Stepwise chain description of polymers and clusters

1988 J. Phys. A: Math. Gen. 21 L849

(http://iopscience.iop.org/0305-4470/21/17/006)

J. Phys. A: Math. Gen. 21 (1988) L849-L855. Printed in the UK

LETTER TO THE EDITOR

Stepwise chain description of polymers and clusters

Z Alexandrowicz

Department of Polymer Research, Weizmann Institute of Science, Rehovot 76 100, Israel

Received 6 April 1988

Abstract. Percolation, Ising critical clusters and branched polymers are described by a stepwise branching-out chain. A mean-field study shows that the chains' filaments become ideal (random-walk-like) at an upper critical dimension $D_c = 6$, 8 and 8, respectively. Ising clusters at D from 8 to 4 exhibit a quasi-ideality. The results reveal a dissimilar geometry: the chains' filaments are strikingly more numerous and stretched for Ising clusters than for both polymers and percolation. Linear analogues are discussed.

Single percolation clusters may be described with the help of a branching-out random chain, growing in a sequence of steps (time), from an arbitrary origin (Alexandrowicz 1980). The construction provides a convenient algorithm for computer simulation and, in addition, enables one to study scaling laws for mass and radius against the 'time' variable. Such a description may be extended to other aggregates, a term which here denotes a connected s-particle random system. Thus it has been applied to study diffusion-limited percolation (Termonia and Meakin 1985), lattice animals (Havlin *et al* 1984, Meirovitch 1987), branched polymers synthesised in an irreversible sequence of steps (Alexandrowicz 1985) and Ising critical clusters (Alexandrowicz 1988). In this connection two different types of aggregates at equilibrium should be distinguished, depending on whether the particle connectivity is permanent or transient. For the 'polymer' type, the ensemble consists of distinct shapes of a permanent macromolecule. For the 'cluster' type, the ensemble consists of distinct allocations of N particles to a volume (lattice), and the clusters constitute transient connected subsets of N. For example, an irreversibly bonded branched polymer is polymer-like and is described by lattice animals (Lubensky and Isaacson 1978) or related models (Zimm and Stockmayer 1949, Alexandrowicz 1985). However, a reversible gel is cluster-like and is described as percolation (de Gennes 1976, Stauffer 1976). The cluster-like aggregates should be further subdivided into athermal, like percolation, in which the connectivity is due to a chancy proximity of particles; and thermal, like Ising, in which it is due to a coupling of interacting particles. Finally, all these aggregates may be branched or linear. This letter studies, in the mean-field approximation, the branching-out (or linear) chains, with the help of which the various aggregate types may be constructed. The goal is to relate the diversity of the aggregate scaling behaviour to the dissimilar nature of the corresponding chains. This leads to an explanation of unequal upper critical dimensions D_c. The results also reveal novel features, such as a quasi-ideality of Ising cluster chains in dimension $D = 4$–8, the scaling with the time variable which throws light on the aggregate geometry, and the possibility of new aggregate types, like linear percolation.

0305-4470/88/170849+07$02.50

Stepwise construction of an aggregate. Empty lattice sites are assigned as A or B, in a sequence of steps $i = 1, 2, \ldots$, with the help of the transition probability p_i. The aggregate consists of connected A. We start from an A which constitutes an arbitrary initial growth 'tip'. Let G_t denote the number of tips at time t. Thus $G_0 = 1$ (figure 1(*a*)). At $t = 1$, near neighbours (NN) to the initial tip are assigned with p_i. Suppose that x are assigned A and become new tips, namely $G_1 = x$ (whereby $\delta G = G_1 - G_0 = x - 1$, cf figure 1(*b*) for $x = 2$). Expended tips constitute the cluster mass s; thus $s_1 = 1$. At $t = 2$ and at subsequent t, the NN sites of each of the G_{t-1} tips are assigned (in any order); termination occurs if $G_t = 0$; $G_t > 1$ implies branching. The branches grow in random trajectories. Suppose that a NN site of a tip turns out to have been already visited via another tip (figure 1(*b*)) and assigned already as an A or B. If the aggregate described is cluster-like, i.e. it constitutes a part of a lattice microstate, the revisited site merely cannot be assigned once again (if it is A, a loop is closed). The chain of steps obeys therefore excluded volume (EV) in the sense of *avoidance* of a repetitious assignment of lattice sites. However, if the aggregate is polymer-like, the assignment of an A at an ith step, to a site already occupied by another A, implies that the configuration is self-intersecting. EV therefore requires its *rejection* from a random sample of shapes of a polymer of mass $s \geqslant i$. As we shall see, this avoidance against rejection causes a fundamental dissimilarity. The construction of a sample of such 'aggregate chains' enables us to evaluate the weight average mass (Stauffer 1979) s_w and radius R. Indefinite growth of chains (at criticality) permits one to study the scaling dependence of s_w and R, upon t, namely upon a length variable (Alexandrowicz 1980)

