Monte Carlo model of polymer chain attached to an interface in poor solvent conditions: collapse to dense globular state

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The coil dimensions of chains up to $N=60$, terminally attached to a rigid, impenetrable boundary in poor solvent and/or low-temperature conditions, are studied by means of the Monte Carlo method. The θ transition and collapse to the dense globular state for model chains at reduced temperature $T^* \equiv kT/\varepsilon_\alpha \simeq 2.0$ has been found.

(Keywords: terminally attached polymer; rigid boundary; segment density distribution; Monte Carlo method; theta temperature)

INTRODUCTION

The structure and properties of a polymer near a surface have received much attention in recent years[1–21]. The influence of microscopic structure on both adhesion and friction of polymers[1], the effect of polymer adsorption on the stabilization of colloidal systems[2] as well as the influence of conformation and dynamics of hydrocarbon tails of phospholipids on the properties and structure of lipid bilayers[3,4] are typical examples of objects of interest.

Computer modelling methods are widely applied in theoretical investigations on this subject. Models of a polymer film in contact with vacuum[5], polymer on a liquid–liquid interface[9,10] or polymer on a liquid–solid interface[7,11,15] have been considered.

The problem of the dimensions and shape of a coil formed by an isolated polymer chain attached to a wall seems to be a basis for considerations of the properties of the polymer near an interface. This model, as in the case of a polymer chain in dilute solution[22,23], allows us to omit some complications relevant to chain–chain interactions.

Guttman *et al.*[16] have investigated the properties of model chains attached to a wall. The simulation results have confirmed the assumption that for large N the mean-square end-to-end separation $\langle R_N^2 \rangle$ is proportional to $N^{2\nu}$, like it is for unconfined chains. For model chains constrained by a tetrahedral lattice in the cited work[16], they have found $1.19 < 2\nu < 1.22$. For comparison, Kremer, Baumgartner and Binder[24] for a free chain model on a tetrahedral lattice in similar conditions have given the value $\nu = 0.59$. The convergence of both values is evident and may attest to the analogy between the properties of the coils formed by both attached and free chains.

In the paper of Eisenriegler, Kremer and Binder[12], which concerns adsorption of a chain on an interface, we also can find a valuation of the dimensions of the coils formed by chains terminally attached to an inert wall. In the terminology of that work, this corresponds to temperature $T=\infty$. In other words, the energy of adsorption is equal to zero. The results have been obtained by the Monte Carlo (MC) method for tetrahedral lattice chains of length $N \leqslant 100$. The dependence of the mean-square radius of gyration, defined by:

$$\langle R_G^2(N) \rangle = \frac{1}{(N+1)^2} \left\langle \sum_{i=1}^{N} \sum_{j=i+1}^{n+1} (r_i - r_j)^2 \right\rangle \tag{1}$$

on the chain length N has been calculated. This dependence has the form:

$$\langle R_G^2(N) \rangle \sim N^{1.22 \pm 0.04} \tag{2}$$

Kremer, Baumgartner and Binder[24] for a similar chain on a tetrahedral lattice have found:

$$\langle R_N^2(N) \rangle \sim \langle R_G^2(N) \rangle \sim N^{2\nu} \tag{3}$$

where $\nu = 0.59$. Kolinski, Skolnick and Yaris[25] for longer (up to $N=800$) athermal self-avoiding walks confined to a tetrahedral lattice have obtained $2\nu = 1.186 \pm 0.004$.

These facts may be used as additional confirmation of the supposition that the properties of free chains under good solvent conditions are similar to those anchored to a wall.

The structure of an isolated polymer coil close to a rigid wall has also been investigated by Cosgrove[11,13]. He has used self-consistent field theory[26,27] to find segment density distributions near the wall[11]. The plots of the segment density functions obtained by him for good solvent conditions without adsorption ($\varepsilon_\alpha = 0$) had a distinct maximum near the wall.

The shape of the segment density distribution functions has been confirmed in experimental studies. Results of small-angle neutron scattering (SANS) studies for polystyrene chains terminally attached on silica in carbon tetrachloride[11] as well as for poly(ethylene oxide) at the polystyrene/water interface[14,15] are good examples.

