Monte Carlo model of a polymer chain attached to an interface in poor solvent conditions

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Coil dimensions of short chains terminally attached to a rigid, impenetrable boundary in poor solvent and/or low temperature conditions are studied by means of the Monte Carlo (MC) method. It is found that the system exhibits a characteristic temperature T_c at which all the chain properties change dramatically. For a given chain length N, the coil dimension above T_c decreases monotonically with decreasing temperature. Below T_c rapid expansion of the chain in a direction orthogonal to the surface can be seen.

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

INTRODUCTION

The influence of a rigid boundary on the conformation of a terminally attached short polymer chain has been extensively studied over the last few years. Gel permeation chromatography, detergents, adhesion and colloid stabilization are typical areas of application. Computer simulation methods can be used to elucidate some of the properties of such systems.

Lal and Stepto[1] studied the properties of a lattice chain by means of the Monte Carlo (MC) method. The mean fraction of adsorbed segments, $\langle v \rangle$, and the mean thickness of the adsorbed layer, $\langle \tau \rangle$, have been measured as a function of the adsorption energy. As a result, the tendency of $\langle v \rangle$ to increase and of $\langle \tau \rangle$ to decrease with increased adsorption energy (modelled by a contact potential characterized by an interaction parameter $\Delta\varepsilon_a$) has been recorded. The dimensions of the chain and its shape have been estimated from analysis of the mean square end-to-end distance $\langle R_{1N}^2 \rangle$ and the radius of gyration $\langle S_N^2 \rangle$. It was found that the chain in an athermal solution tends to assume an expanded conformation near the boundary.

Clark and Lal[2] analysed the model, including the effect of the surface coverage. This parameter was defined as $\tilde{A} = A/A^*$, where $A^* = R_{\max}^2$, $R_{\max}$ is the length of the fully stretched chain and A is the area of the MC box wall. In this way, variations in the surface coverage can be modelled by modifications of the MC box dimensions. Interactions between 20-segment chains have been subjected to periodic boundary conditions[3]. The polymer dimensions, as well as the thickness of the adsorbed layer, have been found to depend on the surface coverage. Two distinguishable regions of the surface coverage can be assumed from analysis of the configurational behaviour of the adsorbed chains: first, for $\tilde{A} \geqslant 0.25$, a region where chain–chain interactions are too weak to manifest themselves in conformational changes; and second, for $\tilde{A} < 0.25$, a region of large coverage, where configurational properties strongly depend on surface coverage density. Characteristic dimensions, such as $\langle R_{1N}^2 \rangle$ and $\langle S_N^2 \rangle$ decrease monotonically up to a limiting value of surface coverage parameter $\tilde{A} = 0.125$. For $\tilde{A} < 0.125$, increase of the surface coverage leads to an extremely rapid expansion of the chains in a direction orthogonal to the surface.

Croxton pays much attention to short chain conformation near a boundary. In his work[4] a MC technique was applied to perfectly flexible self-avoiding hard sphere sequences terminally attached to a rigid plane. The existence of a discontinuity in a segment density distribution $\rho(z|N)$ down the coordinate normal to the boundary, defined as

$$\rho(z|N) = \sum_{i=1}^{N} Z(z_i|N) \qquad (1)$$

is revealed, where $Z(z_i|N)$ is the normalized spatial probability distribution of the ith segment within the N-mer normal to the boundary. The mean square end-to-end distance, the mean square radius of gyration and thickness of the adsorbed layer were investigated too. The data for short chains (up to 20 segments) lead to the conclusion that both $\langle R_{1N}^2 \rangle$ and $\langle S_N^2 \rangle$ scale as n^{γ}, where $n = N - 1$ is the number of bonds of the N-mer and $\gamma = 1.20$ is the mean square length exponent. The structure of the chain in such a system may be resolved into three classes: loops, trains and tails. Croxton[5] noted that structure of the chain is dominated by tails, which account for most of the observed structure.

