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A scaling theory of the collapse transition in geometric cluster models of polymers and vesicles

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Abstract. Much effort has been expended in the past decade to calculate numerically the exponents at the collapse transition point in walk, polygon and animal models. The *crossover* exponent ϕ has been of special interest and sometimes is assumed to obey the relation $2-\alpha=1/\phi$ with the α the canonical (thermodynamic) exponent that characterizes the divergence of the specific heat. The reasons for the validity of this relation are not widely known.

We present a scaling theory of collapse transitions in such models. The free energy and canonical partition functions have *finite-length* scaling forms whilst the grand partition function has a tricritical scaling form. The link between the grand and canonical ensembles leads to the above scaling relation. We then comment on the validity of current estimates of the crossover exponent for interacting self-avoiding walks in two dimensions and propose a test involving the scaling relation which may be used to check these values.

1. Introduction

The number of models of a polymer molecule in a dilute solution of a good solvent is growing rapidly [1]. Many are constructed to model the collapse phase transition that the polymer undergoes as the temperature or the quality of the solvent is reduced. At temperatures above the critical temperature the polymer is in an extended or 'coiled' phase, whilst below, it collapses to a compact 'ball' shape. Another system with similar features is vesicles in solution. These are formed by closed surfaces of lipid membranes the shape of which can be controlled by changing the surface or volume fugacity. If a distinct shape change occurs at a particular temperature or fugacity then we have a phase transition. This behaviour is analogous to the polymer collapse (if we understand surface fugacity as playing the role of temperature) and we expect some universal features.

Our paper is concerned with the scaling theory of the phase transition occurring in geometric cluster models of linear, ring and branch polymers and of vesicles. We shall argue that this class of models has a similar mathematical structure which enables us to present a generic set of scaling forms. In particular, we present scaling forms for the grand partition function (strictly it is a generalized partition function), the canonical free energy and the canonical partition function. The generalized partition function has a tricritical scaling form whilst the free energy and partition function have a

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finite-size crossover scaling form. These scaling forms apply in *both* the expanded and collapsed phases. In the collapsed phase the surface of the polymer plays a significant role in the low temperature finite-size scaling form. The scaling forms in the high temperature phase lead to the tricritical scaling relation

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

where α is the specific heat exponent and ϕ the crossover exponent. This scaling relation enables us to make some strong comments on recent attempts to numerically evaluate the two dimensional crossover exponent of the interacting self-avoiding walk model (ISAW) of the collapse of linear polymers.

The scaling functions we present occur in two forms. The first form is more general and assumes the specific heat exponent α exists on both sides of the phase transition. The second form assumes α exists only in the high temperature phase. Although the second is a particular case of the first, we present it because for several of the models the low temperature specific heat is *analytic* at the collapse transition (and so has no singularity there). The models which are known to have this unusual property include all vesicle models [2] and the interacting partially directed walk model (IPDSAW) [3]. We will refer to the models whose specific heat is singular on both sides of the transition as the *symmetric* models, and those whose specific heat is analytic in the low temperature phase as the *asymmetric* models. It is not known whether the ISAW model or interacting lattice animal models [4] of branched polymers (ILA) are symmetric or not.

2. Generic structure

We now define the geometric cluster models more carefully and argue that they all have a similar mathematical structure which is conveniently represented by a singularity or 'phase' diagram. This diagram shows the radius of convergence of the generating function of the canonical partition functions. This diagram is important as it is here that the tricritical structure of the collapse transition is apparent. The diagram differs significantly depending on whether the model is symmetric or not.

2.1. *The models*

The models considered in this paper are defined by two principal ingredients: (i) the monomers of the polymer or lipid layer of the vesicle are represented by a 'cluster' of sites or bonds on a lattice and (ii) the agent responsible for the phase transition is modelled by a nearest-neighbour interaction or equivalent fugacity, such as the surface fugacity in vesicles. For example, the cluster of branched polymers is a lattice animal, for linear polymers it is a self-avoiding walk, for ring polymers and vesicles it is a self-avoiding polygon (though in the latter the cluster size and collapse agents are different). Mathematically, each system is characterized by some cluster size n and some other parameter that varies the strength of the collapse agent. We now provide some concrete and typical examples of the above.

The ISAW model of polymer collapse consists of a n-step self-avoiding walk with an attractive interaction energy $-J<0$ between any two nearest-neighbour sites of the walk (not connected by a bond of the walk). An example of such a walk is shown in figure 1(a). The canonical partition function for the model is given by

$$Z_n^p(w) = \sum_{\text{config.}} c_m^{(n)} w^m \tag{2}$$

where the Boltzman factor $w = \exp(\beta J)$, $c_m^{(n)}$ is the number of configurations with n steps and m interactions and the sum is over all configurations of the n-step walk.

