Tricritical points in polymer systems

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Abstract. We consider a lattice model for equilbrium polymerisation in a solvent proposed by Wheeler and Pfeuty. We include attractive interactions between first-neighbour monomers which belong to polymer chains but are not consecutive along a chain. In the limit of no dilution this model describes the collapse transition of a polymer in a poor solvent (Θ-point). When no attractive interaction is present the model is appropriate for sulphur solutions,. where a dilution tricritical point is observed. The thermodynamic properties of the model were studied by two kinds of calculations. The solution on the Bethe lattice shows a locus of tricritical points, including the Θ and dilution tricritical points. On a fractal lattice (3D Sierpinski gasket), the exact real space RG solution reveals that the Θ-point and the dilution tricritical point belong to the same universality class.

1. Introduction

We consider two different physical situations where polymeric systems display a tricritical point. The first case is the so-called collapse transition of polymeric chains in a poor solvent (Flory 1966), which may be modelled by attractive interactions between monomers competing with the repulsive, excluded volume interactions (De Gennes 1975, 1979). This tricritical point, known in the literature as theta point, has been the subject of a variety of theoretical investigations such as mean-field calculations (Lifshitz *et al* 1978), exact enumerations on lattice models (Rapaport 1974, 1977), Monte Carlo simulations (Webman *et al* 1981), real space RG (Maritan *et al* 1989), and transfer matrix methods in two dimensions (Derrida and Saleur 1985, Saleur 1986). We should remark that the exact tricritical exponents for this model in two dimensions were also obtained (Duplantier and Saleur 1987). On the other hand, elemental liquid sulphur exhibits a polymerisation transition somewhat below 160 °C. At this temperature long chains of sulphur atoms start to be formed. If sulphur is diluted in certain organic solvents, with increasing dilution the continuous polymerisation transition moves towards a higher temperature and, eventually, turns into a first-order phase transition at sufficiently low sulphur concentration (Larkin *et al* 1967, Knobler and Scott 1984). The lower critical solution point associated with this coexistence line was initially discussed in a framework of chemical equilibrium theories (Scott 1965), with good qualitative agreement between theoretical results and experimental data. Later, the analogy between magnetic and polymeric systems (De Gennes 1972) allowed the identification of the lower critical solution point in sulphur solutions with the tricritical point in the underlying diluted $n \to 0$ vector model (Wheeler and Pfeuty 1981). There

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are fewer theoretical results in the literature regarding this tricritical point (Wheeler and Pfeuty 1981, Stilck and Wheeler 1987), which we will call dilution tricritical point.

In this paper we investigate a model displaying both tricritical points mentioned above. It is a generalisation of the lattice model proposed for sulphur solutions (Wheeler and Pfeuty 1981). Besides considering equilibrium polymerisation with annealed dilution, we introduce attractive interactions between monomers which are first neighbours on the lattice, but which are not consecutive along a chain. We perform two distinct calculations to investigate the thermodynamic properties of this model. First, we obtain an exact solution on the Bethe lattice (Baxter 1982). In the general parameter space this solution shows a tricritical surface, the dilution and the theta points belonging to this surface. On the other side, we solve the model on the 3D Sierpinski gasket (Dhar 1978), whose fractal dimension is equal to 2. From a real space RG calculation, which is exact on the 3D Sierpinski gasket, we obtain the eigenvalues of the linearized transformation near the fixed points. The Θ-point of this model on the 4-simplex lattice, which is equivalent to the 3D Sierpinski lattice regarding critical properties of polymer chains, was investigated previously (Dhar and Vannimenus 1987). In our opinion it is a nice example of a non-mean-field tricritical point which may be studied analytically.

This paper is organized as follows. In section 2, the model is defined, and in section 3 the Bethe lattice solution is obtained. The solution of the model on the fractal 3D Sierpinski gasket may be found in section 4; in section 5 we present final discussions and comments, and in the appendix we show a relation between the diluted non-interacting polymer system and non-diluted interacting polymer system reported recently (Maes and Vanderzande 1990) for the particular case of the solution on the Bethe lattice.

2. Definition of the model

We consider a lattice model, proposed some time ago (Wheeler and Pfeuty 1981), for equilibrium polymerisation of sulphur in a solvent, including attractive interactions between monomers on first-neighbour sites which are incorporated into chains but are not consecutive monomers of the same chain. In this lattice polymer model with annealed dilution each site i may be occupied either by a monomer ($\nu_i = 1$) or a solvent ($\nu_i = 0$). The polymeric chains are represented by mutually and self-avoiding walks, which are constrained to visit only lattice sites where monomers are present. For each pair of first-neighbour sites occupied by monomers, a statistical weight y is considered, and the fugacity of a monomer will be denoted by z. A statistical weight $\tilde{x}$ will be associated with a polymer bond, and the attractive interaction between chains will be introduced by multiplying the statistical weight of a configuration by a factor ω for each pair of first-neighbour sites occupied by polymers which are not adjacent on a chain. In figure 1, an allowed configuration is depicted on the square lattice and its statistical weight is given. The end points of the chains are confined to the boundary of the lattice. In terms of the analogy between the polymer model and the $n \to 0$ limit of the magnetic n-vector model (Wheeler and Pfeuty 1981), this corresponds to allowing a non-zero magnetic field only at the boundary sites.