The problem of the dimensions and structure of a coil formed by a polymer chain anchored to a rigid wall has been considered in Croxton's work as well[17–21]. Relatively short, freely jointed chains (up to $N=20$) have been

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examined there. Results of MC simulations[18] and estimations by the 'iterative convolution' (IC)[17] method show that equation (3) is asymptotically valid for the chains considered. The value of exponent $\nu = 0.6$ was obtained.

The last findings lead to the conclusion that, under athermal conditions ($\chi = 0$ in Flory–Huggins notation[28]), the influence of a geometrical constraint (an inert wall) on the excluded-volume effect of anchored polymer chains is not too big. This is a confirmation of the earlier statement of Tanaka[29]. In 1977 he worked out, in the framework of first-order perturbation theory, an equation for the coefficient of volume expansion, α, for chains anchored to a wall (tails):

$$\alpha^2 = 1 + 1.26z + \cdots \tag{4}$$

where z is the excluded-volume parameter (defined e.g. in ref. 23).

A similar equation for a spatially unrestricted chain has the form:

$$\alpha^2 = 1 + \tfrac{4}{3}z + \cdots \tag{5}$$

One can see that in the above conditions the presence of the wall changes the coefficient α only a little even for large values of z (order of 10). Napper[2] has been of the opinion that this small influence results from great expansion of the tails in the direction perpendicular to the wall. This fact reduces the possibility of realization of the excluded-volume effect.

Data published by Croxton[18–21] confirmed the assumption. Calculations by the IC method and MC simulation, for terminally attached hard-sphere sequences $N \leqslant 24$ segments near a wall, have allowed us to note that the segment concentration in the range of $z = R_F$ has a value about half of the maximum and in athermal conditions drops out at low speed.

There is a question whether the analogy between the behaviour of the tails and the free chains found for athermal conditions is true for a poor solvent range (close to the theta (θ) point defined e.g. in refs. 23–25).

The results of the MC simulation of 20-segment tails constrained to a tetrahedral lattice[30] allowed us to find some similarities, but for a low temperature, where the excluded-volume effect is increasing, one can observe some distinct differences in properties.

In this work we have investigated chains (up to $N = 60$) confined to the half-space. We have carried out the analysis of the dependence of the coil dimensions on the chain length, for temperatures close to the theta point.

DESCRIPTION OF THE MODEL AND SIMULATION METHOD

Description of the model

A detailed description of the model can be found in our previous work[30]. Here we give only a brief summary for the reader's convenience. The model consists of one chain placed in an MC box. It is attached, by one end, to a wall of the MC box. The investigated macromolecules, composed of $N = 16$, 20, 30, 40 and 60 segments, are self-avoiding walk (SAW) type chains restricted to a tetrahedral lattice (details can be found elsewhere e.g. ref. 12). All lattice points unoccupied by polymer segments were considered as solvent molecules.

The polymer–polymer interaction was simulated by the mean force potential, described by the equation:

$$V(r_{ij}) = \begin{cases} \infty & r_{ij} = 0, i \neq j \\ \varepsilon_\alpha & r_{ij} = l, |i-j| \neq 1 \\ 0 & r_{ij} > l \end{cases} \tag{6}$$

where r_{ij} is the distance between ith and jth segments, l is the model bound length and ε_α is an interaction parameter.

The configurational energy of the system has been counted as the sum of the binary interactions between segments:

$$\frac{E}{kT} = \frac{\varepsilon_\alpha}{kT} \sum_{i \neq j} \nu_{ij} = \frac{1}{T^*} \sum_{i \neq j} \nu_{ij} \tag{7}$$

where ν_{ij} is the number of contacts between beads and $T^* \equiv kT/\varepsilon_\alpha$ is the reduced temperature of the system.

The MC box, with periodic boundary conditions[31,32] on the lateral walls, was assumed sufficiently large in order to make chain–chain contacts marginally probable. The wall, where the model chain was anchored, is impenetrable to polymer (the hard-wall potential).

The dynamics of the model macromolecule is simulated by the 'kink–jump' method[33,34]. The conformation of the model chain was changed by two-bead[24] and three-bead[35] jumps (*Figure 1*). The method allows us to simulate the behaviour of the lattice chain near the θ point for free chains[24,25,31,36,37]. Our previous work[30] has confirmed the applicability of this method for short tails.

