LETTER TO THE EDITOR

Single-scaling-field approach for an isolated polymer chain

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Abstract. We develop an approach for describing an isolated polymer chain in solution, without appeal to the $n \to 0$ limit of the n-vector model. Our approach treats the generating function for self-avoiding walks as a grand partition function. In this description, the fugacity per monomer plays a fundamental role as the unique scaling field in the problem. A physical picture of a polymer chain in both an ordered and disordered phase emerges naturally from the resulting thermodynamic relations. This picture turns out to be similar to percolation, and leads us to classify the phases of a single polymer chain according to their fractal dimensionality. We identify the monomer density as the order parameter. Furthermore, since we have only a single scaling field—the fugacity per monomer—we can relate all the critical exponents to a single exponent. We find $\alpha = \gamma$, $\beta = 1 - \alpha = d\nu - 1$. We emphasise that this theory is not equivalent to the $n \to 0$ limit of the n-vector model, though the underlying generating function, and hence the correlation functions, are the same.

1. Introduction

The statistical properties of self-avoiding walks (SAWs) — random walks constrained never to self-intersect — have been the focus of extensive investigation for two principal reasons. First, the SAW model has been extremely successful in describing the properties of an isolated polymer chain. The self-avoiding condition enforces the 'excluded-volume' constraint, which prohibits different monomers within a polymer from occupying the same position (see e.g. Flory 1953, de Gennes 1979 and references therein). Second, the configurational properties of such SAWs, in the limit that the number of steps N tends to infinity, can be described in terms of the critical behaviour of an n-component magnet in the limit $n \to 0$ (de Gennes 1972, Domb 1972, des Cloizeaux 1974).

From this analogy of the SAW model with critical phenomena, there has arisen considerable interest in calculating various properties which characterise the large-N scaling behaviour of SAWs (see e.g. references in McKenzie (1976)). For example, in Monte Carlo studies configurational properties are calculated by sampling SAWs with a *fixed* number of steps N. This procedure may be repeated for several different (relatively large) values of N to deduce the asymptotic dependence on N of the quantity under study. Series expansion studies, on the other hand, involve enumerating *all* lattice SAWs (beginning at some fixed origin) for $1 < N < N_{max}$, where N_{max} is lattice dependent and determined by constraints of computer time. For each N one calculates

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the various configurational properties, and then extrapolates in order to infer $N \to \infty$ behaviour. Thus, in such studies scaling behaviour is expressed as the dependence of a given property on the number of monomers or steps, N.

While these investigations are very useful, the analogy with critical phenomena is not immediate; N, rather than a temperature-like variable, is the fundamental parameter. An important conceptual advance was provided by the $n \to 0$ magnetic correspondence, which showed that $1/N$ is equivalent to $(T - T_c)$ in the magnetic model (de Gennes 1972, des Cloizeaux 1974). This identifies criticality with the limit $N \to \infty$. Unfortunately, this correspondence is valid only for $T > T_c$. In particular, the interpretation of an analogue of a low-temperature phase for an isolated polymer chain has not been adequately addressed (de Gennes 1979).

In this Letter we develop an approach to the isolated polymer chain problem which is of considerable simplicity, and is valid for all values of a temperature-like variable. It is based on treating the SAW generating function as a grand partition function (Shapiro 1978). Within the grand canonical ensemble, the fugacity per monomer, p, is the unique scaling field in the problem. As we shall see, the fugacity plays a temperature-like and a magnetic field-like role simultaneously.

In this thermodynamic description, a simple picture of the ordered and disordered phases of a polymer chain emerges naturally (see figure 1). For $p < p_c$, only a chain of finite length can occur; this corresponds to the disordered or high-temperature phase in the $(n = 0)$-vector magnet. For $p > p_c$, on average a chain occupying a *finite* fraction of the total lattice volume occurs. In this phase, we identify the monomer density as the order parameter, and derive an expression for the associated exponent. Since there is only one chain, the monomer density is just the probability that a given bond (either occupied or empty) belongs to an infinite chain. This is similar to the order parameter in percolation[†]. Our description of the single polymer chain resembles percolation in several ways, and so we use here ideas from percolation to describe geometric features of the chain.
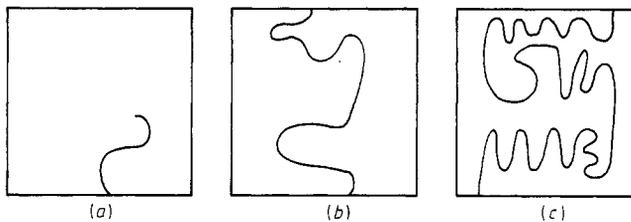
Figure 1. The three 'temperature' regimes for a polymer chain described in the text. (a) In the high-temperature region $(p < p_c)$ only a finite-length chain can occur. (b) At criticality $(p = p_c)$ an infinite chain with a ramified structure occurs. (c) In the low-temperature region $(p > p_c)$ an infinite chain with a compact structure occurs.

