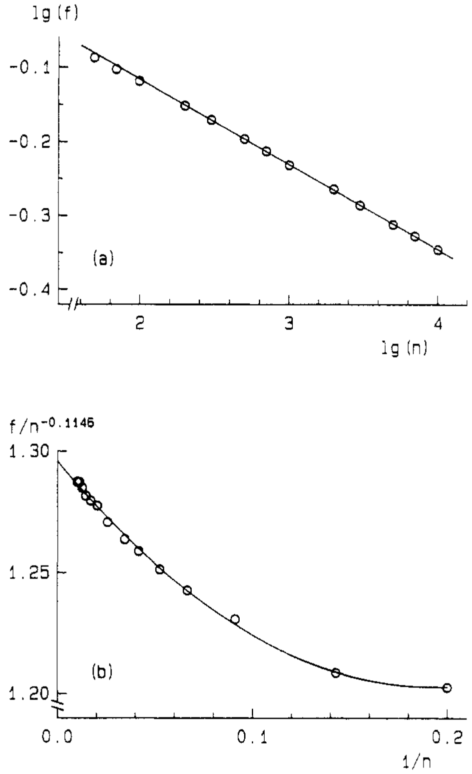

Figure 2. (a) Double-logarithmic plot of (average) acceptance fraction f versus number of bonds n (O). The straight line is the result of a linear regression of the data in the range $199 \leq n \leq 9999$. (b) $f/n^{-0.1146}$ versus $1/n$ (O) and a polynomial fit of the data in the range $6 \leq n \leq 99$ (—).

tive recombination in any other relative position than by combining two independent self-avoiding chains with chain lengths xn and $(1-x)n$. Indeed, $f(x)$ exhibits the same qualitative behavior as $f'(x)$, reaching a plateau at a *larger* value than $f'(x)$, namely 0.45 (average value in the range $0.4 \leq x \leq 0.5$). The overwhelming majority of pivot positions are subject to nearly equal acceptance fractions $f(x)$, which are only ≈10% smaller than the average value $f = 0.4872$, except for the very ends of a chain which clearly have an increased mobility compared to longer subchains. In Table II average values of $f(x)$ and $f'(x)$ in the range $1/n \leq x \leq 1/2$—average acceptance fractions f and f', respectively—and in the range $0.4 \leq x \leq 0.5$—average plateau values g and g', respectively—are presented. As $f \sim n^{-0.1146}$ and $f' \sim n^{-0.162}$, f/f' and g/g' increase with increasing chain length, but there is only a very slight dependence of f/g and f'/g' on chain length, $f'/g' \approx f/g \approx 1.1$. The latter suggests we describe $f(x)$ by an empirical expression $f''(x)$, which is of the same form as $f'(x)$ (eq 2), however, with an exponent $\alpha = 0.1146$ instead of 0.162.

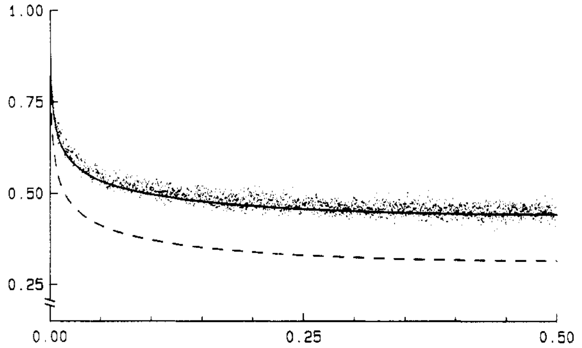

Figure 3. Position-dependent acceptance fraction for pivot algorithm and for combining independent self-avoiding walks: (•) $f(x)$; (- - -) $f'(x)$, eq 2; (—) $f''(x)$, eq 2a. All for $n = 4999$.