Method of simulation

In order to account for polymer–solvent interaction in the model chain, we use an 'importance sampling' method. This method was described e.g. in chapter 1 of the work edited by Binder[32]. It is extensively used for modelling of polymer systems at temperature below the θ point (e.g. refs. 24 and 32). The probability of change of the conformation from x_i to x_j depends, in this method, on change of conformational energy and is described

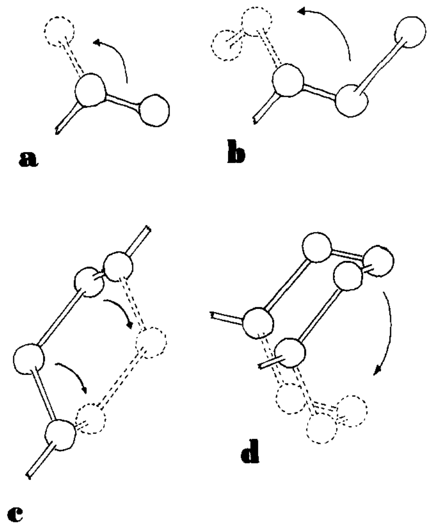

Figure 1 Elementary conformational jumps of polymer chain restricted to the tetrahedral lattice: (a) one-bead motion of end units; (b) two-bead motion of end units; (c) two-bead jump of $G^{\pm} \rightarrow G^{\mp}$ type; (d) three-bead jump

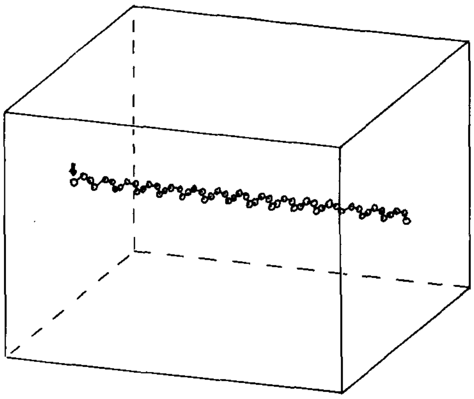

Figure 2 Monte Carlo box with a tail in expanded conformation for $N=60$

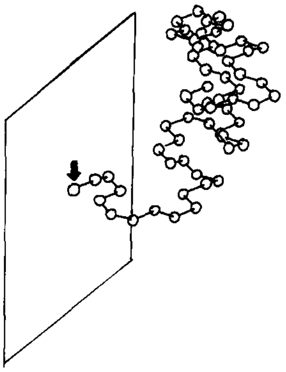

Figure 3 Polymer chain anchored to a wall after relaxation in the athermal condition, for $n=60$

by the equation[32]:

$$p(x_i \rightarrow x_j)=\begin{cases}\exp(-\Delta E_{ij}/kT) & \text{for}\,\Delta E_{ij}>0\\ 1 & \text{for}\,\Delta E_{ij}\leqslant 0\end{cases} \qquad (8)$$

where ΔE_{ij} is the difference of the conformational energy between conformation x_i and x_j.

The simulation process has been based on generating random paths in the space of states with probability of the transition as described above. The mean value of the parameter A is described by the arithmetic average[32]:

$$\bar{A}=\frac{1}{M}\sum_{i=1}^{M}A(x_i) \qquad (9)$$

where M is the number of steps of the random path (number of simulated conformations).

At the beginning of the simulation, the chain has been put in the MC box in an expanded conformation (*Figure 2*). In the next stage the chain, through the changes described above, has passed into the equilibrium conformation. The process has been conducted under athermal conditions (i.e. $\varepsilon_\alpha=0$) to speed it up. The examined value of ε_α has been set up after relaxation (*Figure 3*) and the system has been equilibrated at adequate temperature. Both processes required $\sim N\times 10^4$ trial modifications of the model system. The equilibrium state obtained at a given temperature (*Figure 4*) was the starting point for the main stage of the simulation. The transition to the equilibrium conformation has been detected by observation of the conformational energy of the system against time. As an example, an initial fragment of the $E_c(t)$ plot for $N=60$ and $T^*=1.0$ and 4.0 is presented in *Figure 5*. The time step of the plot $\Delta t=1$ corresponds to $10N=600$ trial modifications of the conformation of the chain.

