

SCRUTINY OF THE CRITICAL EXPONENT PARADIGM, AS EXEMPLIFIED BY GELATION

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ABSTRACT

The conflict between classical and modern theories of criticality is resolved by recognising that both theories work with approximate models, whose relative merits can be assessed by their response to efforts to refine them. Contrary to many claims, critical exponents are not tools fitted to discriminate between different models. True, Riemannian theory which characterises analytic functions in terms of their singularities, can be mapped into experimentally measured functions, that have finite ranges, finite errors, and replace singularities by rounded corners. Under the mapping, the uniqueness of series expansions is not preserved. Weierstrassian theory shows that a single infinite series is mapped into a non-denumerable set of series, each with a finite number of terms, which are equivalent in fitting experimental functions uniformly within any ϵ however small, and whose leading exponents x range over $-\infty < x < +\infty$. From the statistical viewpoint this means that tests for or against a theory, by a null-hypothesis based on the critical exponent, fail because this parameter is not identifiable, or (in other variants of the test) inconsistently estimated, or lacking in robustness.

We illustrate these principles by reference to gelation data in the literature, and exemplify the refinement processes envisaged by classical and modern theories. Modern theories aim to discover universal features, working outward from the critical point by addition of successively larger corrections to the Hamiltonian or free energy. Classical theory works inward towards the critical point by adding successively smaller corrections, and with due regard to system-specific features. The classical gelation theory of Flory and Stockmayer has long since been refined in this way in respect of cycle formation and substituent effects and fits some good data almost within experimental error. The parameters of the refined theories, used in such fittings, are available from measurements independent of gelation.

1. INTRODUCTION

A theory may be wrong, in a weak sense, like Newtonian mechanics, in that it requires refinement to eliminate hidden or overt approximations. A theory may be wrong, in a strong sense, like Phlogiston, by starting from wrong concepts. The founders of our classical mean field theories for gelation (Refs. 1,2), phase equilibrium (Refs. 3,4), swelling (Ref. 5), etc. emphasised from the beginning the overt simplifying approximations they had made. For more than thirty years, they and their followers have laboured to secure progressive refinements by the interplay of theory with experiment. Thus the classical mean field theories have been known to be wrong in the weak sense from their inception.

The rise of a new paradigm, the critical exponent (Ref. 6), has been instrumental in suggesting that the mean field theories are, for important purposes, wrong in the strong sense, namely beyond redemption by any process of refinement.

The resulting strong divergence of opinions on a purely scientific topic, between protagonists for the modern paradigm and the 'classicists' adhering to the mean-field-approximation paradigm, may seem surprising. In an earlier generation, outstanding theoreticians made outstanding contributions to both paradigms. In particular, Landau (7) formulated a general mean-field approach to criticality, while Onsager (8) gave great impetus to modern theory by his solution, which still provides the main reference point, of the Ising model for a two-dimensional lattice graph. These fore-runners cannot be held

responsible for whatever confusion now exists.

The discord between classicists and modernists conceals different conceptions of the criteria for testing and refining a model. Such methodology may appear to be a meta-scientific subject, in which exercise of opposing options is perhaps not surprising and even has heuristic value. Nevertheless, a review of the controversial field of gelation in network-forming polymers, including some principles of mathematical analysis, statistical inference, and physical model-building, may be helpful. The main conclusion we reach is that critical exponents cannot be suitable instruments for discriminating absolutely between rival physical models, however large the difference in the exponents which characterise these models *mathematically*. Classical and modern theories are both useful as approximations. They are testable, not by exponents, but by their response to refinement. Classical gelation theory has a long history, and has proved its power of refinability to accommodate highly system-specific effects, especially ring-formation. Such effects can cause deviations from the crude initial approximation theory of the 1940's, and can be made large or almost vanishingly small, in accordance with quantitative prediction, by varying the chemical structure of the system. The modern theories of Ising or lattice percolation models, of the phenomenological scaling theories (Ref. 9) or the more microscopic renormalisation group approach (Ref. 10), can also be refined as we exemplify in figs. 2 and 8. If this turns out to be more convenient or more powerful than the classical approach via refinement of the model of percolation on a Caley tree, then the classical theories will fall into disuse.

1.1 The two directions of refining critical models

Classical theory aims at progressive refinements by moving inwards towards criticality, while modern theories work outwards from a critical singularity. For theories which start from the classical Flory-Huggins model, this was recently illustrated (Ref. 11). In rubber elasticity, early classical theory was aimed at substantial degrees of cross-linking, but through chain-end corrections at first (Ref. 12) and then through the definition of elastically active network chains (Refs. 13,14,15), applicability of the classical model was extended towards the critical (gel) point. The present stage of this process will be illustrated below in figs. 5 and 7. For modern theory, on the other hand, the opposite direction of refinement is quite evident, since the critical exponent is an asymptotic quantity, strictly valid for a mathematical model at the critical point only, i.e. at minus infinity in a conventional log-log plot. As Stanley (6) points out: "It is important to stress that the relation $f(\epsilon) \sim Ae^\lambda$ does not imply the relation

$$f(\epsilon) = Ae^x, \quad x=\lambda, \quad [3.3]$$

although of course the converse is true...in general we find that there are correction terms, and eq. [3.3] is replaced by

$$f(\epsilon) = Ae^x(1+Be^y + \dots), \quad y > 0 \quad [3.4]'$$

Stanley sums up the rationale of modern 'out-going' procedures thus: 'We may rightly question why we should focus on a quantity such as the critical-point exponent, which contains considerably less information than the complete functional form. The answer seems to lie in the experimental fact that sufficiently near the critical point the behaviour of the leading term dominates. Therefore log-log plots of experimental data display straight-line behaviour sufficiently near the critical point, and hence the critical point exponent is easily determined as the slope of the straight-line region. Hence critical point exponents are measurable while the complete function may not be...'. This is a fair and cautious summary of views often accepted less questioningly. Although we present an analysis which overturns these conclusions, and which challenges the critical-exponent paradigm altogether, it leaves untouched the role of the exponent in characterising an analytic function, and the basic role of Ising-type and similar theories in physics. Indeed we present a case for the claims that the exponent deduced from an *experimental* log-log plot does not reflect the dominance of the leading term in series (1), and that the whole function may be measurable while the critical exponent in isolation is not.

For the analysis of Stanley's eq. [3.4] just cited, we specialise the series appropriately with minor change in notation:

$$f(\epsilon) = A\epsilon^x(1+a_1\epsilon^y + a_2\epsilon^{2y}\dots), \quad y > 0 \quad (1)$$

Before giving the more technical details, we summarise in section 2 qualitatively the obstacles which the analysis brings to light against the use of measured exponents in refining theoretical models and discriminating between their merits. The qualitative summary should enable experimentalists to skip the technicalities in the subsequent section 3. Experimentalists are likely to be familiar already with the vagaries of double-logarithmic plots, and in any case we shall illustrate the obstacles to the application of exponents with practical examples of data, taken from network theories of gelation, in section 5.

2. QUALITATIVE CRITIQUE OF CRITICAL EXPONENTS AND OF THEIR ESTIMATION FROM RELEVANT LOG-LOG PLOTS

The main argument emerges by looking in more detail at the series expansion in eq. 1. Classical and modern theories can describe the critical region by series of this general form. Undoubtedly the critical exponent x is the most important parameter of such an expansion about the critical point from the standpoint of the mathematics of the assumed model. Besides, x is often different for classical and modern models. The idea of treating the expansion as test functions for comparison of different models has been widely canvassed.

Unfortunately, it has emerged that even when we give arbitrary values to x (finite but arbitrarily large, positive or negative) the series (1) can still fit with any desired precision, over any desired finite range of ϵ , both any given continuous curve and any finite set of data. And in practice, this means that if such a series is used as test function, then all theories are compatible with each other and with all data. The reader may object that in this age of computers, a good theory may predict not only the exponent x but also y and perhaps the first 101 coefficients A, a_1, \dots, a_{100} , say. Alas, the conclusions are totally unaffected: all theories are still compatible with each other and with all data, even if they differ in x and y and the first 101 coefficients (or any finite number of coefficients, however large!).

