

CAN PERCOLATION THEORY BE APPLIED TO CRITICAL PHENOMENA AT GEL POINTS ?

D. Stauffer

Institut für Theoretische Physik, Universität, 5000 Köln 41, W.-Germany

Abstract - A review is given on controversial gelation problems very close to the sol-gel transition. For several quantities the concept of critical exponents like β and γ is introduced. For example, the gel fraction vanishes as ϵ^β and the weight-average degree of polymerization diverges as $\epsilon^{-\gamma}$ where ϵ is the small distance from the gel point. Classical theory (Flory, Stockmayer, Gordon,...) predicts $\beta=\gamma=1$ whereas recent percolation theories give $\beta=0.4$, $\gamma=1.7$. Who is right ?

INTRODUCTION

Since nearly 40 years (Ref. 1,2) we know that branching polymers may have a sharp gel point separating the sol phase without an infinite network from the gel phase with an infinite network of monomers bound together. But only since a few years (Ref. 3,4) it is explicitly asserted by reference to percolation theory that these older theories, which we call classical, may have serious deficiencies close to the gel point. For example, if ϵ measures the distance from the gel point, then the fraction G of monomers belonging to the infinite network, i.e. the gel fraction, vanishes for $\epsilon \rightarrow 0$ as ϵ in Flory-Stockmayer theory, but as $\epsilon^{0.4}$ in percolation theory. Who is right ?

In the next section we will define what critical phenomena are, namely the asymptotic behavior of systems very close to the phase transition point. Only with these critical phenomena does this review deal. The next section describes the results of classical and percolation theory and we will see that in many respects percolation can be viewed as a generalization of classical theory. Then we look at the present theoretical and experimental situation of gelation to see which theory is better. M. Adam in these conference proceedings is giving a review of gelation experiments near the critical point; earlier reviews of percolation theory (Ref. 5) and classical gelation theory (Ref. 6), in particular near critical points, are already published. An appendix gives a short introduction to scaling and universality.

WHAT ARE CRITICAL PHENOMENA ?

If a system of branching polymers approaches the gel point, many quantities like the gel fraction approach zero, and many other quantities like the (weight-average) degree of polymerization approach infinity. Since in the latter case the reciprocal of that quantity vanishes we may restrict ourselves first to properties vanishing at the gel point. Let $G(p)$ be such a quantity, for example $G(p)$ = gel fraction = fraction of monomers belonging to the infinite network. Here p is the conversion factor, i.e. the fraction of bonds which have reacted, and p_c is the critical conversion factor at the gel point and is also called the percolation threshold. For $p \rightarrow p_c$ the quantity G may vanish linearly,

$$G = B \cdot (p - p_c)$$

but more generally,

$$G = B \cdot (p - p_c)^\beta$$

with a general critical exponent β which may differ from unity. The prefactor B is often called a critical "amplitude". If p is not extremely close to p_c it may be necessary to add correction terms:

$$G(p) = B \cdot (p - p_c)^\beta + B_1 \cdot (p - p_c)^{\beta_1} + B_2 \cdot (p - p_c)^{\beta_2} + \dots \quad (1a)$$

with $\beta < \beta_1 < \beta_2$ (1b)

We define for the purpose of this review "critical phenomena" as the properties connected with the leading asymptotic term, i.e. with $B \cdot (p - p_c)^\beta$ in Eq. (1a). And for simplicity we restrict

our discussion to critical behavior in this sense, even though recent theories exist (Ref. 8) also for the leading correction terms.

Of course, in this sense our considerations are unrealistic since they refer to the theoretical asymptotic limit $p \rightarrow p_c$, not to an experimental situation at finite distance from the gel point. Similarly, chemistry usually deals with pure substances, whereas all real materials have some impurities. And physics is usually concerned with the thermodynamic limit of infinite volume, whereas any real system is finite and thus has surfaces. It seems that in the natural sciences, differently perhaps from sociology or psychotherapy, a discussion of asymptotically pure situations is more fruitful than the incorporation of all the complexities of a real situation right from the beginning of the research.