The influence of solvent molecular diameter on density distribution and the dimensions of a chain composed of a hard sphere sequence, terminally attached to a rigid boundary, have been determined by Croxton[6]. Short chain (up to 14 segments) properties have been analysed using the iterative convolution technique[7]. Both $\langle R_{1N}^2 \rangle$ and $\langle S_N^2 \rangle$ have been observed to decrease with increasing

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packing fraction and/or increase of the diameter of solvent molecules.

The structure of the adsorbed polymer chain in poor solvent conditions at temperatures below Flory's theta (θ) point is less well explored[8]. This model is very important in understanding the steric stabilization of colloidal systems[9]. Presumably, a critical level of flocculation in colloidal systems stabilized by polymers is related to the collapse transition of polymer chains. The study of the collapse transition near a non-adsorbing interface is of some interest in biophysics too. Good examples are the problems related to the influence of the cellular membrane on biopolymer structure and transport through the lipid bilayers[10].

In this paper we present a Monte Carlo analysis of the dimension and shape of short chains terminally attached to a rigid plane in poor solvent conditions. Conformational properties, the energy of the isolated chain and the structure of the adsorbed layer as function of the temperature have been investigated.

MODEL AND SAMPLING PROCEDURE

Description of the model

A model system consists of a single polymer chain, composed of 20 segments, terminally attached to the MC box wall. Lattice points unoccupied by polymer are considered to be occupied by solvent molecules. Therefore, the model system corresponds to the case of a relatively dilute solution. A self-avoiding walk (SAW) type chain is restricted to the diamond lattice. The details of the construction of the diamond lattice SAWs can be found elsewhere[11]. The interactions between polymer beads in the solvent are described by the potential of mean force of the following form:

$$V(r_{ij})=\begin{cases}\infty & r_{ij}=0,\ i\neq j\\ \varepsilon_a & r_{ij}=l, |i-j|\neq 1\\ 0 & r_{ij}>l\end{cases} \tag{2}$$

where r_{ij} is the distance between the ith and jth beads of the chain, l is a chain bond length (in our case $3^{1/2}$) and ε_a is an attractive parameter. For poor solvents $\varepsilon_a<0$. The total reduced configurational energy of the system is defined as a sum of binary interactions:

$$\frac{E}{kT}=\frac{\varepsilon_a}{kT}\sum_{i\neq j}^{N} v_{ij} \tag{3}$$

where v_{ij} is the number of polymer–polymer contacts and $\varepsilon_a/kT=-1/T^*$, where T^* is the reduced temperature of the system.

A cubic Monte Carlo box has edge length $-L$ greater than the anticipated coil dimension. The chain is attached to the chosen wall of the MC box, which is assumed to be impenetrable for the chain segments (*Figure 1*). Periodic conditions[3] are forced upon the lateral walls.

Three- and four-bond conformational jumps of inner segments and two- and one-bond jumps of the free end of the chain are used for MC modelling of the chain dynamics[11,12]. As shown by Iwata and Kurata[13], this set of elementary jumps enables the entire spectrum of chain conformational transitions within the diamond lattice approximation to be covered. The four-bond conformational jumps seem to be necessary in order to cut down the computation time and lead to a relaxation time of the chain proportional to N^2 (similar to the Rouse chain behaviour) instead of the N^3 dependence when only three-bond motion is present[11–14] (a related problem is discussed by Hilhorst and Deutch[15]). This effect is more important for our system, where mobility of the chain is further restricted by the wall effect.

Computational method

Present computations are focused on the properties of the system for relatively strong polymer–polymer interactions. The energetically privileged conformations, in such conditions, span only a small fragment of the conformational space. Static MC methods are inefficient in such a case[11,14] and, therefore, we employ a dynamic MC method, within the framework of the Metropolis scheme.