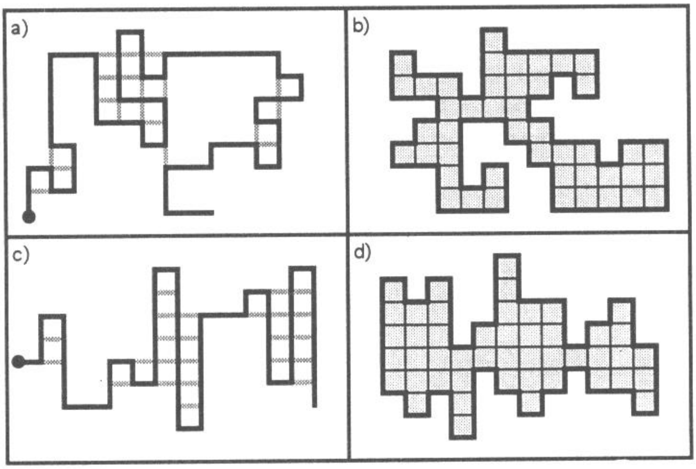

Figure 1. A selection of cluster models illustrating a typical configuration: (a) interacting self-avoiding walk model of linear polymers—light lines show the nearest neighbour interactions, (b) self-avoiding polygon model of vesicles—shaded squares show the area, (c) interacting partially directed self-avoiding 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.

From the partition function we construct the generating function,

$$G^p(w, z) = \sum_{n=1}^{\infty} Z_n^p(w) z^n. \tag{3}$$

The generating function can also be interpreted as a 'generalized' partition function with z a fugacity controlling the average length of the walks. A 'generalized' partition function differs from a grand partition function in that there is no parameter, analogous to the volume, which can be used to take the thermodynamic limit.

Expressions similar to (2) and (3) occur for the interacting polygon models except now the configurations are self-avoiding polygons and n is the length or perimeter of the polygons.

The geometric cluster model of vesicles consists of a self-avoiding polygon with a perimeter and area fugacity. As opposed to ring polymers here the area plays the role of the size n of the system. An example of such a polygon is shown in figure 1(b). The canonical 'partition function' is

$$Z_n^v(x) = \sum_{\text{config.}} p_m^{(n)} x^m \tag{4}$$

where $p_m^{(n)}$ is the number of polygons with area n and perimeter m. The sum is over all configurations of the polygon with fixed area, n. The generating function is

$$G^v(x, y) = \sum_{n=1}^{\infty} Z_n^v(x) y^n. \tag{5}$$

If G^v is interpreted as a generalized partition function then y is an area fugacity. Similar expressions are obtained for the lattice animal models of branched polymers.

2.2. *The singularity diagram*

Many features of these cluster models are concisely represented by a 'phase', or singularity, diagram. This diagram shows the radius of convergence of the generating function which is of particular relevance as it is directly related to the canonical free energy. Both equations (3) and (5) for the generating functions are of the same form, that is, a generating function of finite polynomials; thus we will use G^p in what follows, but the derivation is general. The ISAW total free energy is

$$F_n^p(w) = -\frac{1}{\beta}\log Z_n^p(w) \tag{6}$$

and assuming the thermodynamic limit exists, we have for the thermodynamic free energy per step

$$f_\infty^p(w) = \lim_{n\to\infty}\frac{1}{n}F_n^p(w) \tag{7}$$

which in turn implies that

$$F_n^p(w) = nf_\infty^p(w) + o(n). \tag{8}$$

Using (3), (6) and (8) gives (for fixed w)

$$G^p(w,z) = \sum_{n=1}^{\infty} e^{o(n)}(z\,e^{-\beta f_\infty^p})^n. \tag{9}$$

If G^p is considered as a function of the generating variable, z (with w a parameter) then (9) implies the radius of convergence of G^p, for each value of w, is given by $z\,e^{-\beta f_\infty^p} = 1$, or

$$z_\infty(w) = \exp(\beta f_\infty^p). \tag{10}$$

Thus a plot of $z_\infty(w)$, in the (w, z)-plane is indirectly a plot of the free energy per step of an infinite length walk.

This plot, showing the radius of convergence of the generating function, for each value of the temperature variable—w in this case—will be referred to as the singularity diagram. Note that the existence of the free energy ensures that $z_\infty(w)$ exists for all $w > 0$ and so (10) implies that $z_\infty(w)$ is always positive. Figure 2 shows two schematic singularity diagrams. The first form (Figure 2(a)) is expected to represent the ISAW and ILA models, and is known to represent the IPDSAW model [5]. The second form (figure 2(b)) is known to represent vesicle models [2, 6].

Different parts of the singularity diagram correspond to distinct features of the model. Thus for the ISAW model, if in the thermodynamic limit, the model undergoes a phase transition at some temperature T_c, the free energy $f_\infty^p(w)$ will be singular at $w_c = \exp(J/k_B T_c)$ and hence so will $z_\infty(w)$. Thus, if $z_c = z_\infty(w_c)$, we can represent the phase transition (in the canonical ensemble) by the point (w_c, z_c). The line $z_\infty(w)$ for $w < w_c$ corresponds to the high temperature phase, whilst the line $z_\infty(w)$ for $w > w_c$ corresponds to the low temperature collapsed phase. As G^p is a partition function in the generalized ensemble we can use it to evaluate averages of thermodynamic variables.