The (grand)partition function will be given by

$$Y_N = \sum_{\{\nu_i\}} \sum_{N_b} \sum_{N_p} \tilde{x}^{N_b} y^{N_m} z^{\Sigma \nu_i} \omega^{N_p} \Gamma_N(N_b, N_p, \{\nu_i\}) \tag{2.1}$$

where the first sum is over all site configurations ($\nu_i = 0, 1$), and N_b, N_p, and N_m are
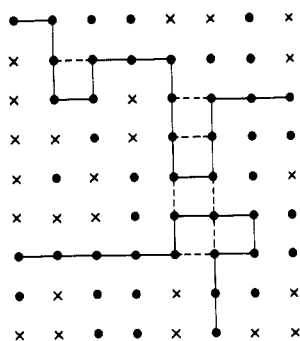
Figure 1. An allowed configuration on the square lattice: (●) monomers, (×) solvent molecules, (I) polymer bonds, (¦) attractive interactions between chains. The statistical weight of this configuration is $x^{26}y^{64}z^{48}\omega^7$.

the numbers of bonds, non-consecutive first-neighbour sites in chains and pairs of first-neighbour sites occupied by monomers, respectively. Finally, Γ_N is the number of configurations on the N-site lattice with the description above.

3. Solution on the Bethe lattice

As in the solution of the Ising model on the Bethe lattice (Baxter 1982), we consider a Cayley tree with coordination number q and M generations built by connecting q-rooted subtrees to a central site (figure 2). We then proceed finding recursion relations for partial partition functions, which are numbered according to the configuration of the root
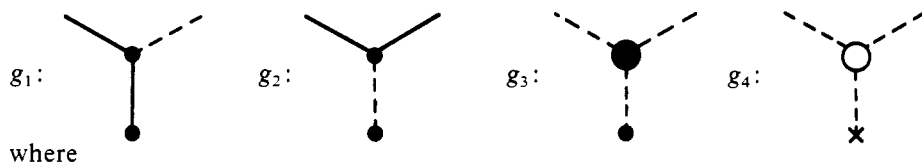
where

- ● : monomer (in a polymer or not)
- | : polymer bond
- × : solvent
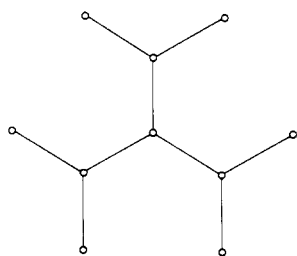- ● : monomer (not in a polymer) or solvent
- ○ : monomer or solvent.

Figure 2. A Cayley tree with coordination number $q = 3$ and $M = 3$ generations.

Let $g_i^{(M)}$ be a partial partition function of a M-generation subtree, which is the sum (2.1) for all configurations of the subtree compatible with the given root. Then $g_i^{(M+1)}$ may be built by attaching $(q-1)$ M-generations subtrees to a new root (figure 3).

This process leads to the following recursion relations

$$g_1^{(M+1)} = (q-1)\tilde{x}yz^{2/q}g_1^{(M)}(\omega g_2^{(M)} + g_3^{(M)})^{q-2} \tag{3.1a}$$

$$g_2^{(M+1)} = \tfrac{1}{2}(q-1)(q-2)yz^{2/q}(g_1^{(M)})^2(\omega g_2^{(M)} + g_3^{(M)})^{q-3} \tag{3.1b}$$

$$g_3^{(M+1)} = z^{1/q}[yz^{1/q}(g_2^{(M)} + g_3^{(M)})^{q-1} + (g_4^{(M)})^{q-1}] \tag{3.1c}$$

$$g_4^{(M+1)} = z^{1/q}[\tfrac{1}{2}(q-1)(q-2)(g_1^{(M)})^2(\omega g_2^{(M)} + g_3^{(M)})^{q-3}$$
$$+ (g_2^{(M)} + g_3^{(M)})^{q-1}] + (g_4^{(M)})^{q-1}. \tag{3.1d}$$

In the first recursion relation, for example, the subtree with $M+1$ generations has a chain incident on the root site. This chain passes through one of the $q-1$ M-generations subtrees, whose partial partition function is $g_1^{(M)}$. The factor $\tilde{x}$ accounts for the new bond on the root and y is the statistical weight due to the two monomers on the root bond. A factor $z^{(1/q)}$ is included for each monomer on the root bond, assuring the correct factor z for a monomer on the tree. Finally, the $q-2$ remaining M-generations subtrees may be of type 2 or 3. In the first case, a factor ω accounts for the attractive interaction between first-neighbour monomers incorporated into chains.
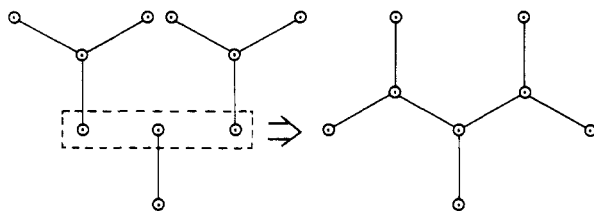

Figure 3. Construction of a $(q=3, M=3)$ subtree from two $(q=3, M=2)$ subtrees.

Considering that the critical value of $\tilde{x}$ for the polymerisation transition in the pure non-interacting case ($\omega = 1$; $z \to \infty$) is $\tilde{x}_c = 1/(q-1)$ (Stilck and Wheeler 1987), it is convenient to define the parameter $x = (q-1)\tilde{x}$, then we will have, in this limit, $x_c = 1$ for all values of q.