Table II
Average Acceptance Fractions for Pivot Algorithm and for Combining Independent Self-Avoiding Walks[a]

n	f	f'^{b}	f''^{c}	g	g'^{b}	g''^{c}
499	0.6360	0.5091	0.6190	0.5934	0.4586	0.5761
999	0.5861	0.4555	0.5721	0.5477	0.4098	0.5320
1999	0.5435	0.4074	0.5287	0.5008	0.3662	0.4914
4999	0.4872	0.3514	0.4761	0.4510	0.3157	0.4424

[a] f, f', and f'' are average values of $f(x)$, $f'(x)$, and $f''(x)$ in the range $1/n \leq x \leq 0.5$, and g, g', and g'' are average values in the range $0.4 \leq x \leq 0.5$. [b] Obtained using eq 2. [c] Obtained using eq 2a.

$$f''(x) = [x(1-x)n]^{-\alpha} \approx f(x) \qquad (2a)$$

$f''(x)$—depicted in Figure 3 by the full line—underestimates the numeric data by a few percent. This is also reflected in the average values f'' and g'' of $f''(x)$, defined in an analogous manner as f and g, which are ≈2.5% smaller than f and g; see Table II. Nevertheless, eq 2a may serve as a rough description for the position-dependent acceptance fraction.

Autocorrelation Functions. In each individual step many segments are transferred into a new position by one elementary motion, but only one three-bond unit is changed. Whereas, therefore, only a few moves will be necessary to produce an appreciable change of the macroscopic structure of the chain, specified by global dimensions (e.g., mean-square radius of gyration $\langle s^2\rangle$ or mean-square end-to-end distance $\langle h^2\rangle$), it will take many more moves to get an effective new chain on a microscopic scale. In other words, local quantities (e.g., the average number of trans units $\langle T\rangle$) will have a much stronger memory than global ones. This qualitative statement can be corroborated by studying the relaxation of properties X

described by the autocorrelation function $A_x(t)$ defined by

$$A_x(t) = \frac{\langle X_0 \cdot X_t \rangle - \langle X \rangle^2}{\langle X^2 \rangle - \langle X \rangle^2} \tag{3}$$

X_0X_t being the product of a property X of two chains successively produced and separated by $t - 1$ intermediate chains. The stronger the correlation is, the slower the decay of $A_x(t)$. Usually, the extent of correlation is specified by relaxation (correlation) times derived from $A_x(t)$. Three measures are widely in use:[17,18] (1) $\tau_{x,\mathrm{int}}$, the integral of the autocorrelation function

$$\tau_{x,\mathrm{int}} = \int_0^\infty A_x(t)\,\mathrm{d}t \approx \sum_0^{t'} A_x(t) \qquad t' \gg \tau_{x,\mathrm{int}} \tag{4}$$

which is actually truncated at some value $t' \gg \tau_{x,\mathrm{int}}$ in order to cut off that part of the autocorrelation function that essentially contains statistical noise only, (2) $\tau_{x,1/e}$, the t-value at which the autocorrelation function has fallen off to $1/e$, and (3) $\tau_{x,\exp}$ defined by the slope in a diagram ln $(A_x(t))$ versus t at large t-values

$$\ln\,(A_x(t)) = \mathrm{constant} - t/\tau_{x,\exp} \qquad t \gg 1 \tag{5}$$

If the *whole* autocorrelation profile is described by one single exponential function, the three autocorrelation times previously defined coincide and the relaxation is called monoexponential. This behavior is expected for the slowest relaxation process, whereas in the autocorrelation function of a faster relaxing quantity its mode is superimposed by the modes of slower processes, leading to $\tau_{x,1/e} < \tau_{x,\mathrm{int}} <(<)\ \tau_{x,\exp}$.

In Figures 4–6 $A_x(t)$ versus t together with a semilogarithmic representation, ln $A_x(t)$ versus t, is shown for the average fraction of trans units $X = T$, for the average number of nearest-neighbor contacts $X = NN$, some intermediate between a local and a global quantity specifying the extent of intramolecular entanglement, and for the mean-square radius of gyration $X = s^2$, all for chains of length $N = 500$. Comparison of the autocorrelation function of T, Figure 4a, with that of s^2, Figure 6a, shows the much weaker correlation in the case of s^2 as stated above. In the beginning $A_{NN}(t)$, Figure 5a, falls off faster than $A_T(t)$ but achieves statistical noise in the same range of t-values as the latter ($t \approx 1500$–2000).