It is a simple corollary, that even if we fix, say, any 101 coefficients and x and y , the adjustment of parameters in the remaining tail of the series suffices to fit data in a log-log plot by a curve which, over as many decades as desired, remains as close to a straight line as we wish to specify. These difficulties remain until a bound can be found for the remainder of the series.

There are serious additional disadvantages for a series such as eq. 1 to be used as a test function for discriminating between models by appeal to data. Statisticians have technical terms for two of these snags: the parameter x , i.e. the critical exponent on which so much hinges, is inconsistently estimated, or not robust, or unidentifiable.

A word of reassurance is in order. Of course, theories *can* be compared and refined, and test functions exist which have been shown to be suitable for this purpose. Also, distinguished experimentalists have produced log-log plots with their data which show impressive linearity over several decades. These are valuable (though more useful plots are available). However, conclusions drawn from them in the past need cautious reinterpretation, especially when the plots have been said to *disprove* some theory; or when it has been assumed that the slope is equal or close to the value of x of that series, theoretically uniquely defined with all its parameters, which would be approached using sufficiently accurate measurements (in the thermodynamic limit ($V \rightarrow \infty$)). This is shown to be most unlikely in practice, since in the experimentally elusive limit of criticality and infinite volume, the Ising model and reality must part company in many ways which may leave the experimentalist unperturbed.

3. THE TECHNICAL CASE AGAINST EXPONENTS IN THE TESTING AND REFINING OF PHYSICAL MODELS

3.1 The untruncated series of eq.(1)

When in eq.(1) the exponents x and y , and the parameters a_i ($i=1,2,\dots$) are calculable from a model, and if the series is convergent, no serious trouble is foreseen. This is already the case in many classical theories, where indeed the series can often be summed into closed form. In most such cases, as illustrated in figs. 4 and 8, the leading term is far from dominating the

total function when fitted to data over present-day ranges available. Unfortunately, only few coefficients are known for most modern theories, and our case concerns the situation where no bound can be assigned to the remainder of the series.

The Weierstrass theorem on uniform convergence of polynomials, which we used in our recent paper on critical and uncritical exponents (Ref. 16), can be readily generalised thus:

Proposition. For any arbitrarily given x in the range $-\infty < x < +\infty$ and $y > 0$ there exists a function

$$f(\epsilon; A, a_1, a_2, \dots, a_r; x, y) = A\epsilon^x (1 + a_1\epsilon^y + a_2\epsilon^{2y} + \dots + a_r\epsilon^{ry}), \quad (r < \infty) \quad (2)$$

which fits any continuous curve $\phi = \phi(\epsilon)$ or any given finite set of data $(\phi_{\text{exp}}, \epsilon_{\text{exp}})$ within any given error bound (however small) over the whole of any *closed* range (however large) in ϵ .

The changes in the usual proofs of the Weierstrass theorem are very minor, since the main requirement of the functions f defined, that they should form an algebra closed under addition and multiplication, is true as it is for polynomials. As a consequence of the proposition, there exists for any critical exponent x such a function whose plot of $\log f$ against $\log \epsilon$ lies as close as desired throughout any closed range (however large) to any given *straight line*. The slope x^* , say, with $x^* \neq x$, of such a line, extending over more than one decade (say) of values of ϵ , was called an '*uncritical exponent*' by us. For a practical case of an uncritical exponent in fitting data to a closed-form theoretical function see Irvine and Gordon (11a, 11b).

To extend the proposition to the case of matching $\phi(\epsilon)$ or $(\phi_{\text{exp}}, \epsilon_{\text{exp}})$, when in addition to the arbitrary assignment of x ($-\infty < x < +\infty$) and of $y > 0$, also A and a_1, a_2, \dots, a_k ($k < \infty$) are to be assigned arbitrarily, requires merely to note that:

$$A\epsilon^x (1 + a_1\epsilon^y + \dots) = A\epsilon^{x - (k+1)y} (\epsilon^{(k+1)y} + a_1\epsilon^{(k+2)y} + \dots) \quad (3)$$

Stanley, in the passage quoted, assigned to the exponent "considerably less information" than to the function as whole. We see that, *in the absence of a bound on the remainder*, the proposition deprives the leading exponent of any information whatever concerning the experimental data to which the whole function has been fitted, or even a function f truncated after a sufficient number of its terms. Any exponent ($-\infty < x < +\infty$) can be equally well fitted to given data by some such "*polynomial*", with arbitrary y, A, a_1, \dots, a_k . The notion, widely canvassed in the literature, that experimental data differ *qualitatively* from predictions of certain theories, is untenable, because it was based on the assumption that any terminal good straight-line segment found must reflect the asymptotic slope due to the leading term $A\epsilon^x$ in the model.

3.2 The truncated series (eq. [3.3] of Stanley)

We have just seen that the untruncated series of eq. (1) is compatible with all possible data for all possible critical exponents. Even the truncated series, with $r \sim 2$, in eq. (2) is likely to fit data within experimental error using any reasonable exponent (cf. fig. 8). Recently, truncation right down to $r=0$ has come into favour, i.e. equation [3.3] of Stanley, against his explicit warning. In what follows we treat the *models* constituted by all truncated variants of eq. 2. This means turning from mathematics to physics and statistics. We shall aim at proving that the truncated series constitutes a new model, which, in a strictly defined sense (section 3.4) is *incompatible* with the modern theories such as the Ising model.

3.3 The physics of criticality

The testing of models is the main concern of the physicist. On approaching the critical point, an ever closer balance is established between the inter-particle potentials taken into account in the mathematical models constructed to simulate the physics. As is well known, the gravitational potential then becomes significant in liquid/gas criticality; chain-end and polydispersity effects in polymer phase equilibria, and higher anharmonic terms in the thermal expansion of magnets are among the untold examples of *disturbances* (Ref. 16) which become significant. Specifically, at spinodal points, the Hessian of the free energy G vanishes in composition space (W. Gibbs). This implies that the G -landscape becomes very flat and signals the vanishing of restoring forces for

displacements from equilibrium as manifested by the macroscopically observed fluctuations. One disturbance, that due to the surface (or wall) effect, is present in all critical phenomena. For gelation, these effects due to finiteness of physical systems were calculated roughly by Covas et al. (17), and treated with combinatorial exactness by Donaghue and Gibbs (18), and Burchard and Nerger (19) seem to have detected the expected effect of finiteness experimentally. (In 1965, Fisher (20) rightly stated that the required accuracy was 'way beyond the possibilities of most experiments'). Perhaps in principle all disturbances can be included in a theoretical model, but they certainly have not been included in models so far tested. Accordingly, Stanley's claim cited above, of an '*experimental* fact that sufficiently near the critical point the behaviour of the leading term dominates' (our emphasis) is not acceptable. It is a weakness of all present models that we are not sure exactly how close to criticality they *lose* their validity; and this invalidates the choice of the critical exponent as a consistent test parameter, as we shall see.

3.4 The statistics of criticality

The testing of models is the main concern of the statistician. Typically he defines a model as a family of functions, viz. as a function containing one or more parameters (whose variation generates the family). A set of experiments are considered as samples from a population, and problems of convergence are paramount in statistical analysis. Experiments are regarded as subject to finite error E , which can be reduced in principle but without reaching zero. A model which fits data everywhere within the current E cannot be refined until E is reduced. We shall now define the notion of *compatibility* of two models. Though compatibility is weaker than mathematical equivalence of functions, equivalent models are not distinguishable by experiment as a matter of principle. Equivalence prevails when *uniform convergence* throughout the experimental range of a sequence of functions, belonging to the family defining the first model, leads to a limit curve not belonging to the first model but to the second model. This is precisely the situation in the proposition concerning $\phi(\epsilon)$ and a sequence of "polynomials" defined in eq.(2). Accordingly, the result derived in 3.1 from that proposition may be stated: all theories expressed in terms of a series of form of eq.(1), in the absence of at least a bound on the remainder, are compatible with each other. Modern or classical theories, so expressed, are compatible with all other theories, and the critical exponent is in the technical terminology of statistics, an *unidentifiable* parameter. Since singular and non-singular models can be *compatible* (though never mathematically equivalent) the implication (Ref. 10) of renormalisation group theory, that the Hamiltonian must have a singular term, is an axiom which cannot be tested experimentally.