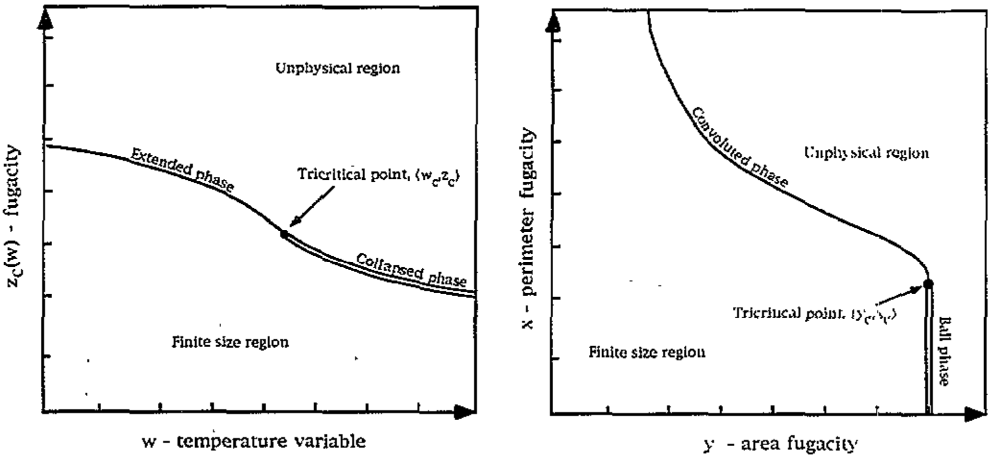

Figure 2. (*a*) The expected form of the singularity or 'phase' diagram for the interacting self-avoiding walk model of linear polymers. (*b*) The singularity or 'phase' diagram for the self-avoiding polygon model of vesicles [2].

In particular, it is possible to show that the average length of the walk is finite in the region $0 \le z < z_\infty(w)$. Thus, the region below $z_\infty(w)$ corresponds to a finite length 'phase'. Similar interpretations occur for the vesicle models. Note that the region above $z_\infty(w)$ is *non-physical* for the class of models considered here. (This can be changed if the models are extended by introducing a bounding box to contain the clusters, that is, a volume parameter.)

2.3. Generic structure of symmetric and asymmetric models

Superficially, the two singularity diagrams (figure 2) appear quite different but by a change of variables the generic structure becomes apparent. Firstly, one considers each singularity diagram in an equivalent way to the (w, z) plane for the walk models: for example, in vesicles the $(1/x, y)$-plane is similar. Let us call the abscissa ω. Now consider the function $z_\infty(\omega)$ at low temperatures, that is large ω, and call this $z_\infty^-(\omega)$. There are two possible cases.

Firstly, if this function is analytic for all ω including ω_c then we can transform our variables to a generic pair (ω, q) where $q_\infty^-(\omega) = 1$ for all $\omega > \omega_c$. (Of course $z_\infty^+(\omega)$ must then have a singularity at ω_c for some transition to exist!) For vesicles we have simply that $\omega = 1/x$ and $q = y$ and in the IPDSAW problem we have $\omega = w$ and $q = wz$. In general we have $q = z/z_\infty^-(\omega)$ and so we can define a generic partition function as $Q_n(\omega) = [z_\infty^-(\omega)]^n Z_n(\omega)$. The generic generating function is

$$G(\omega, q) = \sum_{n=1}^{\infty} Q_n(\omega) q^n \tag{11}$$

and the corresponding singularity diagram in the (ω, q) plane is shown in figure 3(a).

Secondly, if this assumption of analyticity of $z_\infty^-(\omega)$ at ω_c is false then let us examine the asymptotic behaviour of $z_\infty(\omega)$ as $\omega \to \infty$, that is, as the temperature approaches zero. Let

$$z_\infty(\omega) \sim z_a(\omega) \tag{12}$$

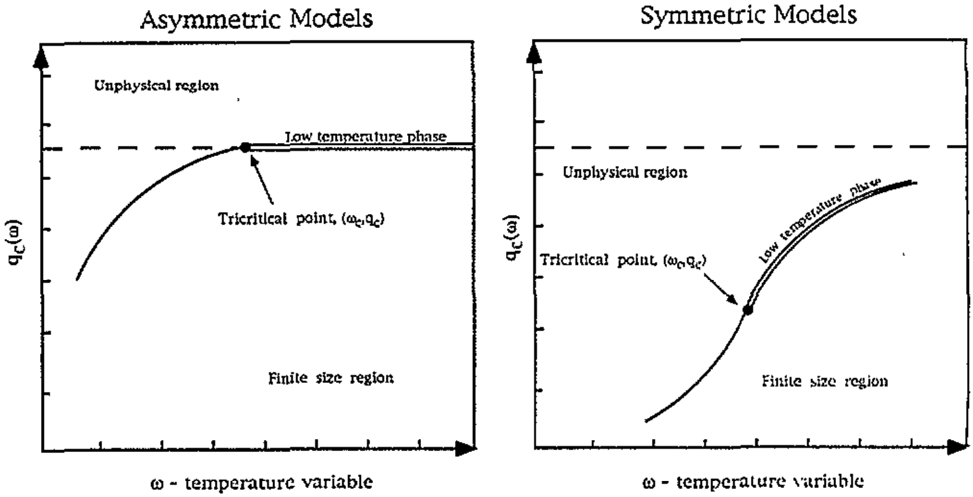

Figure 3. The schematic singularity diagrams, in the generic variables ω and q, (a) for the asymmetric models and (b) for symmetric models (the low and high temperature lines are curved but whether they are concave or convex will be model dependent. The dashed line in both figures is the line $q=1$.

so by using a suitably chosen $z_a(\omega)$ in this case, in the same fashion as $z_\infty^-(\omega)$ for the previous case, we obtain a phase diagram as shown in figure 3(b). Hence $q = z/z_a(\omega)$ and $Q_n(\omega) = [z_a(\omega)]^n Z_n(\omega)$.