We note that g_3 is equal to zero only in the unimportant case $z = 0$, which implies no monomers on the lattice. Therefore we can reduce the number of equations by defining the quantities

$$A = \frac{g_1}{g_3} \qquad B = \frac{g_2}{g_3} \qquad C = \frac{g_4}{g_3}. \tag{3.2}$$

The recursion relations for A, B, C will be

$$A' = xyz^{2/q}(\omega B + 1)^{q-2}\frac{A}{D} \tag{3.3a}$$

$$B' = \tfrac{1}{2}(q-1)(q-2)yz^{2/q}(\omega B + 1)^{q-3}\frac{A^2}{D} \tag{3.3b}$$

$$C' = \frac{1}{D}\{z^{1/q}[\tfrac{1}{2}(q-1)(q-2)(\omega B + 1)^{q-3}A^2 + (B+1)^{q-1}] + C^{q-1}\} \tag{3.3c}$$

with

$$D = z^{1/q}[yz^{1/q}(B+1)^{q-1} + C^{q-1}]. \qquad (3.3d)$$

From the exact solution for $M = 1$, we find the initial conditions

$$A^{(0)} = \frac{xyz^{1/q}}{(q-1)(1+yz^{1/q})} \qquad B^{(0)} = 0 \qquad C^{(0)} = \frac{1+z^{1/q}}{z^{1/q}(1+yz^{1/q})}.$$

The partition function for the M-generation Cayley tree is obtained by attaching q subtrees to the same central site (figure 4). This leads us to

$$Y_M = \tfrac{1}{2}q(q-1)(g_1^{(M)})^2(\omega g_2^{(M)} + g_3^{(M)})^{q-2} + (g_2^{(M)} + g_3^{(M)})^q + (g_4^{(M)})^q. \qquad (3.4)$$

The thermodynamic properties of the model on the Cayley tree may be obtained from the partition function (3.4) in the limit $M \to \infty$. It may be useful, at this point, to stress that on Bethe lattice calculations the iteration of the recursion relations produces the partition functions of the model on larger and larger trees. The recursion relations have thus a different character of the ones obtained in RG calculations, where the relations between the parameters of the original and the renormalised Hamiltonians keep the partition function invariant.
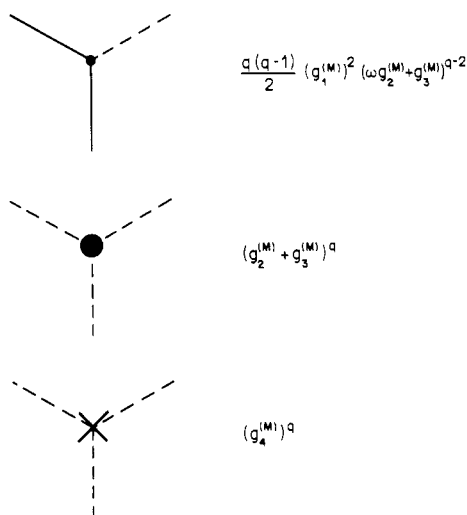

Figure 4. Configurations of the vicinity of the central site that contribute to the partition function.

In the thermodynamic limit the vector $V_i^{(M)} \equiv (A^{(M)}, B^{(M)}, C^{(M)})$ tends to a stable fixed point V^* of the relations (3.3), that is, all the eigenvalues of the matrix

$$\mathcal{M} = \left.\frac{\partial V'}{\partial V}\right|_{V^*} \qquad V \equiv (A, B, C) \qquad (3.5)$$

have to be less than one.

The Bethe lattice solution is obtained studying the behaviour of the model deep inside the tree in the thermodynamic limit. We may write down the average numbers

of monomers and bonds per site in the central region

$$\Phi_m = \frac{1}{Y}\left[\tfrac{1}{2}q(q-1)g_1^2(\omega g_2+g_3)^{q-2}+(g_2+g_3)^q\right]$$

$$\Phi_b = \frac{1}{Y}\left[\tfrac{1}{2}q(q-1)g_1^2(\omega g_2+g_3)^{q-2}\right]$$

or, using (3.2)

$$\Phi_m = \frac{1}{\Delta}\left[\tfrac{1}{2}q(q-1)(\omega B+1)^{q-2}A^2+(B+1)^q\right] \tag{3.6}$$

$$\Phi_b = \frac{1}{\Delta}\left[\tfrac{1}{2}q(q-1)(\omega B+1)^{q-2}A^2\right] \tag{3.7}$$

with

$$\Delta = \tfrac{1}{2}q(q-1)(\omega B+1)^{q-2}A^2+(B+1)^q+C^q.$$

Therefore, the Bethe lattice solution of the model is reduced to finding the stability region for the fixed points of equations (3.3), and then looking for the relevant averages in the central region.

3.1. Limiting cases

(a) Non-interacting polymers. This case corresponds to $\omega = 1$ and the recursion relations (3.1) have only terms in g_1, (g_2+g_3), and g_4. Therefore we can define

$$\tilde{g}_1 = g_1 \qquad \tilde{g}_2 = (g_2+g_3) \qquad \tilde{g}_3 = g_4$$

and the problem is reduced to the non-interacting polymer system (Stilck and Wheeler 1987). There are, of course, no attractive interactions in the one-dimensional case, $q = 2$, which has already been studied (Pfeuty and Wheeler 1983, Stilck and Wheeler 1987).

(b) Pure polymer case. In the limit $z \to \infty$, we have only monomers on the lattice sites. The equations (3.1) turn into

$$\frac{g_1^{(M+1)}}{yz^{2/q}} = xg_1^{(M)}(\omega g_2^{(M)}+g_3^{(M)})^{q-2}$$

$$\frac{g_2^{(M+1)}}{yz^{2/q}} = \tfrac{1}{2}(q-1)(q-2)(g_1^{(M)})^2(\omega g_2^{(M)}+g_3^{(M)})^{q-3}$$

$$\frac{g_3^{(M+1)}}{yz^{2/q}} = (g_2^{(M)}+g_3^{(M)})^{q-1}+O(1/z^{1/q})$$

$$\frac{g_4^{(M+1)}}{yz^{2/q}} = O(1/z^{1/q})$$

and, up to lowest order in z^{-1}, we can define

$$A = \frac{g_1}{g_3} \qquad B = \frac{g_2}{g_3}.$$

The recursion relations for A and B are given by

$$A' = xA \frac{(\omega B + 1)^{q-2}}{(B+1)^{q-1}} \tag{3.8a}$$

$$B' = \tfrac{1}{2}(q-1)(q-2)A^2 \frac{(\omega B + 1)^{q-3}}{(B+1)^{q-1}}. \tag{3.8b}$$

The unpolymerised fixed point $A_U = 0$, $B_U = 0$ gives

$$\lambda_U = \frac{\partial A'}{\partial A} \bigg|_{v_U} = x.$$

The unpolymerised stability line is given by the condition $\lambda_U = 1$ ($x_U = 1$).