Let us now take a simple mathematical example, the function

$$f(p) = (1 + \frac{1}{2} (p-p_c)^{-1/2})^{-1}, \quad p_c = 1/4 \quad (2a)$$

Its critical behavior for p close to p_c is

$$f(p) = 2(p-p_c)^{1/2} - 4(p-p_c) \quad (2b)$$

In the notation of Eq. (1a) we have $B = 2$ and $\beta = 1/2$, $B_1 = -4$ and $\beta_1 = 1$, etc.. Instead of expanding in powers of $(p-p_c)$ we may also try an expansion in $1/p$ for $p \rightarrow \infty$:

$$f(p) = 1 - 1/2\sqrt{p} \quad (2c)$$

a function which vanishes at $p = p_c = 1/4$ as

$$f(p) = 2(p-p_c) + \dots \quad (2d)$$

i.e. $B = 2$ again but $\beta = 1$ instead of the correct $\beta = 1/2$. Everybody will agree that such an expansion for $p \rightarrow \infty$ is no longer good for p near $1/4$, and that the critical exponent $\beta = 1$ in Eq. (2d) is erroneous. People who believe that percolation theory can be applied to gelation may think that Eqs. (2c,d) correspond to classical theory and Eqs. (2a,b) to percolation theory in this loose analogy. At finite $p-p_c$ it is not longer clear which equation is better. For example, at $p = 2p_c = 1/2$ the exact value of $f(p)$ is 0.5, the "correct" approximation of Eq. (2b) gives $f(p) = 0$ and the "wrong" approximation (2d) gives $f(p) = 0.3$, which is a better approximation! Thus far away from the gel point the results of this article should not be applied; one has to restrict oneself to critical phenomena close to the gel point if one wants to distinguish between different theories on the basis of critical exponents like β . (See Ref. 9 for more discussion of these points.) See in particular Schmidt and Burchard (27).

Another sort of critical phenomena, which we will also deal with, appears if we look at properties of finite macromolecules as a function of the number s of monomers in the macromolecule, at fixed $p=p_c$. (One can also look at such quantities at fixed $p \neq p_c$, but for our review here this is not necessary.) For example, we may wonder how the typical radius R_s of a macromolecule with s monomers (called an s -cluster in percolation theory) varies with size s at the gel point:

$$R_s = rs^\rho + r_1 s^{\rho_1} + r_2 s^{\rho_2} + \dots; \quad \rho > \rho_1 > \rho_2 \quad (3)$$

In such a case we define "critical behavior" as the leading term for $s \rightarrow \infty$, i.e. as the property of very large but finite macromolecules; in the example above this is the term rs^ρ . Few experiments seem to exist for this type of quantity, which is therefore mainly of theoretical interest (Stauffer (5)).

After this preliminaries we may define the critical exponents $\beta, \gamma, \delta, \nu, \rho, \sigma, \tau, t$ for $p \rightarrow p_c$ and $s \rightarrow \infty$, respectively, by (Ref. 4)

$$G^\alpha (p-p_c)^\beta; \quad DP_w^\alpha |p-p_c|^{-\gamma}; \quad \xi^\alpha |p-p_c|^{-\nu}; \quad s_\xi^\alpha |p-p_c|^{-1/\sigma}; \quad E^\alpha (p-p_c)^t \quad (4a)$$

$$R_s^\alpha s^\rho (p=p_c); \quad N_s^\alpha s^{-\tau} (p=p_c); \quad DP_w^\alpha G^{1-\delta} (p \geq p_c) \quad (4b)$$

