1 Aims, Expected Outcomes and Significance

In a recent review on the theoretical understanding of long chain polymer molecules in dilute solution two of the pioneering workers [1] in the field began their abstract with "No modern theory of polymer excluded volume adequately describes the crossover from poor to good solvent conditions". On the other hand, there are other workers who would contend that the excluded volume problem and the collapse transition have been more or less solved with the three-parameter Edwards model [2, 3], and with the correspondence to a tricritical O(n) field theory [4, 5, 6], providing an adequate description. Why, after several decades of study, is the three-parameter Edwards model still the subject of controversy? Undoubtedly it is partly due to the difficulty of analysing the model, but more fundamentally is it because the domain of applicability of the model is not understood? It is certainly the case that if one could solve the model of *interacting self-avoiding walks* (ISAW) on any regular lattice one would have a complete description of the *universal* features of the collapse transition of dilute polymers. However, the ISAW model has proved even more intractable - only partly yielding to numerical studies. Recently, however, new methods and advancing computer power have combined to give the opportunity to sensibly attack the questions alluded to above.

- *The general aim of this project is to gain an understanding of the universal features of long chain polymers in dilute solution. In particular, this project aims to delineate the domains of validity of competing models, and by so doing help resolve the controversies surrounding the subject.*

Many of the models of polymer conformations other than ISAW, such as the Domb-Joyce model [7], have *random walks* as the set of allowed configurations (or a diffusing chain in the case of the Edwards Model) from which the model is constructed. By themselves random walks do not have excluded volume (they intersect freely) and to mimic real polymer conformations some type of repulsive interaction is added. When modelling the universal features of self-avoiding walks with a repulsive random walk model it is well accepted that as soon as the repulsion is turned on one gets self-avoiding walk critical properties. However, to model the collapse transition an additional attractive interaction has to be included. In models based on random walks (or chains) these two interactions are *simultaneously* added as perturbations. It is then hoped or assumed that the repulsive interaction produces rigid self-avoidance (ie self-avoiding walks) after which the attraction acts. Clearly if the repulsion is first taken to infinity and then the attraction is added, one gets ISAWs, however this is *not* how the Domb-Joyce (with appropriate attraction) or three parameter models are analysed. It is thus difficult to separate "geometric" (excluded volume) from "thermal" (attractive forces) effects in these models [1].

When only attraction is added, as for example in the Domb-Joyce model, the resulting phase is characterised by walks that on average are bounded in some region in space no matter how long they are or what the spatial dimension is [8] ie a "dot" phase results, which is clearly unphysical. This is also the case for the (ultraviolet limit of a) cut-off two-parameter Edwards model in dimensions greater than two [9], which is a random walk model. Real polymers in a collapsed state are compact balls (in three dimensions or discs in two dimensions) not "dots" as implied by the attraction-only random walk models. Thus attraction alone is insufficient to describe this system.

Recently, evidence has come to light that challenges [10, 11] the predictions of the three-parameter Edwards model/tricritical O(n) field theory in three dimensions. It is

unclear whether the Edwards model, being based on a continuum random walk, can correctly represent the collapse transition of ISAW. It is clear that the two-parameter Edwards model and the Domb-Joyce model with repulsion only do *not* give a description of the collapse transition in two dimensions (since the θ-state has a fractal dimension of 7/4 and not 2). However, the question remains as to the suitability of a Domb-Joyce model with repulsive contact but attractive nearest-neighbour interactions. Some evidence that unexpected results may be obtained comes from another model of excluded volume and its extension to describe collapse, being that of trails and interacting trails respectively. It can be seen in the model of interacting trails that the change in the types of excluding volume (trails are bond-avoiding not site avoiding) and attractive interactions (these are contact interactions) changes the nature of the collapse transition [12, 13, 14, 10].

