Lattice Models of Interacting Polymers and Vesicles

Habilitationsschrift

zum Erwerb der Venia Legendi für Theoretische Physik

Vorgelegt der Mathematisch-Naturwissenschaftlichen Fakultät der

Technischen Universität Clausthal

von

Thomas Prellberg

Institut für Theoretische Physik

Technische Universität Clausthal

April 2001

Acknowledgements

As my habilitation thesis is the fruit of nearly a decade of research while I was employed at five different universities in as many countries, there are numerous people to give thanks to. While the list of names is too long to mention everybody, I should like to explicitly mention my employers and coworkers.

In chronological order, I am indebted to my PhD adviser Joseph Slawny for preparing the groundwork for my future research career, Tony Guttmann and Richard Brak for providing me with an extremely productive research environment in the Statistical Mechanics Group in Melbourne, Heinz Siedentop for furnishing me with an EU Fellowship at the Mathematics Department in Oslo, Alan McKane for taking me into the Condensed Matter Group at Manchester, Alan Middleton and Cristina Marchetti for giving me the opportunity to start doing some "real" teaching, and, finally, Dieter Mayer, who enabled me to come back to Germany and close the circle of research started with my PhD thesis. They all helped to create a stimulating environment for me to engage in independent research and to exercise and sharpen my skills while working on many different problems.

Co-authors on my papers not included in the list above are Heiko Harborth, Philipp Oertel, Debbie Bennett-Wood, Barbara Drossel, and Aleks Owczarek. Of all these I would like to give a special thanks to my friend and colleague Aleks Owczarek, with whom I have entered a singularly rewarding collaboration which has resulted in 24 joint research papers so far. During my international odyssey, the continuity of working with him has provided a strong basis for productive long-term research; the work presented here would not be the same without his input.

Finally, I am very grateful to my wife Sheila. Without her marvellous flexibility, encouragement and support I would never have been able to sustain such an international career.

Contents

1 Introduction

Over the last decade, a large part of my research in statistical mechanics has been devoted to the study of polymers and vesicles in the framework of lattice statistical mechanics. The focus of my attention hereby has been on the polymer collapse transition, where a polymer in a dilute solution changes its conformation from a swollen coil to a collapsed globule. Because of the tri-critical nature of this collapse transition, it is advantageous to also consider a similar phase transition in vesicles.

For the purposes of this research, I have considered a large variety of models, ranging from exactly solvable models, where a great deal of information can be obtained, to the analytically intractable "canonical lattice model of polymer collapse," which is given by interacting self-avoiding lattice walks. In doing so, I have developed and applied a vast spectrum of techniques, ranging from rigorous statistical mechanical calculations to the design and analysis of large-scale Monte-Carlo simulations.

As an example of the results obtained, I would like to highlight the explicit calculation of a tri-critical scaling function (described in Section 4) and the uncovering of a novel type of second-order phase transition with first-order like finite-size correction terms (described in Section 7). This *pseudo-first-order* phase transition is of general interest well beyond the realm of polymer physics.

The presentation of my research in Sections 2 to 7 follows a loosely chronological sequence, with the research in each section providing sufficient motivation for the subsequent sections. (Topically, the oriented ISAW discussed in Section 6 could have been described right after Section 4, but the discussion relies on some of the results presented in Section 5.) The topics chosen, as well as the different emphases made among them, necessarily reflect my personal preference.

After a brief overview of the physical phenomena behind this research, as well as a description of the canonical lattice models used in the theoretical description of these phenomena, the remaining part of Section 1 provides a brief outline of the research described in more detail in Sections 2 to 7.

Polymers in dilute solution constitute one of the fundamental and most well studied systems in statistical mechanics [1, 2, 3]. They attract continuing interest from theoreticians attempting to understand the subtleties inherent in this phenomenon and experimentalists wanting a firm foundation for interpreting their results on more complicated systems.

A polymer is a long chain molecule consisting of a large number of units (atoms or groups of atoms), joined by covalent bonds. The units may all be the same (homopolymer) or different (heteropolymer). Because of the variety of conformations possible for a long polymer, the effect of interactions between different segments of a long polymer chain poses a significant challenge to the theoretical analysis; along the chain, inherently non-local effects are introduced.

There are various ways to describe polymers theoretically; one approach is the modelling of polymer systems using lattice models of various types of self-avoiding paths [4, 5]. This is justified, as long as one is interested in mainly universal properties, which depend only on large scale quantities associated with a long linear polymer chain, rather than on the specific characteristics of the monomers which constitute a polymer.

The canonical lattice model of a polymer in a good solvent is given by the model of self-avoiding walk (SAW), where one considers the subset of random walks (RW) which never return to the same site [2]. The lattice sites visited by the random walk are thought of as a coarse-grained description of monomers (or some larger functional units of a polymer), and the self-avoidance constraint models the solvent-mediated repulsion between these "monomers". That is to say, in a good solvent it is energetically favourable for the monomers to be surrounded by solvent molecules rather than be close to other monomers. This is the so-called excluded volume effect, which is an essential ingredient in any theory of polymers.

Because of its intriguing "non-Markovian" properties, SAW is much studied by mathematicians [6], albeit with the strongest results available in large spacial dimensions which are not of primary physical interest. This is essentially due to the fact that in high dimensions the excluded volume effects are sufficiently weak to consider SAW as a perturbation of RW.

Generically, a solvent at high temperatures is a good solvent. If one lowers the temperature, the quality of the solvent gets reduced and in addition to the solvent-mediated excluded volume, an attractive monomer-monomer interaction becomes relevant. As the temperature is lowered, the polymer collapses. There is an associated phase transition, at which the polymer changes from a swollen coil to a collapsed globule. The point at which the polymer collapses is usually called the θ-point. It is an example of a tri-critical phenomenon, being described by the $n \to 0$ limit of the $\phi^4 - \phi^6$ $O(n)$ field theory [7, 8, 9]. This θ-point is experimentally observable [10, 11].

The canonical lattice model of polymer collapse is given by the model of interacting self-avoiding walk (ISAW), where one associates an attractive interaction with non-consecutive nearest-neighbour interactions of a self-avoiding walk. For obvious reasons it is not sufficient to model the collapse by simply weakening the self-avoidance, as this allows for the possibility of an unphysical buildup of density in small spacial regions.

This model is even less tractable mathematically, due to the intricate interplay of the excluded-volume repulsion and the short-range attraction. Indeed, not even a general proof of the existence of the thermodynamic limit is available.

However, the general theory of critical phenomena can be put to work, and one can extract a great deal of information from the application of its ideas. SAW has been argued to be described by the statistics of the magnetic $O(n)$ model in the limit of $n \to 0$ [12, 13]. Especially in two spacial dimensions, one can use Coulomb gas techniques [14], the theory of conformal invariance [15], and, last but not least, exactly solvable models [16], to get a wealth of precise information about SAW.

Conformal invariance in exactly solvable models has been utilised by Duplantier and Saleur to derive a set of critical exponents for the polymer collapse point in two dimensions [17]. However, there exists controversy about whether the

Duplantier-Saleur model is the correct one to describe polymer collapse. Their model consists of loops on the honeycomb lattice with annealed vacancies which mediate the attractive interaction, and it turns out that this model possesses a particular subset of next-nearest neighbour interactions. It is not clear whether these unusual interactions could be relevant in the renormalisation group sense, which could affect some or all critical exponents.

As the upper critical dimension for the tri-critical $O(n)$-model is $d_u = 3$, one expects that polymers at the θ-point show mean-field behaviour for $d \geq 3$ with logarithmic corrections at $d = 3$. Above the upper critical dimension therefore some type of self-consistent mean-field theory based on a suitable tri-critical Landau-Ginzberg Hamiltonian [18] should adequately describe polymer collapse. However, there also exist competing mean-field theories, notably the one by Lifshitz, Grosberg, and Khokhlov [19, 20, 21] which is based on a phenomenological free energy description. Above the upper critical dimension, the differences between these theories turn out to be rather significant.

As analytical approaches cannot give a full description of polymer collapse, there is also much need for numerical simulations. SAW has been simulated on computers for over 50 years [22], but only recently have both algorithms and computer technology advanced enough to facilitate high-precision simulation of SAW critical behaviour using Monte Carlo methods [23]. An alternative to the Monte Carlo simulation of SAW is given by exact enumeration of small systems and subsequent application of sophisticated extrapolation methods [24]. The advantage of this method is that in contrast to Monte Carlo methods the data to be analysed is known exactly. It is fair to say that while Monte Carlo methods usually give good results in large dimensions, exact enumeration results generically give more precise estimates in two dimensions [25].

Lattice vesicles are caricatures of physical vesicles, which consist of fluid membranes enclosing a spherical volume. A physical realization is given by lipid bilayer membranes consisting of phospholipids. Phospholipids have a hydrophilic polar head and a hydrophobic tail consisting of a hydrocarbon chain. When mixed with water, phospholipids arrange in lipid bilayers. The lipid bilayer constitutes a fluid membrane, with a vesicle being a lipid bilayer membrane which encloses a spherical volume. The physics of vesicles is determined by temperature, solvent quality, and chemical properties of the phospholipid. Vesicles have a very rich phase diagram [26].

A two-dimensional lattice vesicle is a self-avoiding lattice polygon of fixed length enclosing a certain area [27]. Depending on an area fugacity, this model exhibits a phase transition between an inflated and a flaccid phase. The interest in this model in this context is due to the fact that this transition shows a certain similarity to the polymer collapse transition.

The research described in this work is structured as follows. Section 2 contains the investigation of a directed two-dimensional model of polymer collapse, partially directed ISAW. This model is sufficiently complex to allow for a collapse transition and simple enough to allow for analytical treatment. From an exact solution and accompanying numerical analysis the complete critical structure of the collapse transition can be determined, and the scaling in the collapsed phase can be analysed.

Building upon the insight gained from this directed model, Section 3 contains a general analysis of the scaling theory of the collapse transition. The generating function (generalised partition function) is shown to have a tri-critical scaling form while the partition function has a finite-size crossover scaling form. Importantly, in the collapsed phase the surface of the globule plays a significant role in the low-temperature finite-size scaling form. This scaling picture also holds for lattice vesicles.

Section 4 describes the solution of a variety of directed lattice vesicles. These models have a special structure which allows for an elegant derivation of exact solutions via q-algebraic functional equations. The special structure of these functional equations has its origin in bijective mappings of these models to structures well known in enumerative combinatorics and the solution generically involves q-generalised classical functions. The partially directed version of ISAW from

Section 2 is shown to have the same structure as the simplest non-trivial directed vesicle model.

Via an involved technical calculation, the scaling function for these models can be extracted rigorously from the exact solution (this derivation has been termed an "analytical tour de force" in [28]). The model of directed lattice vesicles is therefore one of the few statistical mechanical models for which a tri-critical scaling function is explicitly known. This section closes with a rigorous treatment of the inflated regime for (undirected) vesicle models.

The observation that certain modified ISAW at particular interaction strengths can be mapped to the statistics of walks weighted by a particular kinetic growth process is the basis for Section 5. Quite generally, it turns out that kinetically grown walks are at the critical point of the associated interacting model, allowing for both determination of the θ-point and highly efficient simulations. Thus, for ISAW on the Manhattan lattice, a complete set of bulk and surface critical exponents can be determined from simulations. Moreover, there is a mapping to an exactly solvable $O(n)$ model by Nienhuis [29], and the scaling exponents can thus be matched to the scaling dimensions.

Next to ISAW, the model of interacting self-avoiding trails (ISAT) is yet another plausible lattice model of polymer collapse, with self-avoidance restricted to bonds and attractive interaction incorporated via contacts. Simulations of kinetically grown trails on the square lattice show that there are logarithmic corrections to scaling at the ISAT θ-point. A variety of kinetic models is studied in three dimensions, showing critical behaviour in each case, but not confirming the scaling predictions from the tri-critical $O(n)$ field theory.

Taken altogether, these results indicate that the choice of lattice, as well as the incorporation of self-avoidance and attractive interaction affect the universality class of the collapse transition in a subtle and not yet understood manner.