It is readily seen now that if the series is truncated, it is not compatible with the so-called modern theories, but constitutes a new model. In other words, with sufficiently accurate (though not perfect data) the model of the untruncated series, when all its coefficients are finally calculated from the theory, can always be distinguished from the truncated-series model, even if its coefficients are freely adjusted.

Operations with the truncated-series model fall into two classes, according to whether we take the measurements directly to determine the exact location of the critical point, or whether we allow some adjustment of this location. Now a number of disturbances are known always to exist close to the critical point (see above), among which surface (or wall) effects are prominent; their contributions have been roughly estimated (Ref.20). If we consider the critical point given exactly and independently without adjustment, the only way in principle in which surface effects can enter the truncated-series model is by injecting a small term of exponent lower than that of real interest to theoreticians. This small term must vanish at $V=\infty$, the thermodynamic limit, which causes a jump in the critical exponent. Since the theory is based on the limit $V\rightarrow\infty$, while the physical system has $V<\infty$, the model estimate of the critical (leading) coefficient of the physical system is *not consistent*, to use the technical term (Refs. 21-23).

The inconsistency can be cured only at the expense of a *lack of robustness* (Ref. 22) of the parameter, by correctly allowing some adjustment in the location of the critical point. As has been noted by several investigators, but is not well enough heeded, a small change in the assumed location causes a large change in the slope of a log-log plot (see e.g. fig. 7). Thus by adjusting the critical point, we are indeed able to fit at will a classical or a modern exponent to the data in many cases. However, the lack of robust-

ness of the exponent is caused by its sensitivity not merely to the location of the critical point, but to the sundry other disturbances also. The contributions to G , which the models do take into account, come into balance as we approach criticality, so that physically it is not surprising that tiny contributions which are neglected in the model may cast their shadows on log-log plots into the experimental region far from the critical point. We describe the inbuilt mathematical mechanism of the ill-conditioning which reflects this physical effect, *to the detriment of the rate of convergence of the series.*

Mathematically, the inbuilt mechanism reflects a collusion between the leading term and a whole dominant packet of successive terms somewhere higher up in the series (eq.1) to simulate a linear log-log plot. The mathematics were exemplified using an exactly computable perturbation of a Flory-Huggins model for phase equilibrium in polymer solutions. There the minute leading term represented a disturbance with physical significance arising from second-neighbour effects. (The paper by Barber (24) on "Non-universality in the Ising Model" arising from second-neighbour disturbances should also be consulted here). In a typical case, the addition of the minute leading term caused the free energy to remain proportional, in the usual experimental range, to its undisturbed value to within 0.04%, but caused the *uncritical* exponent of the disturbed model to differ by about 25% from the *critical* exponent of the undisturbed model. The Ising model has a rapidly convergent series, as shown by Monte-Carlo studies. But a slightly perturbed Ising model might well have a much more slowly convergent series. For just such a transformation from rapid to slow convergence by virtue of a small perturbation, see the virial expansion of the chemical potential in section V.4 of reference (11).

The following typical effects ensue on letting the disturbance tend to zero ($a_0 \rightarrow 0$); where $a_0 \epsilon^{x^*}$ is the small term added on the right of eq.(1) ($x^* < x$).

- i) the theoretical curves $f=f(\epsilon)$ converge uniformly upon their unperturbed limit curve, in any finite range including the critical point.
- ii) the curves $\log f = \log f(\epsilon)$ do *not* converge uniformly upon their limit curve, because the critical point $(-\infty, -\infty)$ belongs to no closed interval.
- iii) the centre of the packet of dominant terms travels forward, from terms of higher powers, to converge upon the single leading term of the unperturbed limit curve.
- iv) the *uncritical* exponent of the log-log plot just mentioned, i.e. the extensive near-linear portion, converges rather slowly on the *critical* exponent of the limit curve, and
- v) the true critical exponent of the perturbed series remains constant up to the limit and then *jumps* to a new value discontinuously at the limit.

We summarise our conclusions on the significance of this section 3 in the Discussion (section 6).

4. GEL POINT LOCI IN THE LITERATURE AND THE REFINEMENT OF THE CLASSICAL MODEL

The classical Flory-Stockmayer theory made two approximations, equireactivity, i.e. absence of substituent effects, and absence of cyclisation through intermolecular reactions. Efforts to refine the model showed that both neglected effects are in practice of about equal import. Both can be measured independently of gelation experiments, and treated for such systems within the classical mean-field theory. Both can also, as foreseen by theory, be reduced to immeasurably small effects by spacing out the chemical linking-sites within the monomers, and cyclisation can be so reduced especially by choice of stiff monomers.

For classical theory, the first-shell (nearest neighbour) substitution effect or FSSE was developed in the framework of cascade theory (Ref.25). The chemical principles involved were generalisations of those already developed for non-gelling systems in biochemistry by Pauling (26) and for micromolecules by Bjerrum (27). Cyclisation in gelling systems was analogously treated by generalising the Jacobson-Stockmayer theory of 1950 for linear systems, in work by several schools, including Kilb (28), Dušek and co-workers (29), and Stepto and co-workers (30). The underlying Gaussian statistics of sub-chains are intended to reflect, as in rubber elasticity theory, their great mobility. The high precision with which Gaussian statistics are applicable to cycle formation was documented in the elegant labour of Semlyen's group (31).

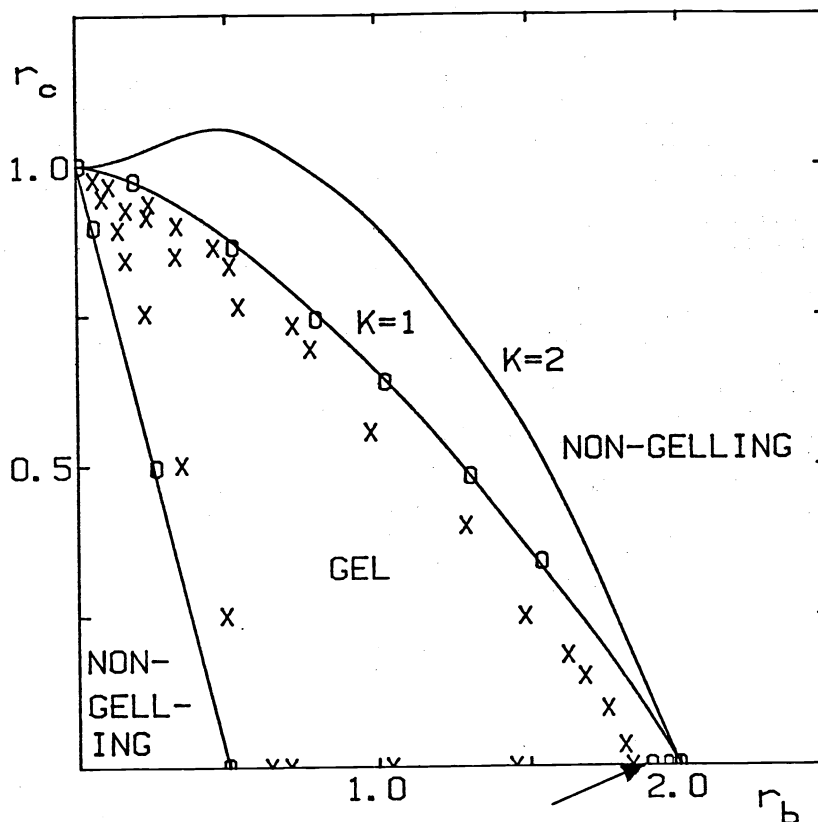


Fig. 1 Phase diagram for the system AA/TMBu/BG by Tang Ao-qing et al. (33).