Figure 4b shows that the average fraction of trans units relaxes strictly monoexponential, which—not unexpectedly—implies that equilibration of the trans/gauche ratio is the slowest process in chain relaxation. Integration of $A_T(t)$ yields $\tau_{T,\mathrm{int}} = 457$, which equals $\tau_{T,\exp} = 461$ within statistical uncertainty. In the beginning ln $A_{NN}(t)$, Figure 5b, is curved but becomes linear at larger t-values having nearly the same slope as ln $A_T(t)$. This is consistent with the idea of superposition of relaxation modes. The autocorrelation function of s^2 yields $\tau_{\mathrm{int}} = 20$. No sensible value can be calculated for $\tau_{\exp}$ since the slowest mode—indicated by the broken line in Figure 6b—is lost in scatter. The integral autocorrelation time for h^2 evaluates to 9, relaxation of h^2 being the fastest process studied (no diagram shown).

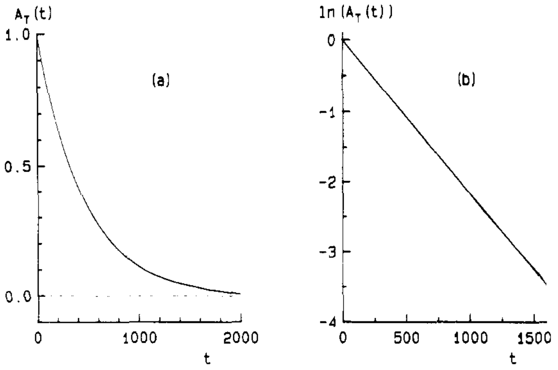

Figure 4. Autocorrelation function of the average fraction of trans units as a function of relaxation trials ("time") t (a) and a semilogarithmic representation (b) for chains of length $N = 500$. The straight line (slope 1/461) is the result of a linear regression of ln $A_T(t)$ versus t in the range $0 \le t \le 1600$.

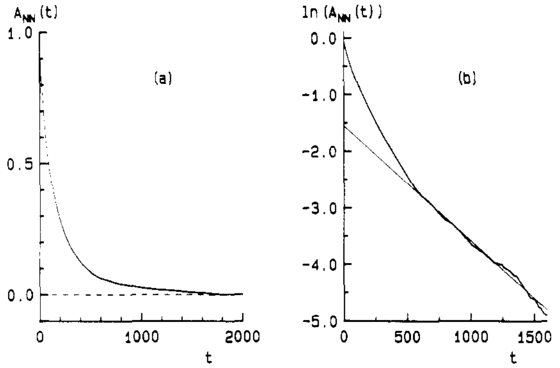

Figure 5. Autocorrelation function of the average number of nearest-neighbor contacts as a function of relaxation trials ("time") t (a) and a semilogarithmic representation (b) for chains of length $N = 500$. The straight line (slope 1/491.9) is the result of a linear regression of ln $A_{NN}(t)$ versus t in the range $600 \le t \le 1600$.

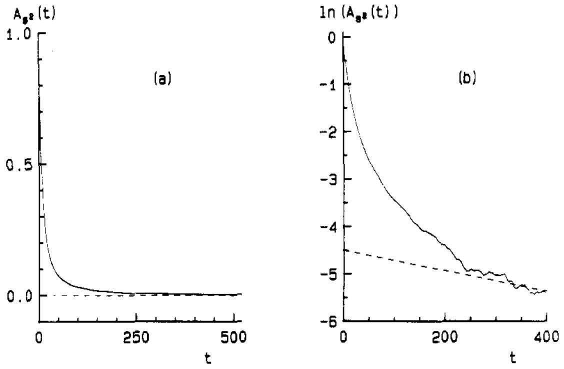

Figure 6. Autocorrelation function of the mean-square radius of gyration as a function of relaxation trials ("time") t (a) and a semilogarithmic representation (b) for chains of length $N = 500$. The broken line (slope 1/460) indicates the expected slowest mode.