Section 6 deals with an oriented version of ISAW in two dimensions. The importance of this model is due to the fact that it combines several models in an enlarged phase diagram. The θ-point of Manhattan ISAW extends to a critical line ending in the θ-point of ordinary ISAW, which is now a higher order critical point. Moreover, the collapsed phase of ISAW is now a critical line between two different collapsed phases. To arrive at these results a new approach to the polymer collapse problem via the consideration of winding angle distribution was used.

Polymer collapse above the upper critical dimension is the topic of Section 7. ISAT and ISAW in four dimensions are simulated using PERM, a clever generalisation of a kinetic growth algorithm [30]. The results of the simulations are most striking: one finds that the expected weak thermodynamic second-order phase transition is masked by strong first-order like finite-size correction terms. An interpretation of the data in the context of the Lifshitz, Grosberg, and Khokhlov mean-field theory [19, 20, 21] clarifies that the origin of the strong correction terms is just an additional term in the free energy due to the surface of the collapsed globule. One consequence is the separation of the scaling region of the collapse transition from the θ-point scaling region. In the thermodynamic limit, the collapse point and the θ-point are identical, however upon approaching the thermodynamic limit the respective scaling regions remain strictly separate.

Selected original publications related to Sections 2 to 7 are enclosed in the appendix. I believe that this particular selection provides a good overview about my work on collapse transitions. It is my hope that this work will leave the interested reader with the impression that this area of research is a rewardingly rich and interesting one.

2 A directed model of interacting polymers

Partially directed two-dimensional SAW as a model of polymers and interfaces has been studied in detail [31]. This is a lattice model of SAW where steps in the negative x-direction are prohibited. As a physical realization, one may think of polymers in a strongly anisotropic setting or of the walk describing an interface between, say, two differently magnetised regions, with no overhangs.

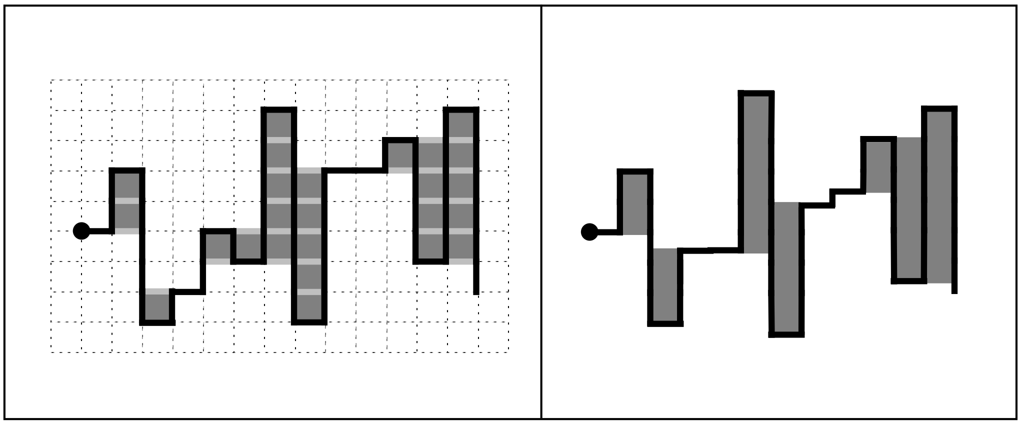

Figure 1: *Typical configurations of partially directed ISAW. On the left hand side is the discrete model with shaded interaction bonds, and on the right hand side is the continuous model with shaded interaction overlap (Figure 1 from [34]).*

The advantage of imposing directedness is that it makes the model analytically tractable.

Adding attractive interactions, partially directed ISAW is a promising model for studying polymer collapse. It simplifies the problem sufficiently to allow for an exact solution while still retaining enough complexity to exhibit a collapse transition. The phase diagram for partially directed ISAW was discussed in [32], and an exact solution in terms of a closed-form expression for a generating function was given in [33].

A typical configuration of partially directed ISAW is shown on the left hand side of Figure 1. For analytical reasons it is advantageous to also consider a semi-continuous version, in which the vertical segments of the walk can have any length. In [34], we give solutions to both the discrete and semi-continuous versions, and more importantly, we extract from the solutions the critical behaviour at the collapse transition.

To fix notation for this section and the subsequent sections, write the canonical partition function for an interacting self-avoiding walk model as

$$Z_N(\omega) = \sum_M C_{N,M}\omega^M \tag{1}$$

where $\omega = \exp \beta J$ is the Boltzmann weight for a single interaction bond with energy $-J$ and $C_{N,M}$ is the number of all configurations of length N with M interaction bonds. The thermodynamic limit is obtained by taking $N \to \infty$.

The thermodynamic quantities of interest relate to the behaviour of the free energy

$$-\beta f = \lim_{N\to\infty} \frac{1}{N} \log Z_N(\omega) \tag{2}$$

and the derived quantities internal energy u and specific heat c. Near a thermodynamic phase transition one expects the singular part of the free energy to behave as

$$f_{sing} \sim \Delta\omega^{2-\alpha} \tag{3}$$

which corresponds to a singular behaviour of the specific heat with exponent α. The partition function scales asymptotically as

$$Z_N(\omega) \sim z_c(\omega)^{-N} N^{\gamma-1} \tag{4}$$

where $z_c = \exp \beta f$ and γ is a critical exponent, whose value depends on whether the system is at or above the transition temperature.

It is advantageous to consider the grand canonical partition function, which is a generating function for $Z_N(\omega)$,

$$G(z,\omega) = \sum_N z^N Z_N(\omega) \tag{5}$$

and from which one can extract the asymptotic behaviour of $Z_N(\omega)$ by Cauchy inversion. In particular, the critical exponent γ is just given by a power law divergence of $G(z,\omega)$.

The directedness of the model allows for an exact solution via an application of transfer matrix techniques [35], leading to

$$1 + G(z,\omega) = \frac{1-\omega}{2[\mathcal{H}(z, z\omega, z^2(\omega-1)) - 1] + (1-\omega)(1-z)} \tag{6}$$

where

$$\mathcal{H}(y,q,t) = \frac{H(y,q,qt)}{H(y,q,t)} \quad \text{with} \quad H(y,q,t) = \sum_{n=0}^{\infty} \frac{q^{\binom{n}{2}}(-t)^n}{(y;q)_n (q;q)_n} \,. \tag{7}$$

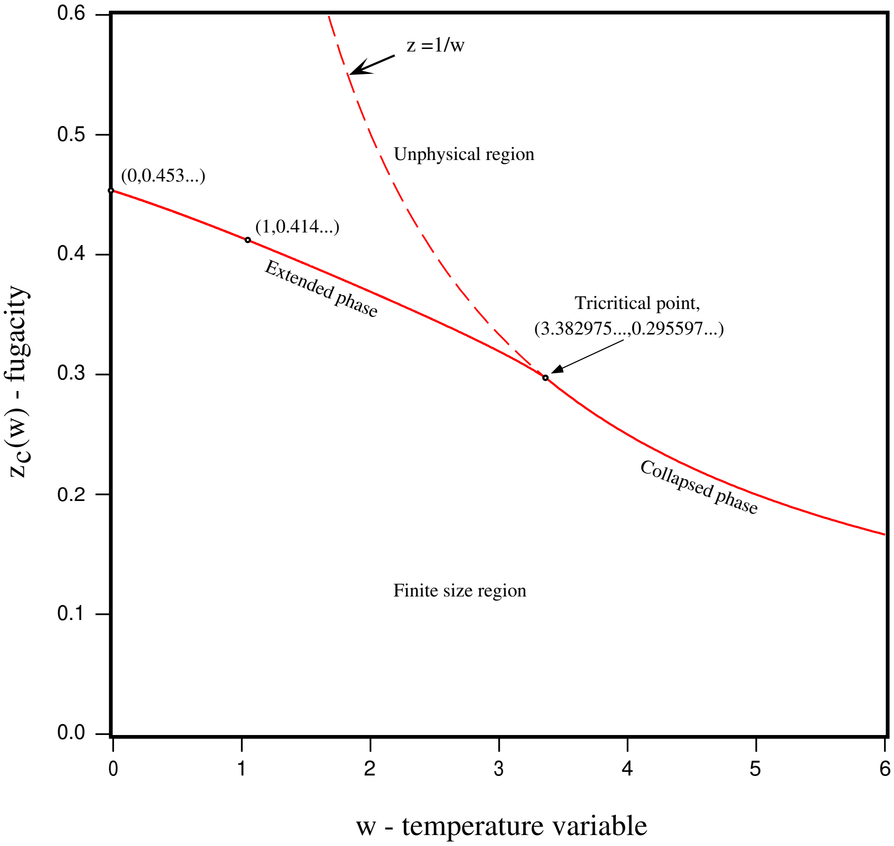

Figure 2: *The singularity diagram for partially directed ISAW (Figure 3 from [34]).*

Here,

$$(t;q)_m \stackrel{def}{=} \prod_{k=1}^{m}(1-tq^{k-1}) \tag{8}$$

is the standard q–product notation. One can recognise here the occurrence of a q-deformed hypergeometric function $H(y,q,t) = {}_1\phi_1(0,y;q,t)$ [36].

A simplified analysis of the critical behaviour can be put forth by observing that the dominant singularity of $G(z,\omega)$ is either $z\omega = 1$, which is an accumulation point of poles, or a simple pole coming from a simple zero of the denominator in Equation (6). For $q = 1$ the generating function simplifies to an algebraic function, and one can use a perturbation expansion around this solution to extract critical exponents. At the critical point, $G(z,\omega_c)$ diverges with exponent $\gamma_t = 1/3$, and the specific heat exponent is $\alpha = 1/2$. A complete analysis gives the phase diagram of Figure 2.

Assuming that the transition point is tri-critical, one can write a scaling form near the transition. (I defer the discussion of this scaling form, along with the definition of the crossover exponent ϕ and the tri-critical scaling relation linking ϕ to α to Section 3.) Computing the precise scaling behaviour from the generating function is a formidable task, which shall be examined in further detail in Section 4. However, for the semi-continuous model one can calculate the scaling behaviour explicitly. The exact solution here involves Bessel functions, and the behaviour around the transition point can be calculated using Airy function asymptotics of Bessel functions [34].

For further analysis we resort to numerical work. In [37] it is observed that the partition function scaling in the collapsed phase is actually given by

$$Z_N \sim \mu^N \mu_s^{N^\sigma} N^{\gamma_c - 1} \tag{9}$$

with $\sigma = 1/2$ and $\gamma_c = 1/4$. (These numerically conjectured values have subsequently been confirmed by a direct calculation [38].) The important point here is that the additional term $\mu_s^{N^\sigma}$ corresponds to an effective surface term in the finite size free energy. As the collapse transition is approached from below, the effective surface term in the finite size free energy becomes weaker. Numerically, it can be seen that $\log \mu_s$ vanishes with an exponent $3/4$.