$$s_w \sim t^{\gamma_t} \qquad \text{and} \qquad R \sim t^{\nu_t}. \tag{1}$$

Clearly the fractal dimension is $d_f = \gamma_t / \nu_t$. Another useful property is the increase of the average number of tips G, with mass s ('growth surface'),

$$G \sim s^g. \tag{2}$$

Since $G = \mathrm{d}s_w/\mathrm{d}t$, (1) and (2) imply

$$\gamma_t = (1-g)^{-1}. \tag{3}$$

Percolation (athermal) clusters. An Ith chain of mass s (s expended tips) has $G_I = 1 + \sum_{i=1}^{s} \delta G_i$ growing tips. In percolation the transition probability is constant, $p_i = p$ and $1-p$, for A and B respectively. We first ignore the occurrence of loops at

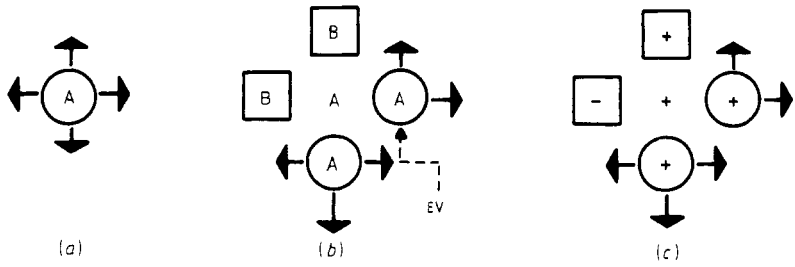

Figure 1. Circles and boxes denote growth tips and perimeter sites, respectively. (*a*) $t = 0$: the initial growth tip, $G_0 = 1$. (*b*) $t = 1$: $G_1 = 2$ and mass (of expended tips) $s = 1$. EV avoidance is displayed. (*c*) As (*b*), for an Ising cluster of *excess* +1 (at zero average magnetisation). The perimeter consists of one −1 and one randomly chosen +1.

$D \geqslant D_c$. The branching-out chain may be therefore constructed on a Cayley tree of coordination z, so that, on average, $\langle \delta G_i \rangle = zp - 1$. (Since the average for an ith step is taken irrespective of steps $i' < i$, it requires that all chains be included, also those that terminate prior to i). At the critical point $p_c = z^{-1}$, $\langle \delta G_i \rangle = 0$ and, on average, the chains grow marginally to infinity, i.e. some terminate and, at correspondance, some attain s with $\sum_{i=1}^{s} \delta G_i > 0$. Hence $G(s)$ of (2), in which the average includes only chains that do attain s (denoted by subscript s in what follows), is estimated by the random s-step deviation from $\langle \delta G_i \rangle = 0$

$$G \sim s^g \sim \sum_{i=1}^{s} \langle \delta G_i \rangle_s \simeq s^{1/2} \tag{4}$$

giving $g^0 = \frac{1}{2}$ (random) and the corresponding mean-field ('ideal') value $\gamma_t^0 = 2$ (cf 3). Since the branches grow purely at random, $\nu_t^0 = \frac{1}{2}$ and $d_f^0 = \gamma_t^0 / \nu_t^0 = 4$. A perturbation due to loops is now considered. The mean-field probability of a loop between a pair of particles $i > j$ is

$$O_{ij}^0 \sim R_{ij}^{-D} \sim (i-j)^{-D/d_f^0}. \tag{5}$$

The loops decrease the number of NN available to a tip (EV). The total decrease of G (introducing positive constants c_1 and c_2) is

$$\Delta G_{\text{loops}} \simeq \sum_{i=3}^{s} \sum_{j=1}^{i-2} O_{ij}^0 \simeq c_1 s - c_2 s^{2-D/d_f^0}. \tag{6}$$