The above is simply describing transformations which allow us to consider the generic forms (figure 3) of the phase diagrams for these models. We have divided the models into two categories, the first we shall call *asymmetric* while the second *symmetric*. This partitioning of the models into two categories becomes logical when we examine the generic free energy $f_\infty = -\lim_{n\to\infty} \log(Q_n)/\beta n$. The radius of convergence of $G(\omega, q)$ occurs for

$$q_\infty(\omega) = \exp(\beta f_\infty(\omega)) \tag{13}$$

and the phase transition occurs at $\omega = \omega_c$ and $q_c = q_\infty(\omega_c)$. If the phase transition is second order, then the singular part of the free energy would be expected to behave like

$$f_\infty \sim t^{2-\alpha'} \qquad t = T - T_c. \tag{14}$$

For the asymmetric models (figure 3(a)) the radius of convergence in the low temperature phase has $q_\infty^-(\omega) = 1$ for all $\omega > \omega_c$. This implies that the low temperature generic free energy, $\beta f_\infty^- = \log[q_\infty^-(\omega)]$ is zero for $\omega > \omega_c$ and hence (trivially) an entire function. Thus the asymmetric models do not have a singular specific heat in the low temperature phase, that is, a non-trivial α does *not* exist. Whereas, for the symmetric models (figure 3(b)) the free energy in the low temperature phase f_∞^- is some *singular* function of ω which gives rise to an α in the low temperature phase. In the high temperature phase the specific heat of both the symmetric and asymmetric models is singular, that is, a non-trivial α exists. Thus the symmetric models have an α in both phases whilst the asymmetric models only have a high temperature α. The nomenclature is therefore self-evident.

While one would normally expect symmetric transitions in other models (such as Ising) recent exact and rigorous results point in the other direction for certain geometric models [2, 6]. There remains the intriguing possibility that all the models might be asymmetric and thus, with appropriate choice of the q variable, figure 3(a) would be the generic form of the singularity diagram.

Whichever category the model falls into we now summarize the mathematical aspects of behaviour of the generating function necessary to produce the scaling forms subsequently given. We conjecture that in the high temperature phase, $q_{\infty}^{+}(\omega)$ is a line of simple singularities (e.g. a pole, branch or log singularity) and hence the generating function diverges, whilst in the low temperature phase $q_{\infty}^{-}(\omega)$ is a line of essential singularities. (We describe these assumptions mathematically later). The essential singularity is such that G remains *finite* on the line $q_{\infty}^{-}(\omega)$. The evidence comes from two sources. Firstly, all the exact solutions of vesicle models [5] and the IPDSAW model [6, 3] have this structure, and secondly there is a very close relationship between the above class of models and the problem of condensation in fluids. (These features do not depend on the symmetry of the transition.) As shown by Fisher [7] the condensation line is a line of essential singularities. The consequences of this relationship have already been shown in Owczarek *et al* [8] and further details may be found in Prellberg *et al* [9].

This singularity structure is significant as it brings to mind the singularity structure of a tricritical phase transition. If a tricritical point is taken to be the meeting point of a line of first order transitions (essential singularities) with a line of second order transitions (simpler singularities), then, at least for $0<q\leqslant q_{\infty}(\omega)$, the singularity structure of G corresponds to that of a tricritical phase transition, with (ω_c, q_c) corresponds to the tricritical point. This leads directly to the tricritical scaling form for the generating function.

3. Scaling forms

We now consider the scaling forms. In the canonical ensemble the partition function and the free energy both depend on the length parameter n. In the limit $n \to \infty$ we have the thermodynamic limit and it is only in this limit that we have the possibility of a phase transition. However, if the thermal correlation length is smaller than the average size of the finite length walk the system behaves thermodynamically as if it was of infinite size. As the critical temperature is approached the thermal correlation length begins to diverge, as if it were an infinite system, and at some stage approaches the size of the system. The finite size aspects of the system then dominate. Thus the system crosses over from one type of behaviour to another. This crossover behaviour is described by the finite-size crossover scaling functions of the free energy and partition function.

As discussed above the generating function or generalized partition function has a tricritical singularity structure and so in the region of the tricritical point is represented by a tricritical scaling function.

We thus have two types of scaling behaviour, finite-size scaling and tricritical scaling, and consequently a large number of critical exponents. This can lead to confusion, not only as to which type of scaling the exponent is associated with, but also because exponents using the same symbol may be confused with those already in use in the general literature. It is for these reasons that we first summarize the structure of a conventional tricritical point and so establish a 'generic' set of tricritical exponents.

