Lattice polymers: behaviour far from θ-conditions

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Two-dimensional Monte-Carlo simulations of lattice polymers were carried out employing Lennard–Jones (LJ) type intramolecular interactions. The shape-dependent properties of these polymers were studied over a large range of interaction parameters and temperatures. The variation of the critical constant was also analysed. Two-dimensional surfaces of sections were used to determine the portions of the parameter space which corresponded to θ-conditions. The behaviour of LJ polymers far from θ-conditions was determined. The investigations were facilitated by a simple scaling argument which resulted in considerable time savings in computations.

INTRODUCTION

It has been observed that the statistical laws governing lattice spin systems and polymers can be described by similar relations[1]. Hence, the previously gained insight from the statistical physics of spin systems coupled to the relative ease of the chain generation on lattices made lattice polymers a very popular model for simulation studies.

Random walk historically has been among the most powerful numerical techniques for studying conformational properties of lattice systems. Starting with the original work of Kuhn[2], various procedures have been employed to approximate the distribution of the configurational space of flexible macromolecules[3,4]. Once the excluded volume effect has been incorporated into the walk generation process, the more realistic procedure of the self-avoiding-walk (SAW) is then created[5]. However the excluded volume effect introduces a certain bias into the sampling process and this bias can be corrected by an early recipe of Rosenbluth and Rosenbluth[6]. SAW, being especially powerful on lattice simulations, has been analysed in detail for various two- and three-dimensional lattices[7–14]. Upon including intramolecular interactions between the repeating units of the chain, one can then study the correlations between the 'numerical' and the 'real' experiments[15–17] and there have been a number of excellent reviews of this field[18–20]. Most of these studies have been carried out in θ-conditions. Under these conditions, contraction of a macromolecule can sometimes compensate its expansion due to volume effects so that the total effect of long range interactions becomes negligible and the polymer behaves like a random coil[21]. These conditions can be achieved by working at a specific temperature for each polymer–solvent pair. However the conformational properties of polymers can also be studied far from θ-conditions by varying the long range interaction parameters as well as the temperature. Here we report our findings in two-dimensional square lattices which self interact via Lennard-Jones (LJ) potential interactions. We analysed the effects of temperature and potential parameters on the shape-dependent properties, such as end to end distance ($\langle r^2 \rangle$) and radius of gyration ($\langle s^2 \rangle$), of chains of varying sizes.

$$\langle r^2 \rangle = \langle (r_N - r_1)^2 \rangle \qquad (1)$$

$$\langle s^2 \rangle = \frac{1}{N} \sum_i (r_i - r_{COM})^2 \qquad (2)$$

where r_{COM} defines the coordinates of the centre of mass.

The critical constant and its dependence on the interaction potential were also analysed.

COMPUTATIONS

The generation of SAW on two-dimensional lattices is rather straightforward[22]. Once a sufficiently large number of configurations are created, the canonical ensemble average of a property can simply be computed:

$$\langle O \rangle = \frac{\sum O_i \exp(-\beta E_i)}{\sum \exp(-\beta E_i)} \qquad (3)$$

where β is $1/kT$, E_i is the energy of individual configurations obtained from two-body interactions and O_i is the measured property for the configuration i.

However the no-self-intersection rule disturbs the randomness of the sampling and a correction factor for each chain has to be included[6]:

$$\langle O \rangle = \frac{\sum W_i O_i \exp(-\beta E_i)}{\sum W_i \exp(-\beta E_i)} \qquad (4)$$

with

$$W_i = \prod_k d_k / q \qquad (5)$$

where d_k is the available number of directions at step k and q is the total number of directions available which is 3 in the case of SAW on square lattices.

The energy of each configuration is computed simply from the sum of two-body contributions. As in common practice, the interaction between two bonded units is considered as constant throughout the simulation. The fact that the vibrational motions of the chemical bonds are excluded does not produce any significant error in the final description of long chains. We have used the LJ potential as the interaction between non-bonded units.

$$V = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \qquad (6)$$

where ε and σ are the potential parameters which define the range and the strength of the interaction. This is not a long range potential in the mathematical sense, however, depending on the size of the cell length, even the interactions between fifth and sixth nearest neighbours contribute to the self energy. In our computations we have used a potential cut-off at eight cell lengths.