Block Averages. Another approach to (integral) autocorrelation times is offered by (1) specification of the connection between autocorrelation function and the variance of correlated data[19] and (2) computation of the variance via block averaging.[20–24] According to the central limit theorem,[25] for large ensembles, the average $\langle X \rangle$ of k *uncorrelated* data is normally distributed with mean $\bar{X}$ and variance σ^2/k. Clearly, in general, σ^2 is unknown but can be estimated by $\langle \sigma^2 \rangle = (1/k)\Sigma(X_i - \langle X \rangle)^2 = \langle X^2 \rangle - \langle X \rangle^2$. If the data are *correlated* $\langle X_iX_j \rangle \neq \langle X_i \rangle \langle X_j \rangle$. This has to be taken into account by replacing $\Sigma(X_i - \langle X \rangle)^2$ by $\Sigma(X_i - \langle X \rangle)\Sigma(X_j - \langle X \rangle) = \Sigma\Sigma(X_iX_j - \langle X \rangle^2)$. Provided that all correlations resulting from the initial configuration have been overcome (by a large number of relaxations, the corresponding chains not being used for data sampling), properties X of consecutively produced chains are distributed according to their *equilibrium distribution* and thus can be interpreted as members of a *stationary* time series. Therefore, the autocovariance $(\langle X_iX_j \rangle - \langle X \rangle^2)$ is not dependent on i but only on $|j - i| \equiv |t|$. Making allowance for the symmetry of the (X_i,X_j) matrix and bearing in mind that the diagonal elements $\langle X_iX_i\rangle$ are counted once only, the expression for the variance of correlated data reads

$$\mathrm{var}(\langle X\rangle) \approx \frac{\langle\sigma^2\rangle}{k}\left\{2\left(\sum_{t=0}^{k}\frac{k-t}{k}\,\frac{\langle X_0X_t\rangle - \langle X\rangle^2}{\langle X^2\rangle - \langle X\rangle^2}\right) - 1\right\} \tag{6}$$

If k is much greater than some value t', $A_x(t')$ being already within statistical noise, the sum in eq 6 can be approximated by $\tau_{x,\mathrm{int}}$ using eq 4, since for all relevant contributions $(k - t)/k \approx 1$ and for $t > t'$ $A_x(t)$ is zero on average. Hence, the integral autocorrelation time can be estimated by

$$\tau_{x,\mathrm{int}} \approx \frac{1}{2}\left(\frac{\mathrm{var}(\langle X\rangle)}{\langle\sigma^2\rangle/k} + 1\right) \tag{7}$$

In order to obtain an estimate for $\mathrm{var}(\langle X\rangle)$, the k data are split into h nonoverlapping blocks, each block containing $m = k/h$ data, and the data in each block are averaged separately. Clearly, if the data X_i are uncorrelated, the block averages $\boldsymbol{X}_j$ in turn are uncorrelated quantities being normally distributed with mean $\bar{X}$ and variance $\mathrm{var}(\boldsymbol{X}_j) = \mathrm{var}(X_i)/m = \sigma^2/m$. But also in the case of correlated data, the $\boldsymbol{X}_j$-values can be regarded as independent provided $m \gg \tau_{\mathrm{int}}$. Of course, $\mathrm{var}(\boldsymbol{X}_j) > \sigma^2/m$ in the latter case. Strictly, $\mathrm{var}(\boldsymbol{X}_j)$ is given by $\sigma^2/m(2\tau_{\mathrm{int}} - 1)$ provided not only $m \gg \tau_{\mathrm{int}}$ but also $m \gg t'$. Thus, $\langle X\rangle$ obtained as an average of h block averages, $\langle X\rangle = (1/h)\Sigma\boldsymbol{X}_j$, is expected to be normally distributed with mean $\bar{X}$ and variance $\mathrm{var}(\langle X\rangle) = (1/h)\,\mathrm{var}(\boldsymbol{X}_j) = (1/h)(1/m)\,\mathrm{var}(X_i) = (1/k)\,\mathrm{var}(X_i)$, which can be easily derived from

$$\mathrm{var}(\langle X\rangle) = \frac{1}{h}\left(\frac{1}{h}\sum_{j=1}^{h}(\boldsymbol{X}_j - \langle X\rangle)^2\right) = \frac{1}{h}(\langle\boldsymbol{X}_j^2\rangle - \langle X\rangle^2) \tag{8}$$