2. Thermodynamic description for a single chain

To introduce our approach, we briefly review the conventional way to study lattice SAWs. Let c_N be the number of N-step SAWs which begin at a fixed lattice site. We may

[†] More precisely, the monomer density corresponds to $pP(p)$ in percolation, where p is the bond occupation probability and $P(p)$, the percolation order parameter, is the probability that an *occupied* bond belongs to the infinite cluster.

define a generating function for all single SAWs by creating a linear combination of the different c_N in the space of polynomials p^N. This is equivalent to assigning a weight, or fugacity, p to each step in the walk. Thus (see e.g. de Gennes 1979)

$$\Gamma(p) = \sum_N c_N p^N. \qquad (2.1a)$$

The asymptotic behaviour of c_N may be written as

$$c_N \sim \mu^N N^{\gamma-1}. \qquad (2.1b)$$

Thus as $p \to p_c \equiv 1/\mu$ from below, $\Gamma(p)$ diverges with the characteristic exponent γ. The exponent in $(2.1b)$ is chosen to be γ because, in the $n \to 0$ magnetic analogy, $\Gamma(p)$ is the susceptibility of the spin system. Thus we write

$$\Gamma(p) \sim (p - p_c)^{-\gamma_{n=0}}. \qquad (2.1c)$$

The subscript $n = 0$ indicates the origin of the exponent from the magnetic analogy. Notice from (2.1c) that p acts as a temperature-like variable in the generating function.

On the other hand, we may also view the generating function $(2.1a)$ as a grand partition function $\mathscr{Z}(p)$. In this sense, the variable $\ln p$ now plays the role of a chemical potential or 'field' which is conjugate to N. We write

$$\mathscr{Z}(p) = \sum_N c_N \, e^{N \ln p}. \qquad (2.2a)$$

This grand canonical ensemble contains *one* chain with a fluctuating number of monomers N. Note that, from equation $(2.2a)$, the canonical partition function for N-step SAWs is simply C_N. Thus we may write

$$Z = c_N = \mathrm{Tr} \, e^{-\mathscr{H}_N}. \qquad (2.2b)$$

If we consider the trace to be taken over the c_N possible (already self-avoiding) states, it follows that the Hamiltonian $\mathscr{H}_N$ is zero; purely entropic considerations determine the statistical mechanics of the system†.

The dual role played by p — both temperature-like and field-like — suggests that one can describe the configurational problem of an isolated chain with only a single scaling field‡. This is not the case in the $n \to 0$ magnetic analogy for the single-chain problem, in which two apparently independent scaling fields exist.

Let us now pursue the consequences of the definition $(2.2a)$ for $\mathscr{Z}(p)$. We define a (normalised) grand potential,

$$G(p) = \lim_{V \to \infty} V^{-1} \ln\left(\sum_N{}' c_N \, e^{N \ln p} \right). \qquad (2.3a)$$

The prime on the summation indicates that the generating function is defined on a finite lattice of volume $V = b^d$, where b is the linear size of the system. Near p_c, we assume that $G(p)$ behaves as

$$G(p) \sim (p - p_c)^{2 - \alpha_{\mathrm{SAW}}}, \qquad (2.3b)$$

where we use the subscript SAW to distinguish our exponents from those of the

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† Alternatively, one could consider the trace in (2.2b) to be over the z^N possible states of a random walk. However, now accounting for the excluded volume interaction leads to a complicated Hamiltonian.

‡ Another scaling field *would* appear, in both the canonical and grand canonical ensembles, if one introduced an actual field in addition to $\ln p$.

$(n = 0)$-vector spin system. We now explore the thermodynamics resulting from our potential $(2.3a)$. In the next section, we indicate how the assumption $(2.3b)$ leads to a consistent thermodynamic formulation of the SAW problem.