- *The specific objective of this project is to elucidate the relationship between models of excluded volume and the collapse transition by studying systematically the competing effects of attraction and repulsion added to a random walk model to determine whether it is a suitable model of polymer collapse.*

Many models of random walks with added attractive or repulsive interactions exist in the literature (see, for example, [7, 9, 15]). It is *our proposal* to consider *the model of Brydges and Slade* [9] as the basis for our studies. The Hamiltonian of this model for an N step walk is given by

$$\mathcal{H}_N = g_1 N^{-p} \sum_{0 \le i < j \le N} \delta_{r_i, r_j} \tag{1}$$

where r_i is the position of the i-th labeled step of the walk. It depends on the coupling g_1 and the exponent p. The cut-off two-parameter Edwards model ($p = (4-d)/2$) and the Domb-Joyce model ($p = 0$) are given by particular cases of the Brydges-Slade (BS) model and so the BS model is a natural choice to study. There are many questions about the BS model with purely repulsive or attractive interactions that remain to be answered [9] and a Monte Carlo study would be an eminently suitable avenue to explore these questions. To study the effect of a second interaction we would add a nearest-neighbour term,

$$- g_2 \sum_{0 \le i < j \le N} \delta_{|r_i - r_j|, 1} \ , \tag{2}$$

to the Hamiltonian. This would allow us to explore the (g_1, g_2, p) parameter space. We will compare these results with a *similar study of a model* which more closely mimics the three parameter Edwards model. This model has an *extended Domb-Joyce* Hamiltonian

$$\mathcal{H}_N = -h_1 \sum_k (n_k)^2 + h_2 \sum_k (n_k)^3 \tag{3}$$

where n_k is the number of times the random walk has visited the site k. The first term is essentially the same as an attractive version of (1), while the second term now provides the repulsion necessary for thermodynamic stability.

There is also controversy over the interpretation of the results of field theoretic calculations [16, 17]. The so-called 'two-parameter theory' (of which the two-parameter Edwards model is one example) of excluded volume (which basically uses the scaling function of the θ-point to describe the full asymptotic expansion of the high temperature state) seems to have no theoretical basis analysed from the point of view of standard critical phenomena ideas [16] and one way of testing the two-parameter theory is to carefully

consider corrections-to-scaling [18] in various excluded volume models. When considering the purely repulsive cases of the BS model we would calculate these corrections in an attempt to test the two-parameter ideas [19, 17].

Our *foci and expected outcomes* are thus twofold:

- To study purely attractive and repulsive random walk models — in particular the Domb-Joyce model — to gain a fuller analysis of their behaviour with a view to comprehend the domain of applicability of two-parameter theories;
- To study the interplay between *finite* repulsion and attraction in a model based on random walks — in particular the extended Brydges-Slade and extended Domb-Joyce models — to determine whether such a model is a viable description of the universal features of collapse;

The *significance* of this work is that it strikes at the fundamental conceptual basis of theories of excluded volume in models of polymer collapse. The problem of excluded volume has been recognised as one of the most subtle in statistical mechanics for the past 50 years. This work would be attempting to decide, using concrete methods (Monte Carlo simulations) on today's high speed computers, which *types* of models are suitable for the task of describing excluded volume and collapse together. If only half of our aims are realised the contribution to the understanding of these central problems of statistical mechanics will be of substance.

2 Research plan, methods and techniques

To study the various interacting random walk models we plan to use two different Monte Carlo methods: The first being the pivot algorithm [20]. The algorithm is as follows: starting from an arbitrary initial walk configuration a vertex of the walk — the pivot point — is chosen uniformly at random, as is one of the symmetry transformations of the particular lattice. The symmetry transformation is then applied to all steps on one side of the pivot point. This generates a new configuration. The energy of the new configuration is then computed. The new configuration is then accepted with the Metropolis probability,

$$\text{Prob}\{\text{Accept}\} = \begin{cases} \exp[-\beta(E_{old} - E_{new})] & \text{if } E_{old} - E_{new} > 0 \\ 1 & \text{if } E_{old} - E_{new} \leq 0 \end{cases} \tag{4}$$

where E_{old} and E_{new} are the old and new configuration energies and β is the inverse temperature. In the original algorithm one also had to check whether the new configuration was self-avoiding. This is not necessary here. This algorithm computes averages for walks of *fixed* length and is thus very well suited to computing quantities like the mean squared end-to-end distance.