The probability of acceptance of a trial conformation in the Metropolis scheme is related to the energy change of the system $\Delta E_{ij}=E_j-E_i$, where E_j is the energy of a new (trial) state and E_i is the energy of the old state. For $\Delta E_{ij}\leqslant 0$ the new conformation is always accepted; for $\Delta E_{ij}>0$ the acceptance probability is equal to $p_{ij}=\exp(-\Delta E_{ij}/kT)$. In the limit of the long MC sequence the energy distribution of the model system approaches the equilibrium Boltzmann distribution. Therefore, all measured properties of the system can be estimated as arithmetical averages.

At the beginning of the MC experiment the model chain was placed into the MC box in fully extended conformation. Then the chain conformation was equilibrated by means of the Metropolis scheme described above, assuming $\varepsilon_a=0$ (athermal system) to speed up the initial stage of equilibration. In the final stage of equilibration a proper (non-zero) value of ε_a was assumed. A dynamic equilibrium of the system after some relaxation period (dependent on the values of ε_a and N) was always achieved. An analysis of the flow charts of simulation was used as a criterion of proper equilibration of the system. The major part of the simulation (sampling run) consisted of a large number (of the order of 10^7) of trial micromodifications of the model chain.

The level of statistical error of the measured properties of the model system was estimated as follows (see, for comparison, the work of Bishop *et al.*[16]). The simulation run consisting of M cycles was divided into a series of subruns consisting of M_p cycles each. Then the average values of measured quantities X were computed for each

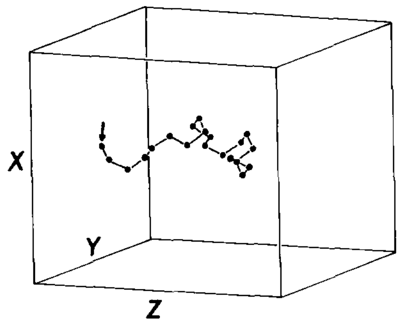

Figure 1 Monte Carlo box with a snapshot of the attached chain ($N=20$, $T^*=4.0$). The arrow denotes the site where the chain is attached to the wall

Table 1 Comparison of coil dimensions obtained in this work and by Clark and Lal[2]

	This work	Ref. 2
$\langle R_{1N}^2\rangle_0/Nl^2$	2.65 ±0.03	2.63 ±0.02
$\langle S_N^2\rangle_0/Nl^2$	0.374±0.003	0.377±0.002

subrun separately, according to the following equation:

$$X_l=\frac{1}{p}\sum_{k=(l-1)p+1}^{l_p} X(k) \qquad l=1,\ldots,M_p \tag{4}$$

where p is the number of cycles (micromodifications of the chain conformation) in a subrun. The mean value of X is the arithmetic average of the subrun result:

$$\langle X\rangle=\frac{1}{M_p}\sum_{i=1}^{M_p} X_l \tag{5}$$

The 95% confidence limit for the X_l distribution was assumed to be an estimation of the statistical error of $\langle X\rangle$.

RESULTS AND DISCUSSION

Chain dimensions

Chain dimensions are described by two parameters: the mean square end-to-end separation $\langle R_{1N}^2\rangle$, which is defined by the following equation:

$$\langle R_{1N}^2\rangle=\langle(\mathbf{\bar{r}}_N-\mathbf{\bar{r}}_1)^2\rangle \tag{6}$$

and the mean square radius of gyration, which is:

$$\langle S_N^2\rangle=\frac{1}{N}\left\langle\sum_{i=1}^{N}(\mathbf{\bar{r}}_i-\mathbf{\bar{r}}_{\mathrm{CM}})^2\right\rangle \tag{7}$$

where r_i is the Cartesian coordinate of ith polymer bead and r_{CM} the coordinate of the centre of gravity of the entire trajectory of the system, i.e. the time average based on a MC run.