To gain further insight about the nature of the collapse transition, we also numerically estimated the length scale exponents for partially directed ISAW in all three scaling regimes. As we have a directed model, we need to consider two length scale exponents. The typical horizontal and vertical extent, $\langle L_x \rangle$ and $\langle L_y \rangle$, respectively, of the walk scale as

$$\langle L_{x,y} \rangle \sim N^{\nu_{x,y}} \tag{10}$$

with length scale exponents $\nu_{x,y}$. In the swollen phase, the walk behaves essentially like a directed random walk, i.e. $\nu_x = 2\nu_y = 1$. As Figure 3 indicates, the attractive interaction causes the occurrence of finite size droplets which form up

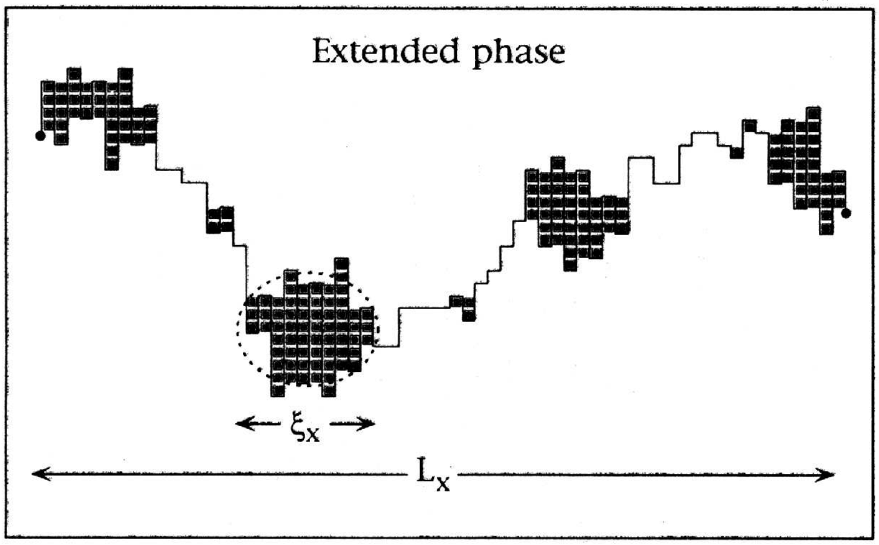

Figure 3: *A picture showing the dominant type of configurations at high temperature for comparison; finite size droplets form up to the size of the thermal correlation length (Figure 15 from [37]).*

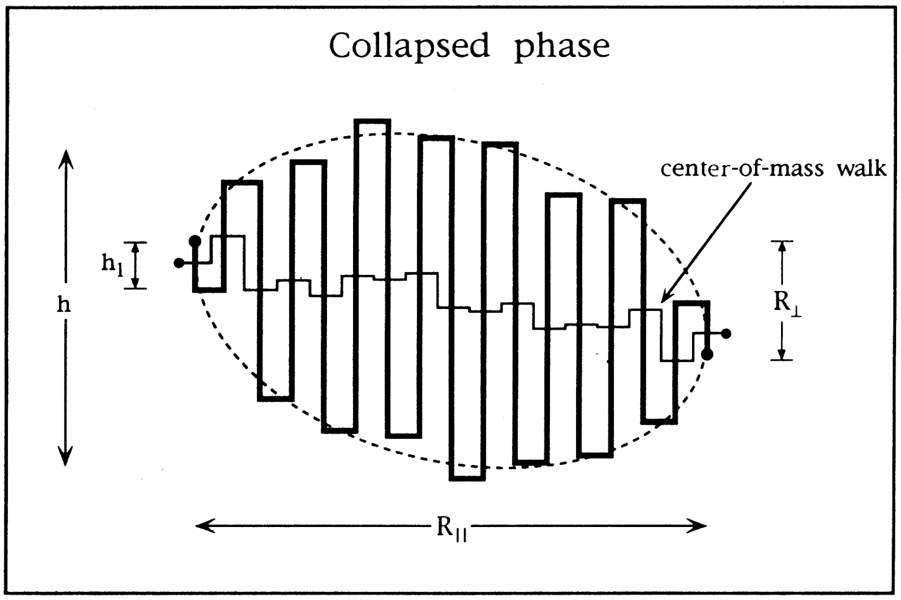

Figure 4: *A picture showing the dominant type of configurations at low temperature; these being described as bubble-like (Figure 14 from [37]).*

to the size of the thermal correlation length. At the transition, the thermal correlation length diverges, and the exponents get modified to $\nu_x = 2\nu_y = 1/3$ [39]. In the collapsed phase we find a rather rigid bubble with a well defined surface. The center of mass of the vertical segments performs a random walk, as indicated in Figure 4. These findings are commensurate with the observed partition function scaling.

Taking all of the above together, the partially directed ISAW is shown to be a useful model for the polymer collapse problem. Many results have been obtained, and it is a rich model indeed. The main drawback of this model is that it has a collapsed phase with maximal density and a rather rigid structure, and therefore low entropy. However, despite this deficiency, it has given information about the scaling behaviour of the collapsed phase, which will directly affect the general scaling theory described in the next section.

3 A scaling theory of the collapse phase transition and scaling in the collapsed phase

The insights gained from partially directed ISAW, as well as aspects of the analysis of vesicle models described subsequently in Section 4, together with general ideas of tri-critical scaling theory [40, 18] are the basis for the development of a scaling theory for generic collapse transitions. In [41] we report on the scaling behaviour in the collapsed phase and in [42] we develop this theory for so-called geometric cluster models, which we argue have similar mathematical structures that enable one to present a generic set of scaling forms.

Figure 5 illustrates the class of models considered here. We consider undirected and directed versions of ISAW and vesicle models, which are self-avoiding lattice polygons enclosing a certain area.

The difference between interacting walk models and vesicle models is that the parametrisation of the two-variable generating function for ISAW is given by

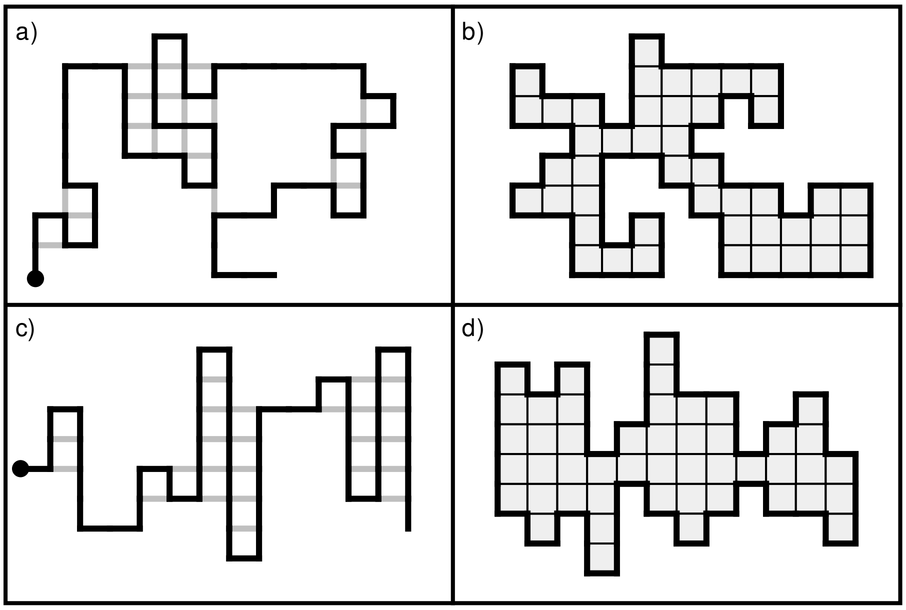

Figure 5: *A selection of cluster models illustrating a typical configuration: a) interacting self-avoiding walk model of linear polymers — light lines show the nearest neighbour interactions, b) self-avoiding polygon model of vesicles — shaded squares show the area, c) interacting partially directed self–avoiding walks (only north, south and east steps allowed) — light lines show the nearest neighbour interactions and d) row-convex self-avoiding polygon model — shaded squares show the area (Figure 1 from [42]).*

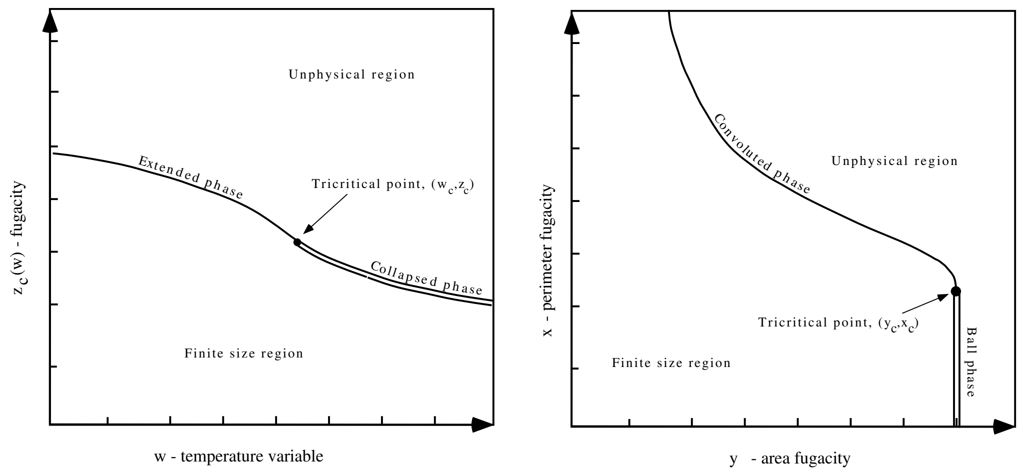

Figure 6: *a) The expected form of the singularity or "phase" diagram for the interacting self-avoiding walk model of linear polymers. b) The singularity or "phase" diagram for the self-avoiding polygon model of vesicles [27] (Figure 2 from [42]).*

fugacity z and interaction weight ω, whereas for vesicles the parametrisation is given by perimeter fugacity x and area fugacity y.

For two-dimensional ISAW, one can make a tentative correspondence with vesicle models by noting that the product $q = z\omega$ corresponds to an "interaction area," so it is natural to identify (z, q) and (x, y).

The singularity diagrams of the respective generating functions are shown in Figure 6. The phase transition for ISAW is the collapse transition between an extended swollen coil and a collapsed globule, whereas the corresponding phase transition for vesicles is the transition between a convoluted flaccid phase where the vesicle shows similarities to branched polymers and an inflated ball-like phase. Even though the phase diagrams look different, there is sufficient similarity to develop a joint theory for both models. There is a principal difference, but it only becomes evident upon rescaling of the variables.

As Figure 7 shows, we find two different generic forms, which for obvious reasons are termed asymmetric and symmetric. ISAW is a symmetric model,

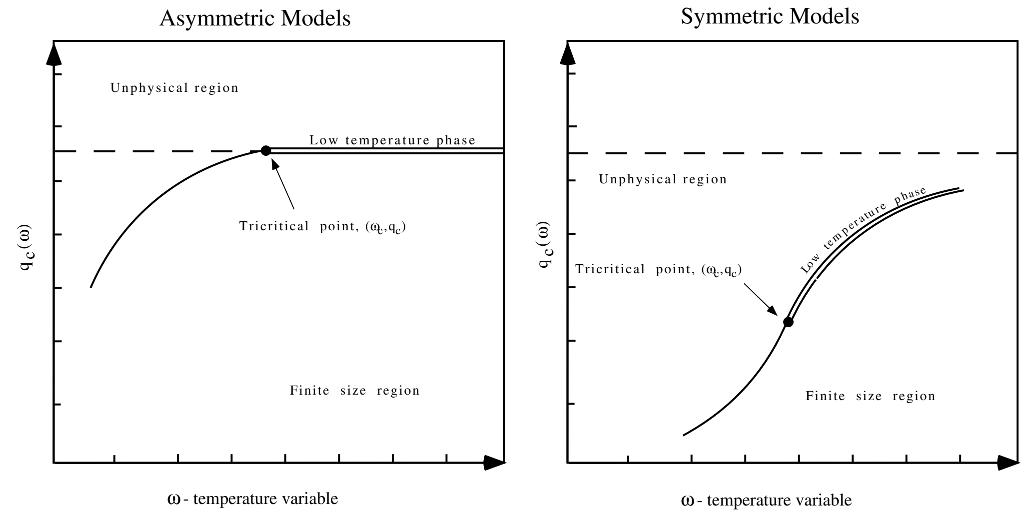

Figure 7: *The schematic singularity diagrams, in the generic variables ω and q, a) for the asymmetric models and b) for symmetric models (the low and high temperature lines are curved but whether they are concave or convex will be model dependent. The dashed line in both figures is the line $q = 1$ (Figure 3 from [42]).*

whereas (directed and undirected) vesicle models, as well as partially directed ISAW are asymmetric models. The reason for this is that for asymmetric models the low-temperature collapsed (respectively inflated) phase is extremely poor in entropy, leading to a degenerate behaviour: the low temperature free energy is an analytic function at the transition point, and hence there is no singular specific heat in the low-temperature phase.

So far, we have interpreted the singularity diagram of $G(\omega, q)$ as a means to extract the singular behaviour of the partition function $Z_N\omega$ in the thermodynamic limit. In this interpretation, the singular line in Figure 7 is the main point of interest, as it is directly related to the free energy of the system.