3.1. *Conventional tricritical scaling*

We shall keep as close to Griffiths [10] and Lawrie [11] as possible. The structure of a conventional tricritical point and the associated exponents is illustrated in figure 4. These exponents are emphasized by superscripting with g (for 'generic'). Here, t is taken as a temperature variable measuring the *tangential* deviation from the tricritical point, and g is the second scaling variable measuring an *angular* (that is, non-tangential) deviation from the tricritical point. Generally a first order phase transition occurs as the τ-line is crossed (and is usually a line of essential singularities) and a second order phase transition occurs as the λ-line is crossed (and is usually a line of branch or pole-like singularities). The τ-line and λ-line are assumed to meet tangentially at the tricritical point. The equation, $g_\lambda(t)$ of the λ-line in the neighbourhood of the tricritical point is characterized by the shift exponent ψ_λ^g through

$$g_\lambda(t) \sim t^{\psi_\lambda^g}. \tag{15}$$

and similarly for the τ-line†.

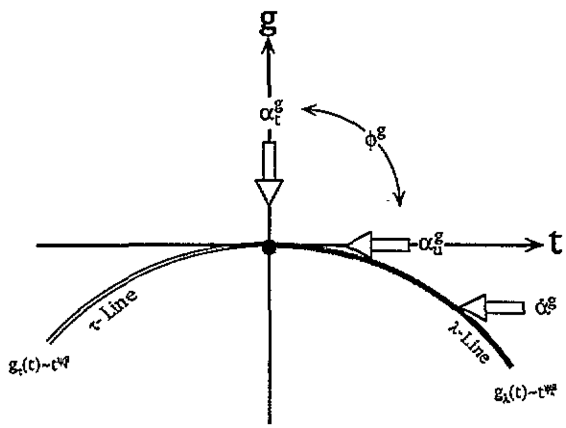

Figure 4. Conventional tricritical scaling diagram showing the two scaling axes g and t and the associated exponents. The large arrows show the path of approach associated with the corresponding exponent.

It is assumed that the free energy is only singular on the τ and λ lines and *analytic* elsewhere in the (t, g) plane. In the neighbourhood of the tricritical point the singular part of the canonical free energy is assumed to have the scaling form

$$\begin{aligned} R^s(g, t) &\sim |t|^{2-\alpha_u^g} \hat{r}^{\pm}(g|t|^{-\phi^g}) \\ \hat{r}^{\pm}(x) &\sim \begin{cases} |x|^{2-\alpha_t^g} & \text{as } x \to \infty \\ 1 & \text{as } x \to 0. \end{cases} \end{aligned} \tag{16}$$

where $\hat{r}^{\pm}(x)$ is the scaling function, which is analytic in the neighbourhood of $x = 0$ and generally depends on the sign of t—as denoted by the $\pm$. The tricritical exponent α_t^g is defined by the relation $2 - \alpha_t^g := (2 - \alpha_u^g)/\phi^g$. The exponent ϕ^g is the tricritical crossover exponent.

† Note that in this paper we take $f(x) \sim g(x)$ to mean $\lim_{x \to x_0} f/g = \textit{constant} \neq 0$ (rather than one). This avoids the frequent introduction of constants.

Along the λ-line, for $t>0$ and for fixed $g<0$ the free energy is assumed to have the asymptotic form

$$R(g,t) \sim r_0(g) + r_1(g)|\tilde{t}|^{2-\tilde{\alpha}^g}. \tag{17}$$

where $\tilde{t} = t - g_\lambda(t)$ and $r_0(g)$ and $r_1(g)$ are analytic functions. Consistency of (16), (17) and the analyticity of the free energy elsewhere in the (t, g) plane require that the shift exponent and crossover exponents be equal:

$$\psi_\lambda^g = \phi^g. \tag{18}$$

The assumed non-cuspish shape of the λ-line implies that $\phi^g \geqslant 1$. A similar argument leads to $\psi_\tau^g = \phi^g$. Note that if the τ line corresponds to the scaling axis then ψ_τ^g is not defined.

3.2. Tricritical scaling of the generating function

We begin by defining the ingredients that go into forming our scaling picture. At high temperatures (small ω) the generating function is assumed to be characterized by the exponent γ_+ as $q \to q_\infty(\omega)$ from below at fixed ω:

$$G(\omega, q) \sim (q_\infty(\omega) - q)^{-\gamma_+}. \tag{19}$$

At the critical point a different exponent γ_t is assumed to replace γ_+ so

$$G(\omega_c, q) \sim (q_\infty(\omega_c) - q)^{-\gamma_t}. \tag{20}$$

However at low temperatures ($\omega > \omega_c$) we assume that G converges in the limit $q \to q_\infty(\omega)$, though with an essential singularity which we describe later. Now, assuming that tricritical scaling holds around the point (ω_c, q_c) we can proceed to write down the scaling forms. Firstly we transform to scaling axes, if necessary. To set up the appropriate coordinate system for scaling we use the notation ε for the thermal scaling field and p for the fugacity field. In the asymmetric case we have simply $\varepsilon = \omega_c - \omega$ and $p = q_c - q$, while in the symmetric case these are chosen appropriately to arrive at a scaling-region-singularity diagram as in figure 5.