According to the anisotropy of the polymer coil at the surface it is useful to compute components of $\langle R_{1N}^2\rangle$ orthogonal and parallel to the surface[17] defined as follows:

$$\langle R_{1N}^2\rangle_{\parallel}=\langle(x_1-x_N)^2+(y_1-y_N)^2\rangle \tag{8}$$

$$\langle R_{1N}^2\rangle_{\perp}=\langle(z_1-z_N)^2\rangle \tag{9}$$

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

Similarly, one defines the radius of gyration in the XY plane, parallel to the surface:

$$\langle S_N^2\rangle_{xy}=\frac{1}{N}\left\langle\sum_{i=1}^{N}(x-x_{\mathrm{CM}})^2+(y-y_{\mathrm{CM}})^2\right\rangle \tag{10}$$

According to the axial symmetry (in the statistical sense) of the attached coil, the last parameter may be considered as more important than $\langle S_N^2\rangle$, which is normally used in the anisotropic case of an isolated coil[11].

The data obtained in the present work for the specific case (used here as a reference state) of the athermal system ($\varepsilon_a=0$) can be compared with the earlier results of Clark and Lal[2]. The values of $\langle R_{1N}^2\rangle/Nl^2$ and $\langle S_N^2\rangle/Nl^2$ from both our work and Reference 2 are given in *Table 1*. Good agreement between the results of the two works (in spite of different simulation algorithms) can be considered as a test of computational methodology, and consequently allows for some conclusions concerning the real systems.

In *Figure 2* the values of $\langle R_{1N}^2\rangle/Nl^2$, $\langle R_{1N}^2\rangle_{\parallel}/Nl^2$ and $\langle R_{1N}^2\rangle_{\perp}/Nl^2$ are plotted against the reduced temperature $-kT/\varepsilon_a=T^*$. *Figure 3* shows the dependence of $\langle S_N^2\rangle/Nl^2$ and $\langle S_N^2\rangle_{xy}/Nl^2$ on T^*. The vertical bars in the figures correspond to the 95% confidence limit estimated according to the method described above.

Two distinct temperature regions of the system behaviour seem to be evident. For relatively high temperatures and/or in good solvent conditions $\langle R_{1N}^2\rangle$ monotonically decreases with decreasing temperature. For low temperatures $\langle R_{1N}^2\rangle$ has a minimum and then increases with further decrease of T^*. Very similar behaviour of $\langle S_N^2\rangle$ can be seen. Analysis of *Figures 2* and *3* shows that the direction of chain expansion in the low temperature regime is highly anisotropic. The main direction of chain expansion is orthogonal to the surface. In contrast, the parallel components, $\langle R_{1N}^2\rangle_{\parallel}$ and $\langle S_N^2\rangle_{xy}$, decrease monotonically. The last observation is typical for the collapse transition of an isolated (not adsorbed) flexible polymer chain (see References 11 and 18). An increase of chain dimensions (the opposite behaviour) with decrease in temperature over some range of T^* has been observed in earlier studies of semiflexible polymers[19,20]. In the above case of an isolated polymer

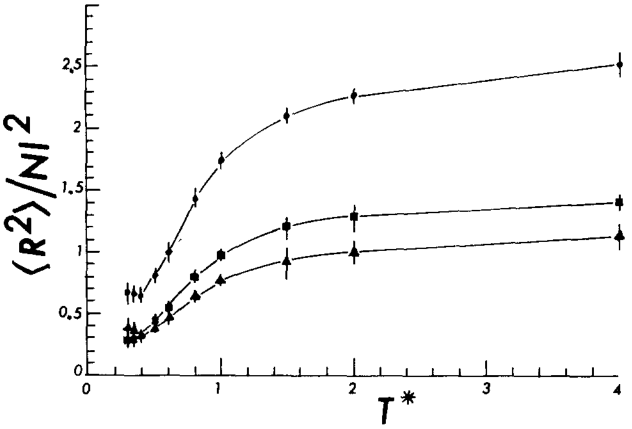

Figure 2 $\langle R_{1N}^2\rangle/Nl^2$ (●), $\langle R_{1N}^2\rangle_{\parallel}/Nl^2$ (■) and $\langle R_{1N}^2\rangle_{\perp}/Nl^2$ (▲) as functions of T^*