However, there is another possibility of interpretation, which is in spirit much closer to the tri-criticality of the model. If one interprets the generating function $G(\omega, q)$ as a partition function in the generalised ensemble, then q is a fugacity in the model and therefore controls the size of the objects. Thus, the area below the critical line $q_c(\omega)$ corresponds to a region in which the average size of the objects

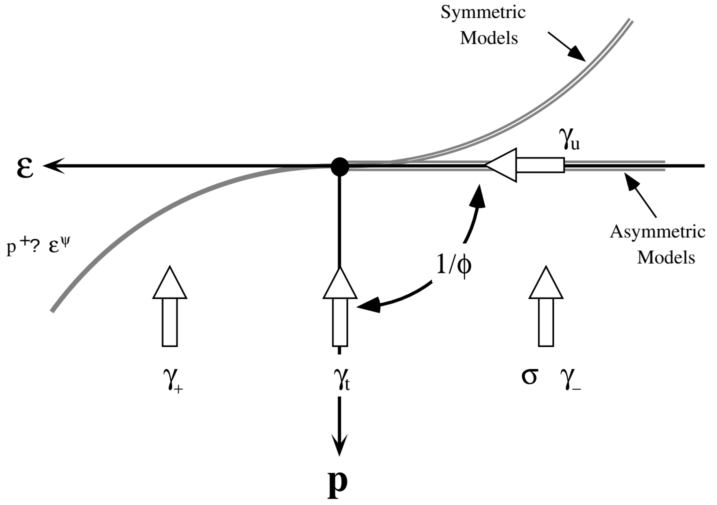

Figure 8: *Schematic tri-critical scaling diagram of the generating function (or generalised partition function) showing the scaling axes p and ϵ and the associated exponents. The low temperature line coincides with the ϵ axis for asymmetric models, but goes above (as shown), or possibly below, for the symmetric models (Figure 5 from [42]).*

is finite. The area above the critical line $q_c(\omega)$ is unphysical for the models considered here, which can be remedied by introducing a containing volume into the theory. In this case, the low-temperature $q_c(\omega)$ can be seen to be a line of first-order transitions and the high-temperature $q_c(\omega)$ as a line of second-order transitions, which meet at the collapse point, which is therefore a tri-critical point.

Mathematically, the character of the line of the first-order transitions is described by the fact that $G(\omega, q)$ exhibits a line of essential singularities on $q_c(\omega)$. This is also reminiscent of the results of an old theory of condensation in a droplet model [43, 44]. In partially directed ISAW this essential singularity emerges directly as an accumulation point of poles approaching the critical line from above. It is crucial in our description that $G(\omega, q)$ is actually finite on the critical line.

Alternatively, one can consider the finite-size crossover forms. Here, the tri-critical scaling behaviour of the generating functions for these models is sum-

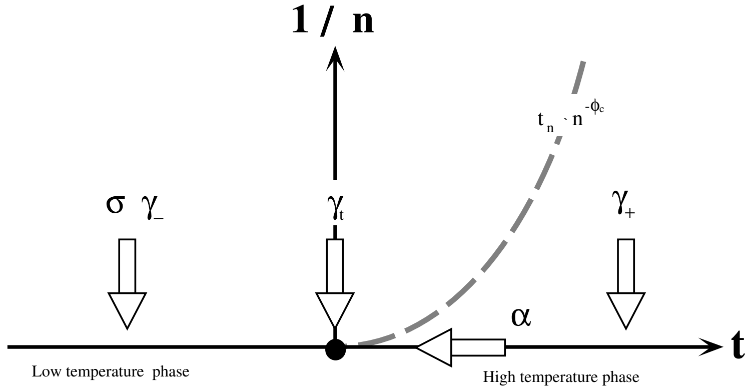

Figure 9: *Finite-size crossover scaling diagram showing the scaling axis* $1/n$ *and* $t = T - T_c$ *and the associated exponents. The large arrows show the path of approach associated with the corresponding exponent. The line* $n^{-\phi_c}$ *is the locus of specific heat maxima. (Figure 6 from [42]).*

marised in Figure 8, and the associated finite size scaling can be found in Figure 9. The key point is that the singular part of the generating function $G(\omega, q)$ can be described by a single-variable scaling function. After transformation to scaling axes, if necessary, we denote the thermal scaling field with ϵ and the fugacity scaling field with p. In these coordinates we then find that

$$G^s(\epsilon, p) \sim |\epsilon|^{-\gamma_u} \hat{g}^{\pm}(p|\epsilon|^{-1/\phi}), \tag{11}$$

where the $\pm$ superscripts refer to temperatures above and below the critical temperature. The exponent γ_u is defined by $\gamma_u := \gamma_t/\phi$ with ϕ being the tri-critical crossover exponent. Performing matching of the expected scaling behaviour leads to a relation between the tri-critical crossover exponent ϕ and the specific heat exponent α, which enters the picture via the shape exponent $\psi = 2 - \alpha$ related to the high-temperature free energy singular behaviour. One obtains $\psi = 1/\phi$ and thus the tri-critical scaling relation

$$2 - \alpha = \frac{1}{\phi} \; . \tag{12}$$

Due to the presence of an essential singularity on the low temperature critical line, the scaling of the finite-size crossover becomes quite involved. Here, I point out only that the postulation of an effective surface term in the free energy corresponding to Equation (9) along with the assumption of simple crossover scaling implies the vanishing of the surface free energy with an exponent $\chi = \sigma/\phi$. I shall return to this point in Section 7, where it will become apparent that for collapsing ISAW in high dimensions the crossover scaling assumption needs to be modified to account for the observed effects.

The scaling theory of [42] along with the numerical evidence of [37] was the basis for an announcement of this collapsed scaling form in [41], which has caused much subsequent discussion, especially regarding the difference between collapsed and dense polymers (see e.g. [45, 46, 47]). The meaning, or indeed the existence of a power law correction term with exponent γ_- in the collapsed phase is still an open question.

4 Vesicle models

The basis of this section are my papers [48, 49, 50, 51, 52, 53], with papers [49, 52, 53] attached in the appendix. These papers describe the exact solution and subsequent asymptotic analysis of a variety of directed lattice vesicle models. An excellent summary of some of this work can also be found in [5].

The vesicle models are of interest beyond the aspects discussed here, because there are deep connections to problems in enumerative combinatorics and algebraic languages. In combinatorial languages, the objects under consideration are called polyominoes. A short review of the history of the solutions of the various types of polyominoes can be found in [54]. It is frequently possible to prove a bijection between words of an algebraic language and the combinatorial objects of interest [55], an idea going back to [56].

All these models possess the characteristic feature that their single variable generating functions are algebraic, whilst the two variable generating functions are expressed in terms of q-series. These are generally q-Bessel functions [57, 58] or q-hypergeometric functions [36]. The q-series solutions to this class of models have been obtained by several techniques. In algebraic language theory the q-series appear as q-extensions or q-grammars [59].

From a scaling point of view, all these models are examples of what was called asymmetric model in Section 3. Partially directed ISAW (see Section 2) can be shown to have the same structure as the simplest non-trivial directed vesicle model, so that the analysis presented here is applicable to that model as well.

In this section, I would like to present three aspects of these models. Firstly, they have a special structure which allows for quite an elegant derivation of their exact solutions via q-algebraic functional equations [49]. Secondly, I succeeded in finding a method for rigorously computing the tri-critical scaling function for this class of models [52]. Finally, in the inflated regime one can obtain rigorous asymptotic results even for undirected vesicle models [53]. Given the general lack of rigorous scaling analysis, the success in the analysis of these models is rewarding.

The directed models under consideration here are shown in Figure 10. The vesicle models are all particular subsets of column-convex polygons, obtained by adding restrictions to the shape of the upper or lower boundary. The simplest non-trivial example is the model of staircase polygons, which is obtained by considering two mutually self-avoiding fully directed walks with common start and end points.

The technique for solving these models is to use a geometrical partition of the set of all polygons into disjoint subsets. These subsets are chosen such that they enable one to give construction rules that can be transformed into equations for the corresponding generating functions. A related method for the derivation of functional equations based on the theory of algebraic languages has been developed in [60].

I illustrate this method with the example of staircase polygons. One needs a three-variable generating function. Let $S(x, y, q)$ be the generating function

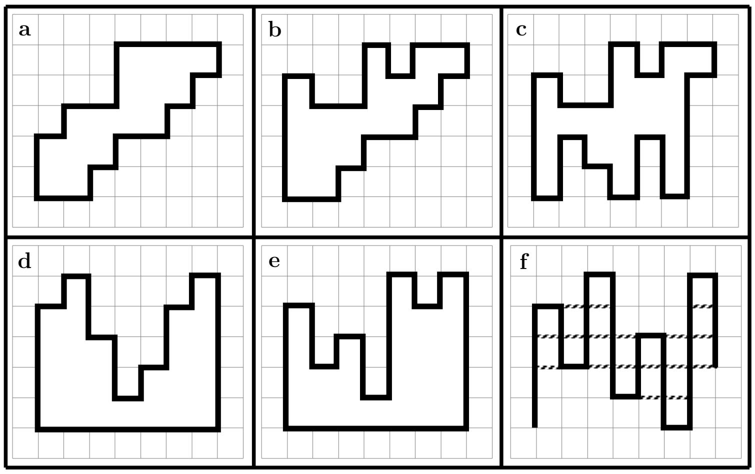

Figure 10: *Typical configurations for a selection of directed geometric cluster models. a) staircase polygons, b) directed column-convex polygons, c) column-convex polygons, d) bar-graph polygons, e) alternating bar-graph polygons and f) partially directed walks (Figure 1 from [49]).*

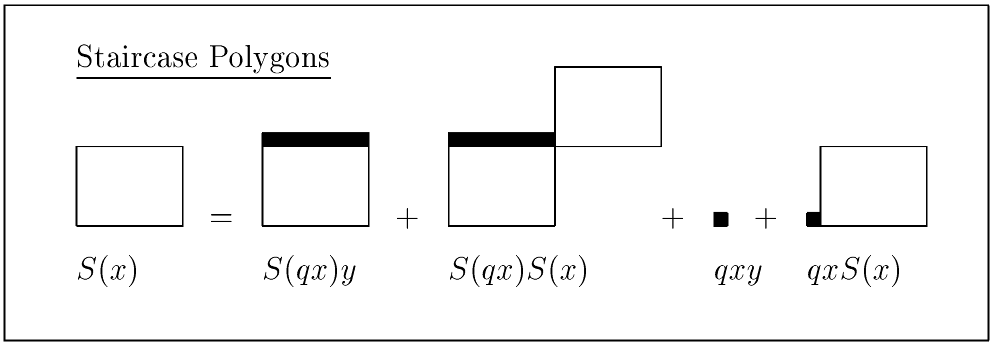

Figure 11: *The diagrammatic form of the functional equations for staircase polygons. Here, $S(x) \equiv S(x, y, q)$ (Figure 5 from [49]).*

for staircase polygons enumerated by width (x), height (y), and area (q). We use an inflation process, where we increase the height of each vesicle column by one. For the generating function, this corresponds to transforming $S(x,y,q)$ to $yS(qx,y,q)$. Using this inflation process, one can decompose the set of staircase polygons as shown in Figure 11, whereby one obtains the functional equation

$$S(x,y,q) = \{S(qx,y,q) + qx\}\{y + S(x,y,q)\} \ . \tag{13}$$

Setting $q=1$, one sees the algebraic nature of the perimeter-only problem.

Solving this functional equation is described in [49]. One obtains

$$S(x,y,q) = y\left(\mathcal{H}(qy,q,qx) - 1\right) \tag{14}$$

with $\mathcal{H}(y,q,t)$ being the same function we encountered in Equation (7) for partially directed ISAW.