For the polymerised fixed point $(A_p, B_p \neq 0)$ we have, from (3.8b)

$$A_p = \left[\frac{2(B_p + 1)^{q-1} B_p}{(q-1)(q-2)(\omega B_p + 1)^{q-3}} \right]^{1/2} \tag{3.9}$$

with B_p a positive root of the polynomial of degree $(q-1)$

$$P(B) = (B+1)^{q-1} - x(\omega B + 1)^{q-2}. \tag{3.10}$$

On the unpolymerised stability line, $x_U = 1$, the zero-order term of $P(B)$ is equal to zero and one of the polymerised fixed points becomes equal to the unpolymerised fixed point both with the largest eigenvalue equal to one. The tricritical point will be the point on that line at which a third fixed point becomes equal to the unpolymerised fixed point. This condition is fulfilled when the zero-order term and the linear term of $P(B)$ are both equal to zero

$$x_\Theta = 1 \qquad \omega_\Theta = \frac{(q-1)}{(q-2)}. \tag{3.11}$$

At the tricritical point, the polymerisation phase transition changes from second to first-order, and this point may also be defined as the limiting point where the stability curves of both phases are coincident.

In particular, for coordination number $q = 3$, we have a polynomial of degree 2 for λ_P,

$$\lambda^2 - \frac{1}{(B_P + 1)^2} [x(\omega B_P + 1) - 2B_P(B_P + 1)]\lambda - 2x \frac{B_P(\omega - 1)}{(B_P + 1)^3} = 0.$$

Then, using (2.10) and making $\lambda_P = 1$ in this equation, we can obtain a simple expression for the stability line of the polymerised phase,

$$x_P = \frac{4(\omega - 1)}{\omega^2} \qquad \omega > \omega_\Theta = 2. \tag{3.12}$$

To obtain the first-order phase transition line we need the bond density at the central region,

$$\Phi_b = \frac{1}{Y} [\tfrac{1}{2}q(q-1)g_1^2(\omega g_2 + g_3)^{q-2}] = 1 - \frac{(B+1)^q}{\Delta} \tag{3.13}$$

with

$$\Delta = \tfrac{1}{2}q(q-1)A^2(\omega B + 1)^{q-2} + (B+1)^q.$$

In the unpolymerised phase Φ_b is equal to zero and in the polymerised phase we can use (3.13) to write $B(\Phi_b)$. Using (3.8), (3.9) and (3.13), we get

$$\ln(x(\Phi_b)) = \ln(2) + (q-1)[\ln(B(\Phi_b)+1) - \ln(\omega B(\Phi_b)+1)].$$

So, we have an analytic expression for $\ln(x(\Phi_b))$ and we may use the equal area rule to calculate the value of $x_C(\omega)$ at the first-order transition by performing the integration $\int \ln(x)\,d\Phi_b$ at $\omega = $ constant (figure 5). All calculations in figures 5–10 were done with coordination number $q = 3$.
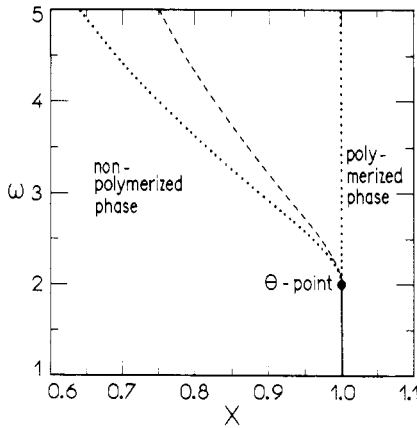
Figure 5. ω against x phase diagram for the pure $(z = \infty)$ case. The stability (spinodal) curves are also shown (dotted curves). The broken curve represents first-order transitions and the full line locates second-order transitions.

3.2. Study of the fixed points

The fixed points of the general problem may be classified into two categories.

(*a*) Unpolymerised fixed point. This case corresponds to $A_U = B_U = 0$, which implies, from (3.3),

$$z^{1/q}C_U^q - C_U^{q-1} + yz^{2/q}C_U - z^{1/q} = 0. \tag{3.14}$$

The non-zero eigenvalues are

$$\lambda_{LG} = \left.\frac{\partial C'}{\partial C}\right|_{v_U} = \frac{(q-1)(y-1)C_U^{q-2}}{(yz^{1/q} + C_U^{q-1})^2} \tag{3.15}$$

$$\lambda_U = \left.\frac{\partial A'}{\partial A}\right|_{v_U} = \frac{xyz^{1/q}}{yz^{1/q} + C_U^{q-1}}. \tag{3.16}$$

λ_{LG} is related to the well known Ising lattice-gas problem (Baxter 1982, Stilck and Wheeler 1987) and we do not consider it here in detail.