The first term affects p_c, the second the s dependence of G. The upper critical dimension D_c, below which the second term dominates the ideal s dependence of G, is

$$2 - (D_c / d_f^0) = g^0 \qquad \text{or} \qquad D_c = (2 - g^0)/[(1 - g^0)\nu_t^0] \qquad \text{(EV avoidance)} \tag{7}$$

giving $D_c = 6$. At and above D_c the mean field holds. The ideal values of the well known exponents in $s_w \sim \varepsilon^{-\gamma}$ and $R \sim \varepsilon^{-\nu}$ ($\varepsilon = |p - p_c|$), notably $\gamma^0 = 1$ and $\nu^0 = \frac{1}{2}$, may therefore be determined in the conventional manner. An interesting relation follows from the fact that, at p_c, G increases as s^g, but some chains terminate before attaining s, so that the average for all chains is $\langle \delta G_s \rangle = 0$. Let us introduce the scaling law for the number of s clusters per lattice site, $n_s \simeq s^{-\tau}$. The probability of an s cluster is sn_s (Stauffer 1979), and that to attain s is $f_s = 1 - \sum_{i=1}^{s-1} in_i$. Hence, in a mean-field approximation $\langle \delta G_s \rangle = (1 + \delta G / \delta s) f_s - 1 = 0$, giving

$$g^0 = 3 - \tau^0 \qquad (= 1 - \beta^0/(\beta^0 + \gamma^0)) \tag{8}$$

the expression in brackets being obtained from finite-size scaling. For percolation $\beta^0 = \gamma^0 = 1$, reproducing $g^0 = \frac{1}{2}$ (4). At $D < D_c$, EV causes an expansion, i.e. a decrease of d_f; thus γ_t decreases from 2 towards 1 (linear chain), while ν_t increases from $\frac{1}{2}$ towards 1 (fully stretched).

Ising (thermal) clusters. An Ising critical cluster may be identified with a randomly picked connected region of excess +1 (−1) spins, demarcated by a perimeter consisting of +1 and −1 at average proportion (Alexandrowicz 1988). Such clusters reproduce the Ising critical behaviour, rigorously so in the mean-field regime, on a Cayley tree. Indeed in that regime they become exactly equivalent to the clusters defined, on the basis of the Fortuin and Kasteleyn (1972) formalism, by Coniglio and Klein (1980) with a subsequent extension (Swendsen and Wang 1987). The clusters of excess +1 are also conveniently constructed with the help of a branching-out chain (cf '*ab initio*' construction in Alexandrowicz (1988)). This first assigns $\sigma_i = \pm 1$ on an empty lattice,

with transition probability p_i, and the second allots the -1 and an equivalent amount of $+1$ to the perimeter, and the remaining $+1$ to the cluster (figure 1(c)). An Ith cluster of mass s is sampled with probability $P_I = \Pi_{i=1}^{s} p_i$. The right definition of p_i requires that P_I be equal to the Boltzmann factor (determined by the Ising Hamiltonian at given T and $H = 0$), divided by the partition function as follows:

$$P_I = Z^{-s} \exp\left(\tfrac{1}{2}K \sum_{i=1}^{s} \sigma_i \sum_{j=1}^{z} \sigma_j\right). \tag{9}$$

Here $K = J/kT$ is the Ising coupling, Z^s the partition function, z the number of NN to σ_i, while index i refers to the $+1$ spins in the cluster). Equation (9) is relatively easy to fulfil in the mean-field regime $D \geqslant D_c$ as follows. Let us take again a construction on a Cayley tree of coordination z. If an ith tip contributes δG_i, the excess of $+1$ among its z NN descendents is $1 + \delta G_i$ and (9) becomes

$$P_I = Z^{-s} \exp\left[K\left(s + \sum_{i=1}^{s} \delta G_i\right)\right]. \tag{10}$$