The scaling behaviour for directed vesicle models can be determined by means of (singular) expansions of the associated functional equations around $q=1$ or by considering semi-continuous versions of the models. In [52], I developed a method which allows one to rigorously calculate the scaling function for directed vesicle models. This method involves rewriting $\mathcal{H}(y,q,t)$ via contour integrals and performing a saddle point analysis on these. This method gives insight into the structure of tri-criticality in this model. The asymptotics is governed by the confluence of two saddle points, which naturally produces the crossover exponent $\phi = 2/3$ and explains satisfactorily the occurrence of Airy functions in the scaling function. In particular, setting $y=x$, I obtain the scaling solution for staircase polygons,

$$S(x,x,q) \sim \frac{1}{2} - x + 4^{-2/3}(1-q)^{1/3}\frac{\mathrm{Ai}'\left(4^{4/3}\{1/4-x\}(1-q)^{-2/3}\right)}{\mathrm{Ai}\left(4^{4/3}\{1/4-x\}(1-q)^{-2/3}\right)} \ . \tag{15}$$

This shows that the scaling function is given as

$$f(z) = -\frac{\mathrm{Ai}'(z)}{\mathrm{Ai}(z)} \tag{16}$$

and that the set of tri-critical exponents is given by

$$\gamma_u = -\frac{1}{2}\ , \qquad \phi = \frac{2}{3}\ , \qquad \gamma_t = -\frac{1}{3}\ . \tag{17}$$

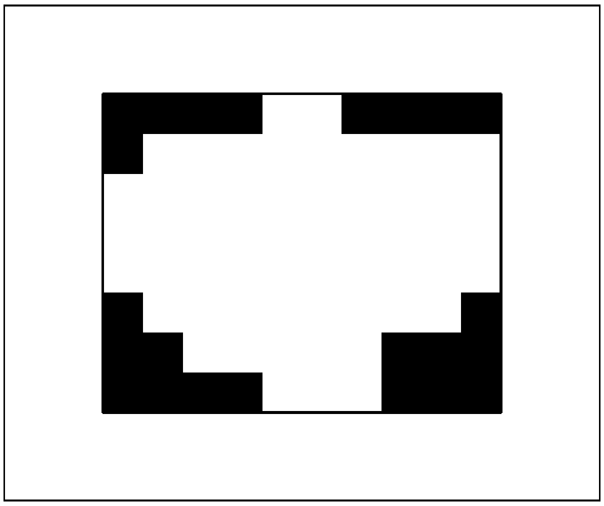

Figure 12: *Pictorial representation of (18): the partition function is asymptotically dominated by convex polygons, which are constructed from rectangles by removing corners made of Ferrers diagrams (Figure 1 from [53]).*

Recently, the phenomenon of coalescing saddle points has been shown to occur in a variety of other problems ranging from Brownian motion to the analysis of algorithms [61].

In [53], the scaling behaviour of the inflated phase of vesicles is revisited. We consider the finite-perimeter partition function $Z_N(q)$ and prove that

$$Z_N(q) \sim \frac{1}{(q^{-1};q^{-1})_\infty^4} \sum_{k=-\infty}^{\infty} q^{k(N-k)} \tag{18}$$

with an exponentially small error.

The asymptotic form (18) has a straightforward combinatorial interpretation (see Figure 12). The infinite sum has its origin in the generating function for rectangles. Convex polygons can be constructed by removing corner sites from these rectangles while preserving the perimeter. These "corners" have an area–generating function

$$F(q) = \frac{1}{(q;q)_\infty} = \prod_{k=1}^{\infty} \frac{1}{1-q^k} \ , \tag{19}$$

which is convergent for $|q| < 1$. A removal of one corner (ignoring overlaps) corresponds to multiplication with this area–generating function with the area weight replaced by q^{-1}. Correspondingly, the simultaneous removal of four corners corresponds to multiplication with $F(q^{-1})^4$, leading directly to the expression in (18). This result improves upon estimates in [27].

Vesicle models have thus been shown to be of great interest for modelling a tri-critical phase transition. Depending on the degree of simplification (directed vs. undirected), one can obtain a wealth of information which allows the phase transition to be investigated in detail. It should be pointed out, however, that too much simplification results in a loss of meaningful physics. In [51] we investigated stacking models of vesicles which, although interesting in their own right, were so degenerate as to destroy any tri-critical forms.

5 Kinetic growth models for polymer collapse

Certain modified interacting walk models at particular interaction strengths can be mapped to the statistics of walks weighted by a particular kinetic growth process. For suitable models, the statistics given by the kinetic growth process places the kinetic walks at the critical point of the associated interacting model.

Kinetic growth walks (KGW) [62, 63, 64] and smart kinetic growth walks [65, 66] were introduced as dynamic models of polymerisation. KGW is a model defined via a random walk which at each time step chooses from the available sites while remaining self-avoiding. On regular lattices these walks were found to eventually stop by entering self-made traps; their size scales in the same way as SAW. In contrast to this behaviour, a smart version of KGW [65] in two dimensions was explicitly constructed not to trap (configurations only close by loop formation). This was done by adding a "dressing" around the walk on the dual lattice that distinguishes the left and right-hand sides of the walk as it is constructed, and forbidding steps that do not allow the further construction of the dressing. This effectively means that a walk can only enter places where there is at least one escape route. Configurations of smart KGW trace out the hulls of percolation clusters at threshold [65], and their size exponent has been later deduced to be the same as that of θ-point polymers. In fact, it was shown [66] that closed smart KGW defined on the honeycomb lattice is equivalent to static interacting self-avoiding loops with nearest-neighbour and next-nearest-neighbour attraction.

In three dimensions, a clever generalisation has been found [67, 68, 69] which is known as tri-colour walks. These are defined on the Wigner-Seitz cells of the body centred cubic (WS-bcc) lattice, and a three colour dressing is added to the dual of this lattice to give the walk the "smart" property. The exact construction of this model is explained in great detail in [68]. It was found that these tri-colour walks have a fractal dimension close to 2 and map onto a version of interacting SAW with nearest and next-nearest-neighbour interactions. It was then deduced that these kinetic walks may provide information about the collapse transition in three dimensions.

Another lattice model of polymer configurations studied extensively is that of self-avoiding trails (SAT) [70, 71, 72, 73]. These are paths on a lattice which have no two steps on the same bond of that lattice but may occupy the same site. This restriction is sometimes referred to as bond-avoiding, in contrast to self-avoiding walks (SAW) which are site-avoiding (that is, no two vertices of the walk may occupy the same site on the lattice). Clearly walks are, by default, also bond-avoiding. Trails possess an excluded volume effect and it is fairly well established that the SAT and SAW are in the same universality class [74] which describes good solvent polymers. It has been shown [71] that there should exist a collapse transition when contact attraction is added to the trail model. Moreover, Shapir and Oono [71] have argued that this point should be tri-critical in nature, as it is at the ISAW collapse point. However, they predict that ISAW and interacting self-avoiding trails (ISAT) are in different universality classes. Importantly, while the upper critical dimension for ISAW is expected to be $d_u = 3$, the Shapir-Oono field theory gives $d_u = 4$ for ISAT. In analogy to KGW, kinetically grown trails (KGT) can also be defined.

Building upon this background, this section describes results coming from utilising kinetic growth models for the investigation of the critical structure of the collapse transition: dressed KGW on the honeycomb lattice [47], KGW on the Manhattan lattice [75, 76, 77, 78] (which is a smart model by virtue of the lattice) and KGT on the square lattice [79] have all provided information about the collapse of two dimensional polymers. In three dimensions, KGT on the simple cubic lattice, the diamond lattice, and on the dual of the WS-bcc lattice, as well as tri-colour walks on the WS-bcc lattice have been studied [80].

From a simulational point of view, studying KGW and KGT is very appealing, as the straightforward kinetic growth process along with a very low attrition (trapping only occurring when the origin is revisited) leads to a highly efficient algorithm for generating very long configurations. One can thus simulate well beyond the system sizes obtainable by alternative Monte Carlo methods, while simultaneously guaranteeing complete independence of the individually grown samples.

The theoretical motivation to study KGW and KGT may be most evident from the cases in which there exists an exact mapping between these and a corresponding, naturally defined version of ISAW and ISAT. For instance, on any lattice with coordination number 4, a KGT can naturally only terminate when it returns to its origin and thus forms a loop. The mapping to an interacting model is then as follows: if a KGT visits a site of the lattice for the first time, each of the three remaining bonds is chosen with probability $1/3$, whereas if a KGT visits a site of the lattice a second time, it must continue on the one remaining bond with probability one. Comparing the statistical weights of KGT with the weights of ISAT configurations, one can then deduce that KGT can be mapped to ISAT with an attractive contact interaction with associated Boltzmann weight $\omega = 3$.

A similar mapping can be made for KGW and ISAW on the Manhattan lattice, which is a directed square lattice of alternating "one-way streets", i.e. neighbouring parallel bonds have opposite direction. KGW on the Manhattan lattice are by their nature smart and map onto ISAW with only nearest-neighbour interactions

Exponent	ν	γ_t	ϕ
Duplantier Saleur model	4/7	8/7	3/7
Manhattan ISAW	4/7	6/7	3/7
square lattice ISAT	1/2(log)	1(log)	0.88(7)

Table 1: *Best estimates and exact conjectures for some of the bulk exponents for the collapse transition of Manhattan ISAW, square lattice ISAT, and, for comparison, the corresponding values for the Duplantier and Saleur model (for the full set of exponents, see [77, 84]).*

at a Boltzmann weight of $\omega = \sqrt{2}$. The study of this model turns out to be most rewarding.

Utilising a mapping to the problem of bond percolation Bradley was able to identify that $\nu = 4/7$ and $\gamma = 6/7$. This applies to the related models of Gunn *et al* [81] and Roux *et al* [82], and series work is in accord with these results [83]. Our simulations [77] extend this work and determine a complete set of bulk and surface exponents. (Kinetic growth also plays a role in the mapping to a surface interaction: absorbing and reflecting boundary conditions can be identified with the ordinary and the special transitions, respectively.) High accuracy simulations were performed with walks up to length 10^6, from which accurate exponent estimates could be made to identify exact values of critical exponents. For example, the estimate for the crossover exponent $\phi = 0.430(6)$ enabled the fraction $\phi = 3/7$ to be identified. This value was substantiated in [77] by a mapping to an exactly solvable $O(n)$ model by Nienhuis [29]. The bulk and surface scaling dimensions for this model are known and the numerically determined critical exponents can thus be matched to these, allowing for a full understanding of the collapse transition in this model.

The situation is much less clear for ISAT on the square lattice, which has been investigated in [84]. Simulating ISAT at $\omega = 3$ using KGT, we find that this is indeed a critical point, indicated clearly by a divergent specific heat. This indicates also a difference with the critical behaviour of Manhattan ISAW, where $\phi = 3/7$ implies that the specific heat does not diverge, as $\alpha = 2 - 1/\phi = -1/3$ is negative. A closer investigation shows that the collapse transition in these two models are indeed in two different universality classes, and even indicates the presence of logarithmic corrections for ISAT. The exponent results are summarised in Table 1. One reason for the difference between Manhattan ISAW and square lattice ISAT may be that in two dimensions there is a significant topological difference between a walk that can not cross itself and a trail that can cross itself. However, so far there has not been any satisfactory explanation for this difference.

A study of various models in three dimensions is reported in [80]. Here, KGT were studied on the diamond lattice and the WS-bcc lattice (both with coordination number 4, which allows a direct mapping to ISAT at $\omega = 3$ as above) and on the simple cubic lattice. Moreover, tri-colour walks on the WS-bcc lattice were simulated for comparison. The results were indicative of critical behaviour in all of these cases, with logarithmically divergent specific heats $C_N \sim (\log N)^{\zeta}$. However, the measured exponent was different for walks ($\zeta_{KGW} = 2.5(5)$) and trails ($\zeta_{KGT} = 1.0(5)$) and quite different from the theoretically predicted value of $\theta = 3/11 \approx 0.27$ from the field-theoretical methods applied to the continuum Edwards model [85, 86].

Summarising, the evidence presented indicates firstly that suitably defined interacting models of polymer collapse can be identified with kinetic growth processes. This is of both analytical and simulational significance. Not only may the additional structure introduced to the models help in the theoretical treatment, but it also enables highly efficient simulations providing a great deal of information.

On the other hand, however, the results also indicate that the choice of lattice, as well as the precise way in which self-avoidance and attractive interaction is incorporated in a lattice model of polymer collapse, affects the universality class of the collapse transition in a rather subtle and not yet understood manner.