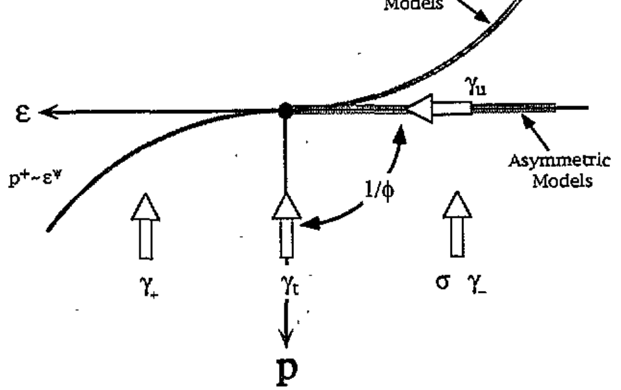

Figure 5. Schematic tricritical scaling diagram of the generating function (or generalized partition function) showing the scaling axes p and ε and the associated exponents. The low temperature line coincides with the ε axis for asymmetric models, but goes above (as shown), or possibly below, for the symmetric models.

The location of the ε scaling axis fall into two cases: (i) for the asymmetric models the ε scaling axis corresponds exactly to the singular line while (ii) for the symmetric models the low temperature scaling axis does not correspond with the singular line (but is tangential at $(0,0)$). In the neighbourhood of the point $(\varepsilon, p) = (0,0)$ the generalized canonical partition function has a singularity structure of the same form as a conventional tricritical point. Thus, for $\varepsilon > 0$, the shape of the $p^+(\varepsilon)$ line (being the transformation of the line $q_\infty^+(\omega)$) defines a shift exponent through

$$p^+ \sim \varepsilon^{\psi} \qquad (\varepsilon > 0). \tag{21}$$

(Note that one must choose p so that the leading order of the asymptotic form is given by the singular part of $p^+(\varepsilon)$.) For the asymmetric models there is no shift exponent for $\varepsilon < 0$ as the first order line coincides with the scaling axis, whilst for symmetric models there is a low temperature shift exponent. The singular part of G has the scaling form

$$\begin{aligned} G^s(\varepsilon, p) &\sim |\varepsilon|^{-\gamma_u} \hat{g}^{\pm}(p|\varepsilon|^{-1/\phi}) \\ \hat{g}^-(x) &\sim \begin{cases} |x|^{-\gamma_u \phi} & \text{as } x \to \infty \\ 1 & \text{as } x \to 0 \end{cases} \end{aligned} \tag{22}$$

where the $\pm$ superscripts refer to temperatures above and below the critical temperature. The exponent γ_u is defined by $\gamma_u := \gamma_t/\phi$ and ϕ is the tricritical crossover exponent. We do not define more precisely the behaviour of $g^-(x)$ as it approaches the essential singularity other than the note that it occurs at some point, $\dot{x}^-$ say, which may be zero.

For $\varepsilon > 0$, G is singular along the line $p^+(\varepsilon)$. Here, for $p \leqslant p^+(\varepsilon)$, G diverges with the asymptotic form

$$G \sim \hat{g}_0(\varepsilon) + \hat{g}_1(\varepsilon)(p^+(\varepsilon) - p)^{-\gamma_+}. \tag{23}$$

This requires the scaling function $\hat{g}^+(x)$ to have a singularity at $x = \dot{x}^+$, where it behaves like

$$\hat{g}^+(x) \sim (x - \dot{x}^+)^{-\gamma_+} \qquad x \to \dot{x}^+. \tag{24}$$

As G is singular along the line $p^+(\varepsilon)$ and analytic below, it ensures that $\psi = 1/\phi$. Note that there is a small difference between the scaling form (22) and the conventional scaling form in that ϕ corresponds to $1/\phi^g$, which we define to be consistent with the literature on walk and polygon problems.

We now compare (21) with (14) and use the fact that the line defined by $p^+(\varepsilon)$ is related to the free energy through (13) and $\varepsilon \sim t$ then considering the singular parts of both functions at the critical point leads immediately to

$$\psi = 2 - \alpha. \tag{25}$$

This is the first relation between exponents in different ensembles: the shape of the high temperature line in the generalized ensemble is related to the specific heat exponent in the canonical ensemble. This relation subsequently leads to the relation (1) because $\psi = 1/\phi$.

A word of explanation on the use of the character 'γ' in the tricritical scaling form: We use γ (as opposed to some other Greek character) because G is a generating function analogous to *non*-interacting self-avoiding walks where the asymptotic form of the generating function is characterized by the exponent γ. Note that for the self-avoiding polygon model of vesicles γ is usually replaced by $2 - \alpha_M$, because this polygon model maps onto a magnetic model where α_M is the magnetic specific heat exponent. This exponent is *not* the same as the α we have previously mentioned.

3.3. Canonical scaling

In this section we consider the scaling form of the canonical partition function and the canonical free energy. Several ingredients have gone into the construction of these scaling forms which we briefly discuss before presenting the scaling forms.