These statistics were incorporated appropriately in the classical tree percolation model, as generalised in the so-called *spanning-tree approximation* (Ref.25) to intramolecular reaction. The resulting theory was verified on several gelling systems without significant adjustment of parameters which were secured independently both by measuring chemical rates and by calculation of relevant conformational statistics. By 1972, it could be claimed (Ref. 32) that 'the approximation is excellent, and that the ring-chain competition problem is solved by the spanning-tree approximation for all but the most searching enquiries'.

4.1 Gel point loci and the classical pure tree-percolation model

In several industries, the mapping of gel point loci by special instruments has become a practical tool. It is fitting to begin our review with a recent academic study by Tang Ao-qing and co-workers (33) on polyfunctional condensates of adipic acid (AA), trimethylol butane (TMBu) and butylene glycol (BG), which are 'of practical significance for the study of the curing process and choice of processing conditions for thermosetting resins...'. Fig. 1 illustrates with their phase diagram the sensitivity of the classical theory to the assumption of equireactivity. Modern theories are not available for the lines in their diagram. The abscissa r_b denotes the stoichiometric ratio of TMBu hydroxyls, and the ordinate r_c that of BG hydroxyls, to AA carboxyls. The parameter K denotes the ratio of rate constants of TMBu hydroxyls and BG hydroxyls for esterification. The upper boundary curve of the gel-forming region is seen to lie close to the value $K=1$ corresponding to the unamended classical theory. With the amendment $K=2$, their calculated curve is seen to fall wide of the data, even though the implied change in relative activation free energy is merely about 2.5 kJ mol⁻¹. The equireactivity postulate is thus confirmed for this reaction with a precision that must be the envy of kineticists working with reactions which are much simpler, but which lack a critical point. The authors remark, however, that the two experimental points indicated by an arrow, manifesting the observation of ungelable samples just inside the calculated gel region, probably reflect a deviation from the independent approximation which neglects cyclisation in the unamended scheme. Indeed a

small positive FSSE in TMBu is to be expected, similar to that in pentaerythritol (PE) described below, and that observed in trimethylol ethane (Ref.34). This would in part counteract the cyclisation effect, as in fig. 2 below, and thus contribute, but only to a minor extent, to the quite excellent fit in fig. 1. However, on the evidence of fig. 2, technologists would be right to resist the argument that classical gelation theory is *basically* wrong.

4.2 Classical and modern gel points as guides to model refinement

The work of several researchers in our group was carried out in the 60's and was reviewed, e.g. in 1971 in the Journal fuer praktische Chemie (35). Fig. 2 up-dates one from that review by including the broken line A, calculated by

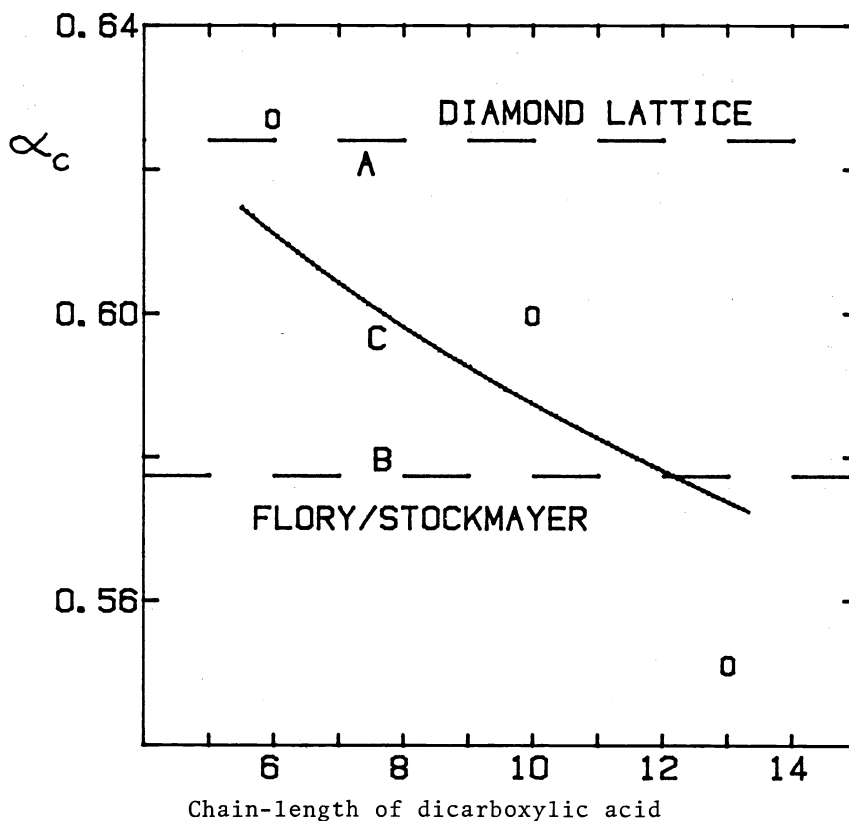


Fig. 2 Gel points of three polyesters. This figure compares two unrefined theories (A and B) with a refined theory (C) allowing for system-specific extent of cyclisation and substitution effects.

adapting the best modern lattice-percolation result available, for comparison with the original Flory-Stockmayer classical tree-percolation result (line B), and its amendment for both FSSE and by the spanning-tree approximation for cyclisation (line C). The best individual fit to any one system is clearly that of the modern theory A to the AA/PE gel point. The line A was derived by placing the units of PE on the sites of a diamond lattice, which most closely mimic the conformations of carbon chains. For this lattice, various estimates for α_c are given by Essam (36) and 0.39 is a reasonable average value.

However, two ester-bonds require to be located between any two lattice points. This rigorously modifies the result to $\alpha_c = (0.39)^{1/2} = 0.624$, since no FSSE has been clearly detected for the carboxyls of the intervening AA unit (Ref.34). For an analogous reason, the classical tree-percolation (line B) gives not 3^{-1} , but $3^{-1/2} = 0.577$. The line B corresponds to this constant value and represents the unrefined classical tree-like model. The line C, for the refined tree-model copes well with the system-specific variations within the set of three

points, bearing in mind the large scale of the ordinates. These points summarise much labour (Ref. 37); e.g., the middle point (sebacic acid) averages ten measurements at four temperatures to give $\alpha_c=0.5988$ with standard deviation 0.0045.

- i) The ring-closure parameter λ was found from chemical rate measurements, and confirmed from calculation based on the appropriate random-flight chain, subject to the constraint of the appropriate bond angles. The parameter then allows the calculation of the -OH groups converted into intra-molecular bonds at the gel point, expressed as a fraction σ_c of the total number of -OH groups. This gave for the PE hydroxyls; 0.0501 with AA, 0.0425 with sebacic acid (SA), and 0.0307 with tridecanoic acid (TDA). Below we review a system for which α_c is about 0.018.
- ii) The FSSE parameter N , measuring the factor by which the rate constant of esterification of an -OH increases for each -OH previously esterified on the same PE monomer, was found from chemical rate measurements on the same systems, and in good agreement on the mono-functional model system lauric acid/PE (Ref.38), and again, independently, from the product analysis by GPC of that model system (Ref.39). The parameter $N=1.4\pm 0.1$ for all these methods was tentatively attributed to intramolecular H-bonding in the unesterified (or singly or doubly esterified) PE monomer. The value $N=1.4$ represents a decrease of only about 0.7 kJ mol⁻¹ in the free energy of activation for each α -methylol already esterified.

Fig. 2 deals with mathematically and statistically sound tests of three theories, not against critical exponents, but against gel points which can be trusted to reflect theoretical quantities calculable from the models. The unrefined classical model (line B) fits about equally well as the unrefined modern model (line A). The refinement of the much older classical theory, to yield the improved fit of line C, throws some light on the pathway for refining the modern theory, which is of course equally capable of refinement. The highly system-specific ring-closure and substitution effect, both measurable independently of gelation experiments, are seen to dominate the refinement process. No limit is foreseeable for the reduction of ring-closures by spacing out the functionalities, or indeed by stiffening the monomer structures (see below). Any hope of sharply discriminating between classical tree-like and modern diamond-like models for the particles are, therefore, foredoomed to failure. To base the discrimination on critical exponents would founder, not only on the difficulties already detailed for the general case, but also because any hope of 'universality' of exponents is here dashed by the highly system-dependent degree of cycle formation σ_c reached at the gel point. Stepto and his group have shown (Ref.30) how accurately σ_c can be measured independently of any gelation theory, using a combination of measurements of freezing-point depression and chemical assay.