The stability limit of the unpolymerised phase is given by (3.14) and (3.16) with $\lambda_U = 1$, which corresponds to

$$z_U = \frac{[1+(x-1)y]^{q-1}}{(x-1)x^{q-1}y^q}. \tag{3.17}$$

(*b*) Polymerised fixed point. In the polymerised region we have A_P; B_P; $C_P \neq 0$, and equations (3.3) lead to

$$A_P = \left(\frac{2xB_P(\omega B_P + 1)}{(q-1)(q-2)}\right)^{1/2} \tag{3.18a}$$

$$C_P = \{yz^{1/q}[x(\omega B_P + 1)^{q-2} - (B_P + 1)^{q-1}]\}^{1/(q-1)} \tag{3.18b}$$

where B_P will be a positive root of a polynomial of degree $(q-1)^2$

$$P(B) = x^{q-1}y^q z(\omega B + 1)^{(q-1)(q-2)}[x(\omega B + 1)^{q-2} - (B+1)^{q-1}]$$
$$- [x(y+B)(\omega B + 1)^{q-2} - (y-1)(B+1)^{q-1}]^{q-1}. \tag{3.19}$$

The stability line must be calculated with the condition $\lambda_P = 1$, where λ_P is the largest eigenvalue of the matrix $\mathcal{M} = \partial V'/\partial V|_{V_P}$.

3.3. Tricritical points

As before, at the tricritical points, the zero-order and linear terms of $P(B)$ in (3.9) are equal to zero. Therefore

$$\omega_{TC} = \frac{(q-1)}{(q-2)} \frac{x^2 - (q-2)(y-1)(x-1)}{yx^2 - (y-1)[q(x-1)+1]} \tag{3.20}$$

and $z_{TC}(x, y)$ given by (3.17).

We note that both known limiting cases are recovered, the Θ-point, which corresponds to the limit $z \to \infty \Rightarrow x \to 1$,

$$\omega_{TC} \xrightarrow[z \to \infty]{} \frac{(q-1)}{(q-2)}\left(1 - \frac{(y-1)}{(yz^{1/q})^2} + O(1/z^{3/q})\right) = \omega_\Theta + O(1/z^{2/q})$$

and the dilution tricritical point, $\omega_{TC} = 1$,

$$x_{TC} = \frac{1}{(q-2)y - (q-1)} + 1.$$

This corresponds to equation (5.16) of Stilck and Wheeler (1987) if we replace x by $(q-1)K_p$ and y by ω_{y}.

We also see that in the limit where there are no lattice-gas interactions present, that is when $y = 1$, ω_{TC} in (3.20) reduces to ω_Θ, and the tricritical dilution point disappears in this case.

The value $\omega_{TC} = 1$ is reached only for $y \geq (q-1)/(q-2)$, and the dilution tricritical point and the Θ-point belong to a line of tricritical points in the ζ-ω plane (figure 6), where ζ is the activity fraction

$$\zeta = \frac{z}{(1+z)}.$$

$\zeta = 1$ corresponds to a pure polymer system, and the simple case of non-interacting polymers without dilution is $\zeta = 1$, $\omega = 1$.

In figure 7 we show the non-monotonical behaviour of a curve ζ_{TC} against y for $\omega = 1$, $\omega = 1.5$ and $\omega = 1.999$. It should be remarked that when $\omega = (q-1)/(q-2)$ ($=2$ for $q = 3$), the tricritical value of ζ is equal to one, for all values of y.
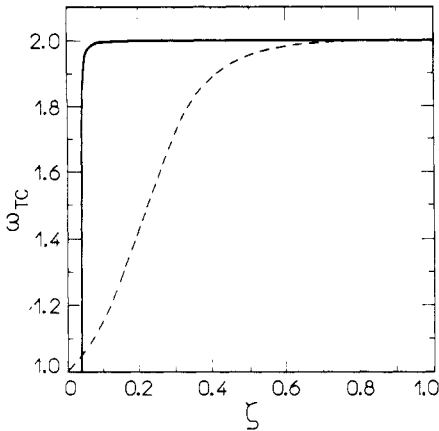
Figure 6. Curves ω_{TC} against ζ at $y = $ constant. Full curve represents results for $y = y_{LG} = (q/q-2)^2 = 9$ and the broken curve corresponds to $y = (q-1)/(q-2) = 2$.
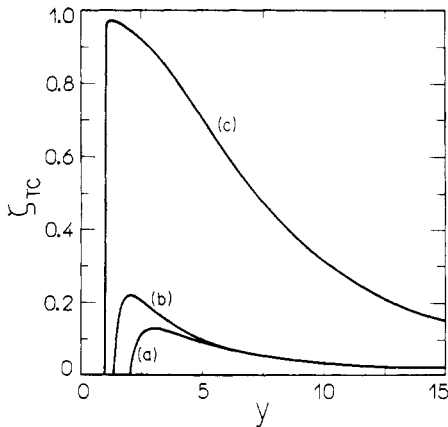

Figure 7. Curves ζ_{TC} against y at $\omega = $ constant: (a) $\omega = 1$, (b) $\omega = 1.5$, and (c) $\omega = 1.999$ $(\omega = 2$ corresponds to $\zeta_{TC} = 1$ for all values of $y)$.