Firstly they must describe finite-size crossover. A finite length walk does not undergo a phase transition. All finite n thermodynamic functions must be analytic functions of the temperature and number of steps. It is only in the thermodynamic limit $n \to \infty$ that we have a phase transition and non-analyticity. The crossover from the finite size behaviour to the infinite size system occurs when the thermal correlation length falls below the average physical size of the walk. The finite-size crossover behaviour is characterized by a crossover exponent, ϕ_c. We show later that ϕ_c in fact equals the tricritical crossover exponent, ϕ.

Secondly, the partition function is generated by $G(\omega, q)$: It is well known that the generating function for non-interacting self-avoiding walks has the asymptotic form $W(z) \sim (z - z_\infty)^{-\gamma}$, which in turn means that the asymptotic number of n-step walks behaves like $z_\infty^{-n} n^{\gamma-1}$. Now, as Q_n is generated by $G(\omega, q)$, this would *suggest* that $Q_n \sim q_\infty(\omega)^{-n} n^{\gamma-1}$. Furthermore, the tricritical scaling of G requires the value of γ to be different for $\omega < \omega_c$ and $\omega = \omega_c$ where the above behaviour of the generating function is believed to hold.

Thirdly, the collapse models are related to the condensation transition of fluids. As already shown [8] we expect a surface area contribution to the free energy in the low temperature phase. The argument presented requires the free energy to have an n^σ term with $0 < \sigma \leqslant 1 - 1/d$ ($\sigma = 1 - 1/d$ occurs if the surface is 'smooth'). This is possible if $Q_n \sim q_\infty^{-n} \mu_s^{n^\sigma} n^{\gamma_- - 1}$, for some μ_s. Note that the factor of $n^{\gamma_- - 1}$ is allowed for the sake of generality but does not imply the $(q - q_\infty)^{-\gamma}$ form in the generating function.

For convenience, figure 6 shows the asymptotic region the canonical scaling functions must represent and the associated exponents. The dashed line is the locus of specific heat maxima and, unlike the tricritical singularity structure, this is *not* a line of singularities. This is a fundamental difference between tricritical scaling and finite-size scaling. For finite n the partition function must be analytic in ω and conventional scaling arguments [11] would suggest that the finite-size scaling function should be analytic at the origin. Putting all the above arguments together gives rise to the partition

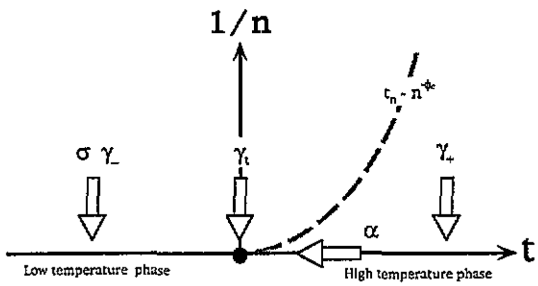

Figure 6. Finite-size crossover scaling diagram showing the scaling axis $1/n$ and $t = T - T_c$ and the associated exponents. The large arrows show the path of approach associated with the corresponding exponent. The line $n^{-\phi_c}$ is the locus of specific heat maxima. Note that this is *not* a line of singularities (unlike the lines in the tricritical scaling diagrams).

function scaling form

$$Q_n(\omega) \sim [q_\infty^a n^{\gamma_t - 1} \hat{z}(\delta\omega n^{\phi_c})$$

$$\hat{z}(x) \sim \begin{cases} x^{-(\gamma_t - \gamma_+)/\phi_c} \mu_+^{x^{1/\phi_c}} & \text{as } x \to +\infty \\ |x|^{-(\gamma_t - \gamma_-)/\phi_c} \mu_-^{|x|^{1/\phi_c}} \mu_s^{|x|^{\sigma/\phi_c}} & \text{as } x \to -\infty \end{cases} \tag{26}$$

where q_∞^a is the analytic part of $q_\infty(\omega)$ and $\mu_\pm$ and μ_s are constants with

$$\begin{aligned} &\mu_- > 1 \qquad \text{(symmetric models)} \\ &\mu_- = 1 \qquad \text{(asymmetric models).} \end{aligned} \tag{27}$$

Given this scaling form for the partition function we can now deduce the scaling form for the free energy. Substituting (26) into (6) and using $\delta\omega \sim t$ gives the finite size scaling of the singular part of the free energy as

$$f_n^s(t) \sim \frac{1}{n} \hat{f}(n^{\phi_c} t)$$

$$\hat{f}(x) \sim \begin{cases} x^{1/\phi_c} & \text{as } x \to \infty \\ |x|^{\sigma/\phi_c} & \text{as } x \to -\infty \text{ (asymmetric models)} \\ |x|^{1/\phi_c} & \text{as } x \to -\infty \text{ (symmetric models).} \end{cases} \tag{28}$$

Let us for a moment focus on the high temperature situation. This scaling form for f_n^s implies that

$$f_\infty^s \sim t^{1/\phi_c} \qquad (T > T_c). \tag{29}$$

This is only consistent with (14), if the tricritical scaling relation

$$2 - \alpha = \frac{1}{\phi_c} \tag{30}$$

is satisfied. Thus, we see that the assumed scaling form of the canonical partition function leads, via the induced free energy scaling, to the tricritical scaling relation. Comparing the tricritical scaling relation (30) with (21) shows that $\psi = 1/\phi_c$ and hence

$$\phi_c = \phi. \tag{31}$$

Thus the tricritical crossover exponent is equal to the finite-size crossover exponent. Furthermore, one can equally well show, although tortuously, that by only assuming a scaling form for the free energy (with some ϕ_c and satisfying (14) in the $n \to \infty$ limit) that consistency with the tricritical scaling of the generating function leads to the two equations above.