Quantities such as the free energy and partition function are more efficiently computed using a variable length algorithm. Therefore, the second Monte Carlo method we propose to use is the Berretti-Sokal method [21]. This was originally designed for athermal models, and so to simulate interacting models we shall add a Metropolis move to give a Berretti-Sokal-Metropolis (BSM) algorithm. It starts with some arbitrary initial walk configuration and adds or deletes a step to or from the walk. The change in length ΔN is chosen with the transition probabilities,

$$\text{Prob}\{\Delta N = \pm 1\} = \begin{cases} z/(1+qz) & \text{if } \Delta N = 1 \\ 1/(1+qz) & \text{if } \Delta N = -1 \end{cases} \tag{5}$$

where q is the coordination number of the lattice and z the length fugacity. The new configuration is only accepted if the length of the walk is non-zero and only with the same Metropolis probability given by (4). Note, there are no self-avoidance constraints as in the original BS algorithm since we are dealing with random walks, not self-avoiding walks. Preliminary studies have shown that this considerably helps to reduce the exponential auto-correlation time compared with a self-avoiding walk model.

As a preliminary feasibility study we employed a student to write a pilot computer program for an interacting random walk model (slightly simpler than those described in the proposal). We were able to successfully simulate walks of length 4048 steps. This length was successful because we were able to simulate a workable sample from an overnight run. Our analysis of the student's data showed the worst case auto correlation time was only 600 Monte Carlo steps, which is small for this type of model. Based on our past experience walks of length 4048 are more than adequate to give good estimates of the critical properties of the model. In another Monte Carlo project, we are undertaking presently on anisotropic walks, samples of greater than 10^5 walks of length 3200 have been generated on an IBM workstation in a couple of days – here the autocorrelation time is much larger. We are thus confident we can produce adequate data to analyse for our requirements.

Both the pivot and BSM algorithms suffer from critical slowing down. For a Markov process one way this manifests itself is through increasing autocorrelation times. The increase generally occurs as a critical point of the model is approached. In order to reduce the autocorrelation time associated with the thermal critical point we propose to enhance both algorithms. The principal enhancement is to convert the single Markov chain to a multiple Markov chain [22]. This requires the simulation of several walks in parallel at a range of temperatures, β_n. At fixed intervals the temperatures of randomly chosen adjacent pairs (in temperature) of walks are "swapped" . This has the effect of increasing the temperature of one of the walks whilst decreasing the temperature of the other. If the probability of the n'th chain being in state S_n is $\pi_{S_n}(\beta_n)$ then the temperatures are swapped with the probability,

$$\text{Prob}\{\text{Accept}\} \ = \min\left(1, \frac{\pi_{S_{n+1}}(\beta_n)\pi_{S_n}(\beta_{n+1})}{\pi_{S_n}(\beta_n)\pi_{S_{n+1}}(\beta_{n+1})}\right) \ . \tag{6}$$

Heuristically, the temperature exchange has the effect of "heating up" one of the walks and thus helps it to escape from a configuration in which it might have got "stuck" (by repeated failure of the Metropolis move). The multiple Markov chain has been used with the pivot algorithm for interacting self-avoiding walks in three dimensions [23] and it considerably reduces the autocorrelation time.

The data produced by the simulations will be analyzed using several techniques. The use of more than one technique is important since it provides a powerful check on the results; if similar results are obtained it considerably increases one's confidence in the results. Conversely, if dissimilar results are obtained then any conclusions based on them must be treated with caution.