5. EXPERIMENTAL SCRUTINY OF EXPONENTS

5.1 The exponent β in gelation

Fig. 3 is by Parker and Dalgleish (40), showing the relationship between the theory of branching processes and the heat-coagulation of milk. Their curve of the 'classical' theory is drawn on the assumption of exact second-order kinetics with respect to functionalities. Brauner (41) urged experimentalists to present their data as log-log plots. He transformed fig. 3 accordingly as part of a survey of gelation data aimed at deciding between classical and modern theories on the basis of exponents. His policy was to accept, in cases like fig. 3, the critical point deduced from extrapolation of the plot provided by the original authors. However, Parker and Dalgleish would hardly feel committed to that location to within a tolerance appreciably less than the accuracy of their actual measurements (as deducible, e.g. from the scatter about the theoretical curve). One could not demonstrate more strikingly the lack of robustness of the critical exponent as a statistical parameter than by replotting on a log-log scale. Thus fig. 4 gives the conventional log-log plot for two different assumed values of t_c . For the crosses, the value of t_c taken was the same as in fig. 3. The straight line drawn is an unweighted linear regression line and has a slope of 0.45, close to the theoretical lattice percolation value of 0.39, and slightly different from the value 0.54 calculated by Brauner using the same method for the same data. (The difference must be due to the sensitivity of reading points near the critical point off a graph). The points styled O represent a decrease of 1.75 per cent in the value of t_c . This adjustment is within the experimental error as is clear from the scatter in fig. 3, and indeed the first six experimental points after the gel point ($t/t_c=1$) mildly suggest such a shift

of t_c . The curve through the circles represents the 'classical' theory. Its slope at the point $(-\infty, -\infty)$ would be 1.0, which represents the classical critical exponent. The lack of practical significance of this exponent is apparent since the slope of the classical curve varies over the experimental range from about 0.9 to about 0.1, and this is adequately fitted to the data points. The classical theory is probably weakly wrong, as Parker and Dalgleish have suggested, especially in the precise values of the (properly averaged) functionality of the casein units. Clearly better data are required to refine the classical theory further. Taking its crude assumption at face value, the modern theory is seen to be weakly wrong also, since the rough averaging of the slope over the systematic deviations of the crosses gives 0.45 rather than 0.39. To be applied with confidence, however, a bound for the remainder of the series must be calculated, to confirm that (*unlike what happens in classical theory*), the leading term dominates the modern theory throughout the experimental range.

Parker and Dalgleish's work in fig. 3 is of interest to the Dairy Industry, because i) it explains convincingly as a single chemical process what was previously thought to be a composite effect involving a delay period, ii) it elucidated the order (and activation energy) of the chemical process involved. Even moderate degrees of cyclisation in the sol would measurably lower the apparent reaction order below the observed value of two. Since the three or so sites on a casein molecule are probably spaced out over intervals larger than those between the carboxyls in TDC (fig. 2), little cyclisation is expected in the sol. iii) Finally, a satisfactory model with an appropriate functionality of 3 in the Cayley-tree being available, 'the exact nature of the reactivity groups should be elucidated more easily' (Ref. 37). Neither of the two replottings in doubly logarithmic coordinates, shown in fig. 4, would have shed any light on these three practical concerns, and such plots are not, therefore, recommended. Note also that the log-log plot depends on accurate knowledge of the location of the gel-time, which is not required when using linear coordinates (fig. 3).

5.2 The exponent in rubber elasticity

Let $G'(0)$ denote Young's modulus, α the fractional conversion of cross-linking sites, and α_c its value at the gel point. The exponent t in the relation

$$G'(0) \sim ((\alpha/\alpha_c) - 1)^t \quad (4)$$

is predicted to be ~ 1.7 - 1.9 by scaling theory, and 3 by a classical theory, hailed as non-trivial by de Gennes (9). We review de Gennes' attempt to discriminate with a series *truncated after a single term* against classical, and in favour of scaling, theory using scattered data on the difficult, because weakly bonded, gelatin system. These data were presented (Ref. 42) by the original authors for purposes substantially less sensitive to experimental scatter than eq. 4, for which they are unsuitable. The modest purposes were (cf. ref. 43) the demonstration that a), the mere placement of the curve in the diagram gave support to the correct multiplicity of the helical cross-linking zones (triple helix), and b) the overall very rough fit of the scattered data was sufficient to suggest that molecular theories of rubber elasticity were generally relevant to weak gelatin gels of this type, a notion hardly yet considered at that time.

Fig. 5 includes the full data of 3 runs together with the line drawn in his text book by de Gennes to obtain 1.7 as the slope for the points (\odot) he selected from one run, and four points (\circ) from that run which he omitted. (He has handsomely apologised for this omission (Ref. 44)). The point seems to have been misplaced in de Gennes' figure from the higher position in the original plot, also shown here just above this triangle. We use this textbook example to illustrate the conclusion, which follows from our adaptation of Weierstrass's theorem, that the series (1) is not a test function that can discriminate between rival theories by reference to experimental data without a bound on the remainder of the series. We recall Stanley's remark that the exponent contains substantially less information than the whole function. The whole function is available for the classical theory and it shows that, *for that theory*, truncation is very far from justified in the experimental range. For the convenience of those who favour series expansions, Gordon and Ross-Murphy (43) published two expansions of classical formulae, of which the one for random cross-linking of long homodisperse chains is sufficiently relevant. From it we find:

$$t = d \ln G / d \ln (\alpha/\alpha_c - 1) = 3 - (22/7) (\alpha/\alpha_c - 1) \dots \quad (5)$$

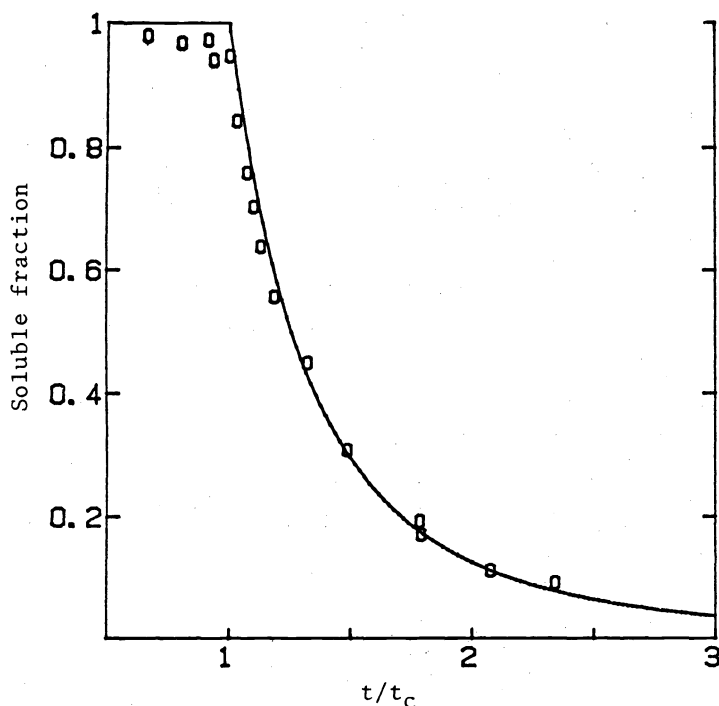


Fig. 3 Soluble fraction of milk as a function of relative heating time t/t_c . O, data of White and Davies, and White and Sweetsur (in Ref. 40). The kinked curve is the theoretical classical result for random trifunctional polycondensation.