because the $\boldsymbol{X}_j$-values are regarded as independent variables. The advantage of this approach is that the $\mathrm{var}(X_i)$, being $\sigma^2(2\tau_{\mathrm{int}} - 1)$, need not be computed directly. Thus, from eqs 7 and 8 an estimate for the integral autocorrelation time reads

$$\tau_{x,\mathrm{int}} \approx \frac{1}{2}\left(\frac{(1/h)(\langle\boldsymbol{X}_j^2\rangle - \langle X\rangle^2)}{(1/k)\langle\sigma^2\rangle} + 1\right) \equiv \tau_{x,\mathrm{blk}} \tag{7a}$$

As mentioned above, eqs 8 and 7a are only valid for large m. In addition, in order to get statistically significant results, h should be as large as possible too. If m is not large enough, a too small variance or τ-value, respectively, is pretended: As m increases from $m = 1$ to $m \gg t'$, $mh = k$ being constant, the numerical result from eq 8 or eq 7a, starting from σ^2/k or 1, respectively, first increases and then forms a plateau, scattering about some value characteristic of $\mathrm{var}(\langle X\rangle)$ or $\tau_{x,\mathrm{blk}}$, respectively. This is shown in Figure 7 where $\tau_{x,\mathrm{blk}}$ ($X = s^2$, h^2, NN, T) obtained from $k = 6000N$ chains of length $N = 500$ is depicted as a function of (reduced) block size m/n. Analogous pictures can be drawn for the other chain lengths examined, $N = 1000$ and $N = 2000$ (not shown). The resulting $\tau_{x,\mathrm{blk}}$-values are summarized in Table III, together with autocorrelation times obtained from autocorrelation functions. The difference between $\tau_{x,\mathrm{blk}}$ and $\tau_{x,\mathrm{int}}$ is seen to be approximately 2–10%. There are too few data to perform an accurate analysis of the chain-length dependence of the integral autocorrelation times, but the data are roughly in accordance with Madras and Sokal's result that the integral autocorrelation time is proportional to n^q, q being $\approx\alpha$ for global and $\approx(1 + \alpha)$ for local quantities.

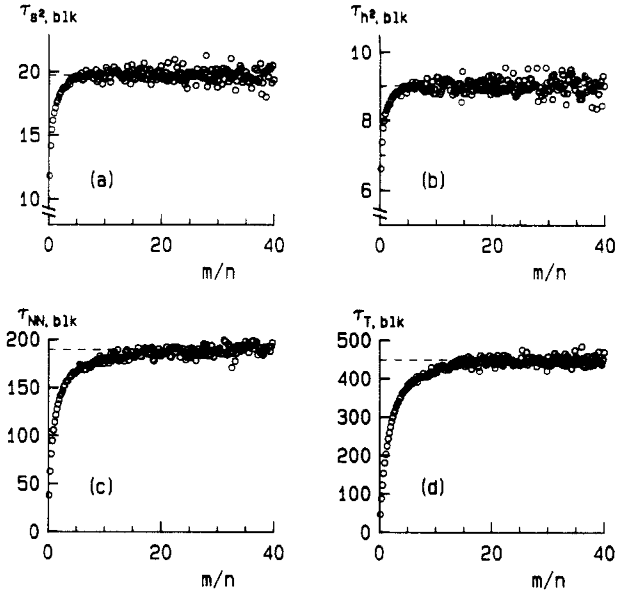

Figure 7. $\tau_{x,\mathrm{blk}}$ estimates for the integral autocorrelation time $\tau_{x,\mathrm{int}}$ according eq 7a as a function of (reduced) blocksize m/n for chains of length $N = 500$: (a) $X = s^2$; (b) $X = h^2$; (c) $X = NN$; (d) $X = T$.