In the 'kink–jump' model one can observe a tendency of the conformational space to divide into some ergodic subclasses[36]. When the modelled system enters in one of the subclasses, it has a very small probability of leaving this area. These 'forbidden configurations', in agreement with equation (8), limit the freedom of movement. Averages in this case are counted not over the whole configurational space but over this selected subclass. To avoid errors resulting from the described occurrence, we used additionally counting of the averages from some (at least five) independent simulations for a given set of data.

From 10^6 to 10^7 elementary trial conformations for every point of measurement have been simulated. The efficiency of the simulation went down very fast with the increasing modulus of the interaction constant, ε_α. We can see this in the plot of conformational energy against time. The efficiency was estimated there as the number of accepted changes of the chain configuration. However, in the investigated range of temperature ($T^*\geqslant 0.8$) the method seems to be productive. This means that the time between configurational jumps is very small in comparison with the time of the simulation.

RESULTS AND DISCUSSION

Dimension of the coil

Figure 6 shows the reduced mean-squared end-to-end distances $\langle R_N^2\rangle/Nl^2$ (where l^2 is the square of the bond

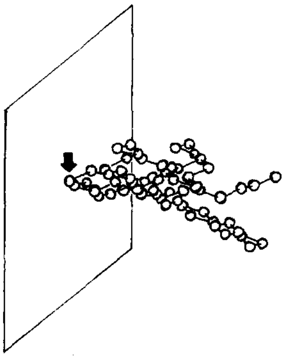

Figure 4 Polymer chain anchored to a wall after relaxation at reduced temperature $T^*=1.0$, for $N=60$

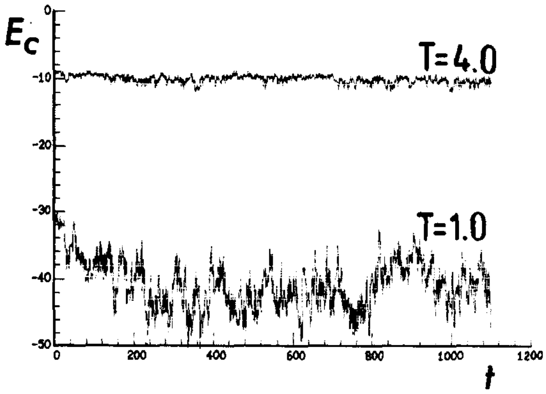

Figure 5 Plot of the conformational energy of the model chains for $N=60$ as a function of time of the simulation

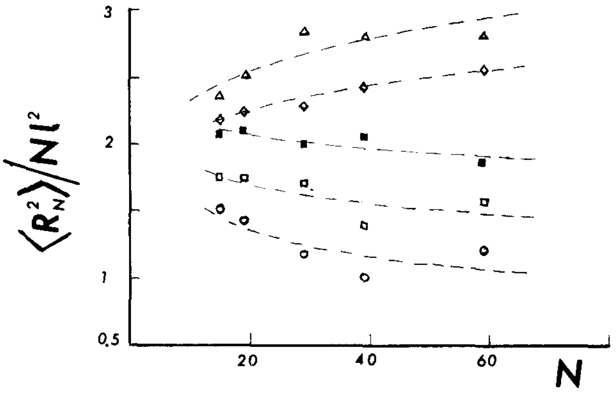

Figure 6 Reduced mean-squared end-to-end distance vs. number of segments of the model chain: (△) $T^*=4.0$; (◇) $T^*=2.0$; (■) $T^*=1.5$; (□) $T^*=1.0$; (○) $T^*=0.8$

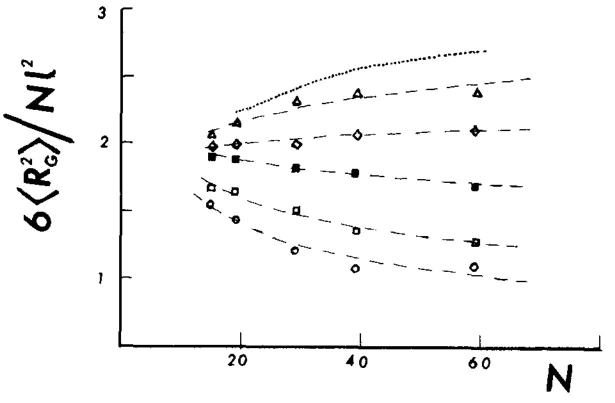

Figure 7 Reduced mean-squared radius of gyration vs. number of segments of the model chain. Symbols as in *Figure 6*. The dotted curve represents values obtained by extrapolation of the data to the temperature $T^*=\infty$

length in a tetrahedral lattice) vs. number of segments in the model chain, N. All the parameters are measured in the reduced temperatures (defined above, in equation (7)) $T^*=4.0$, 2.0, 1.5, 1.0 and 0.8.