(For our purposes the most important exponents are β, γ and t .) Here G is the gel fraction and vanishes for p below p_c , DP_w is the weight-average degree of polymerization, s_ξ is the number of multifunctional monomers in a typical macromolecules, i.e. in that size $s=s_\xi$ of macromolecules which gives the largest contribution to the sum for DP_w , and ξ is the average radius of such "typical" s -clusters. (One may also define s_ξ as the z -average of s , and ξ as the z -average of the cluster radius.) R_s is the average radius of gyration for macromolecules, N_s the average number of macromolecules with s monomers each, and E is the elasticity constant. (Essam (5) discusses more precisely the relation between the correlation length ξ and the cluster radius R_s .) In the last relation of Eq. (4b) we assume that gel fraction and molecular weight are measured simultaneously and that the usually unknown $p-p_c$ is eliminated from the relations. Thus from Eq. (4a) we find trivially

$$\gamma = \beta(\delta-1) \quad (5)$$

This relation is one of many "scaling laws" relating critical exponents. By assuming

$$N_s = s^{-\tau} f((p-p_c)s^\sigma) \quad (6a)$$

for $s \rightarrow \infty, p \rightarrow p_c$ (Stauffer (5)) with a suitable "scaling function" f , and a similar expression for the cluster radius one can derive easily (Ref. 4,5) in addition to Eq. (5):

$$\tau = 2+1/\delta, \quad \sigma = 1/\beta\delta, \quad \rho = \sigma\nu \quad (6b)$$

(The number average A_n of some quantity A_s depending on the cluster size s is defined as $A_n = \sum A_s N_s / \sum N_s$; its weight average is $A_w = \sum A_s s N_s / \sum s N_s$, and its z-average is $A_z = \sum A_s s^2 N_s / \sum s^2 N_s$, where all sums start from $s = 1$ and extend over all finite cluster sizes s . The sum $\sum s N_s$ equals the total number of monomers in the sol, since isolated monomers are counted as clusters with $s = 1$; thus it varies as $1-G$.)

Because of these scaling laws, Eqs. (5,6b) only three of the exponents $\beta, \gamma, \delta, \nu, \rho, \sigma, \tau$ are independent. The number of independent exponents reduces from three to two by assuming (Ref. 4,5) that the interior structure of very large clusters is for p above p_c the same as that of the infinite network. Then a "hyperscaling" law can be derived for d dimensions, where $d = 3$ of course is what we are most interested in:

$$d\nu = \gamma + 2\beta \quad (7)$$

Perhaps this hyperscaling law is less reliable than usual scaling laws, Eqs. (5,6). For the exponent t the Skal-Shklovskii-De Gennes hypothesis (Ref. 10,3) is still controversial:

$$t = 1 + (d-2)\nu \quad (8)$$

These scaling relation between $\beta, \gamma, \delta,$ and ν are nothing peculiar to gelation. They have been part of the standard body of knowledge of second order phase transitions (i.e. those without latent heat) more than ten years, for example for the transition from a ferromagnet to a paramagnet near the Curie temperature, or for the liquid-gas phase transition near a critical point. Table 1 summarizes this analogy and also compares the usual gelation notation with the notation customary in percolation theory.

TABLE 1. Analogies in the critical behavior of different phase transitions.

Gelation	Percolation	liquid-gas	ferromagnet
G	P_∞	Δ_ρ	M_0
DP_w	S	κ	χ
ξ	ξ	ξ	ξ
$P-P_c$	$P-P_c$	T_c-T	T_c-T

P_∞ = fraction of units belonging to infinite network; Δ_ρ = difference between densities of liquid and vapor; M_0 = spontaneous magnetization;
 $S = \sum s^2 N_s / \sum s N_s$; κ = isothermal compressibility; χ = isothermal susceptibility; ξ = correlation length.

The concepts of critical exponents and scaling laws are believed to apply to all these transitions, only perhaps with different values for the exponents.