In this averaging process, only those walks which mature to the specified length are considered, that is, in the case of a ring closure the complete walk is discarded from the sampling. This procedure causes severe computational restrictions on the chain generation process[23]. For example, in the case of a chain length of 200, as many as 80% of the configurations are discarded. Since chain generation is the most time-consuming step of the computation, a technique was used which enabled Monte-Carlo averages over a wide range of parameters to be obtained with considerable savings in computer time[24].

Since chain generation is independent of the interaction parameters or temperature, from one calculation at fixed temperature, ε and σ values, it is possible to generate averages for any given set of temperature, ε and σ. To achieve this, a calculation with a fairly large sample space is carried out. During the calculation the following sums are saved for each configuration as well as any desired property of that configuration.

$$S_1^i = \sum_{p>q} \left(\frac{1}{r_{pq}} \right)^{12} \qquad S_2^i = \sum_{p>q} \left(\frac{1}{r_{pq}} \right)^6 \qquad (7)$$

Then the total energy of the configuration i can be written as

$$E_i = 4\varepsilon(\sigma^{12} S_1^i - \sigma^6 S_2^i) \qquad (8)$$

with the corresponding Boltzmann probability factor of $\exp(-\beta E_i)$. Then, once these configurations are generated, any average property at a different temperature (or β), ε and σ can be computed without regenerating these configurations. The new energy at ε' can be computed as:

$$E_i(\varepsilon', \sigma) = \frac{\varepsilon'}{\varepsilon} E_i(\varepsilon, \sigma) \qquad (9)$$

the Boltzmann factor for a different temperature is

$$\exp(-\beta' T) = \exp(-\beta T) \exp(-\delta\beta T) \qquad (10)$$

with $\beta' = \beta + \delta\beta$.

In the case where σ is varied, the energy expression is slightly more time consuming:

$$E_i(\varepsilon, \sigma') = 4\varepsilon[(\sigma')^{12} S_1^i - (\sigma')^6 S_2^i] \qquad (11)$$

Combining these equations, any energy, Boltzmann factor, $\langle r^2 \rangle$ or $\langle s^2 \rangle$ can be computed for a wide range

of parameters with substantial savings in computational time. To give an example, the initial run of generating 100 000 configurations takes ~ 4000 s on IRIS 4D/20, where 900 sets of calculations of various temperature, ε, and σ take ~ 5000 s. Equations (9)–(11) are exact for the uniform sampling used here. However it is possible to employ such a scaling for the case of standard importance sampling of the Metropolis Monte-Carlo in a perturbation-like scheme. That is, the results would be reliable within a radius of convergence which depends on the size of the configuration space sampled. Work along these lines is in progress in our laboratories.

RESULTS AND DISCUSSION

We have carried out simulations of chains ranging from 100 to 200 repeating units. In each case, 100 000 configurations are generated and the summations S_1 and S_2 are stored as well as the end-to-end distances and radii of gyration for each configuration of the fixed length. The length of the unit cell in the square lattice is kept constant and the σ parameter of the LJ potential is expressed in terms of this length L. For these calculations we have used $T = 300$ K, $\varepsilon = 0.3$ kcal mol^{-1} and $\sigma = L$. Although the number of chains does not seem to be very large, a convergence study showed that the fluctuations of energy and the other properties remain in an acceptable range for 300 K. Then around 1000 sets of parameters are tested again at every chain length, for $T = 150$–450 K, $\varepsilon = 0.1$–1.1 kcal mol^{-1} and $\sigma = 0.7$–1.1L. *Figure 1* shows the results for the variation of $\langle r^2 \rangle$ as a function of the three parameters for a chain length of 200. It is seen that at ε values above 0.5 kcal mol^{-1}, almost independent of temperature and σ, collapsed polymers are obtained (these observations are also valid for various chain lengths). This is not unexpected as high ε means high attractive energy especially for the nearest neighbours. Only for very large σ, can this effect be compensated. Also temperature does not seem to play a great role in the high ε regime. Therefore we concentrate on small ε, i.e. $\leqslant 0.5$ kcal mol^{-1}. In that case, a plot of σ–T displays a valley which resembles θ-conditions. From scaling-theoretical arguments, this can be understood since there is always a set of parameters which should give the same measurements. However the question is whether these parameters are found in physically reasonable ranges. For $\varepsilon = 0.3$ kcal mol^{-1}, the collapsed polymers are found between $\sigma = 0.8L$ and $0.9L$ and below 200 K. The transition from collapsed to random flight is rather steep and occurs for $\varepsilon < 0.28$ kcal mol^{-1}, $\sigma > L$ and $T > 450$ K. The conclusions from plots of $\langle s^2 \rangle$ are along the same lines. The variation of average energy does not produce any unexpected behaviour with high ε and low T resulting in low energy regimes.