Figure 7 shows a similar plot for the reduced mean-squared radius of gyration $6\langle R_G^2\rangle/Nl^2$. As we can see on both of the figures, flat regions exist between temperature $T^*=2.0$ and $T^*=1.5$. These regions, in agreement with Kremer, Baumgartner and Binder[24], define the θ region. In this case, the θ region is understood as the region where a chain anchored to the wall (tail) has properties close to the properties of the tail without polymer–polymer interactions. The $\langle R_N^2\rangle_\theta$ and $\langle R_G^2\rangle_\theta$ fulfil relations:

$$\frac{\langle R_N^2\rangle_\theta}{Nl^2}\simeq 2 \tag{10}$$

and

$$\frac{\langle R_G^2\rangle_\theta}{Nl^2}\simeq \frac{2}{6} \tag{11}$$

Values of $\langle R_N^2\rangle_\theta/Nl^2$ for single random walk without excluded volume can be found e.g. in the work of Livne and Meirovich[38].

The broken curves in *Figures 6* and *7* represent the linear least-squares fit of the data with adjustable parameters A, B, $2\nu_R$ and $2\nu_G$ in equations:

$$\ln\langle R_N^2\rangle = \ln A + 2\nu_R \ln N \tag{12}$$

and

$$\ln\langle R_G^2\rangle = \ln B + 2\nu_G \ln N \tag{13}$$

The results, with the standard errors and correlation coefficients, are given in *Tables 1* and *2*. The values of $\langle R_G^2\rangle$ for $T^*=\infty$ have been obtained by extrapolation of the data. The value of 2ν in these conditions (1.170 ± 0.015) is in good agreement with the data of Kolinski, Skolnick and Yaris[25]. For long, unrestricted chains they have obtained $2\nu=1.186\pm0.004$. This convergence may be understood as the test of the used algorithm.

Anisotropy of the coil

In the case of tails, anisotropy results from the presence of the surface. We can distinguish the parallel and perpendicular parts of the mean-squared end-to-end distance[12], defined as:

$$\langle R_N^2\rangle_\parallel \equiv \langle (x_1-x_N)^2+(y_1-y_N)^2\rangle \tag{14}$$

$$\langle R_N^2\rangle_\perp \equiv \langle (z_1-z_N)^2\rangle \tag{15}$$

where x_i, y_i, z_i are the Cartesian coordinates of the ith bead.

Similarly, the parallel component of the mean-square radius of gyration can be defined as:

$$\langle R_G^2\rangle_\parallel \equiv \left\langle \sum_{i=1}^{N} (x-x_{\mathrm{CM}})^2+(y-y_{\mathrm{CM}})^2 \right\rangle \tag{16}$$

where x_{CM} and y_{CM} are the centre-of-mass coordinates.

Plots of the reduced values of the defined quantities are given in *Figures 8*, *9* and *10*. The broken curves are obtained similarly as in the preceding paragraph. The values of the fitted quantities are given in *Tables 3* to *5*. It is evident, from the presented data, that a θ transition occurs for both parallel components close to $T^*=2.0$. This value is qualitatively consistent with the theta temperature obtained by Kremer, Baumgartner and Binder[24] for free chains. For unrestricted SAWs they have obtained $k\theta/\varepsilon_\alpha=2.25\pm0.05$; Kolinski, Skolnick and Yaris[25] for SAWs up to $N=800$ have given $k\theta/\varepsilon_\alpha=2.12\pm0.02$. This convergence may confirm the supposition that

Table 1 The results of the linear least-squares fit of $\ln(\langle R_N^2\rangle/Nl^2)$ (see text for further details)

T^*	2ν	$\ln A$	Corr. coeff.
4.0	1.131 ± 0.045	1.640 ± 0.150	0.9976
2.0	1.114 ± 0.015	1.570 ± 0.050	0.9997
1.5	0.930 ± 0.030	2.038 ± 0.100	0.9885
1.0	0.877 ± 0.077	1.998 ± 0.260	0.9885
0.8	0.782 ± 0.115	2.059 ± 0.389	0.9692