It follows that the product of p_i on the LHS of (10) has to depend on $\Sigma\, \delta G_i$. Let the transition probability for the initial tip at the critical point $K = K_c$ be defined as

$$p_c = \Xi^{-1} \exp(K_c) \qquad \Xi = 2 \sinh(K_c). \tag{11}$$

The corresponding average excess of $+1$ spins (p_c) over -1 spins ($1 - p_c$) is $z(2p_c - 1)$. Hence $\langle \delta G_0 \rangle = z(2p_c - 1) - 1 = z \tanh(K_c) - 1 = 0$ (implying $zK_c \simeq 1$ for $z \gg 1$). Let index k denote the (G_t) tips created during time t, and δG_t be the corresponding mean fluctuation

$$\delta G_t = G_t^{-1} \sum_{k=1}^{G_t} \delta G_k. \tag{12}$$

A (mean-field) transition probability for the G_t tips, utilised during time $t+1$, is then defined by

$$p_{t+1} = p_c \exp(K_c \delta G_t). \tag{13}$$

In this manner the product of the p_{t+1} for time $t+1$ precisely compensates $\Sigma\, \delta G_k$ accumulated during the preceding time t. The Ith cluster contribution to the partition function (the Boltzmann factor divided by the sampling probability P_I) is constant and equal to Ξ^s. This makes the latter equal to Z^s (per cluster), showing *ipso facto* that P_I defined with (11)-(13) indeed fulfills (10). Let us now consider the consequences of (13) upon the tips' creation, δG_l, during time $t+1$. From (11)-(13), $\langle \delta G_l \rangle = z(2p_t - 1) - 1 \simeq \langle \delta G_t \rangle$. The mean random fluctuation $\langle \delta G_t \rangle$ scales as $\langle G_t \rangle^{-1/2} \sim s^{-g/2}$, where $s = s(t)$. Hence

$$G \sim s^g \sim \sum_{i=1}^{s} \langle \delta G_i \rangle_s \sim s^{1-g/2} \tag{14}$$

giving $g^0 = \frac{2}{3}$ (coupled) and $\gamma_t^0 = 3$. (The result is independent of our choice of a mean field p_{t+1} in (13), e.g. the same result would be obtained with a choice of p_i depending of δG_j alone, where j immediately precedes i on the tree.) The striking conclusion is that, due to the coupled connectivity, the branching-out of Ising cluster chains is not purely random even in the mean-field regime $D \geqslant D_c$. The perturbation due to loops cannot be ignored below $D/d_f = \frac{4}{3}$ (see (7), (14)). As before, in the absence of loops $\nu_t^0 = \frac{1}{2}$. Hence $d_f^0 = \gamma_t^0/\nu_t^0 = 6$ and the corresponding D, we call it D_{rand}, is $6 \times \frac{4}{3} = 8$.

Below that value, EV expansion makes d_f decrease. This decrease may result from a decrease of γ_t or an increase of ν_t, or both. Since $\nu_t^0 = \frac{1}{2}$ is purely random, while $\gamma_t^0 = 3$ is not, it is conjectured that the initial effect of EV will increase ν_t just sufficiently to keep EV still marginally negligible, that is to preserve $D/d_f = \frac{4}{3}$ and, by this token, the mean-field behaviour. If so, $\gamma_t^0 = 3$ (14) remains unaffected. Summarising, in the quasi-ideal regime at $D_c \leqslant D \leqslant D_{rand}$, $\nu_t (= \gamma_t^0/d_f)$ just compensates the decrease of D and preserves

$$D/d_f = \tfrac{4}{3} \qquad \gamma_t = \gamma_t^0 = 3 \qquad \text{giving } \nu_t = 4/D. \tag{15}$$

Due to the mean-field behaviour, the conventional exponents γ and ν also retain their ideal value. Equation (8) also holds, reproducing $g^0 = 1 - [\frac{1}{2}/(1+\frac{1}{2})] = \frac{2}{3}$ (14). The compensation halts at $D_c = 4$, when $\nu_t = 1$ (fully stretched). Below that point a further decrease of d_f causes $\gamma_t(g)$ to decrease, while ν_t cannot increase any more and presumably remains at, or close to, $\nu_t = 1$. Recent simulation results (Alexandrowicz 1988) support this very unexpected behaviour at $D < D_c = 4 \leqslant D \leqslant D_{rand} = 8$.