By differentiating $G(p)$ with respect to $\ln p$, our field-like variable conjugate to N, we obtain an 'order parameter',

$$\frac{dG(p)}{d(\ln p)} = \lim_{V \to \infty} \frac{\langle N \rangle}{V} \equiv \langle \mathcal{N} \rangle. \tag{2.4a}$$

The notation $\langle \ldots \rangle$ indicates an average in the grand canonical ensemble defined by equation $(2.2a)$. Assuming equation $(2.3b)$, as $p \to p_c$ from above, the order parameter $\langle \mathcal{N} \rangle$ varies as

$$\langle \mathcal{N} \rangle \sim (p - p_c)^{1 - \alpha_{SAW}}. \tag{2.4b}$$

From this equation we identify

$$\beta_{SAW} = 1 - \alpha_{SAW}. \tag{2.5}$$

Furthermore, the derivative of the order parameter with respect to its conjugate field is simply related to the fluctuation in the order parameter,

$$d\langle \mathcal{N} \rangle / d(\ln p) = V(\langle \mathcal{N}^2 \rangle - \langle \mathcal{N} \rangle^2). \tag{2.6a}$$

Thus we may identify equation $(2.6a)$ as the 'susceptibility' of the single chain polymer. Then from equation $(2.4b)$ we obtain

$$d\langle \mathcal{N} \rangle / d(\ln p) \equiv \chi_{SAW} \sim (p - p_c)^{-\alpha_{SAW}}, \tag{2.6b}$$

from which we find a susceptibility exponent

$$\gamma_{SAW} = \alpha_{SAW}. \tag{2.7}$$

If we have viewed p as a temperature-like variable in the thermodynamic relations instead of a field-like variable, then $(2.4a)$ and $(2.6a)$ would be the entropy and the specific heat respectively. Hence, in this formalism, the entropy is equivalent to the order parameter and the specific heat is equivalent to the susceptibility. This equivalence is a direct consequence of the existence of a single scaling-field.

3. Scaling laws and order parameter

In order to study the consequences of the single-scaling-field approach, we now relate the SAW exponents to the correlation length exponent ν. Our argument emphasises the physical interpretation of the order parameter. Consider an ensemble of isolated polymer chains at the critical value, $p_c(b)$, for a finite system of linear dimension b. From finite size scaling, the deviation of $p_c(b)$ from p_c of an infinite system may be written as (Fisher 1971, Sur *et al* 1976, Reynolds *et al* 1978)

$$(p_c(b) - p_c) \sim b^{-1/\nu}. \tag{3.1a}$$

Since (cf equations $(2.1a, c)$)

$$\langle N \rangle = (p/\Gamma) \, d\Gamma/dp \sim (p - p_c)^{-1}, \tag{3.1b}$$

we may combine equations $(3.1a)$ and $(3.1b)$ to obtain

$$\langle \mathcal{N} \rangle = \langle N \rangle / b^d \sim b^{1/\nu - d}. \tag{3.2a}$$

On the other hand, finite size scaling arguments show that the order parameter for a finite system at p_c varies as

$$\langle \mathcal{N} \rangle \sim b^{-\beta/\nu}. \tag{3.2b}$$

Combining equations (3.2a) and (3.2b), we obtain $\beta = d\nu - 1$. This may also be derived from hyperscaling ($d\nu = 2 - \alpha$) together with equation (2.5). Since the correlation length is the *same* for both our formulation of the SAW problem and the formulation from the $n \to 0$ magnetic analogy, ν does not require a distinguishing subscript. Employing the Flory (1953) values of ν yields the numerical values of the SAW exponents shown in table 1.

Table 1. Relationship of the SAW exponents to ν for general d. The numerical results for $1 \leq d \leq 4$ are obtained from the Flory formula $\nu = 3/(d+2)$. Above $d = 4$, mean-field theory gives $\nu = \frac{1}{2}$.

Dimension	α	β	γ	ν
$d \leq 4$	$2 - d\nu$	$d\nu - 1$	$2 - d\nu$	$3/(d+2)$
1	1	0	1	1
2	0·5	0·5	0·5	0·75
3	0·2	0·8	0·2	0·6
≥ 4	0	1	0	0·5

The problem of identifying the order parameter has been addressed previously by de Gennes (1979), who proposed that the order parameter *squared* is the monomer density. This proposal is based on making an equivalence between the magnetisation of the $(n = 0)$-vector spin system (the presumed order parameter), and the square root of the monomer density. However, our identification of $\langle \mathcal{N} \rangle$ as the order parameter allows one to find the exponent β simply. Moreover, the resulting physical picture is similar to both percolation and gelation (de Gennes 1976, Stauffer 1976). In these theories the order parameters are the percolation probability and the gel fraction — the probabilities that a monomer belongs to an infinite cluster or to an infinite gel molecule respectively. For the single chain, the monomer density is the same as the probability that a bond (occupied or empty) belongs to an infinite chain. Thus the similarity with percolation and gelation is quite close.