Table 2 The results of the linear least-squares fit of $\ln(\langle R_G^2\rangle/Nl^2)$ (see text for further details)

T^*	2ν	$\ln B$	Corr. coeff.
∞	1.170 ± 0.015	-0.379 ± 0.052	0.9998
4.0	1.113 ± 0.026	-0.257 ± 0.088	0.9992
2.0	1.049 ± 0.010	-0.145 ± 0.032	0.9999
1.5	0.919 ± 0.011	0.179 ± 0.038	0.9998
1.0	0.799 ± 0.021	0.389 ± 0.071	0.9990
0.8	0.729 ± 0.064	0.456 ± 0.217	0.9887

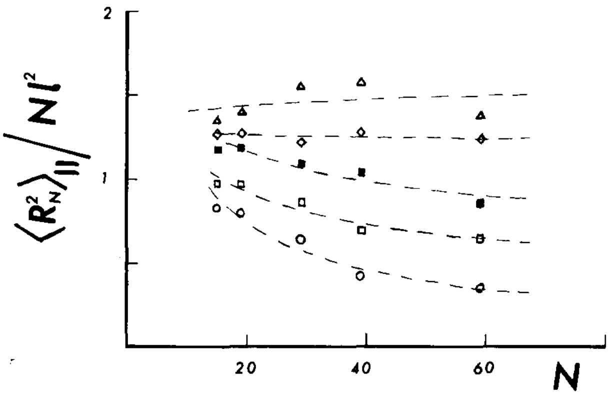

Figure 8 Reduced parallel component of the mean-squared end-to-end distance vs. number of segments of the model chain. Symbols as in *Figure 6*

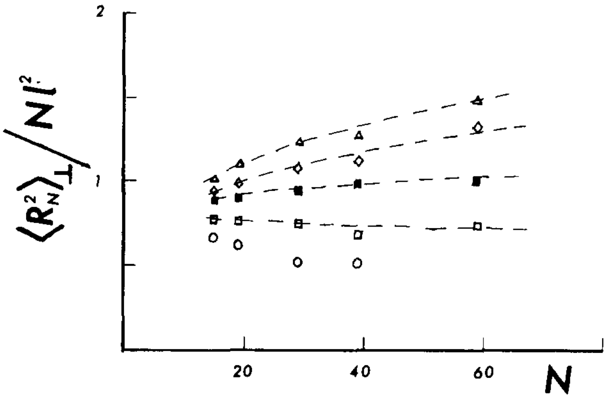

Figure 9 Reduced perpendicular component of the mean-squared end-to-end distance vs. number of segments of the model chain. Symbols as in *Figure 6*

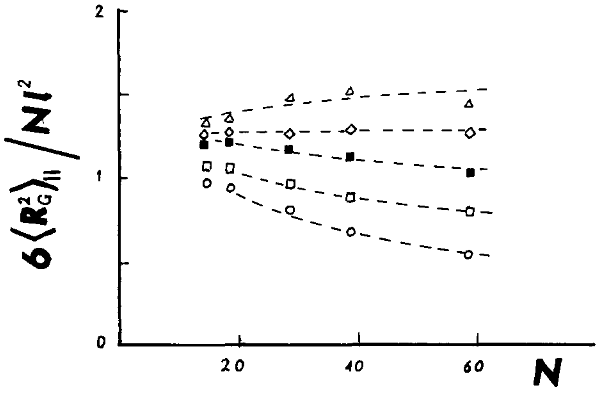

Figure 10 Reduced parallel component of the mean-squared radius of gyration vs. number of segments of the model chain. Symbols as in *Figure 6*

parallel components of $\langle R_N^2\rangle$ and $\langle R_G^2\rangle$ are independent of the surface and they behave like in bulk[38]. The data obtained by us do not permit us to perform a quantitative calculation of the θ point.

Reduced values of the parallel components in the flat regions, close to θ condition, lie near to 1.0. This is in good agreement with the data obtained by Livne and Meirovich for tails without excluded volume[38].

For the perpendicular component of $\langle R_N^2\rangle$ we can also see a flat region but it is shifted in the direction of lower temperatures (between $T^*=1.0$ and $T^*=1.5$).