A reader who wants to check these scaling laws and does not want in their derivation (Ref. 5) to work with the general scaling function f in Eq. (6a) may simplify his task (Ref. 11) if he is interested in critical exponents only: Take $N_s \propto s^{-\tau}$ for $s < s_\xi$, and $N_s = 0$ for larger s . Then, for example $|p-p_c|^{-\nu} \propto \xi^\alpha \sum s^2 R_s N_s / \sum s^2 N_s \propto \int s^{0+2-\tau} ds / \int s^{2-\tau} ds \propto \xi^\alpha |p-p_c|^{-\rho/\sigma}$, or $\rho = \sigma\nu$ as required in Eq. (6b). (Here the integrals run from zero to s_ξ only.) Of course this simple approximation does not describe correctly the asymptotic exponential decay of the number N_s of macromolecules, which seems to follow $\log(N_s) \propto -s$ above p_c and $\propto -s^{1-1/d}$ below p_c (Ref. 5) for percolation.

The principle of universality asserts that the many different materials exhibiting critical phenomena can be grouped into a few universality classes having the same exponents. For example, all liquid-gas phase transitions in as different materials as helium, CO₂ and water seem to belong to the same universality class (Ref. 12). Also the Ising model for magnets (i.e. the lattice gas approximation) belongs to this universality class according to our present knowledge. On the other hand, isotropic magnets (i.e. the Heisenberg model) belong to a different class than anisotropic magnets, and both do not belong to the same universality class as percolation (see table 2 below). Systems in different dimensions, like the two- and the three-dimensional Ising model, belong to different universality classes. Three-dimensional percolation problems in general all seem to have the same exponents, but some exceptions exist (Ref. 13). Thus for our purposes we should regard universality as an empirical classification which works for most cases.

Thus far this discussion has centered about the critical exponents, like β . What about the critical amplitudes, like B , or the position p_c of the critical point? These quantities are not universal within one universality class, and if they can vary for different materials they are more difficult to predict and therefore of less interest. In particular they are not suited to distinguish between classical and percolation theories. However, certain combinations of amplitudes can be shown to be universal, the simplest being the "susceptibility ratio": If $DP_w = C_+(p-p_c)^{-\gamma}$ for p above p_c , and $DP_w = C_-(p_c-p)^{-\gamma}$ for p below p_c , then the ratio

C_+/C_- is hoped to be universal, i.e. to be the same for all members of one universality class. After all these definitions, what do the values for these quantities look like in classical and in percolation theory? This is discussed in the next section.

COMPARISON OF CLASSICAL AND PERCOLATION THEORY

Both classical and percolation theory usually assume the bond distribution to be random. Also we neglect here the particular problem of very long chains with few crosslinks only and look at the simple polymerization of f-functional monomers. Classical theory neglects all or some possibilities for cyclic bonds within one macromolecule, whereas percolation theory knows no such restriction. (If percolation is studied on the Bethe lattice or Cayley tree, Essam (5), then cyclic bonds are impossible, too, and the results are equivalent to Flory-Stockmayer theory. In this sense classical theory is a special case of percolation theory.)

Although percolation has been studied (Ref. 15) without restriction to a lattice, most of the work and in particular the determination of critical exponents used periodic lattices. (It does not seem to matter (Ref. 5,16) what type of lattice is used as long as one does not change its dimensionality.) In that lattice case, percolation, or more precisely, bond percolation between nearest neighbors, is defined as follows:

All lattice points are occupied, and between two lattice points which are nearest neighbors one bond exists. This bond is randomly closed with probability p , and open with probability $1-p$. A cluster or macromolecule is a group of lattice sites connected directly or indirectly by closed bonds.

The infinite cluster, which appears for p larger than a percolation threshold p_c , is then identified with the gel, i.e. with the infinite network of connected monomers.

Since in classical theory cyclic bonds are not allowed and other bonds are closed randomly, the monomers in a macromolecule have to get the closer together the larger the macromolecule is. On the other hand, for percolation the lattice structure takes into account automatically the excluded volume effect, that no monomer can exist on the place already occupied by other monomers. (We thank M. Adam for pointing out to us the importance of that difference.)