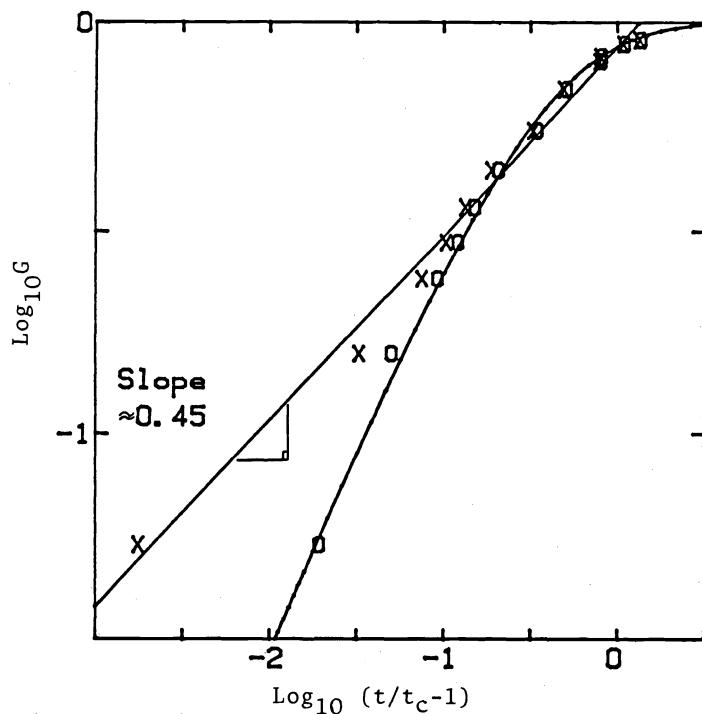


Fig. 4 Conventional critical-exponent plots for fig. 3 of $\log G$ (G =gel fraction = 1- soluble fraction) plotted against $\log (t/t_c - 1)$, for two different assumed values of t_c . X, linear regression with t_c taken as value used in fig. 3; O, the same data fitted to the classical curve by adjusting t_c downwards by 1.75 per cent of its value.

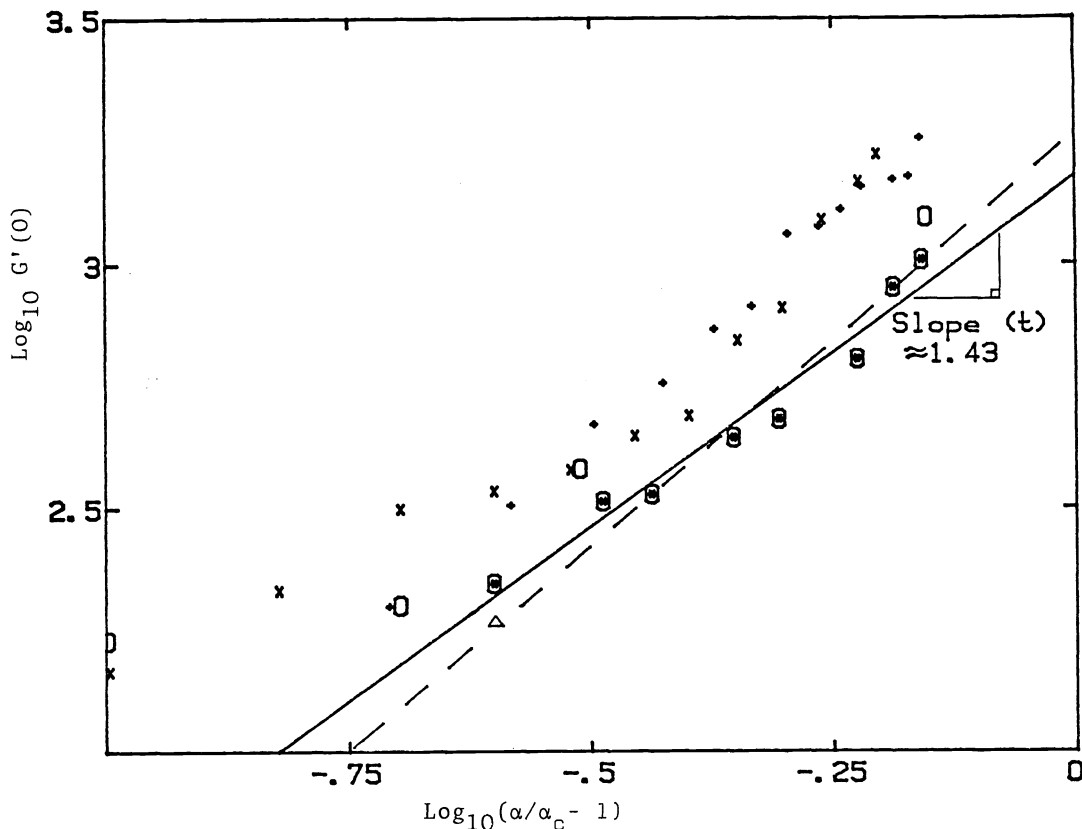


Fig. 5 Conventional critical-exponent plot for the data of Judd (see ref. 17) on the modulus ($E = G'(0)$) of three gelatin gels. \odot , points chosen by de Gennes (9) to estimate the slope as $t = 1.7$ (broken line), the left-most point \odot of Judd's data having accidentally been misplaced to the position of the triangle Δ . The solid line is a linear regression of the chosen data after correcting this misplacement.

Many terms of the series are required at the end of the experimental range, where $(\alpha/\alpha_c)-1=1$; *illicit* truncations at this point of the series give $t=3$ at the first term and $t=-0.14$ at the second term. Thus the slope of the chord drawn by de Gennes does not disprove the classical theory. The whole classical function is also plotted (fig. 6) to show that the predicted slope in the experimental range is variable, decreasing from about 2.5 to 2.2. It is, of course, sensitive to the assumed position of the gel point also, which is displaced in the top plot ($\alpha_c=1.025$) to show that the 'uncritical' exponent could be 2.33. Neither, of course, does it disprove the scaling theory, which we prefer, however, to fit successfully to the much better data on a well characterised system below.

5.3 A better test system: esterification of decamethylene glycol/benzene-1,3,5-triacetic acid

Fig. 7 shows five plots of the storage modulus $G'(\omega)$ as a function of frequency ($0.1 < \omega < 25 \text{ s}^{-1}$) for decamethylene glycol/benzene-1,3,5-triacetic acid (DMG/BTA) polyester condensates. Measured by Roberts using a Weissenberg Rheogoniometer, these results are taken from a recent paper (45). They confirm, with increased accuracy, earlier plots for the same system taken with a microsphere rheometer essentially at $\omega=0$, published in several reviews (Refs. 35, 47) and quoted as background for the gelatin work (Ref. 43) (cf. fig. 5). The system DMG/BTA has been carefully characterised by several chemical and physical methods. Its bulk-state esterification in stoichiometric mixtures has a

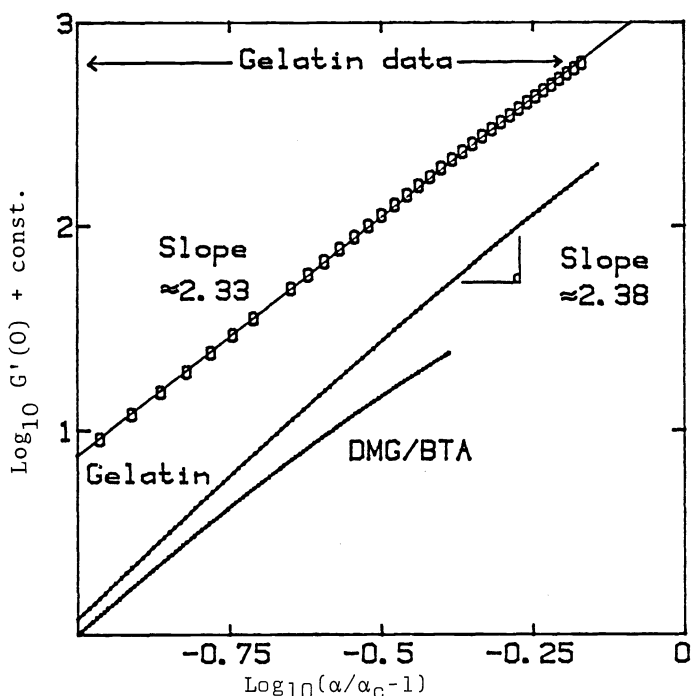


Fig.6 Classical theory ($\log G'(0)$ against $\log(\alpha/\alpha_c - 1)$) for different cross-linking mechanisms and different assumed gel points, in the range of the data ($1.1 < \alpha/\alpha_c < 1.7$) by Judd et al. (17) on gelatin (fig. 5). Polycondensation (bottom) and helix-formation (middle) give different degrees of curvature and positions. Top (displaced upward): "uncritical" exponent due to shift of gel point $\alpha_c = 1.025$. O, theoretical points, and regression line