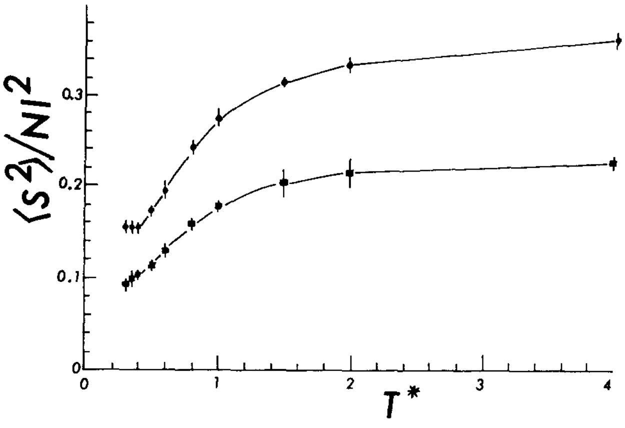

Figure 3 $\langle S_N^2\rangle/Nl^2$ (●) and $\langle S_N^2\rangle_{xy}/Nl^2$ (■) as functions of T^*

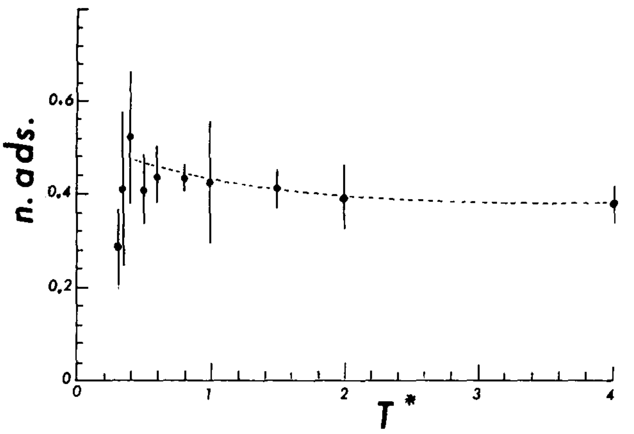

Figure 4 Mean number of segments in contact with the inpenetrable surface as a function of T^*

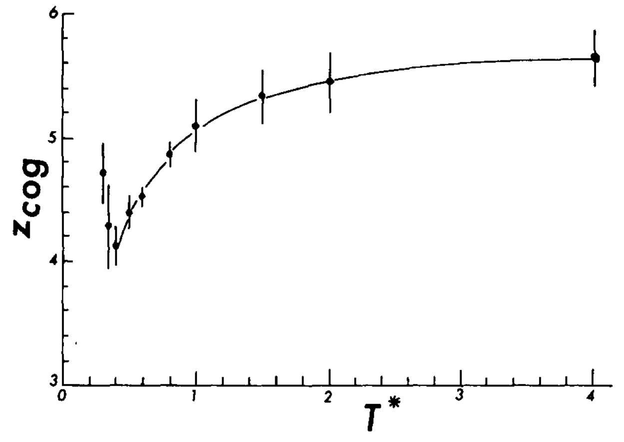

Figure 5 Distance between centre of mass of the coil and surface as a function of T^*

molecule this reflected the increasing effect of short range interactions (stiffness of the chain) with decreasing temperature. In the present work the reason for such behaviour is quite different. Here, a repulsive effect of the surface is responsible for chain expansion in a direction perpendicular to the surface. More detailed analysis of polymer segment density distribution confirms the last statement.

Structure of adsorbed coil

Inspection of *Figure 4*, in which the fraction of adsorbed segments in contact with the surface is plotted against temperature T^*, provides additional information concerning the structure of the coil at the surface.

The fraction of the adsorbed segment slowly increases with decreasing temperature over the entire high temperature range. Below a characteristic point (where the orthogonal expansion becomes significant) the number of polymer–surface contacts decreases rapidly.