Branched polymer. The scaling laws for a polymer of mass s are $R \sim s^{\nu}$ (i.e. $\nu = 1/d_f$) and $n_s \sim s^{-\tau}$. Its description by a branching-out chain is straightforward. Lattice sites NN to a tip are assigned as belonging, or not belonging, to the polymer with the help of a constant transition probability $p_i = p$ or $p_i = 1 - p$ respectively. The chain grows marginally to infinity when $zp_c = 1$. Such a construction essentially corresponds to the 'termination-limited' polymer (Alexandrowicz 1985). Again we consider first the mean-field regime $D \geqslant D_c$, loops are ignored and the construction proceeds on a Cayley tree. The evaluation of $G(s)$ is therefore precisely as in (4), giving $g^0 = \frac{1}{2}$, $\gamma_t^0 = 2$, $\nu_t^0 = \frac{1}{2}$ and the well known result $d_f^0 (= 1/\nu) = 4$ (Zimm and Stockmayer 1949, Lubensky and Isaacson 1978). The result $g^0 = \frac{1}{2}$, together with (8), agrees with $\tau^0 = 2.5$ (Parisi and Sourlas 1981). The effect of loops, however, is radically different from that for cluster-like aggregates. To recall, if a chain that describes a polymer-like aggregate self-intersects, it is rejected. The probability for a chain to attain s therefore is (for O_{ij} cf (5)),

$$f_s = \prod_{i=3}^{s} \prod_{j=1}^{i-2} (1 - O_{ij}) \tag{16}$$

and clearly $n_s = z^s f_s$. If $O_{ij}^0 \sim (i-j)^{-2}$, $f_s \simeq \Pi_{i=3}^{s} \exp(-c_1 + c_2/i) \simeq [\exp(-c_1)]^s s^{c_2}$ which conserves the scaling law $n_s \sim s^{-\tau}$. Hence at D_c (5),

$$D_c/d_f^0 = 2 \qquad \text{or} \qquad D_c = 2/[(1-g^0)\nu_t^0] \qquad (\text{EV rejection}) \tag{17}$$

which gives $D_c = 8$ (Lubensky and Isaacson 1978). Below D_c, due to EV, d_f decreases, so as to preserve the scaling law form of $\Pi\,\Pi\,(1 - O_{ij})$ and of n_s (it appears that at D_c itself $c_2 = 0$).

Linear chains. In the branching-out chains, the critical point strikes a balance between a decrease of the correlation in 'time' (as p^t), and its increase as the number of participating NN particles increases (as z^t). This stochastic balance controls $\langle \delta G_i \rangle = 0$ but leaves the fluctuation $G(s) > 1$, leading to branching. A similar balance is also possible with linear chains. The following linear analogue of percolation, called here the 'woodworm', offers an example. A lattice consists of wood and holes, with initial probabilities p and $1 - p$ respectively. The woodworm burrows a random walk through the lattice, consuming wood, and producing more holes instead. At each step, if it encounters wood, its weight G_t increases by 1; if a hole, it slims down by -1. Irrespective of its weight it occupies one lattice site; it terminates when $G_t = 0$. At D_c and for p_c (when $\langle \delta G_i \rangle = 0$), the average weight of walks reaching s steps is $G(s) \sim s^{1/2}$

or $g^0 = \frac{1}{2}$ (cf (4)). The walk shows a complete similarity to the chain describing percolation, exhibiting EV avoidance (7). The only difference is that, for a linear chain $d_f \equiv 1/\nu_t$. In consequence, for the woodworm the first equation (7) gives $D_c = (2-g^0)/\nu_t^0 = 3$. Another instructive example is an Ising lattice consisting of $\sigma_i \equiv 1$ alone. The probability to belong to the cluster is $p \equiv 1$ and therefore $z_c = 1$. There is no stochastic balance of p_c and z, no attendant $G(s) > 0$ and no branching; so $g^0 = 0$ and (equation (7) again) $D_c(= D_{rand}) = (2-0)/\nu_t^0 = 4$. This explains the formal equivalence of the $n = 0$ vector model, perceived here as a linear analogue of the Ising cluster to linear SAW. But the SAW also constitutes the linear analogue of the branched polymer, i.e. $g^0 = 0$ and, from (17), $D_c = 2/\nu_t^0 = 4$. This dual role, both cluster- and polymer-like, is possible because, when the linear SAW self-intersects it terminates automatically, be it due to an avoidance of the sole available choice $z_c = 1$ or to rejection.