3.4. Phase diagrams

For second-order phase transitions the stability borders of both phases are coincident at the phase transition line. At the tricritical point the curves split and the stability limit lines are the spinodal curves associated with a first-order phase transition. The coexistence line may be calculated using an equal area rule, by performing the integration $\int \ln(x)\, d\Phi_b$ at ω, y, $z = $ constant. In figure 8 we show three curves of x as a function of Φ_b, with ω, y, z held constant. The curves (a), (b), and (c) were calculated for $\omega < \omega_{TC}$, $\omega = \omega_{TC}$, and $\omega > \omega_{TC}$ respectively, a thermodynamically unstable region being observed in curve (c), signalling a first-order phase transition. Some ω against x phase diagrams are displayed in figure 9. Curve (a) corresponds to the pure case $\zeta = 1$, so that the tricritical point in this diagram may be identified with the Θ-point. In curve (b) $\zeta = 0.065$ and curve (c) was obtained with $\zeta = 0.0551$, since $\omega_{TC} = 1$, the tricritical point in this curve is the dilution tricritical point. Therefore, a continuous line of tricritical points exists between the Θ-point and the dilution tricritical point.
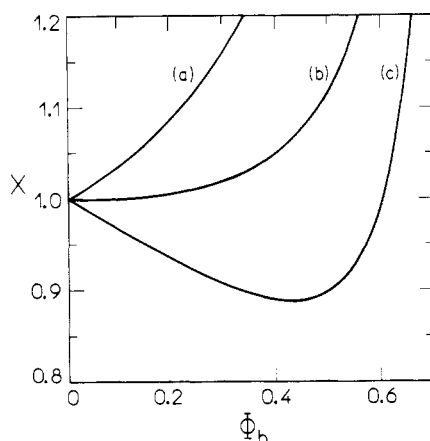
Figure 8. Curves x against Φ_b for $\zeta = 1$ at $\omega = $ constant: (a) $\omega = 1$, (b) $\omega = \omega_{TC} = 2$, (c) $\omega = 3$.
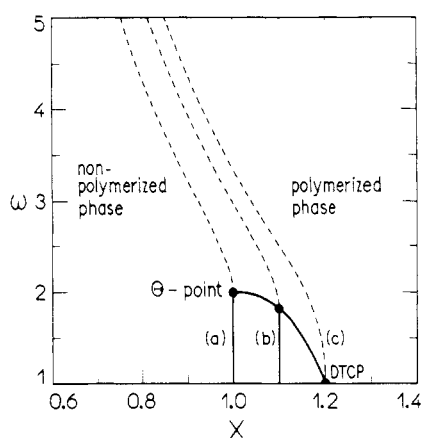

Figure 9. ω against x phase diagrams at $y = $ constant $= 7$: (a) $\zeta = 1$ (pure case), (b) $\zeta = 0.065$, and (c) $\zeta = 0.0551$ ($\omega_{TC} = 1$). The line of tricritical points joining the Θ-point $(x = 1)$ and the tricritical dilution point $(\omega = 1)$ is also depicted.

All curves were calculated with $y = 7$. The corresponding Φ_b against ω diagrams are shown in figure 10.

It should be remarked that qualitatively different phase diagrams are obtained for large values of y. This feature is already present in the mean-field calculation for the dilute polymerisation model (Wheeler and Pfeuty 1981), where critical endpoints are found. For shortness, we do not present here results for $y > q^2/(q-2)^2$ ($=9$ for $q = 3$), but there is no difficulty in obtaining them.

4. Solution on a fractal lattice

The problem of pure ($z \to \infty$) interacting polymers was studied on several fractal lattices (Dhar 1978, Dhar and Vannimenus 1987, Rammal *et al* 1984, Vannimenus 1989, and
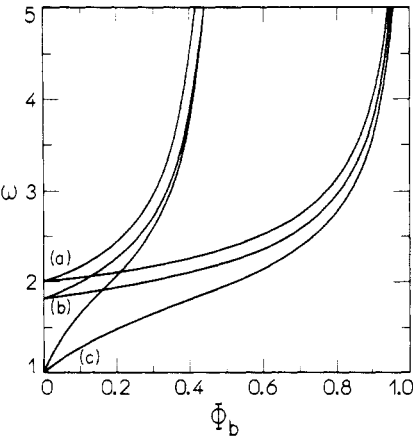
Figure 10. ω against Φ_b phase diagrams corresponding to the same values of y and ζ as in figure 9.

references therein). In particular it is known that (Rammal *et al* 1984) the polymerization phase transition is of second order for all values of ω in the solution on the 2D Sierpinski gasket and in the equivalent solution on the 3-simplex lattice. But it was found (Dhar and Vannimenus 1987) that the Θ-point is present in the 3D Sierpinski gasket solution (they obtained the equivalent solution of the model on the 4-simplex lattice). In this section, we will study the thermodynamic properties of the dilute polymerization model with attractive interactions on the 3D Sierpinski gasket, which gives simpler equations for the dilute case than the equivalent 4-simplex lattice. A projection of the 3D Sierpinski gasket is depicted in figure 11.

The model is solvable through an exact real space renormalization calculation. On this lattice, the critical Ising temperature is equal to zero (Gefen *et al* 1980), but the lattice-gas problem is equivalent to an Ising model with non-zero magnetic field, therefore we need to enlarge the dimensionality of the space in which we perform the decimation transformation, defining five partial partition functions (not only three as
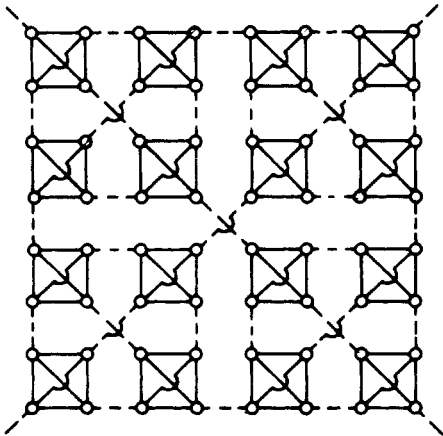

Figure 11. The 4-simplex lattice.

in Gefen *et al* 1980) g_1, g_2, g_3, g_4 and g_5 for configurations without polymers and corresponding to tetrahedra with 0, 1, 2, 3 or 4 vertices occupied by solvent, respectively.