It turns out that in nearly all classical theories investigated so far the same critical exponents appear independent of dimensionality; in other words, all classical gel-to-sol transitions belong to a single universality class, apart from a few possible exceptions. In percolation theory as defined above, at least two different universality classes are known: $d = 2$ and $d = 3$ systems. (Also higher dimensions have been studied and belong to different universality classes, but they are of no relevance to gelation (Ref. 17). Table 2 summarizes our present knowledge of these universal properties; for completeness we included liquid-gas transitions (where the Van der Waals equation is a classical theory and the modern Ising model theories are the analog of percolation; the two-dimensional Ising exponents are exact, the others are numerical estimates.)

Table 2 Numerical values of critical exponents and susceptibility ratio

	Model	β	γ	ν	t	C_+/C_-
gelation	Classical	1	1	1/2	3	1
	$d=3$, percolation	0.4	1.7	0.8	1.7	9
	$d=2$, percolation	0.14	2.4	1.3	1.1	200
liquid-gas tr.	Classical	1/2	1	1/2	-	2
	$d=3$, Ising model	0.3	1.24	0.63	-	5
	$d=2$, Ising model	1/8	7/4	1	-	37.7

We see that for both gelation and liquid-gas transition drastic differences occur between classical and modern exponents. Since the two-dimensional Ising results are exact and not just a spurious result of insufficient accuracy, and since three-dimensional liquid-gas experiments agree roughly with the corresponding Ising exponents, we can conclude that classical theory fails for liquid-gas transitions. However, for three dimensions the exponents are closer to their classical values than in two dimensions. Similarly, three-dimensional percolation exponents are closer to classical gelation than two-dimensional ones. The differences in the exponents are much larger than the differences in the exponents for linear polymers, where for the radius of gyration R_s of chains with s links and excluded volume effects the classical Flory theory predicts a value only two percent above the modern prediction:

$$R_s \propto s^{0.6} \text{ (classical) , } R_s \propto s^{0.59} \text{ (modern)} \quad (9)$$

According to Cotton (18) experiments were able to distinguish between these nearly equal exponents and to confirm modern theory. Thus an experimental distinction between the drastically different percolation and classical gelation exponents should be possible, too.

(The reader can calculate exponents missing from Table 2 by scaling laws, Eqs. (5,6); for example, $\delta = 1 + \gamma/\beta$ is about 5 in three-dimensional percolation. Inspection of classical theory shows that it also follows the scaling laws with the exception of hyperscaling: In 3 dimensions, ν is not equal to $\gamma/2\beta$ classically. Only in six dimensions is hyperscaling compatible

with classical exponents, and one expects, Ref. 17, classical exponents to be valid for percolation in more than six dimensions.)

Why does classical theory follow the scaling laws, which usually are not employed in classical theories. The reason is simple: The cluster size distribution follows the assumption (6a) and thus gives all the scaling laws following from that equation. Application of Stirling's law to the factorials appearing in the classical results for N_s gives (Ref. 7,19)

$$N_s \propto s^{-5/2} \exp(-\text{const} \cdot (p-p_c)^2 s) \quad (10)$$

and one immediately sees that this result agrees with Eq. (6a) if $\tau=5/2$ and $\sigma=1/2$. Thus one can regard classical theory as a special case of percolation theory apart from hyperscaling. Only the exponents differ, not the scaling laws. Of course, for three- and two-dimensional percolation the detailed shape of the scaling function f in Eq. (6a) is more complicated than the simple Gaussian curve of Eq. (10). See Stauffer (5) for details.