fractional conversion of 0.722 ± 0.006 . The fraction of links formed intramolecularly up to the gel point is about 0.018. This reduction in degree of cyclisation in comparison with PE/TDA (0.0307, see above), despite the chain-length of DMG being lower than that of TDA, is due to the greater stiffness of BTA when compared with PE. This is shown both by calculations of the conformational statistics of the chains and by the case of self-etherification of 1:3:5 trimethylol benzene (TMB). This compound closely resembles BTA in structure. Although this self-etherification proceeds without a 'long-chain' component bearing widely-spaced functionalities like the carboxyls in TDA, the cyclisation degree is found to be so low as to lie between 0.01 and 0.02. The gel point was found to be 0.508 ± 0.006 by Temple (35,48), while the classical theory gives $1/2$, and the spanning-tree refinement raises this merely to 0.502.

The five curves in fig.7 were superposed by Kästner (49) using his elegant frequency-reduction theory, which also confirmed that the lowest curve ($0.1s^{-1}$) is an adequate approximation to $G'(0)$ as a function of time. The classical-theory curve drawn through the points adjusted (slightly) only one parameter, the front factor. Theoretical reasons were given to accept the value of unity as in Flory's early theory. The value chosen in fig.7 was 1.336 by way of optimising the fit. However, over the best 10 runs taken, the average front factor found by optimisation was 1.041 ± 0.157 , very close to Flory's early prediction. The gel point was also adjusted for optimal fit within the narrow visco-elastic range where viscometry and elastic measurements overlap, the critical conversion estimated by back-extrapolation of the modulus to zero being between 0.002 and 0.005 lower than the critical conversion estimated by forward extrapolation of the reciprocal low-shear viscosity to zero. Thus the bottom curve is after all a *practically parameter-less fit* of the classical tree-like theory.

We do not recommend the transformation to a log-log plot, which renders the experimental errors less uniform, spaces out experimental points in an undesirable way, and wrongly debases the front-factor. Nevertheless, we present the log-log plot in fig. 8 with a very satisfactory fitting to the modern theory of critical exponent 1.8. This illustrates that the modern theory (which is as yet equivalent to all possible data) could fit with essentially two parameters.

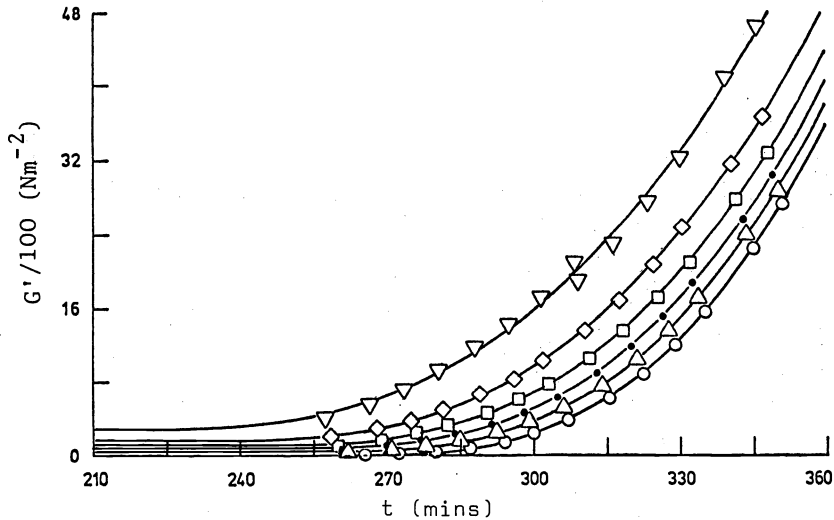


Fig. 7 $G'(\omega)$ against time for run 23 of Roberts and Gordon (46) on stoichiometric DMG/BTA. These data are in a range ($1.005 < \alpha/\alpha_c < 1.02$) much closer to the gel point than shown in fig. 6. Frequencies, from left to right $\omega = 25, \omega = 10, \omega = 5, \omega = 2.5, \omega = 1.0, \omega = 0.1$ Hz. The rightmost curve ($\omega = 0.1$ Hz) shows the classical theory, fitted by optimisation with respect to the front-factor (here $g = 1.38$, predicted (ref.46) $g = 1$).

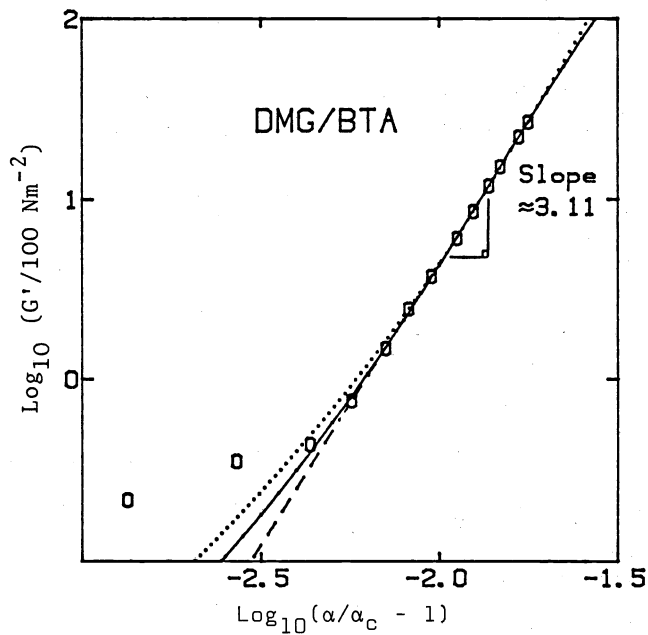


Fig. 8 Fit of the modern theory (eq. 1) to the low frequency data of Roberts (the circles in fig. 7), on stoichiometric DMG/BTA, using a critical exponent plot: $\log G'(0.1)$ against $\log(\alpha/\alpha_c - 1)$. The first three points show large deviations from the linear behaviour exhibited by the remaining points. This reflects the artificiality of log-log plots wherever absolute rather than percentage errors tend to be uniform, plus the finite-frequency effect, etc. Dotted line: $G'(0)/104 = 0.61939z^{1.8} + 4510.6z^{3.6}$, where $z = (\alpha/\alpha_c - 1)$. This implies that the second term contributes up to 5 times the amount of the first term, while in the expansion of the closed-form classical equation, fitted in fig. 7, the second term contributes a maximum of 5%. Continuous line: $G'/104 = 0.39418z^{1.8} + 5531.9z^{3.6} - 10.436 \cdot 10^7 z^{5.4}$.

6. DISCUSSION

We discuss first the status of classical and modern theories within the context of natural philosophy, and answer some fundamental and specific objections to the classical approach which have been put forward. This leads on to a brief statement for the claim that the response of models to refinement is a better guide to progress than selected acts of curve-fitting. Finally, we return to the case for treating log-log plots and their slopes as tools to be avoided wherever possible, and certainly tools unfitted to give a firm verdict for or against either the classical or the modern approach to critical phenomena.

A constructive philosophy views classical and modern theories not as qualitatively different and mutually exclusive, but as two methods of crudely averaging for a first approximation. Classical theory typically replaces the configurational phase integrals by random-flight or Gaussian-chain approximations, thereby exploiting the factorisation of multivariate integrals of that kind. Modern theories place the moving particles at fixed average positions, viz. at lattice points of an embedding space. There is no intrinsic reason why either approach should not be refined by higher approximations (cf. figs.2,8). Both methods of averaging have some theoretical appeal. The modern theorist can draw on the vast array of solid-state models which have served well for crystalline materials. The classicist may take comfort from the invariance principle (Ref.50), which sanctions the reduction of molecules moving in a three-dimensional embedding space with freely rotating inter-unit links, to the classical unembedded tree-graphs in terms of invariance to such reduction of the relevant ratios of symmetry numbers. It also seems that this reduction can be widely, and perhaps always, expressed as a degeneracy of the Riemann metric to a graph metric (Ref.51).