Table III
Autocorrelation Times Obtained from Autocorrelation Functions and Block Averaging

	$X = h^2$	$X = s^2$	$X = NN$	$X = T$
$n = 499$				
$\tau_{x,\mathrm{int}}$	9.08	20.07	190.2	456.9
$\tau_{x,\mathrm{exp}}$			491.9	461.0
$\tau_{x,1/e}$	4.70	10.20	149.1	465.8
$\tau_{x,\mathrm{blk}}$	9.00	19.75	189.5	449.1
$n = 999$				
$\tau_{x,\mathrm{int}}$	9.68	23.40	410.3	1063.1
$\tau_{x,\mathrm{exp}}$				1036.4
$\tau_{x,1/e}$	5.15	11.30	316.4	1051.8
$\tau_{x,\mathrm{blk}}$	9.48	23.09	366.8	969.5
$n = 1999$				
$\tau_{x,\mathrm{int}}$	10.87	25.70	962.3	2381.5
$\tau_{x,\mathrm{exp}}$				2368.5
$\tau_{x,1/e}$	5.70	12.45	722.3	2354.7
$\tau_{x,\mathrm{blk}}$	11.15	24.40	909.1	2335.1

Chain Length Dependence of Global and Local Quantities. Long ago Flory[26] calculated the chain-length dependence of $\langle h^2\rangle$ using a mean-field approximation and found a scaling relation $\langle h^2\rangle \sim n^\nu$, ν being 1.2. Since then, a lot of effort has been undertaken in order to get more rigorous results, both theoretically and numerically. In the limit of long chains, all approaches yield the same relation in principle with different values for the exponent ν. From renormalization group theory[27,28] now a value $\nu = 1.176$ has been established which is slightly smaller than $\nu = 1.2$ predicted by Flory. Early Monte Carlo results[29] yielded values ranging from 1.18 to 1.22. The latest series extrapolation result[14] reads $\nu = 1.184$, and the most recent Monte Carlo calculation[2] predicts an exponent of 1.181 for $\langle h^2\rangle$ and 1.188 for $\langle s^2\rangle$, the range of chain lengths being $200 \leq n \leq 3000$. There is still a small gap between numerical and theoretical predictions, and, therefore, it seems valuable to add a further result to the existing ones: in Figure 8 double-logarithmic plots of $\langle h^2\rangle$ and $\langle s^2\rangle$ as a function of n ($99 \leq n \leq 9999$, the largest range of chain length hitherto examined) are shown. No deviation of the symbols from a

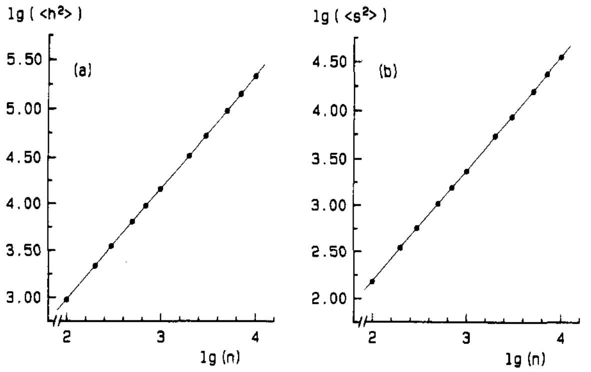

Figure 8. Double-logarithmic plots of (a) the mean-square end-to-end distance, $\langle h^2\rangle$, and (b) the mean-square radius of gyration, $\langle s^2\rangle$, as a function of the number of bonds n (●). The straight line (the slope being (a) 1.1802 for $\langle h^2\rangle$ and (b) 1.1832 for $\langle s^2\rangle$) is the result of a linear regression in the range $99 \leq n \leq 9999$.

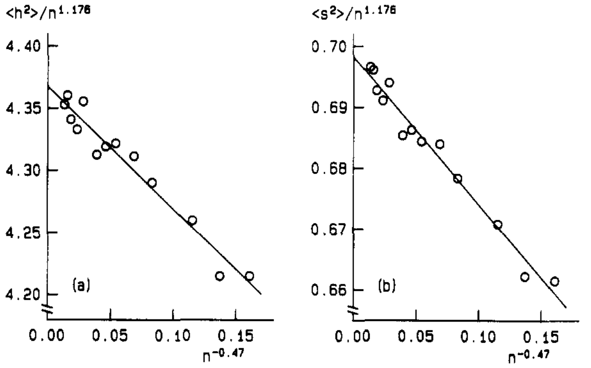

Figure 9. (a) $\langle h^2\rangle/n^{\nu}$ versus $n^{-\Delta}$ and (b) $\langle s^2\rangle/n^{\nu}$ versus $n^{-\Delta}$ using the renormalization group predictions[28] $\nu = 1.176$ and $\Delta = 0.47$; the straight lines are the result of a linear regression of the data.