Table 1 summarises the main findings obtained in the mean-field regime at $D \geqslant D_c$. The different nature of the chains that describe three types of aggregates is traced to two causes. First, transient cluster-like against permanent polymer-like connectivity, requires, respectively, EV avoidance or rejection. The former leads to (7) for $D_c = D_c(g^0, \nu_t)$, the latter to (17). Second, the cluster-like connectivity may be athermal or thermal, giving rise, respectively, to a random or coupled 'growth' (construction) of the chain. The former leads to (4) for g^0, the latter to (14). In this sense table 1 tries to provide an intuitive 'who's who in random cluster chains'. The intuitive approach relies on a set of geometric exponents g, γ_t and ν_t (one of which only is independent). Their general connection to conventional exponents, if any, is presently unknown, though in the mean-field approximation $g^0 = 3 - \tau^0$ (8). The intriguing findings are, the quasi-ideality of Ising cluster chains from $D_c = 4$ to $D = 8$ (15), and their growth at D_c in filaments that are strikingly more numerous ($g^0 = \frac{2}{3}$, $\gamma_t^0 = 3$) and more stretched ($\nu_t = 1$!), than both in percolation and in branched polymers ($g^0 = \frac{1}{2}$, $\gamma_t^0 = 2$ and $\nu_t^0 = \frac{1}{2}$). This geometric difference extends also to $D < D_c$ (Alexandrowicz 1980, 1985, Havlin *et al* 1984). All these aspects are not brought to light by the conventional γ and ν and indeed are largely obliterated in the fractal dimension, since $d_f = \gamma_t/\nu_t$.

Table 1.

Type of aggregate	Percolation athermal cluster	Ising spins thermal cluster	Branched polymer
Connectivity and EV effect	Transient → avoidance	Transient → avoidance	Permanent → rejection
Growth at D_c	Random	Coupled	Random
g^0	$\frac{1}{2}$ (4)	$\frac{2}{3}$ (14)	$\frac{1}{2}$ (4)
ν_t at D_c	$\frac{1}{2}$ (ideal)	1! (15)	$\frac{1}{2}$ (ideal)
$D_c(g_{id}, \nu_t)$	6 (7), (4)	4 (7), (14)	8 (17), (4)
Linear analogue	Woodworm $D_c = 3$	SAW $D_c = 4$	SAW $D_c = 4$

References

Alexandrowicz A 1980 *Phys. Lett.* **80A** 284
—— 1985 *Phys. Rev. Lett.* **54** 1420

—— 1988 *Phys. Rev. Lett.* **60** 669
Coniglio A and Klein W 1980 *J. Phys. A: Math. Gen.* **13** 2775
de Gennes P G 1976 *J. Physique Lett.* **37** 1
Fortuin C M and Kasteleyn P W 1972 *Physica* **57** 536
Havlin S, Djordjevic Z V, Majid I and Stanley H E 1984 *Phys. Rev. Lett.* **53** 178
Lubensky T C and Isaacson J 1978 *Phys. Rev. Lett.* **41** 829
Meirovitch H 1987 *J. Phys. A: Math. Gen.* **20** 6059
Parisi G and Sourlas M 1981 *Phys. Rev. Lett.* **46** 871
Stauffer D 1976 *J. Chem. Soc. Faraday Trans. II* **72** 1354
—— 1979 *Phys. Rep.* **54** 1
Swendsen R H and Wang J S 1987 *Phys. Rev. Lett.* **58** 86
Termonia Y and Meakin P 1985 *Phys. Rev. Lett.* **54** 1083
Zimm B and Stockmayer W H 1949 *J. Chem. Phys.* **17** 1301