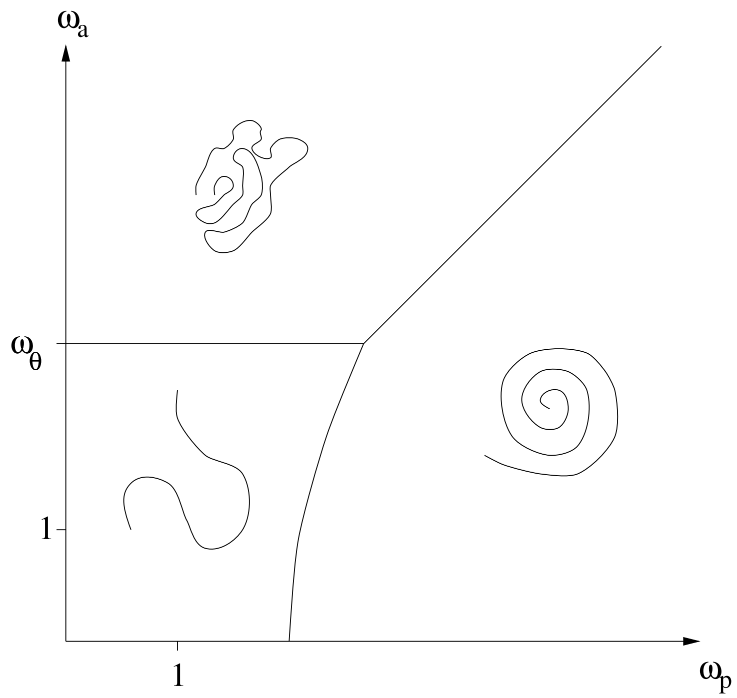

Figure 13: *Qualitative phasediagram of oriented ISAW (Figure 2 from [87]).*

6 Collapse of oriented polymers

The phase diagram for polymer collapse becomes more complex when the polymers are *oriented*, i.e., when they look different in the two directions along the chain, as, e.g., for A–B polyester [88]. In this situation, the interaction energy between nearby monomers depends in general on whether their relative orientation is parallel or antiparallel. When the attractive interaction between parallel monomers is sufficiently strong, the collapsed polymer winds up to form a spiral. A phase diagram, based on numerical work and exact results, was suggested in [89]. It contains three phase boundaries, separating the swollen, the normal collapsed, and the spiral phase (the latter being also a collapsed phase), and meeting at one point 13.

Oriented ISAW attracted much controversy after Cardy suggested (using conformal field theory arguments) that the exponent γ associated with the partition function may depend continuously on the parallel interaction energy in the swollen phase, while the exponent ν remains constant [90]. This supposed nonuniversality of γ in the swollen phase is complemented by the observation that at the collapse transition γ assumes different values on different lattices, which was discussed in the previous section. Orientation dependence of interactions may be relevant, as on the Manhattan lattice each bond of the lattice has a preassigned orientation, thus naturally excluding parallel interactions. Numerical studies of the swollen phase [89, 91, 92, 93, 94], however, show no indication of a variation of γ with the parallel interaction strength. This investigation has been continued involving other types of lattices [95, 96, 97]. In all these studies, the (very small) variation of γ with the parallel interaction strength decreases with increasing polymer length, making it unlikely that γ should show non-universal behaviour for much larger polymer length.

In [87] a study of winding angle distributions is utilised to clarify the precise location of the transition lines as well as their nature. (The results of this study have been confirmed independently by numerical simulations [93, 94].) The motivation for this is that the winding angle distribution for RW and SAW shows universal scaling features [98].

Since the winding angle is so closely related to the occurrence of parallel interactions, it should be equally sensitive to a change in the parallel interaction strength as the exponent γ. In fact, we find analytically a different winding angle distribution at the collapse transition on the Manhattan lattice and on the square lattice. Using universality arguments, we consider instead the problem of finding the winding angle distribution of parts of percolation cluster hulls, leading to a calculation which can be conveniently performed using the $O(n)$ model on a hexagonal lattice [99, 100]. We find that the winding angle distribution is Gaussian with universal variance $6/7 \log N$ which is different from the winding angle distribution variance $24/7 \log N$ for square lattice ISAW [99]. The validity of the calculation for critical Manhattan ISAW is confirmed using KGW simulations, as shown in Figure 14.

Using a combination of rigorous results, renormalisation group flow arguments, and phenomenological statistical physics arguments, we build a discussion

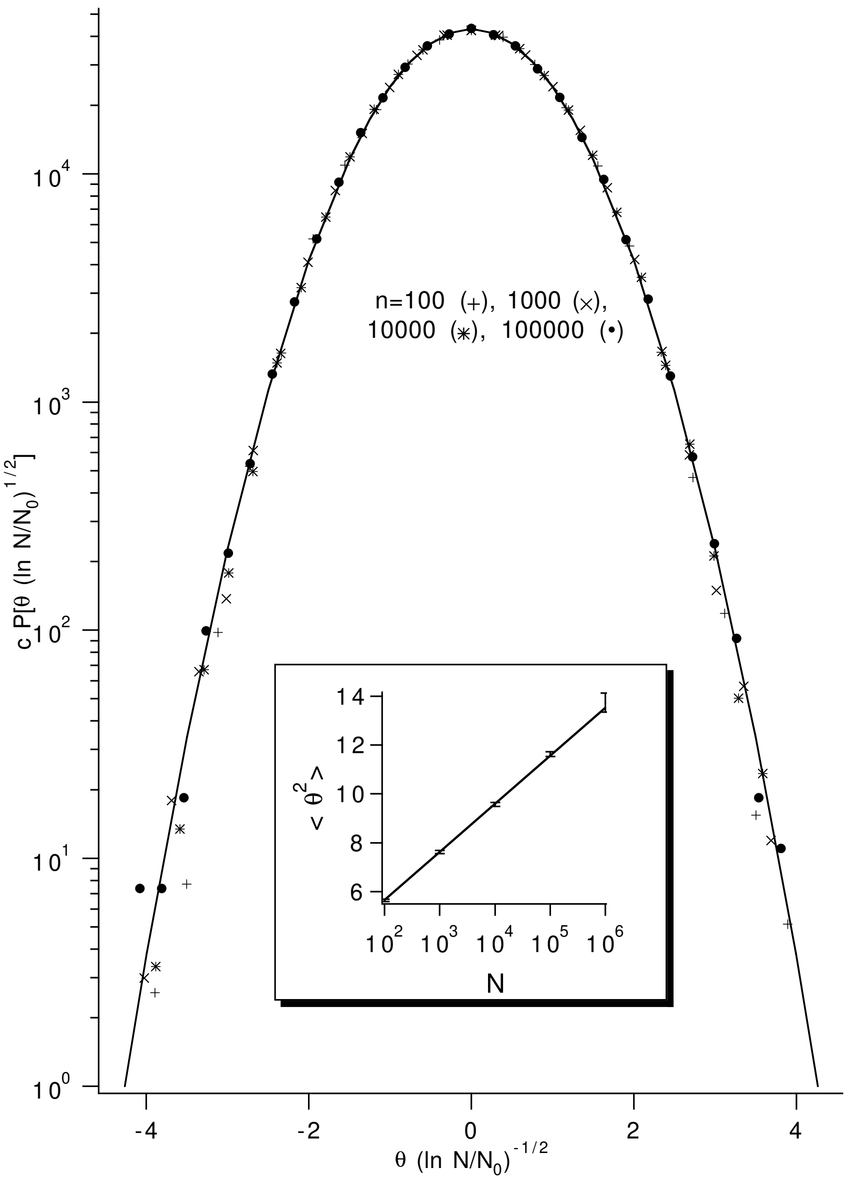

Figure 14: *Winding angle distribution at the collapse transition on the Manhattan lattice. When rescaled, the distributions collapse onto a Gaussian. The unit length* N_0 *is determined from a linear fit of* $\langle\theta^2\rangle$ *versus* $\ln N$. *(Figure 5 from [87]).*

of the full phase diagram upon this result. The important conclusion of [87] is that the winding angle distributions for oriented interacting polymers are also universal. The main evidence for this comes from the collapsed phase. Minimising the free energy, we find that the winding angle distribution in the collapsed phase depends only on whether the symmetry between parallel and antiparallel interaction energies is broken. This fixes the phase boundary between the normal collapsed and the spiral phase on the symmetry line, where parallel and antiparallel interactions are equally strong. Our argument shows also that the phase transition along this line is continuous. The θ–point is the point where the three phase boundaries meet. Due to its special role, it can have an exponent γ and a winding angle distribution that is different from all other points, without leading to non-universal behaviour.

Our work gives insights into the underlying physics of oriented polymers: whenever the antiparallel interaction energy is more negative than the parallel one, the winding angle of the polymer decreases during the collapse. It is confined in the collapsed phase and becomes zero in the ground state, where the end points must be at the surface. When the two interactions are equal, however, the variance of the winding angle increases during the collapse, and is always proportional to $\ln N$. When the parallel interaction is stronger than the antiparallel one, the collapsed phase has an overall spiral shape, the number of parallel interactions being proportional to the length of the polymer.

While the winding angle distribution in both collapsed phases of this model is well understood, little is known about the transition line; as this transition line corresponds to the collapsed phase of ordinary collapsed ISAW without orientation dependence, this is an important open question.

7 Polymer collapse in high dimensions

In the previous sections we have discussed polymer collapse models in the physically important dimensionalities two and three. In addition to general tri-critical scaling theory, results from conformal field theory and exactly solvable models have given a thorough understanding of the polymer collapse transition, leaving but a few open questions. At the upper critical dimension $d_u = 3$ results from field-theoretical work and simulations also confirm the tri-critical scaling behaviour [101, 30, 102].

Until recently [103], polymer collapse above the upper critical dimension has attracted little attention, presumably because it was generally accepted that it is described by standard mean field theory and therefore should be of little interest. However, our work in [104, 105, 106] uncovers a surprisingly interesting scenario.

Mean-field theory is generally applicable to second-order phase transitions above their upper critical dimension, and so is believed to provide an adequate description of the approach to such critical points. One type of transition where mean-field theory should hold are tri-critical points [18] for dimension $d > 3$. The region around a tri-critical point in general dimension is described by crossover scaling forms, where quantities depending on two relevant parameters can be essentially described by functions of a single scaling combination of those two parameters.

The application of the mean-field theory of a tricritical point to polymer collapse predicts that at the transition point the polymer actually behaves as if it were a random walk. In the thermodynamic limit, one expects a weak transition with a jump in the specific heat $\alpha = 0$. For finite polymer length there is no sharp transition for an isolated polymer and so this mean-field transition is rounded and shifted. In four and higher dimensions one may expect pure mean-field behaviour with a crossover exponent of $1/2$ [7].

On the other hand, for $d > 3$ Sokal [107] has pointed out that the alternative method of analysing collapse which has been shown to be equivalent to the field theoretic approach, namely the continuum Edwards model, has difficulties: in fact, an analysis of the Edwards model shows that the crossover exponent is given by $\phi_E = 2 - d/2$, which for $d = 4$ gives $\phi_E = 0$! In passing we note here that the same analysis predicts the shift of the θ-point, defined say via the universal ratio of the radius of gyration to the end-to-end distance equalling its Gaussian value, should scale as $N^{-(d/2-1)}$ so $\psi_E = (d/2-1) \neq \phi_E$. This difference between the shift and the crossover exponent implies that strict crossover scaling has broken down. Of course, the theoretical fact that the swollen phase should also be Gaussian for $d > 4$ does raise the suspicion that the analysis of the Edwards model for polymer collapse may be subtle for $d > 3$.

To consider such issues, we have simulated ISAW and ISAT on the four-dimensional hyper-cubic lattice [104, 106], and report on the implications for collapse scaling in [105]. The simulations are performed using PERM, a clever generalisation of a kinetic growth algorithm [30].

We find that there is a rather dramatic breakdown of the simple crossover scaling for the case of the coil-globule transition of an isolated polymer. It is likely that the build up of the tri-critical point is through the forming of singularities that have more in common with a (non-critical) first-order transition! However, this can be explained by a different kind of mean-field approach (not starting with an explicitly tri-critical Landau functional); moreover, the region around the tri-critical point needs to be described by more complex scaling forms. This second issue is in fact separate from the first-order nature of the scaling approach: we speculate that this behaviour is intimately related to the general description of systems where mean-field theory is used, so may have more general applicability.