Mean number of polymer–polymer contacts

Plots of the mean number of polymer–polymer contacts, against the reduced temperature T^*, are given in *Figure 11*. For all the observed values of N we can see that the number of polymer–polymer contacts remains about constant at high temperature, and begins to grow at temperatures below the θ point. The temperature of the transition increases with increasing length of the model chain from $\simeq 1.0$ for $N=16$ to $\simeq 2.0$ for $N=60$. This may be proof of the collapse to the dense globular state[25] in such systems for $N\rightarrow\infty$, and indicates that the range of model chain lengths is too small to calculate a quantitative value of the point of the phase transition.

The mean segment density profile

The mean segment density profile in the vicinity of the surface was another quantity of interest in the presented work. *Figure 12* shows, as an example, plots of the segment density profile obtained at temperatures $T^*=4.0$ and 1.0, for tails with length $N=60$. The shape of the segment density profile is consistent with the data published by Cosgrove *et al.*[11,14,15] obtained experimentally by using the SANS method and by MC analysis and the data obtained by Croxton[18–20] for free jointed chains.

On the presented plot one can state the decrease of the thickness of the polymer layer on the wall, and the increase of the density maximum for decreasing temperature.

In *Figure 13* one can see the density profiles obtained at temperature $T^*=4.0$ for chain lengths $N=20$, 40 and 60. In the examined range of chain lengths we cannot observe any qualitative changes of the segment density

Table 3 The results of the linear least-squares fit of $\ln(\langle R_N^2\rangle_{\parallel}/Nl^2)$ (see text for further details)

T^*	2ν	$\ln A$	Corr. coeff.
4.0	1.038 ± 0.080	1.343 ± 0.271	0.9912
2.0	0.986 ± 0.024	1.370 ± 0.081	0.9991
1.5	0.769 ± 0.056	1.936 ± 0.190	0.9921
1.0	0.670 ± 0.060	2.005 ± 0.203	0.9882
0.8	0.316 ± 0.094	2.844 ± 0.094	0.8882

Table 4 The results of the linear least-squares fit of $\ln(\langle R_N^2\rangle_{\perp}/Nl^2)$ (see text for further details)

T^*	2ν	$\ln A$	Corr. coeff.
4.0	1.270 ± 0.027	0.394 ± 0.092	0.9993
2.0	1.238 ± 0.032	0.388 ± 0.109	0.9990
1.5	1.100 ± 0.008	0.714 ± 0.028	0.9999
1.0	0.953 ± 0.045	0.972 ± 0.152	0.9967
0.8	1.101 ± 0.212	0.308 ± 0.720	0.9484

Table 5 The results of the linear least-squares fit of $\ln(\langle R_G^2\rangle_{\parallel}/Nl^2)$ (see text for further details)

T^*	2ν	$\ln A$	Corr. coeff.
4.0	1.083 ± 0.044	-0.615 ± 0.148	0.9976
2.0	1.010 ± 0.015	-0.484 ± 0.053	0.9996
1.5	0.882 ± 0.028	-0.158 ± 0.094	0.9985
1.0	0.770 ± 0.024	-0.025 ± 0.080	0.9986
0.8	0.551 ± 0.048	0.556 ± 0.163	0.9887

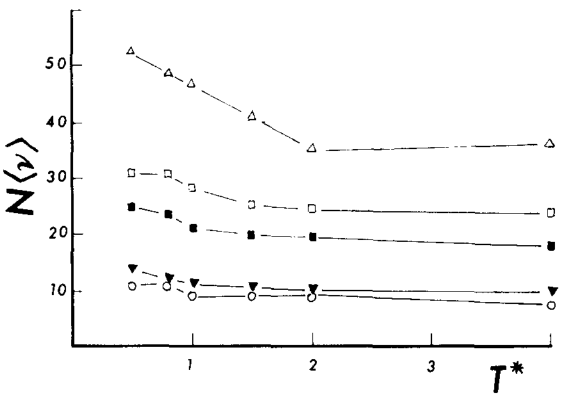

Figure 11 Plot of the mean number of polymer–polymer contacts against the reduced temperature T^* for chain lengths $N=16$, 20, 30, 40 and 60: (○) $N=16$; (▼) $N=20$; (■) $N=30$; (□) $N=40$; (△) $N=60$