The cluster radius R_s according to scaling should vary as $s^{\sigma\nu}$ at $p=p_c$ for large clusters, which means

$$R_s \propto s^{1/4} \text{ (classical)}, \quad R_s \propto s^{0.4} \text{ (percolation)} \quad (p=p_c, d=3) \quad (11)$$

in three dimensions. Computer data confirm roughly the percolation prediction (Ref. 11). The classical result, with its exponent 1/4, was also known already (Ref. 20). Of course, no experiment, however accurate, will ever confirm this classical prediction for $s \rightarrow \infty$, since it would require that the density within the cluster approaches infinity if the cluster size s goes to infinity. This inconsistency vanishes for higher dimensions, and therefore it is quite possible, although not yet confirmed directly, that the classical result in Eq. (11) will be correct for d larger than six dimensions. In three-dimensions, on the other hand, the cluster radius must increase at least as $s^{1/3}$ for large s , a condition fulfilled only by percolation theory.

The elastic constant in both classical (Ref. 21) and percolation (Ref. 3) theory varies as the conductivity of a mixture of conducting and insulating bonds; only the exponents (3 versus about 1.7) differ.

The viscosity (more precisely, the intrinsic viscosity) does not seem at present a suitable quantity to distinguish different theories. One may assume the viscosity to be a suitable average of the viscosity due to the contribution η_s of macromolecules of a given size s . Free draining gives $\eta_s \propto R_s^2$ and a weight average, the equivalent sphere limit gives $\eta_s \propto R_s^3$ and a number average. (See Refs. 20,22,23 for details.) In the first theory we get

$$\eta \propto \sum R_s^2 s N_s \propto (p_c - p)^{\beta - 2\nu} = (p_c - p)^{1.3} \text{ (percolation) and } \propto \log(p_c - p) \text{ (classical);}$$

in the other theory we have

$$\eta \propto \sum R_s^3 N_s / \sum s \cdot N_s \propto \log(p_c - p) \text{ (percolation) and finite (classical)}$$

Closer inspection (Ref. 22) shows that the second choice should be better near the gel point where the molecules become large. But still these theories neglect interaction between different macromolecules. Perhaps it is better to regard the viscosity as the analog of the conductivity of a random mixture of superconducting and normal conducting links (De Gennes (24)). In that phase percolation predicts the viscosity to diverge as $(p_c - p)^{-0.7}$ in three dimensions. Thus the viscosity cannot help us much in distinguishing between classical and percolation theory, at least not at present, since it is not yet understood theoretically.

DISCUSSION

With so widely differing predictions for the critical exponents it should, at first sight, be easy to find from the existing literature which describes reality better. Why is this not the case?

Experiment

In real experiments, most of the chemical literature in the past did not concern itself with critical behavior as discussed here, and thus little information was gained by Brauner (25) from a short literature review except that there does not exist a wealth of information confirming the exponents of the then widely accepted classical theory. More recent experiments are reviewed by Adam (26) at this conference and give a more optimistic outlook. We thus mention here only one recent result: The Freiburg group (27) measured gel fraction and molecular weight simultaneously, Eq. (4b), for p above p_c , and found $\delta \approx 4$, in excellent agreement with $\delta - 1 = 4.0 \pm 0.8$ from percolation theory but not with the classical prediction $\delta - 1 = 1$. But other data agreed better with classical theory, and the exponent δ was perhaps an "accident". Clearly progress could come quicker if in the future the chemical literature would report sol-gel phase transition experiments in log-log plots near the gel point, after the unique phase transition point has been determined as accurate and unbiased as possible.

The Colchester group (9) pointed out that experimental determinations of critical exponents can be seriously wrong. Their discussion centers not on gelation but on phase separation in polymer solutions, which we did not cover here. For gelation, the difference between the two competing theories ($\beta=1.0$ classically, $\beta=0.4$ for percolation) is larger and thus easier to measure than for phase separation ($\beta=0.5$ classically, $\beta=0.3$ in modern theories). Critical

exponents for phase transitions other than percolation have been discussed in numerous papers in the last 20 years, and in general an accuracy of ± 0.1 can be achieved in good experiments where the position of the phase transition point has been determined carefully.

