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LETTER TO THE EDITOR

The graph-like state of matter XI. Electrical conductivity of random networks, gelation and elasticity

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Abstract. The analogy between the branching model of electrical conductivity and the graph theoretical treatment of *f*-functional polycondensation in chemistry is quantified by an application of the concept of elastically active network chains in rubber theory to random resistor networks.

The analogy between the branching model of electrical conductivity in random networks and the graph theoretical treatment of *f*-functional random polycondensation (Flory 1941) in chemistry has been drawn by a number of workers, notably Stinchcombe (1973), Stauffer (1976) and de Gennes (1976) to whose expositions the reader is referred. In essential detail both models have connection with others, especially the percolation model, and all can be described in terms of the probability α that an edge linking two vertices in a graph or a lattice exists, or for example in an initially saturated random resistor network, that all but a fraction α of resistors have been removed. The 'critical conversion' α_c is given by equation (1).

$$\alpha_c = \frac{1}{f-1} \tag{1}$$

where f is the 'functionality' or maximum degree of a vertex.

Stauffer (1976) remarked that 'presumably the elasticity problem is similar to the percolation evaluation of electrical conductivity'. The purpose of this paper is to quantify the quite rigorous physical analogy within the framework of the general attack of one-dimensional ('graph-like state') models.

More generally, the result of this quantification tends to reverse the usual view of the embedding lattice graphs (i.e. one-dimensional structures) in spaces of more than one dimension for treating amorphous systems. The view that *f*-functional polycondensation is a deficient model for treating critically branched materials, because it is a purely one-dimensional theory, is not acceptable in the light of experiment, as will be explained below; equally, the formulae based on integral transforms for two- or three-dimensional models (Stinchcombe 1973, 1974) for electrical conductivity are shown to fit computer experiments (Kirkpatrick 1973) no better than the much simpler one-dimensional formulae, based on combinatorial algebra, and 'classical' rescaling. As exemplified throughout this series, we regard the use of an embedding

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space as a part of certain models, but not as an *a priori* part of the reality the models attempt to fit. Mackenzie (1976) was surely right in suggesting that discrimination between models using continuum and discrete space lies in experimental work.

The elastic modulus of a polycondensate gel is very satisfactorily assumed by the model to be proportional to the number of Scanlan–Case (Scanlan 1960, Case 1960) elastically active network chains (EANC). An EANC is defined as a chain segment lying between two active branch points. An active branch point is one from which at least three independent paths can be traced to infinity on the infinite Cayley tree (Bethe lattice graph). One of these paths always goes from the branch point along the EANC itself; the others—at least two in number—radiate *outwards* to infinity.

The randomly branching electrical model likewise should assume that conductivity is proportional to the number of 'EANC' defined in terms of the graph in the same way. This is readily seen by imagining the graph embedded in three-dimensional space, though the calculation of the number of EANC itself takes no cognisance of this embedding. Thus the number of EANC of the embedded random network crossing (an odd number of times) a cross section of a unit cube is proportional to the number of EANC in the cube. Each EANC crossing the cross section carries a finite current in parallel across the section. This is because the statistical theory of branching processes (cf Dobson and Gordon 1965) shows that if a point is connected by at least two non-overlapping outward paths to the surface of the specimen, there will be (with overwhelming probability) a great multitude of further connections to the relevant end face of the cube, as these paths branch out into more (partly overlapping ones).

The Dobson–Gordon (1965) method enables the calculation of the number N_e of EANC per repeat unit (i.e. per vertex of the lattice graph) to be made, using the concept of the tie generating function. The result obtained is given as equation (2):

$$N_e = 3\alpha(1-v)^2(1-\beta)/2, \tag{2}$$

where α is the conversion parameter, v is the extinction probability (the probability that a link chosen at random in the statistical forest leads, in one chosen direction to a finite sub-tree)—and is given as the lowest positive root of

$$v = (1-\alpha+\alpha v)^{f-1} \tag{3}$$

and

$$\beta \equiv (f-1)\alpha v/(1-\alpha+\alpha v). \tag{4}$$

This result has been tested experimentally against data in a number of weak gel networks, and shown to give good agreement (Gordon and Ross-Murphy 1975). The treatment as given above is for tree-like networks only (absence of cycles)—but recent work shows that by appropriate rescaling it can give good agreement even in the presence of cycles. The rescaling strategy adopted is widely applied (Dušek *et al* 1978, Dušek and Vojta 1977). Let α_c' be the observed critical value of α and α_c that predicted from the condition of equation (1) (generally $\alpha_c' > \alpha_c$), then we rescale in terms of the derived variable α/α_c', and assume the results for this new variable are the same as predicted theoretically in terms of the variable α/α_c (Dušek *et al* 1978).

Figures 1(*a*) and (*b*) present competitive fittings of well known computer data by Kirkpatrick (1973) on the relative conductivity of random resistor networks against the fraction α of resistors present.