Since all the algorithms are stationary Markov processes it is necessary to estimate the exponential and integrated autocorrelation times. This will be done principally by auto-regression analysis backed up by the method of batches and spectral analysis. Having obtained estimates of the autocorrelation times, τ_i, and dismissing the data for the first five to ten autocorrelation time steps (roughly the time it takes before the process is stationary) the remaining data can then be sampled at intervals of two or three τ_i. The latter ensures that the samples are effectively independent and hence the conventional independent sample estimators can be used to calculate averages and variances.

The variance gives the statistical error, but we will also have to contend with systematic errors produced by corrections-to-scaling. The latter can be reduced by simulating very long walks. The corrections-to-scaling will be estimated by fitting the data to appropriately chosen asymptotic forms.

We expect such a Monte Carlo approach to this project to be very suitable. We have had a significant experience with such Monte Carlo simulations having successfully applied them to simulate ISAW and anisotropic spiral walks (see Track Record section). The results of both these projects are currently being written up for publication.

The plan of the project is as follows: We shall begin the project by programing the pivot and BSM algorithms for the models with only *one* interaction, in particular the repulsive Domb-Joyce model. Since much is known about certain aspects of these models we can use these known results as a test of the programs and the analysis techniques. We will then use the data to obtain new results. Of particular interest is the crossover behaviour of the Brydges-Slade model from random walk behaviour to self-avoiding behaviour. It is believed to be a continuous transition. We will verify this and estimate the associated critical exponents. A major effort will be put into calculating the corrections-to-scaling.

Having obtained results for the simpler models we shall move on to the models which have both repulsion and attraction. There are many ways of implementing these forces. In particular, we will study the Brydges-Slade model with nearest-neighbour attraction and contact repulsion (see equations (1) and (2)), and the three-parameter Domb-Joyce model (see equation (3)). We will determine the phase diagrams and the order of the various phase transitions. Following this we will obtain estimates of the various critical exponents associated with the continuous transitions.

The above work will be carried out for two dimensional models since this is where any discrepancies will be greatest, as mentioned in the previous section. Monte Carlo simulations of the models with attraction and repulsion have not been reported in the literature before. Thus any results we obtain will be new. We also plan to study the three dimensional versions of each of the models using the same Monte methods.

On a technical note, we will also carry out an extensive study of the multiple Markov chain as an algorithm in itself. This will be necessary as little is known about it. The optimal number and range of temperatures has to be determined as well as the frequency of swapping. (Optimal being that combination which minimises a chosen autocorrelation time.)

3 Budget Justification

The project calls for a deep knowledge of Monte Carlo methods, Markov Processes, time series analysis, lattice statistics and a general knowledge of the statistical mechanics of phase transitions. The problems associated with the Edwards model are intimately connected with the renormalization group and field theory of tricritical points. Accordingly, support is requested for a Research Associate on a full time basis who has some Monte Carlo experience and an understanding of the renormalization group approach to critical phenomena.

The investigators consider travel to international conferences and academic visits to be a vital part of any project. Conferences are a powerful source of new ideas as well as a means of disseminating the results of the work. Discussions with international experts in the field frequently lead to a significant increase in understanding. We believe this is an essential part of this project, it being at the cutting edge of developments in the field.

We do conduct electronic mail exchanges on a regular basis but this does not lessen the need for face-to-face contact. The investigators request travel as a priority B item. We point out that we are not requesting the full amount of travel costs but rather are asking for a *partial* contribution.

The X-station requested will be for the use of the research associate as s/he will need full-time access to our computing facilities for the conduct of the day-to-day progress of the project. While some communal terminals are available in the department these simply are not adequate for the heavy usage we require. Hence, this item is requested as priority B.

The items reluctantly listed with priority C under the heading of maintenance are important to the project and logically should be funded as part of the project. The computer maintenance costs cover the necessary upkeep costs for the special high-end workstations (which are not part of the department's general machines) available to us here in Melbourne, and that will be used for the project.