In a few cases like the two-dimensional Ising model or the ideal Bose gas in d dimensions the critical behavior can be calculated exactly (Ref. 28) and has been proved to differ from classical theory, whereas it agreed within minor error bars with earlier numerical studies. For gelation we already mentioned that the classical exponent $\rho=1/4$ (Ref. 20) for the radius of macromolecules right at the gel point cannot be true geometrically in three dimensions since it would require the density to grow to infinity. Thus the pessimistic view cited by Gordon and Turkington (9) "Ulteriora in rerum natura nec evinci nec cognosci possunt" (free translation: Don't trust those theoretical physicists) does not apply to all critical phenomena.

Of course the Colchester group could be right (but so far has presented no evidence) that gelation is a phase transition very much different from most other phase transitions, and that it is not possible, by the general methods which were successful in other cases, to distinguish between the competing theories through careful experiments. If this statement were true, it would still not justify the belief (Ref. 7) that critical phenomena are described by classical theory. Also, if one mistrusts the universality hypothesis, as the Colchester group (9) does, then one should believe in that type of theory where universality is valid less, and that is percolation; for in classical theory we have $\beta=1$ for all dimensions, whereas in percolation theory β varies with dimensionality d .

Theory

To what extent do computer simulations and other calculations on more realistic models than percolation (as described above) confirm or reject one of the previous theories?

Most computer simulations for percolation assume a lattice where all points are equal. But gelation happens not on a lattice, and is often a copolymerization of bifunctional and multifunctional monomers. In a general field theory (Ref. 29) this copolymerization had the same critical exponents as percolation, and that theory needed no lattice. More directly relevant to three dimensions is a Monte Carlo study of polymers growth reported at this conference (Ref. 30) which showed that for rather large concentration of multifunctional units the correlation length (average radius) is described by the exponent $\nu=0.8$ of percolation theory and not the classical exponent $\nu=1/2$, whereas for a smaller concentration the exponent ν is even larger.

Percolation on a lattice usually allows bonds between nearest-neighbors only. No change in critical exponents was observed thus far if bonds over larger distances were allowed (Ref. 31). In the limit of very long-ranged bonds the lattice structure becomes unimportant, and one approaches percolation on a continuum (Ref. 15). In contrast to earlier assertions by Stauffer (4) based on the Ginzburg criterion, recent speculations (Ref. 31) suggest that even in this limit the usual percolation exponents hold. A direct test by Monte Carlo simulation in a continuum is in preparation (Ref. 32). It seems likely, that the lattice structure is not very important for percolation exponents, for it turned out to be quite unimportant for liquid-gas critical points (Ref. 12) and linear polymers (Ref. 33, 18).

Simultaneously to chemical bonding processes, thermal concentration fluctuations can happen, which may lead to a combination of gelation and phase separation. A recent classical theory (Ref. 34) predicted a phase diagram which was confirmed experimentally (Ref. 35). At the gelation line the same exponents as in simple percolation seem to result according to more detailed theories of this site-bond percolation problem, which is a more realistic gelation model (Ref. 36). In this review we ignore these complications, since H.E. Stanley is present at the conference.

Both classical and percolation theory usually assume that each bond is closed or open randomly, without reference to its neighbors. If instead correlations exist between different bonds, according to some thermal equilibrium probability $\propto \exp(-\text{energy}/kT)$, then (Ref. 37) this correlated percolation problem does not belong to the same universality class as random percolation. Perhaps correlated percolation is a better model for reversible gelation in thermal equilibrium, and correlated site-bond percolation should be even more realistic.