straight line—the slope being 1.180 and 1.183, respectively—is detectable by eye. Nevertheless, splitting the data into two parts and performing separate regressions in the range $99 \leq n \leq 999$ and $999 \leq n \leq 9999$, respectively, reveal a slightly larger slope for shorter chains (1.182 and 1.185) compared with longer chains (1.179 and 1.182). Of course, these values are equal within statistical uncertainty, but obviously there exists some trend toward smaller exponents for still larger chains. Thus, although a double-logarithmic plot of mean-square dimensions versus chain length is nearly perfectly linear, an appropriate correction to the scaling law seems to be necessary even for very long chains. From renormalization group theory one expects

$$\langle h^2\rangle = n^{\nu}(C_0 + C_1 n^{-\Delta} + ...) \qquad (9)$$

where $\nu = 1.176$ is the scaling exponent as described above and $\Delta = 0.47 \pm 0.03$[28] is some correction to the scaling exponent. Therefore, a plot of $\langle h^2\rangle/n^{1.176}$ or $\langle s^2\rangle/n^{1.176}$ versus $n^{-0.47}$ should be approximately linear if the chains are large enough that no further correction term is apparent. Such diagrams are shown in Figure 9. Indeed, the data—although scattering is rather large—lie on a straight line. A linear regression yields $C_0 = 4.367$ and $C_1 = -0.982$ for $\langle h^2\rangle$ and $C_0 = 0.698$ and $C_1 = -0.242$ for $\langle s^2\rangle$; the deviations of $\langle s^2\rangle$ or $\langle h^2\rangle$ predicted by use of eq 9 using these C-values from the Monte Carlo data are in the same order of magnitude as the statistical error of the latter. This result proves the validity of the scaling relation, eq 9, in principle, even though the accuracy of the data is not good enough to ultimately confirm the renormalization result for the leading correction to the scaling exponent. A value of -0.47 seems to be highly reasonable, but slightly larger or smaller values would be in accordance with the data too.

The ratio $\langle s^2\rangle/\langle h^2\rangle$—being $^1/_6$ for infinite random walks—increases slightly with increasing chain length. From a least-squares fit of $\langle s^2\rangle/\langle h^2\rangle$ versus $1/n$ ($499 \leq n \leq 9999$) a limiting value ≈ 0.16 is obtained which is in good agreement with recent Monte Carlo data (see ref 2 and literature cited therein).

Due to the excluded-volume condition, parts of the chain have to avoid each other not only on a global but also on a local scale. Therefore, the fraction of trans units is larger than 0.33, the value expected for random walks: $\langle T\rangle$ first increases with increasing chain length and then converges to approximately 0.372.

The number of nearest-neighbor contacts, $\langle NN\rangle$, increases approximately proportionally with chain length; if the chain length is doubled, the number of contacts is doubled too. As mentioned above, two subchains constituting a chain are a little less compact than isolated chains with the same chain length. This should be reflected in some decrease of intramolecular contacts within the subchains. Obviously, this decrease is exactly compensated by contacts between the two subchains.

4. Conclusions

The pivot algorithm has proved most valuable for constructing very long chains and determining their properties, both in cubic and in tetrahedral lattice due to (1) a very slow decrease of acceptance fraction with increasing chain length, (2) comparable acceptance fractions for nearly all pivot positions (except for very small values), and (3) small (integral) relaxation times of global quantities, which increase only slightly with increasing chain length. As the integral relaxation time is directly reflected in the statistical error of the results, the latter fact makes it possible to get significant results within reasonable computer time.