In addition to the above findings we have studied the size problem of macromolecules as a function of the length. It is well established that $\langle r^2 \rangle$ of random walk polymers changes by a power law

$$\langle r^2 \rangle = a N^\nu \qquad (12)$$

where ν is a universal constant which depends only on the lattice dimensionality but not on the type of the lattice. In the case of random walk on two-dimensional lattices, this constant ν is ~ 1.5. This value, however is not a universal constant when there are interactions
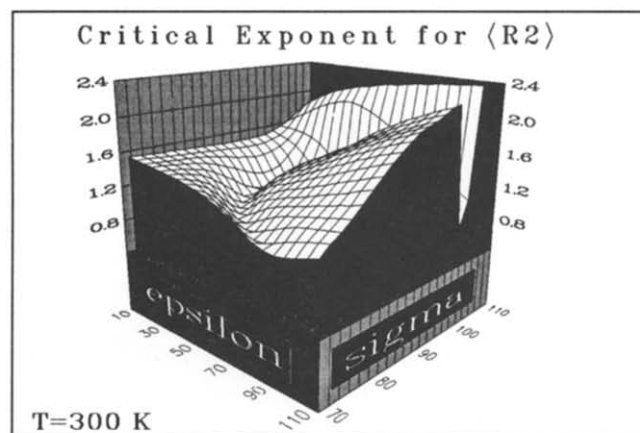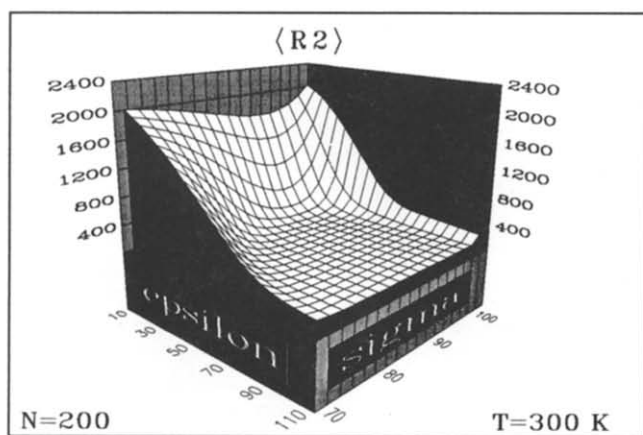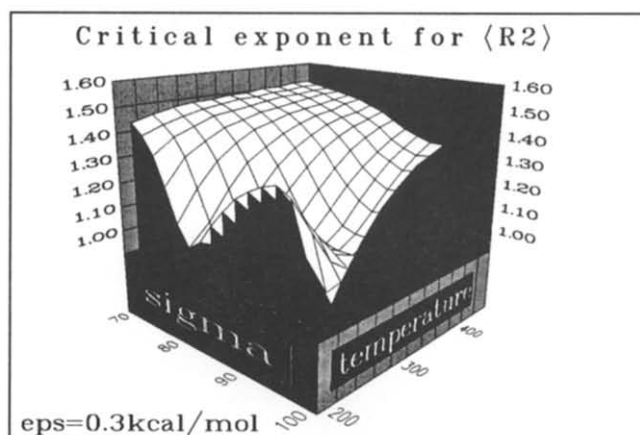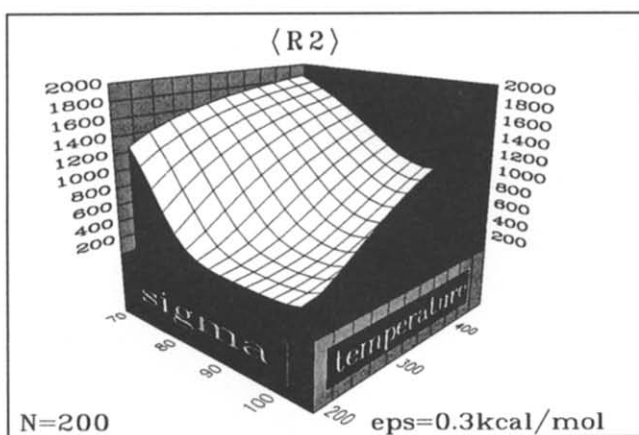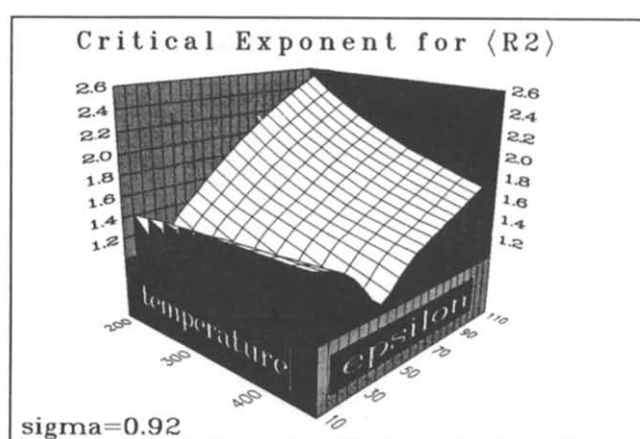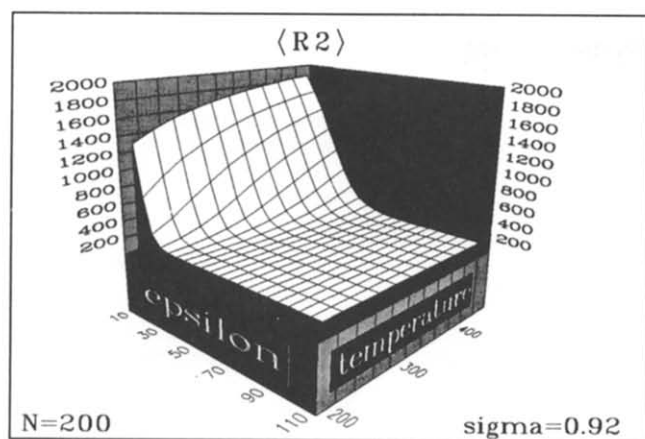
Figure 1 Two-dimensional surfaces of the variation of $\langle r^2 \rangle$ as a function of σ, ε and T