The comparison is between the calculations of Stinchcombe (1973) (curve A), using his integral transform equations (7) and (8), and equation (5) of this paper

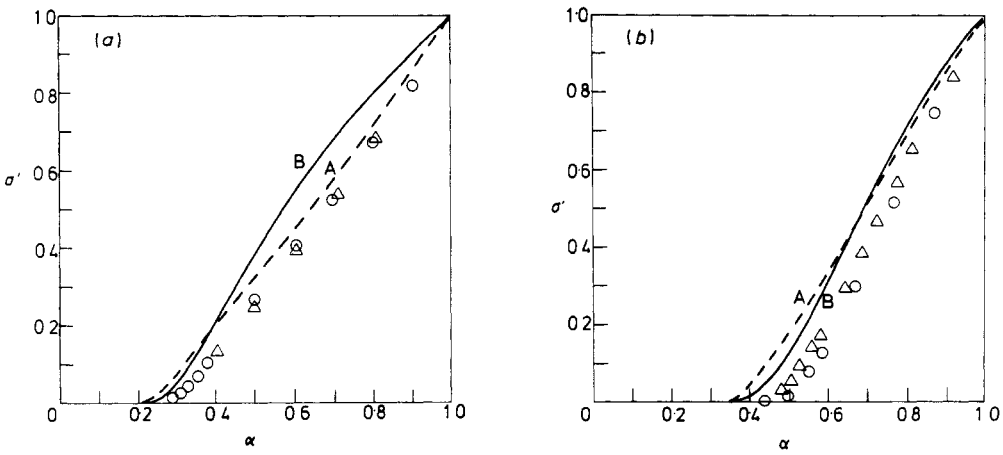

Figure 1. Kirkpatrick's Monte Carlo data for relative conductivity σ' in a random resistor network on: (*a*) a cubic lattice; and (*b*) a square lattice; plotted against α the degree of conversion. Δ and ○: see Kirkpatrick (1973) for details. Broken curve, calculation of Stinchcombe (1973); full curve, calculated from equation (5).

denoted by curve B. Figure 1(*a*) shows the results for a cubic lattice, figure 1(*b*) for the square lattice, and figures 2(*a*) and (*b*) respectively show the improvement in fit on rescaling. These correspond to Stinchcombe's figures 2 and 3. The rescaled discrete graph-like state calculation gives better fits than the unscaled integral transform calculation which attempts to cope with the effects of embedding in two or three dimensions. In fact, the results suggest that the coordination number of the lattice graphs, rather than the dimensionality of the assumed embedding space, dominates the shapes of these curves. For discussion of the relative effects on various physical theories of assumed coordination numbers and assumed dimensionality, see e.g. Domb and Sykes (1961) and Gordon *et al* (1976). (Note that the maximum value of N_e per repeat unit is (Dobson and Gordon 1965) 3/2, as found by substituting $\alpha = 1$,

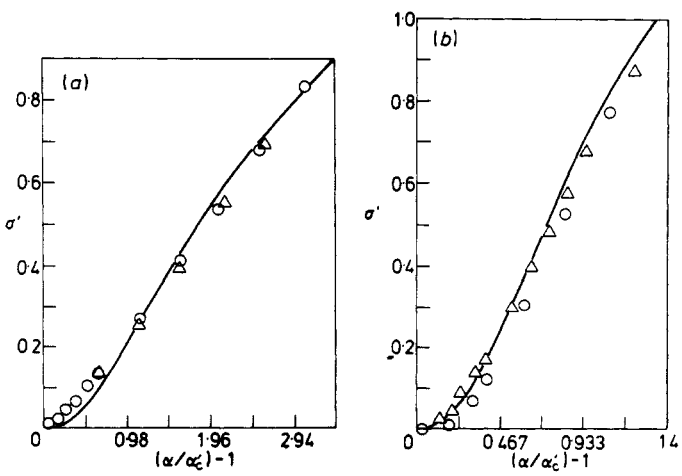

Figure 2. As figure 1 except that σ' is plotted against $(\alpha/\alpha_c')-1$. The critical conversion α_c' was taken to be 0·255 and 0·43 on the cubic and square lattices respectively.

and thus $v = 0$, in equations (2) and (4).) In the conductivity analogue, the maximum value of σ', the relative conductivity, is defined to be unity. We therefore write

$$\sigma' = \alpha(1-v)^2(1-\beta) \tag{5}$$

where v and β are calculated as before from equations (3) and (4).

Even if the results of the integral transform approximation were also rescaled, no worthwhile improvement in fit over the much simpler combinatorial approach (exact for the regular Bethe lattice graph) would result. We also note that Stinchcombe's figure 1 calculates probabilities relating to an unembedded graph (exactly equivalent to sol and gel fractions in condensation theories (Flory 1941)). The sol fraction curve (i.e. Stinchcombe's $R(p)$), with $z = 3$, has been shown to fit admirably the thermal coagulation behaviour of milk (Dalgleish and Parker 1977).

Stauffer (1976) has argued that classical calculations, i.e. from unembedded graphs, by Covas *et al* (1974) of the size of the largest molecule in a critically branched finite polycondensate sample, were incorrect by a factor of about 200. His argument is based on the assumption that such materials can be treated in terms of repeat units fixed at lattice sites in three dimensions, with the large bias in favour of cyclisation reactions which this entails. The need for monomers in dilute solutions to move about in order to collide is regarded as a complication from his viewpoint. However, the physical facts of rubber elasticity reveal the great mobility of the segments of a network, and chemical reactions in gels have been experimentally shown (Gordon and Roe 1956) to proceed with collision rates requisite for the law of mass action to apply, rather than to become diffusion controlled in their rate behaviour. Only if both colliding partners exceed a large critical size, will diffusion control prevail, although this still means that the reactants are moving. The growth of polycondensate molecules in critically branched materials is largely mediated by collisions in which one partner is quite small. It is not, therefore, surprising that critical exponents derived from scaling theories based on multi-dimensional continua have not, to our knowledge, been verified by gelation experiments.

At the same time, constant progress is being made in refining models based on scaling regular lattices, e.g. by Young and Wallace at Oxford. We are grateful to a referee for pointing out that for such models the critical exponent is now known to be of order 1·7 (cf Stauffer 1976). Since the exponents are valid only very close to the critical point (cf figure 2(*b*) where the critical exponent is 3), an experimental discrimination by conductivity measurements is a challenging task.

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