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(11) If rotation occurs around one of the three central bonds, the subchain to be rotated is chosen at random to avoid the central bond remaining fixed.
(12) It should be mentioned that no effort was made in order to find the true leading correction-to-scaling exponent. As the pivot algorithm is primarily intended as a tool for generating long chains, this problem seems to be only secondary and so one should be content with a semiempiric treatment.
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Screening of Interactions in Homopolymer Blends and in Diblock Copolymer Systems

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ABSTRACT: The screening of interactions is compatible binary homopolymer blends A and B and in the diblock copolymer A–B system is studied. A systematic comparison between both cases is presented, and a general expression for the effective screened potential $U_{AA}{}^{s}$, acting on one chain of type A, is given as a function of the compositions Φ_A and Φ_B for both components, their Flory interaction parameter χ_F, the degrees of polymerization N_A and N_B, and the wave vector $|\mathbf{k}|$. The theoretical variation of the screened potential $U_{AA}{}^{s}$ as a function of the composition and the wave vector is considered in the case of homopolymer blends A and B and in the case of the diblock copolymer system. The main result of this study is the Gaussian behavior of a single chain in the system ($U_{AA}{}^{s} = 0$) before the spinodal is reached. In the particular case where the composition is chosen to be 50/50, this is achieved at $|\mathbf{k}| = 0$ and at the critical value of $(\chi_F N)_c = 2$ in the case of binary homopolymer blends A and B and at the values of $|\mathbf{k}| = |\mathbf{k}^*| \simeq 2^{1/2}/R_{gA}$ and $(\chi_F N)_c \simeq 5.25$ in the case of the diblock copolymer A–B system, where R_{gA} is the radius of gyration of one block chain of species A. These values of $|\mathbf{k}^*|$ and $(\chi_F N)_c$ are identical with those obtained by Leibler using a theoretical approach dealing with the scattering properties.

I. Introduction

In a previous paper,[1] the screening of interactions in compatible blends of two homopolymers A and B was discussed. In that paper, mean-field and perturbation theory was used to derive general expressions for the effective screening potential $U_{AA}{}^{s}$ and for the radius of gyration $\langle R_{gA}{}^2 \rangle$ as a function of the compositions Φ_A and Φ_B of both components and their Flory interaction parameter χ_F. The main conclusion of that work was the Gaussian behavior (when the effective screened potential $U_{AA}{}^{s}$ is equal to zero) of one chain within the system before the phase separation (spinodal decomposition) takes place.

In the present paper we mainly discuss the case of diblock copolymer A–B and show that the screening of interactions in such systems provides a similar effect. In this theoretical approach, one treats the fluctuations in the Gaussian approximation. Whereas the Gaussian "point" described above occurs at $|\mathbf{k}| = 0$ for the blend of A and B homopolymers, the total screening or the zero of the effective interaction potential of the A part for the diblock copolymer system at 50/50 composition is obtained at the value of the wave vector $|\mathbf{k}| = |\mathbf{k}^*| \simeq 2^{1/2}/R_{gA}$, where R_{gA} is the radius of gyration of one block chain of species A. This result is in perfect agreement with the theoretical approach regarding the scattering properties.[2–5]

The present paper is organized as follows: In the next section we calculate first the mean-field Hamiltonian explicitly for the dense melt of diblock copolymers. This Edwards Hamiltonian will provide the generalized random phase approximation (RPA) for diblock copolymer systems. Similar calculations have been attempted in refs 6 and 7. The knowledge of the Edwards Hamiltonian allows us to carry out the screening calculation. This is done in section III of the paper. Hence we integrate out all terms coming from the B parts of the diblock copolymers and we are left with an effective A system in the presence of the mean field coming from the B system. Then the "effective A chains" will screen their effective interaction themselves. Finally, we are left with a single A chain taking into account the presence of all the other A and B species. The final result is therefore the effective Edwards Hamiltonian for one chain, i.e., the configurational part and an effective interaction potential acting on this chain. This effective interaction potential is called the screened potential. In the remainder of the paper we analyze the effective interaction potential and discuss the consequences.

II. Calculation of the Edwards Hamiltonian for Diblock Copolymers

Let us consider a melt system of a diblock copolymer. First we have to derive the mean-field Edwards Hamil-

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