Figure 2 Two-dimensional surfaces of the variation of the power v as a function of σ, ε and T

between monomers, since the randomness of the walk is heavily disturbed[25,26].

The variation of the critical constant (*Figure 2*) with interaction strength is somewhat more interesting. At constant σ, there is a valley which presumably represents the θ-conditions with $v = 1.0$ for all temperature values studied. This valley corresponds to the $\varepsilon/kT = 0.5$ line with fairly good accuracy. For constant ε, the behaviour of v is not so simple. At low temperature, there seem to be two different minima bracketing a maximum at $\sigma = 0.9L$. This maximum corresponds to the case where the length of the unit cell L coincides with the minimum of the LJ potential ($2^{-1/6} = 0.891$). A similar double minimum behaviour is also observed when a one-

dimensional variation of σ is carried out. At low σ values (large distance between successive units), the polymer is like a random flight polymer since the interactions are very low, and for the high σ values, then the interactions become very repulsive again resulting in fairly random walks. In the intermediate region, collapsed polymers are detected. This double minimum type plot is seen also in the $\varepsilon-\sigma$ surfaces, however a clear explanation of the rather irregular surface eludes us.

In summary, we have shown that by a very simple strategy, we were able to analyse the variation of shape-dependent properties and the critical constant as functions of temperature and interaction parameters on square lattices. The regions for the collapsed and random walk polymers are recognized as well as the ranges corresponding to θ-conditions. From the variation of the

critical constant v, the transitions away from θ-conditions can also be studied.

ACKNOWLEDGEMENTS

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