The main evidence for this scenario stems from the internal energy density distribution near the collapse transition, which is shown in Figure 15. The character of that transition is particularly intriguing; we find a distinct double peak distribution for the internal energy, which becomes *more* pronounced as the chain length is increased. This would seem to suggest a first-order transition. If this were the case there would be a delta function peak forming in the specific heat but we find that while a peak is indeed forming it does not seem to be growing linearly with the size of the polymer, see Figure 16. Moreover, there is a θ-point scaling region distinct from the collapse transition (the location of which is indicated in Figure 16), a scenario which is incompatible with a first-order transition.

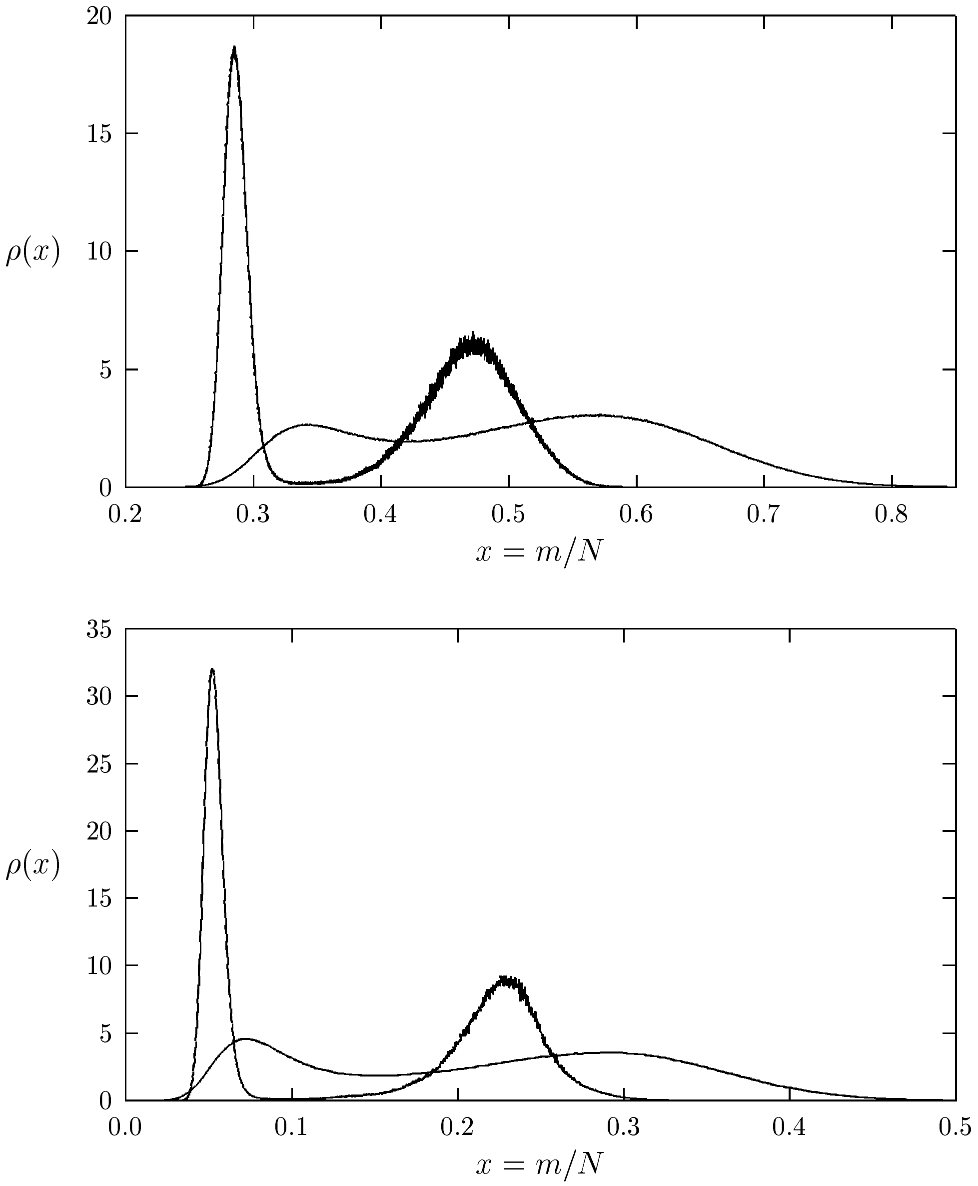

Figure 15: *Internal energy density distributions for ISAW at lengths 2048 and 16384 (above) and ISAT at lengths 512 and 4096 (below) on the four-dimensional hyper-cubic lattice, at their respective transition temperatures. The more highly peaked distribution is associated with the longer respective length (Figures 11 from [104] and 7 from [106]).*

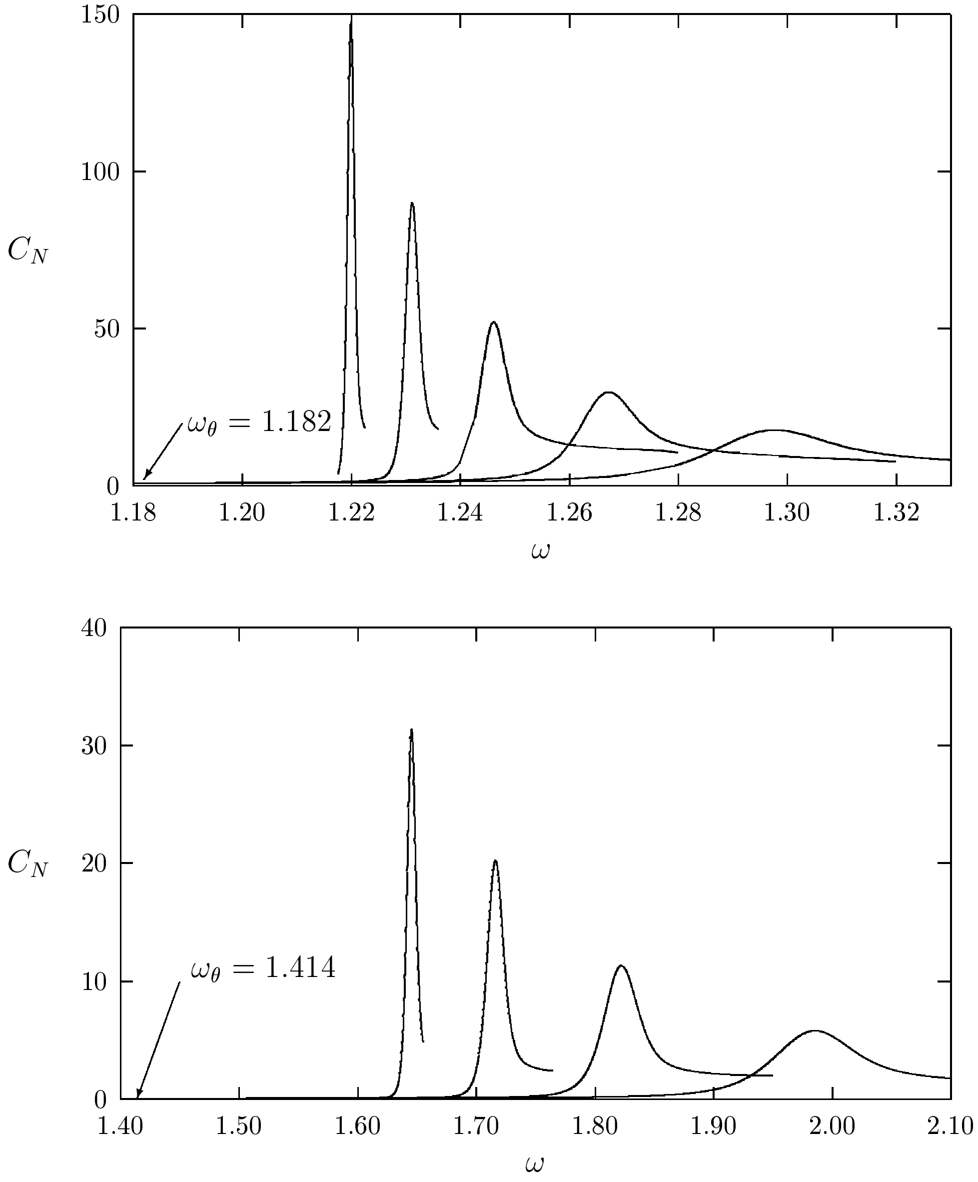

Figure 16: *Specific heat C_N versus ω for ISAW at lengths 1024, 2048 , 4096, 8192 and 16384 (above) and for ISAT at lengths 512, 1024, 248, and 4096 (below) on the four-dimensional hyper-cubic lattice. (Figures 9 from [104] and 5 from [106]).*

Fortunately there is a (suitably extendable) theoretical framework that is consistent with the evidence we present. This framework was explained in a paper by Khokhlov [108] who applied the mean-field approach of Lifshitz, Grosberg and Khokhlov [19, 20, 21] to arbitrary dimensions. This theory is based on a phenomenological free energy in which the competition between a bulk free energy of a dense globule and its surface tension drive the transition. Until recently [41] the consequences of this surface free energy were largely ignored in the polymer literature.

The implications of this theory for polymer collapse above the upper critical dimension are described in [104, 105]. The major conclusions are that the finite-size character of the coil-globule transition in four dimensions is first-order despite the thermodynamic limit being probably adequately described by mean-field tricritical behaviour. We propose to call this a *pseudo-first-order transition.*

References

[1] P. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, 1953.

[2] P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, 1979.

[3] J. des Cloizeaux and G. Jannink, *Polymers in Solution*, Clarendon Press, Oxford, 1990.

[4] C. Vanderzande, *Lattice Models of Polymers*, Cambridge University Press, Cambridge, 1998.

[5] E. J. Janse van Rensburg, *The Statistical Mechanics of Interacting Walks, Polygons, Vesicles, and Animals*, Oxford University Press, Oxford, 2000.

[6] N. Madras and G. Slade, *The Self-Avoiding Walk*, Birkhauser, Boston, 1993.

[7] P.-G. de Gennes, J. Physique Lett. **36**, L55 (1975).

[8] P.-G. de Gennes, J. Physique Lett. **39**, L299 (1978).

[9] B. Duplantier, J. Physique **43**, 991 (1982).

[10] S. T. Sun, I. Nashio, G. Swislow, and T. Tanaka, J. Chem. Phys. **73**, 5971 (1980).

[11] S. F. Sun and J. R. Fan, Polymer **38**, 563 (1997).

[12] P.-G. de Gennes, Phys. Lett. **38A**, 339 (1972).

[13] J. des Cloizeaux, J. Physique **36**, 281 (1975).

[14] B. Nienhuis, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz, volume 11, Academic Press, London, 1987.

[15] J. L. Cardy, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz, volume 11, Academic Press, New York, 1987.

[16] R. J. Baxter, J. Phys. A. **19**, 2821 (1986).

[17] B. Duplantier and H. Saleur, Phys. Rev. Lett. **59**, 539 (1987).

[18] I. D. Lawrie and S. Sarbach, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz, volume 9, Academic, London, 1984.

[19] I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **55**, 2408 (1968), [Sov. Phys. - JETP, **28**, 545, 1969].

[20] I. M. Lifshitz, A. Y. Grosberg, and A. R. Khokhlov, Zh. Eksp. Teor. Fiz. **71**, 1634 (1976), [Sov. Phys. - JETP, **44**, 1976].

[21] I. M. Lifshitz, A. Y. Grosberg, and A. R. Khokhlov, Rev. Mod. Phys. **50**, 683 (1978).

[22] G. W. King, in *Monte Carlo Method*, volume 12 of *Applied Mathematics Series*, National Bureau of Standards, 1951.

[23] B. Li, N. Madras, and A. D. Sokal, J. Stat. Phys. **80**, 661 (1995).

[24] A. J. Guttmann, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz, volume 13, Academic Press, 1989.

[25] A. Conway and A. J. Guttmann, Phys. Rev. Lett. **77**, 5284 (1996).

[26] E. Sackmann, H.-P. Duwe, and H. Engelhardt, Faraday Discuss **81**, 281 (1986).

[27] M. E. Fisher, A. J. Guttmann, and S. Whittington, J. Phys. A **24**, 3095 (1991).