For the configurations with polymer chains going through the tetrahedron we define seven partial partition functions, six of them for configurations with a chain going once through the tetrahedron, namely:

if the four vertices are occupied by monomers we define P_1, P_2, P_3 for chains visiting four, three or two vertices respectively;

if just one vertex is occupied by a solvent we define P_4 and P_5 for chains visiting three or two vertices respectively;

if two vertices are occupied by solvent we define P_6 for a chain visiting those two vertices.

Finally we need a seventh partial partition function P_7 for chains going twice through a tetrahedron.

The initial conditions for the lattice-gas partition functions g_i and for the polymer partial partition functions P_i are shown in figure 12.

$$g_{1,0} = y^6 z^2 \qquad g_{2,0} = y^3 z^{3/2}$$

$$g_{3,0} = y\, z \qquad g_{4,0} = z^{1/2}$$

$$g_{5,0} = 1$$

$$P_{1,0} = g_{1,0}\,\bar{x}^3\,\omega^3 \qquad P_{2,0} = g_{1,0}\,\bar{x}^2\,\omega$$

$$P_{3,0} = g_{1,0}\,\bar{x} \qquad P_{4,0} = g_{2,0}\,\bar{x}^2\,\omega$$

$$P_{5,0} = g_{2,0}\,\bar{x} \qquad P_{6,0} = g_{3,0}\,\bar{x}$$

$$P_{7,0} = g_{1,0}\,\bar{x}^2\,\omega^4$$

Figure 12. Initial condition for the partial partition functions. (●) monomers, (○) solvent, (|) polymer bond.

Due to the dimension of the combinatorial problem the recurrence relations have to be obtained by computer, and their derivation may be understood by observing figure 13. In figure 13(*a*) we show the original and renormalized cells of a renormalization step. In figure 13(*b*) the contributions to one of the terms of the recursion relation are depicted. Note that, as in the non-dilute problem (Dhar and Vannimenus 1987), we do not include a factor ω for first-neighbour sites occupied by a chain which are not in the same tetrahedron; this would lead to more difficulties in solving the problem without any qualitative difference in the results (see Klein and Seitz (1984) for self-interacting chains on the 2D Sierpinski gasket). There are typically of the order of one hundred terms in the recursion relations, but their analysis shows that at the
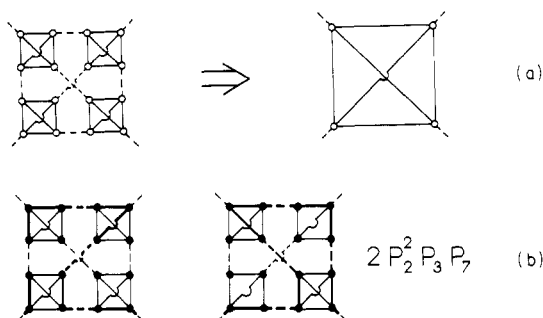
Figure 13. (*a*) Two-dimensional projection of the original and the renormalized cells of the exact RG calculations on the 3D Sierpinski gasket. Points at the end of the same broken line are actually the same point in the lattice. (*b*) One of the contributions to P'_1.

relevant fixed points, the lattice-gas partial partition functions are in the $T \to \infty$ fixed point values:

$$f_1^* = f^4 \qquad f_2^* = f^3 \qquad f_3^* = f^2 \qquad f_4^* = f$$

$$f_i \equiv \frac{g_i}{g_5} \qquad i = 1, \ldots, 4 \tag{4.1}$$

where the parameter f is defined as a function of y and z through the recurrence relations. In particular, if $y = 1$ in the initial conditions ($T = \infty$ or non-interacting lattice gas) it follows that $f = z^{1/2}$ at the fixed point for all values of z. Defining the quantities

$$R_i \equiv \frac{P_i}{g_5} \qquad i = 1, \ldots, 7 \tag{4.2}$$

we obtained the fixed point values

$$R_1^* = R_2^* = R_4^* = 0 \qquad R_3^* = f^2 R_6^* \qquad R_5^* = f R_6^* \tag{4.3}$$

where the equations for R_6^*, R_7^* are

$$u^6 R_6^* = u^5 R_6^{*2} + 2u^4 R_6^{*3} + 2u^3 R_6^{*4} + 4u^2 R_6^{*3} R_7^* + 6u R_6^{*2} R_7^{*2} \tag{4.4a}$$

$$u^6 R_7^* = u^4 R_6^{*4} + 4u^3 R_6^{*3} R_7^* + 22 R_7^{*4} \tag{4.4b}$$

with $u \equiv 1 + f^2$. Now we can define

$$A \equiv \frac{R_6^*}{u} \qquad B \equiv \frac{R_7^*}{u^2}$$

and the relations for A and B will be given by

$$A = A^2 + 2A^3 + 2A^4 + 4A^3 B + 6A^2 B^2 \tag{4.5a}$$

$$B = A^4 + 4A^3 B + 22 B^4. \tag{4.5b}$$

These equations are identical to the fixed point equations obtained for the pure case (Dhar and Vannimenus 1987) and we see that the fixed point values are functions of f (and therefore of y and z) but the eigenvalues of the three fixed points are universal.

(*a*) Second-order phase transition fixed point: the eigenvalues are

$$\lambda_1^a = 2.796 > 1 \qquad \lambda_2^a = 0.254 < 1.$$

(*b*) First-order phase transition fixed point:

$$\lambda_1^b = 0 \qquad \lambda_2^b = 4 = 2d_f.$$

(*c*) Tricritical point: this fixed point is fully unstable

$$\lambda_1^c = \frac{100}{27} \qquad \lambda_2^c = \frac{20}{9}.$$

In figure 14 we compare the pure cases $z \to \infty$ on this lattice and on the $q = 6$ Bethe lattice solution.