The apparent repulsive effect of the surface is even more evident after analysis of the temperature dependence of the distance between the centre of the mass of the coil and the surface. Again, below the characteristic temperature $T_c^* = 0.4$ this distance increases with decreasing temperature (*Figure 5*). In *Figure 6* polymer density $\rho(z)$ is plotted as a function of T^*. The data obtained from MC simulation are in qualitative agreement with experimental findings for small surface coverage[21] for segment density profiles calculated according to the Monte Carlo method for a cubic lattice model[22], and with the theoretical predictions of de Gennes[23]. Indeed, all the simulation data indicate the existence of the characteristic temperature T_c^*. The thickness of the layer of adsorbed polymer exhibits a minimum at this temperature. Decrease of temperature, as well as increase of T^*, leads to a more diffuse layer. However, the causes in the two cases differ. It is interesting that the location of the maximum polymer density region remains almost unaffected by temperature. It is not clear if the last observation is limited to the particular range of chain lengths studied, especially when one considers changes in the absolute value of the density maximum with reduced temperature (*Figure 7*). The data illustrated in *Figure 7* also confirm the statement that at very low temperatures (below the characteristic point T_c^*) the observed layer of adsorbed polymer becomes diffusive again.

CONCLUSION

An idealized model of polymer chains terminally attached to an impenetrable surface was studied by means of the dynamic Monte Carlo method. Earlier studies were extended to the region of lower temperature, and additional information was given concerning the structure of the coil near the surface. However, asymptotic behaviour ($N \rightarrow \infty$) cannot be deduced from the present

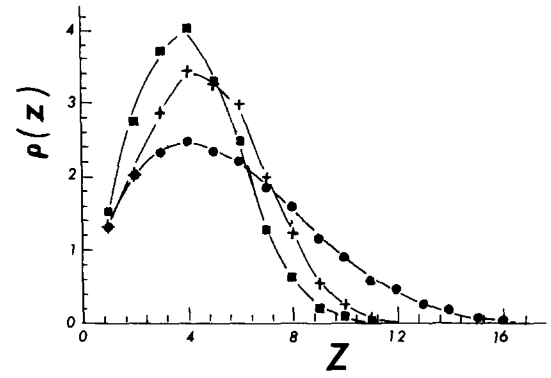

Figure 6 Segment density distribution for attached chain as a function of distance to the surface: ●, $T^* = 4.0$; ■, $T^* = 0.4$; ×, $T^* = 0.3$

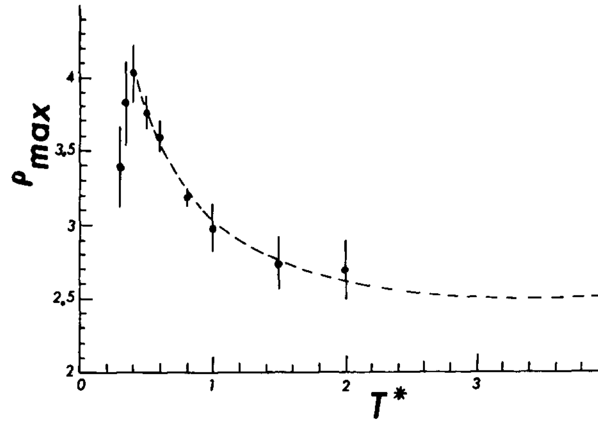

Figure 7 Absolute value of the density distribution maximum as a function of T^*

studies. There seems to be some reason to expect a strong effect of the surface on the character of the collapse transition of the polymer coil[24]. We hope that the findings of the present work explain some features of short polymers at the surface.

In particular it has been found that:

(1) For short chains terminally attached to the impenetrable rigid plane two temperature regions can be distinguished.

(2) At relatively high temperatures, where the repulsive force of the wall is not too strong, the chain behaves like an isolated, non-attached, polymer.

(3) Below a characteristic temperature T_c^* properties of the chain change dramatically. The chain expands in a direction orthogonal to the surface.

The results for longer chains (up to $N=60$) with an analysis of the chain length effect on system behaviour will be published soon[24].

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