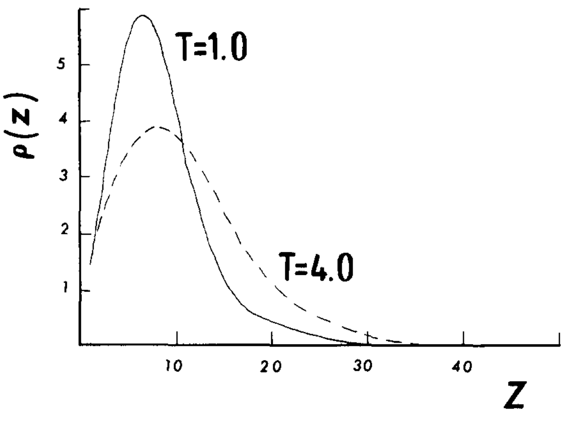

Figure 12 Plot of the segment density profiles obtained at temperatures $T^*=4.0$ and $T^*=1.0$ for tails $N=60$

shape. All segment density profiles procured in the presented work have a distinct maximum away from $z \simeq \langle R_G^2 \rangle^{1/2}$. This dependence persists over the entire range of observed temperatures.

CONCLUSIONS

The statistical properties of isolated model chains constrained to a tetrahedral lattice were investigated. The chains were anchored to a rigid wall without attractive force to polymer. A short-range attractive force (defined by equation (6)) between polymer beads was assumed. We pay special attention to the region around the θ temperature, where the chain anchored to the wall has properties of the chain without polymer–polymer interaction (in a sense of quasi-ideal scaling of chain dimensions). We have considered the dimensions of the coil and its shape as well. Values of $\langle R_N^2 \rangle$, $\langle R_G^2 \rangle$, and their parallel and perpendicular components $\langle R_N^2 \rangle_{\parallel}$, $\langle R_N^2 \rangle_{\perp}$ and $\langle R_G^2 \rangle_{\parallel}$ are calculated. We have also shown the mean number of polymer–polymer contacts *versus* temperature and mean function of segment density for all modelled chains.

In particular the following points have been found:

(i) The θ transition occurs for tails in poor solvent conditions between the reduced temperatures $T^*=1.5$ and $T^*=2.0$.

(ii) Chains confined to the half-space are governed by the same characteristic power laws as free chains.

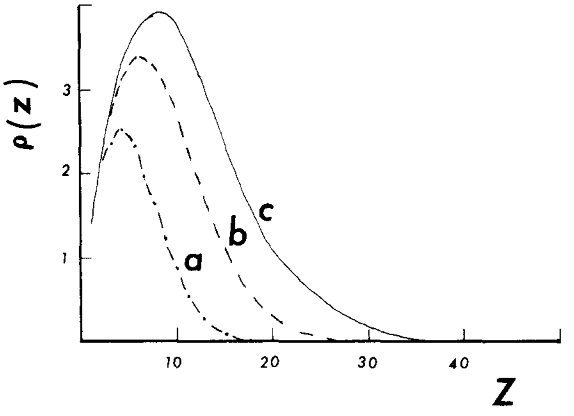

Figure 13 Plot of the segment density profiles obtained at temperature $T^*=4.0$ for tails $N=$ (a) 20, (b) 40 and (c) 60

(iii) The data obtained do not permit us to make a quantitative calculation of the θ point for tails. We think that, to obtain the phase transition point precisely, the length of the studied tails should be longer by an order of magnitude.

(iv) The parallel components $\langle R_N^2 \rangle_{\parallel}$ and $\langle R_G^2 \rangle_{\parallel}$ are independent of the surface and they behave like in the free-chain case.

(v) The mean number of polymer–polymer contacts in the observed systems remains constant up to the temperature about the θ condition and begins to grow below this point.

(vi) Segment density profiles for tails over the entire temperature range under all conditions have the same shape, with a distinct maximum away from the wall, at the distance close to $\langle R_G^2 \rangle^{1/2}$.

Taken together, we point out that the presented method may be successfully used to examine the systems just as depicted above, but it would be very important to study longer systems, which is unfortunately beyond our present computer resources. The presented work can provide the basis for a more complete description of the θ transition for non-interacting tails.

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The INSWELL microcomputer, with Intel 80386 processor and floating-point co-processor, was used for the simulation. Typical simulation (for one chain length and one temperature) required 25 to 35 h CPU time.

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