[28] P. Flajolet and R. Sedgewick, Functional equations, rational and algebraic functions, INRIA Res. Rep. #4103, planned Chapter 8 of *Analytic Combinatorics*, 2001.

[29] B. Nienhuis, Int. J. Mod. Phys. B **4**, 929 (1990).

[30] P. Grassberger, Phys. Rev. E **56**, 3682 (1997).

[31] V. Privman and N. M. Švrakić, *Directed Models of Polymers, Interfaces, and Clusters: Scaling and Finite–Size Properties*, volume 338 of *Lecture Notes in Physics*, Springer–Verlag, Berlin, 1989.

[32] A. R. Veal, J. M. Yeomans, and G. Jug, J. Phys. A **23**, L109 (1990).

[33] R. Brak, A. J. Guttmann, and S. G. Whittington, J. Phys. A **25**, 2437 (1992).

[34] A. L. Owczarek, T. Prellberg, and R. Brak, J. Stat. Phys. **72**, 737 (1993).

[35] H. N. V. Temperley, Phys. Rev. **103**, 1 (1956).

[36] G. Gasper and M. Rahman, *Basic Hypergeometric Series*, Camb. Univ., 1990.

[37] T. Prellberg, A. L. Owczarek, R. Brak, and A. J. Guttmann, Phys. Rev. E. **48**, 2386 (1993).

[38] A. L. Owczarek, J. Phys. A. **26**, L647 (1993).

[39] P. M. Binder, A. L. Owczarek, A. R. Veal, and J. M. Yeomans, J. Phys. A **23**, L975 (1990).

[40] R. B. Griffiths, Phys Rev. B **7**, 545 (1973).

[41] A. L. Owczarek, T. Prellberg, and R. Brak, Phys. Rev. Lett. **70**, 951 (1993).

[42] R. Brak, A. L. Owczarek, and T. Prellberg, J. Phys. A. **26**, 4565 (1993).

[43] M. E. Fisher, Physics **3**, 255 (1967).

[44] M. E. Fisher and B. U. Felderhof, Ann. Phys. **58**, 176 (1970).

[45] B. Duplantier, Phys. Rev. Lett. **71**, 4274 (1993).

[46] A. L. Owczarek, T. Prellberg, and R. Brak, Phys. Rev. Lett. **71**, 4275 (1993).

[47] D. Bennett-Wood, R. Brak, A. J. Guttmann, A. L. Owczarek, and T. Prellberg, J. Phys. A. **27**, L1 (1994).

[48] R. Brak, A. L. Owczarek, and T. Prellberg, J. Stat. Phys. **76**, 1101 (1994).

[49] T. Prellberg and R. Brak, J. Stat. Phys. **78**, 701 (1995).

[50] T. Prellberg and A. L. Owczarek, in *Proceedings of the Conference 'Confronting the Infinite'*, pages 204–214, World Scientific, (1995).

[51] T. Prellberg and A. L. Owczarek, J. Stat. Phys. **80**, 755 (1995).

[52] T. Prellberg, J. Phys. A **28**, 1289 (1995).

[53] T. Prellberg and A. L. Owczarek, Commun. Math. Phys. **201**, 493 (1999).

[54] M. Delest, J. Math Chem **8**, 3 (1991).

[55] M. Delest and G. Viennot, Theo. Comp. Sc. **34**, 169 (1984).

[56] M. P. Schutzenberger, in *Proc. Symp. on Mathematical Theory of Automata, Lecture notes in Computer Science*, pages 246–264, Polytechnic Institute of Brooklyn, 1962.

[57] F. H. Jackson, Trans. Roy. Soc. Edin. **41**, 1 (1903).

[58] M. Rahman, J. Math Analysis and Applications **125**, 58 (1987).

[59] M. P. Delest and J. M. Fédou, in *Proc. Workshop on Attribute grammars*, edited by P. Deransart and M. Jourdan, pages 46–60, 1990.

[60] M. P. Delest and J. M. Fédou, Discrete Math. **112**, 65 (1993).

[61] C. Banderier, P. Flajolet, G. Schaeffer, and M. Soria, Submitted to Random Structures and Algorithms, March 2001.

[62] I. Majid, N. Jan, A. Coniglio, and H. E. Stanley, Phys. Rev. Lett. **52**, 1257 (1984).

[63] J. Lyklema and K. Kremer, J. Phys. A. **17**, L691 (1984).

[64] K. Kremer and J. Lyklema, J. Phys. A. **18**, 1515 (1985).

[65] A. Weinrib and S. A. Trugman, Phys. Rev. B **31**, 2993 (1985).

[66] A. Coniglio, N. Jan, I. Majid, and H. E. Stanley, Phys. Rev. B **35**, 3617 (1987).

[67] R. M. Bradley, J.-M. Debierre, and P. Strenski, Phys. Rev. Lett **68**, 2332 (1992).

[68] R. M. Bradley, J.-M. Debierre, and P. Strenski, J. Phys. A. **25**, L541 (1992).

[69] R. M. Bradley, P. Strenski, and J.-M. Debierre, Phys. Rev. A **45**, 8513 (1992).

[70] A. Malakis, Physica **84**, 256 (1976).

[71] Y. Shapir and Y. Oono, J. Phys. A. **17**, L39 (1984).

[72] H. A. Lim, A. Guha, and Y. Shapir, J. Phys. A **21**, 773 (1988).

[73] I. S. Chang, A. Guha, H. A. Lim, and Y. Shapir, J. Phys. A **21**, L559 (1988).

[74] I. Guim, H. W. J. Blöte, and T. W. Burkhardt, J. Phys. A. **30**, 413 (1997).

[75] R. M. Bradley, Phys. Rev. A **39**, 3738 (1989).

[76] R. M. Bradley, Phys. Rev. A **41**, 914 (1990).

[77] T. Prellberg and A. L. Owczarek, J. Phys. A. **27**, 1811 (1994).

[78] M. T. Batchelor, A. L. Owczarek, K. Seaton, and C. M. Yung, J. Phys. A **28**, 839 (1995).

[79] A. L. Owczarek and T. Prellberg, J. Stat. Phys. **79**, 951 (1995).

[80] T. Prellberg and A. L. Owczarek, Phys. Rev. E. **51**, 2142 (1995).

[81] J. M. F. Gunn and M. Ortuno, J. Phys. A. **18**, L1095 (1985).

[82] S. Roux, E. Guyon, and D. Sornette, J. Phys. A. **21**, L475 (1985).

[83] S. S. Manna and A. J. Guttmann, J. Phys. A. **22**, 3113 (1989).

[84] A. L. Owczarek and T. Prellberg, Physica A **205**, 203 (1994).

[85] B. Duplantier, Europhys. Lett. **1**, 491 (1986).

[86] B. Duplantier, J. Chem. Phys. **86**, 4233 (1987).

[87] T. Prellberg and B. Drossel, Phys. Rev. E **57**, 2045 (1998).

[88] J. Miller, J. Stat. Phys. **63**, 89 (1991).

[89] D. Bennett-Wood, J. L. Cardy, S. Flesia, A. J. Guttmann, and A. L. Owczarek, J. Phys. A. **28**, 5143 (1995).

[90] J. L. Cardy, Nuc. Phys. B. **419**, 411 (1994).

[91] S. Flesia, Europhys. Lett. **32**, 149 (1995).

[92] G. T. Barkema and S. Flesia, J. Stat. Phys. **85**, 363 (1996).

[93] A. Trovato and F. Seno, Phys. Rev. E **56**, 131 (1997).

[94] G. T. Barkema, U. Bastolla, and P. Grassberger, J. Stat. Phys. **90**, 1311 (1998).

[95] D. Bennett-Wood, J. L. Cardy, I. Enting, A. J. Guttmann, and A. L. Owczarek, Nuc. Phys. B **528**, 533 (1998).

[96] H. Frauenkron, M. S. Causo, and P. Grassberger, Phys. Rev. E. **59**, R16 (1999).

[97] S. Caracciolo, M. S. Causo, P. Grassberger, and A. Pelissetto, J. Phys. A. **32**, 2931 (1999).

[98] B. Drossel and M. Kardar, Phys. Rev. E **53**, 5861 (1996).

[99] B. Duplantier and H. Saleur, Phys. Rev. Lett. **61**, 1521 (1988).

[100] H. Saleur and B. Duplantier, Phys. Rev. Lett. **58**, 2325 (1987).

[101] P. Grassberger and R. Hegger, J. Chem. Phys. **102**, 6881 (1995).

[102] J. Hager and L. Schäfer, Phys. Rev. E **60**, 2071 (1999).

[103] A. L. Owczarek and T. Prellberg., Physica A **260**, 20 (1998).

[104] T. Prellberg and A. L. Owczarek, Phys. Rev. E. **62**, 3780 (2000).

[105] A. L. Owczarek and T. Prellberg., Europhys. Lett. **51**, 602 (2000).

[106] T. Prellberg and A. L. Owczarek, Four-dimensional polymer collapse ii: Interacting self-avoiding trails, Submitted to Physica A., 2001.

[107] A. D. Sokal, Europhys. Lett. **27**, 661 (1994).

[108] A. R. Khokhlov, Physica A. **105**, 357 (1981).

8 Appendix: Selected own papers

1. [34] "The Tricritical Behaviour of Self-Interacting Partially Directed Walks," J. Stat. Phys. **72** (1993) 737-772, A. L. Owczarek, T. Prellberg, and R. Brak.

2. [37] "Finite Length Scaling of Collapsing Directed Walks," Phys. Rev. E **48** (1993) 2386-2396, T. Prellberg, A. L. Owczarek, R. Brak, and A. J. Guttmann.

3. [41] "New Scaling Form for the Collapsed Polymer Phase," Phys. Rev. Lett. **70** (1993) 951-953, A. L. Owczarek, T. Prellberg, and R. Brak.

4. [42] "A Scaling Theory of the Collapse Transition in Geometric Cluster Models of Polymers and Vesicles," J. Phys. A: Math. Gen. **26** (1993) 4565-4579, R. Brak, A. L. Owczarek, and T. Prellberg.

5. [49] "Critical Exponents from Non-Linear Functional Equations for Partially Directed Cluster Models," J. Stat. Phys. **78** (1995) 701-730, T. Prellberg and R. Brak.

6. [52] "Uniform q–Series Asymptotics for Staircase Polygons," J. Phys. A: Math. Gen. **28** (1995) 1289-1304, T. Prellberg.

7. [53] "On the Asymptotics of the Finite-perimeter Partition Function of Two-dimensional Lattice Vesicles," Commun. Math. Phys. **201** (1999) 493-505, T. Prellberg and A. L. Owczarek.

8. [77] "Manhattan Lattice Θ-point Exponents from Kinetic Growth Walks and Exact Results from the Nienhuis $\mathrm{O}(n)$ Model," J. Phys. A: Math. Gen. **27** (1994) 1811-1826, T. Prellberg and A. L. Owczarek.

9. [79] "The Collapse Point of Interacting Trails in Two Dimensions from Kinetic Growth Simulations," J. Stat. Phys. **79** (1995) 951-967, A. L. Owczarek and T. Prellberg.

10. [80] "Models of Polymer Collapse in Three Dimensions: Evidence from Kinetic Growth Simulations," Phys. Rev. E **51** (1995) 2142-2149, T. Prellberg and A. L. Owczarek.

11. [87] "Winding Angles for Two–dimensional Polymers with Orientation Dependent Interactions," Phys. Rev. E **57** (1998) 2045-2052, T. Prellberg and B. Drossel.

12. [103] "Existence of four-dimensional polymer collapse I: Kinetic growth Trails," Physica A **260** (1998) 20-30, A. L. Owczarek and T. Prellberg.

13. [104] "Four-dimensional polymer collapse: Pseudo-First-Order Transition in Interacting Self-avoiding Walks," Phys. Rev. E **62** (2000), 3780-3789, T. Prellberg and A. L. Owczarek.

14. [105] "First-order scaling near a second-order phase transition: Tricritical polymer collapse," Europhysics Lett. **51** (2000), 602-607, A. L. Owczarek and T. Prellberg.

15. [106] "Four-dimensional polymer collapse II: Interacting self-avoiding trails," preprint cond-mat/0104134, submitted to Physica A, T. Prellberg and A. L. Owczarek.