Following this similarity further, we may classify the phases of a single chain according to its effective or fractal dimensionality (Stanley 1977, Mandelbrot 1977). This quantity may be defined as the exponent relating the volume Ω occupied by the chain to the characteristic linear dimension of the system b, i.e. $\Omega \sim b^{d_f}$. This effective dimension is one of many parameters which helps to describe the ramification and spatial extent of an object (Gefen *et al* 1980), and has provided useful insights into the geometric aspects of the percolation transition.

When $p < p_c$, the probability of having a chain with N monomers decreases exponentially with N (see equations (2.1a, b)). Hence $\langle N \rangle$, which is the volume occupied by the chain, is *finite* even in an infinite system, and $d_f = 0$. At the point $p = p_c$, the average number of bonds in a SAW varies asymptotically as $b^{1/\nu}$. Hence $d_f = 1/\nu$ for 'critical' SAWs. Finally, for $p > p_c$ we have the ordered phase for which $\langle \mathcal{N} \rangle > 0$. This implies that $\langle N \rangle$ must scale linearly in the volume of the system, yielding $d_f = d$. Thus, in the condensed phase, the SAWs are compact. This geometric picture for the shape of a

polymer chain as a function of p is qualitatively the same as that in percolation and gelation.

Finally, we discuss briefly the nature of the mean-field theory that is appropriate for the isolated polymer chain. From table 1, we see that for spatial dimensions $d \geq 4$, the exponents remain constant. This indicates that mean-field theory holds above an upper critical dimensionality $d_c = 4$. In fact, from the Ginzburg (1960) criterion we verify, by substituting the mean-field values $\beta_{SAW} = 1$ and $\gamma_{SAW} = 0$, that $d_c = (2\beta + \gamma)/\nu = 4$. Such a mean-field theory can be described by a phenomenological Landau–Ginzburg expansion of the form

$$F(\langle \mathcal{N} \rangle) = a \langle \mathcal{N} \rangle + b \langle \mathcal{N} \rangle^2 + \dots, \tag{3.3}$$

where $a \propto (p - p_c)$, b is non-zero at p_c, and the potential $F(\langle \mathcal{N} \rangle)$ is the Legendre transform of $G(p)$. The linear term is admitted into this expansion because a polymer chain has the same spatial symmetry for all values of $p \neq 0$ (Landau and Lifshitz 1969). This expansion yields the SAW exponents in table 1 for $d \geq 4$.

A similar single-scaling-field treatment can be applied equally well to any single element system whose configuration is controlled by a constant fugacity for each of its constituents. Such a system will also satisfy the exponent relations, equations (2.5) and (2.7). In this description, one may think of ν as fundamental, depending on the physical details of the system. Once the value of ν is determined, the remaining exponents follow. As an example, we can apply these ideas to the lattice animal problem and predict the value of d_c. While it was first thought that for animals $d_c = 6$ as in percolation, recent evidence points to $d_c = 8$ (Lubensky and Issacson 1978, 1979, Issacson and Lubensky 1980, de Gennes 1980). To derive this, we use the known value $\nu = \frac{1}{4}$ from mean-field theory (de Gennes 1980). From the same symmetry argument used for the single polymer chain, a Landau theory for animals also has the form of equation (3.3), from which the mean-field values are $\beta = 1$ and $\gamma = 0$. Substituting these into the Ginzburg criterion yields $d_c = 8$.

4. Summary

We have formulated a description of the single polymer chain problem through an approach in which the fugacity per monomer is the only scaling field in the problem. We have treated the generating function for lattice self-avoiding walks as a grand partition function. Our treatment appears to have applicability to any configurational problem with a generating function controlled by a fugacity per monomer. For the single chain problem, the thermodynamic relations following from our definition of the grand partition function have led naturally to a percolation-like picture of the ordered and disordered phases for a polymer chain, and to the identification of the monomer density as the order parameter. Moreover, since there is only one scaling field in the problem, all the exponents may be related to each other.

Acknowledgments

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