The modernists sometimes put their basic case more philosophically. They feel the advantage of starting from an *exact solution* of a well-defined model, the 2D Ising model, or a variant for which a very close approximation to the true exponent seems assured. If it did not fit the data, they would not wish to refine further a model whose exact first term was known to be wrong. This, in the modernist's view, is just the flaw in the process of refining a mean-field theory: the unrefined results of mean-field theories, even where they admittedly fit certain types of measurement, do so demonstrably by cancellation of large errors among the terms contributing to the mean-field solution (cf. the large numbers of terms in fig.6, see above). A superstructure erected on such foundation is a poor tabernacle for physics. The argument is persuasive. But is it really correct? The mean field is, of course, an average by definition. (The terms in its series expansion can very often be *summed!*). And a good model succeeds in averaging correctly, for some defined purpose, over some broad distribution. In other words, a large cancellation of errors is the mark of a good theory, not a flaw. But the theory will need refinement when we require it to fulfill more demanding purposes.

As a more specific objection to classical models, it has been thought that a tree-percolation model cannot in principle deal with cyclic structures. Electrical circuits also contain cycles, yet their properties are analysed in terms of the basic graph-theoretical notion of a *spanning-tree*. The success of the spanning-tree approximation, illustrated in dealing with the system-specific cycle formation in polymerisations, essentially parallels a model approach to the statistics inherent in certain epidemics put forward long ago by no less a statistician than Neyman (52).

Again, certain graph-models are rejected by modernists as being overcrowded in a three-dimensional embedding space. Especially, a *tree-like* gel of Flory-Stockmayer type acquires infinite packing density in such a space when the atoms are assigned a volume. This Malthusian Packing Paradox has been resolved (Ref. 43). Essentially the resolution depends on the fact that, for the purpose of physical theories, a formal accountancy procedure simplifies the calculations by classifying large ring closures in a gel as if they occurred intermolecularly, thus generating the overcrowded tree structure as a convenient and useful picture.

6.1 Refinement versus fit

The notions of "correct" or "wrong" theory cannot rest on the quality of fit of a crude first approximation. After all, melts of adipic acid and PE do not fix their highly mobile particles on a diamond lattice, and thus the modern theory is crude, as well as the classical, even though it can predict the gel point a little better (fig. 2). The correctness of a theory rests, instead,

on its response to the refinement process. This was realised early on by the leaders of the field of studies in which particles obediently *do* occupy lattice sites. For instance, Pauling and co-workers (53) detected that a crystal structure assigned to β -Se was indeed *wrong*: although the fit of the relevant Fourier synthesis had been remarkably good, indeed good enough to achieve publication in *Acta Crystallographica*. Pauling et al. noted that even fifteen successive refinements of the Fourier synthesis had not removed some disturbing features. Only by a wholesale displacement of the molecule in the unit cell could a new trial-structure be generated which rapidly refined under slight shifts of the new assumed atomic coordinates. This structure, now accepted as *correct*, unlike the earlier one, had the correct bond lengths everywhere, which means precisely that the bond lengths found were those upon which properly *refinable* models converge in other molecules containing Se-Se bonds...

As a general quantitative measure of refinability, the reduction in standard deviation of experiment from theory should be divided by the change in the free enthalpy G or Hamiltonian per relevant particle in the model responsible for this reduction. It was recently shown (Ref. 17) that further theoretically inspired refinements of an already-refined (Ref. 54) Flory-Huggins model for phase equilibrium in a polymer solution, resulted in substantial improvements in fit of spinodal and critical point data. The corresponding adjustments in G descended rapidly down to $0.05kT$ per polymer chain. Such minute adjustments will still cause displacements of several centigrade degrees in the location of spinodals at the dilute end of the experimental range. The process of refinement of the classical theory has followed the path of moving inward towards the critical point with successively smaller adjustments in G . This mode of model refinement is classical in the widest sense, and the converse procedure seems yet to have to prove itself in polymer science.

6.2 Critical and uncritical exponents

It is time to return to the impressive log-log plots in the literature sometimes spanning several decades, which verify modern exponents. In favourable cases, the experiments concerned do provide evidence that the Ising or percolation model, the phenomenological scaling models, or microscopic modelling through the renormalisation group approach, lead to truncated series whose leading term models the physical behaviour over the observed range. The truncation implies mathematically, and the limited range of effects built into the model implies physically, that the location of the critical point assumed in these plots is not exact, if the correct procedure is used to adjust it. This correct procedure selects that location of the critical point, which gives the most linear tail-piece to the plot. The procedure is correct for locating an experimental range over which the model, in its stark simplicity, reflects the physically dominant effect, provided the slope agrees with that deduced from the model. If so, the critical point selected by this straightening routine may be that of a *hypothetical substance* which harbours no effects beside those built into the model. It is never the exact critical point of the physical system taken to infinite volume. Thus all measured exponents are uncritical in a strict sense. The straightening of the plot by adjusting the critical point will tend to extend the apparent range of linearity, and may do so substantially, as shown in the top plot of fig. 6, without reflecting the properties of any specifiable model.

Experiments which have been precise enough to lead to a 'verification' of modern exponents remain an achievement of which experimentalists can be proud. It should now be clear that the log-log plots in question in no way preclude a classical theory from being refined to fit just as well (see, e.g. fig. 2 of Ref. 11b). Equally, a log-log plot with a classical slope can in principle be fitted just as well to a refined modern theory (e.g. fig. 8). The two ways, mean-field and modern, of tackling the process of initial averaging and successive refinements, are available. The experimentalist will be aware already of the need to keep this process in tune with the system-specific features of his materials. Burchard and his school have demonstrated (Ref. 55) that a wide range of physical properties can be calculated to serve for judicious testing of mean-field model refinements, and Dušek's school has been successful in using model systems of technological interest in this process (Ref. 56); and the whole wide programme of research into gels at Prague has greatly benefitted from constant efforts to build specific features into mean-field theories.

Theoreticians, for their part, have every cause to be proud of the Ising model, among the most useful and exciting in physics. With remarkably simple forms for its Hamiltonian, this model succeeds in mapping well-defined and sharp

singularities into experimental plots, in which the corners must always be rounded off to some degree. A set of well-defined singularities, was shown by Riemann to define uniquely an analytic function and its series expansions, with all their exponents and coefficients. But caution is required in attempts to preserve Riemann's conclusions while we pass through the mapping just described. Once we enter the experimental plots with their visible or implied roundings, their finite ranges and their experimental errors (however small), we pass from Riemann's unique series to Weierstrass's non-denumerably infinite set of equivalent series resembling polynomials, with no restriction on the leading exponent. Our message is not merely that the error limits on the slope of a log-log plot are easily underestimated by a power of ten or more, but rather that, without application of a remainder theorem, the critical exponent cannot be restricted to any range between $-\infty$ and $+\infty$. The need for such a theorem to give a bound on the truncation error is reinforced by the proven effects of minute perturbations on this error when it can be calculated, and the realisation that near the critical point all physical systems do become subject to disturbances.

Finally we summarise the results of tests for rejecting model theories by citing the conclusions of two recent surveys on the use of exponents in discriminating between classical and modern theories of gelation. Brauner (41) concluded: 'No clear confirmation of one of the two theories is found'. In this conference, Stauffer (57) ends thus: 'At present the outcome which seems most likely to me would be that for some materials classical theory results to be valid, for other cases percolation-like exponents are found, and for some gelation experiments both competing theories are wrong.' These conclusions are indeed to be expected from statistical principles in any situation where a yes-no decision (null-hypothesis) is being tested in terms of a parameter which, according to different variants of the test, is either unidentifiable, estimated inconsistently, or lacking in robustness.

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