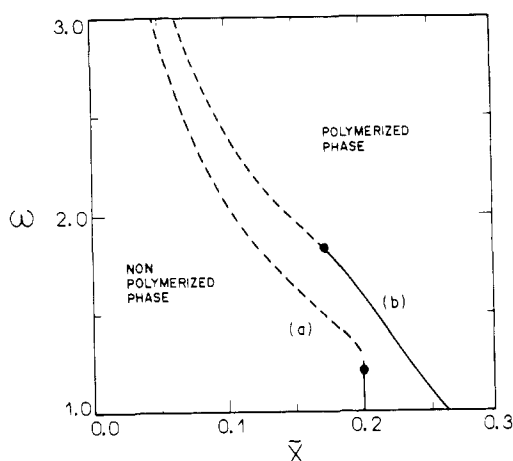**Figure 14.** ω against $\tilde{x}$ phase diagrams for the pure case, calculated on (*a*) the Bethe lattice with $q = 6$, and (*b*) the 3D Sierpinski gasket.

5. Discussion and conclusion

A generalisation of a model for equilibrium polymerisation in a solvent (Wheeler and Pfeuty 1981) with attractive interactions between monomers incorporated into polymers is solved exactly on the Bethe lattice (Baxter 1982) and on the fractal 3D Sierpinski gasket. In the solution of the model on the Bethe lattice, the Θ and the dilution tricritical points belong to the same tricritical surface in the general parameter space. Also, both tricritical points are related to the same fixed point of the real space decimation RG transformation for the model defined on the 3D Sierpinski gasket.

It should be stressed that actually the model of polymers with attractive interactions for the collapse transition (De Gennes 1975) and the model for equilibrium polymerization in a solvent (Wheeler and Pfeuty 1981), are quite similar in their physical background. Both models take into account the interactions between the polymer chains and the solvent. In the first model these interactions are considered indirectly, by introducing attractive interactions inside and between chains which tend to collapse the polymers, therefore reducing their area of contact with the poor solvent. In the second model, the effect of the solvent is considered explicitly, in the form of a lattice gas interaction. Also, sites which are not occupied by solvent not incorporated into

chains are allowed (non-activated monomers). So, it is not surprising that the dilution tricritical point and the Θ-point are two particular points in the same locus of tricritical points in the Bethe lattice solution of the model with both attractive interactions and annealed dilution; also, the Θ-point may be obtained as a limiting case of thé dilution (non-interacting) tricritical point (see the appendix).

It is interesting to study the model on two-dimensional regular lattices; we are actually working in that direction.

Acknowledgments

Appendix. Pure interacting polymer case as a limit of the dilute non-interacting polymer system on the Bethe lattice

Recently (Maes and Vanderzande 1990) showed that the high-temperature expansion of the partition function of the dilute classical n-vector model in the $n \to 0$ limit, for $z \to 0$; $x \to \infty$; and $xz = $ constant is equivalent to the grand partition function of the interacting non-dilute polymer problem.

In this appendix we show how this limit is realized in the particular case of the Bethe lattice solution. For the solution on the Bethe lattice we have that equations (3.1) are equivalent to equations (3.8) when

$$\omega = 1 \qquad z \to 0 \qquad x \to \infty \qquad xz = \text{constant}.$$

If $\omega = 1$ in (3.1) we may define

$$h_1 = z^{(q-2)/2q} g_1 \qquad h_2 = z^{-1/q}(g_2 + g_3) \qquad h_3 = g_4$$

and so the recursion relations may be written as

$$h_1' = \alpha h_1 h_2^{q-2}$$
$$h_2' = \tfrac{1}{2}(q-1)(q-2) y h_1^2 h_2^{q-3} + h_3^{q-1} + \mathrm{O}(z) \qquad\qquad (A1)$$
$$h_3' = \tfrac{1}{2}(q-1)(q-2) h_1^2 h_2^{q-3} + h_3^{q-1} + \mathrm{O}(z)$$

where $\alpha \equiv xyz$.

Now we will change variables in a different way from the one adopted in section 3.1, since in the limit $z \to \infty$, with $\omega \neq 1$, g_4 vanishes. So, we define

$$f_1 = h_1 \qquad f_2 = \frac{h_2 - h_3}{y - 1} \qquad f_3 = \frac{y h_3 - h_2}{y - 1}$$

and the recursion relations for the f_i are

$$f_1' = \alpha f_1 (y f_2 + f_3)^{q-2}$$
$$f_2' = \tfrac{1}{2}(q-1)(q-2) f_1^2 (y f_2 + f_3)^{q-3} \qquad\qquad (A2)$$
$$f_3' = (f_2 + f_3)^{q-1}.$$

Now, as was done in section 3, we may deduce the number of equations by defining

$$A = \frac{f_1}{f_3} \qquad B = \frac{f_2}{f_3}$$

and the new recursion relations will be

$$A' = \alpha A \frac{(yB+1)^{q-2}}{(B+1)^{q-1}}$$

$$B' = \tfrac{1}{2}(q-1)(q-2)A^2 \frac{(yB+1)^{q-3}}{(B+1)^{q-1}}.$$

(A3)

Replacing α by x and y by ω, equations (A3) are identical to equations (3.8).

A similar calculation does not hold for our solution on the 3D Sierpinski gasket, since we did not consider interactions between first-neighbour sites occupied by chains and situated in different tetrahedra on the lattice. Thus, the parameter ω appears only in the initial conditions, being not present in the expressions for the recursion relations. This simplifies somewhat the solution of the problem, but breaks down the exact relationship between both models in the limit stated above.

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