As an aside, to which we shall return, the scaling form (28) is frequently used in numerical procedures to estimate the value of the crossover exponent. With this scaling form it is possible to show that if the finite length intensive specific heat has a maximum height at some temperature, t_n, then the height, h_n and t_n behave (given $\alpha > 0$), for $n \to \infty$ like,

$$\begin{aligned} h_n &\sim n^{\alpha\phi_c} \\ t_n &\sim n^{-\phi_c}. \end{aligned} \tag{32}$$

(Note that if $\alpha < 0$ then $h_n \sim 1$.) We make further comments on the use of (32) in the discussion section.

4. Discussion

We have shown that the simple assumption of a generic crossover phenomenon places restrictions on commonly defined exponents at the collapse transition in an interacting geometric cluster model. In particular the relationship $2-\alpha=1/\phi$ is a straightforward consequence of this mild and common assumption. The conclusion of this clear argument is now used to throw light on a wide range of problems which have been investigated in the literature.

The crossover exponent at the collapse transition is a value of perennial interest in many problems (especially in two dimensions where it should take on a non-trivial value) such as interacting self-avoiding walks [12–21] and (the related problem of) rings [22], interacting self-avoiding trails [23–26], vesicles [27, 2], interacting walks and trails on a Manhattan lattice [28, 29], interacting partially directed walks [30] and site lattice animals/branched polymers [31–35]. Attempts at discovering its value in these systems has been made with a variety of methods including transfer matrix [12, 14, 29–31], exact enumeration/series extrapolation [13, 22, 23, 27, 2, 35], Monte Carlo [16–21, 24–26, 32–34] and renormalization group techniques [12, 16–19]. The assumptions involved in considering the collapse transition as a generic crossover phenomena are widespread. Importantly, often the relationship (1) is assumed in these calculations. For reasons of later comparison we note that one prominent technique involves finding ϕ from specific heat data (as explained in the previous section and hence the use of (1)). In the problem of interacting self-avoiding walks and rings in two dimensions, for example, the range of values calculated for the crossover exponent range from 0.48 ± 0.07 [12] through 0.577 ± 0.007 [21] to 0.90 ± 0.02 [22]. To place the above values in some context we mention that an exact value has been conjectured [15] for the ISAW/ISAR problem of $\phi=3/7\approx0.429$.

In a recent development the case of partially directed walks was solved exactly [3] and the collapse transition exponents extracted. In addition, a complete discussion of each phase and the numerical behaviour of quantities in a finite size scaling analysis [9] have also been presented. It is clear from these discussions that, while the exact values of α and ϕ do indeed satisfy the relationship, estimates made from small walk lengths n up to about 100 are far off their actual values. This discrepancy arises even when the exact critical temperature is known. If one instead utilizes the common procedure of using the position and value of the specific heat maxima of finite length walks to estimate the two exponents then, with some reasonable extrapolation, the values $\alpha=1.30\pm0.05$ and $\phi=0.45\pm0.03$ are obtained [36]. These are extravagantly different from the correct values of $\alpha=1/2$ and $\phi=2/3$ obtained from the exact solution! Only by knowing the exact critical temperature and series expansions up to 6000 terms do numerics begin to yield estimates for these exponents within 1% of their correct values [9]. Remembering that for the wider problem of interacting SAW the critical temperature must also be estimated, and present exact enumeration data extends to walks of length 40 or so [37], there may be a case for reappraisal of the values of ϕ given in the literature. These considerations, we feel, override the usual gain one obtains from considering an undirected problem. In the directed problem it was noted that large corrections to scaling were apparent and that knowing the correction to scaling exponent a reasonable extrapolation for ϕ can be obtained with walks up to 1000. It is often believed that the calculation of the crossover exponent using series and Monte Carlo methods is fraught with difficulty due to the strong effect of the collapsed phase. In directed walks this can be seen directly by the asymmetry of the scaling forms and the size of corrections to scaling (of the order $n^{-1/3}$).

We suggest that to check the reliability of estimates of ϕ that both α and ϕ be calculated *independently* in a problem. Whether the relationship $2-\alpha=1/\phi$ holds or not will be a significant test of these estimates. We also suggest that estimates be calculated as a function of the size and extrapolated against a best estimate for the correction-to-scaling exponent (for example corrections-to-scaling in ISAW/ISAR may be of the order $n^{-1/7}$, which we add is hardly distinguishable from a constant for $n<100$). This technique will, of course, result in larger error bounds on the estimate, though hopefully these bounds will encompass the true value! In any case, the relationship $2-\alpha=1/\phi$ provides a potent test for numerical data in these problems.

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