4 Proposed Timing

The project will begin with the programing of the pivot algorithm for the single interaction two dimensional models. Results from the simulations will be compared with known results of these models away from any critical points. This part is expected to take about six months. This will be followed by the programing of the BSM algorithm. The data from both algorithms will then be extensively analysed to give accurate results for both canonical and grand canonical quantities for long walks. This stage is expected to take a further six months.

The second stage will involve the extension of the programs to models with an attractive interaction. Both algorithms will then be boosted to a multiple Markov chain to reduce thermal critical slowing down. There are several models to study and for each of these the phase diagram and critical exponents need to be calculated. Since little is known about the correlations involved in the multiple Markov chain the algorithm itself will also be studied in this stage which is expected to take at least eighteen months.

The final six months (if available) of the project will be used to study the three dimensional versions of the previous models. In parallel with all the Monte Carlo work we will study the renormalization group aspects of the models.

5 Track record

Our track records are manifest in our publication records which are dominated by work on lattice walk problems in statistical mechanics, which is precisely the context of this proposal.

One of us (ALO) can be classed as an early career researcher and to supplement the publication/distinctions record we mention the following points. ALO has been invited to speak at several venues (Universities of Bordeaux and Leuven, and the Second Taipei International Symposium on Statistical Physics) and worked in the Condensed Matter Theory Group of the Department of Theoretical Physics, University of Oxford between 1989 and 1991. ALO is currently a regular registered referee for the Journal of Physics A and have refereed many articles for Physical Review E and Physical Review Letters. ALO is currently collaborating with Associate Professor C. Soteros of Saskatoon, Canada,

Dr. J. Essam of the University of London and Dr. T. Prellberg of the University of Oslo. ALO has co-supervisored the doctoral student D. Bennett-Wood who is currently writing up after completing successful research in lattice statistical mechanics. A list of other distinctions can be found in ALO's curriculum vitae.

Since the project depends heavily on Monte Carlo methods we shall provide our track record with this technique. We have both worked extensively on five Monte Carlo projects covering the last two years. The projects are:

- Work on kinetic growth simulations has led to the elucidation of the collapse transition of interacting SAW on the Manhattan lattice and interacting trails on the square lattice in two dimensions, and some tantalising new evidence for ISAW collapse in three dimensions. It has concomitantly led to several publications (see references 19, 21, 24, and 27 of ALO's Curriculum Vitae – see attached). This Monte Carlo technique, which is essentially a type of stochastic enumeration, has been utilised successfully now for several years.

- The Metropolis-pivot algorithm has been used the study random walks with a hierarchical angle interaction. This simulation was done in conjunction with a renormalisation group analysis of the model and was used primarily to find the critical temperature.

- Another project has been the study of Interacting self-avoiding walks (ISAW). One of us (RB) has a Ph.D student doing very large simulations on the Paragon 80-node supercomputer. The methods used in the simulation have been written up and are about to be submitted for publication. We have further obtained very good results which will form the content of least two more papers: one for ISAW in two dimensions and a second for the more complicated simulations at the upper critical dimension. This simulation uses Beretti-Sokal-Metropolis, Multiple chains and the reptation algorithm (suitably modified for ergodicity to hold).

- A Monte Carlo study of the droplet distribution of ISAW is underway. The runs for these simulations have just been completed and we are currently analysing the data. The results have produced excellent evidence for a completely new way of understanding the collapse phase, so much so that we shall be submitting a manuscript to "Physical Review Letters" in the near future. This simulation uses Multiple chains with a Metropolis-reptation algorithm.

- The final project is a collaboration with Prof. C. Soteros of the University of Saskatoon (Canada). The project is a pivot algorithm study of anisotropic spiral walks. These simulations are currently in progress, however even the preliminary results show the method is working extremely well.

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