For irreversible gelation, the macromolecules grow in time, and both percolation theory and classical theory assume that a random distribution of closed bonds results. That assumption is questionable; for example Monte Carlo simulation (Ref. 38) of such a growth process at very low p ("growing animals") gave macromolecules much more compact ($\rho=1/d$ for $d=2$ and 3) than those in percolation theory for the same p ("random animals"). Quite possibly (Ref. 39) both percolation and classical theory are wrong for this reason, and we need a calculation as a function of time for this kinetic process.

Finally, it should not be forgotten that this whole discussion centered about critical behavior, and in particular critical exponents. If one is merely interested in the position of the critical point, or in the structure of phase diagrams, then perhaps classical theory is sufficient, even though exceptions exist for other phase transition (Ref. 40). Present percolation theory does not make "universal" predictions for the percolation thresholds p_c . See (15).

CONCLUSION

For liquid-gas transitions, experiments have indicated for nearly one century (see Levelt Sengers (41), for a historical review) that classical theory is wrong; but these data were not taken seriously for a long time because classical theory was widely accepted. Only for about 20 years, in a development widely ignored by the chemical literature on gelation, have the critical exponents at these and similar phase transitions been measured carefully and taken seriously without such theoretical bias. These experiments, and numerical "experiments" like series expansions etc, have in turn lead to the now widely accepted concepts of scaling, universality, and renormalization group, which can be regarded as a generalization of classical theory. Gelation seems to be the last bastion of classical theory where the more modern concepts are not yet fully taken into account. It would be nice if for gelation we would not have to wait another 50 years until unproven theories are challenged by experiment. The progress during the last year (Ref. 26) makes a much quicker resolution likely. 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.

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APPENDIX

A SHORT INTRODUCTION TO SCALING AND UNIVERSALITY

This appendix explains on an elementary level the formalism of modern phase transition theory (without renormalization group technique). The reader can inform himself in Ref. (28) on applications and variants.

Let i and j denote points on an infinite simple lattice with coordination number z (= number of nearest neighbors for each lattice site). S_i is a variable which we identify with a spin (localized magnetic moment) and which can take on the values $+1$ (magnetic moment upward oriented) or -1 (spin down). Equivalently, $S_i=1$ can mean an occupied lattice site and $S_i=-1$ an empty one in the lattice gas model, where molecules jump freely from one lattice site to the other. An interaction energy J tends to make nearest neighbor spins parallel, and a magnetic field H (corresponding to a chemical potential in the lattice gas) wants to align all spins. In this Ising model the interaction energy E is therefore (with $|\text{magnetic moment}|=1$):

$$E = -\sum_i J S_i S_j - H \sum_i S_i \quad (\text{A1})$$

where the first sum runs over all nearest-neighbor pairs. Thermal probabilities are proportional to $\exp(-E/kT)$ and have to add up to unity. Thus for $J=0$, when we can look at each spin separately, the probability for S_i to be in the direction of the field H is $\exp(H/kT)/(\exp(H/kT) + \exp(-H/kT))$, and the average magnetization M per spin is the difference of the "up"-probability and the "down"-probability:

$$M = \langle S_i \rangle = \tanh(H/kT) \quad (\text{A2})$$

For $J \neq 0$ the mean-field approximation (which corresponds to the van der Waals equation) neglects the influence of S_i on its neighbor S_j if one calculates the interaction energy $-JS_i S_j$. Thus S_j in Eq. (A1) is replaced by its average value $\langle S_j \rangle = M$, giving

$$E = -\sum_i S_i (H + J \sum_j \langle S_j \rangle) = -H_{\text{eff}} \sum_i S_i \quad (\text{A3a})$$

with the effective field

$$H_{\text{eff}} = H + J \sum_j M = H + MzJ \quad (\text{A3b})$$

Comparison with Eq. (A2) gives immediately the self-consistent equation for M :

$$M = \tanh(H_{\text{eff}}/kT) \quad (\text{A4a})$$

For small M and small H we can expand the hyperbolic tangent:

$$M = H_{\text{eff}}/kT - \frac{1}{3}(H_{\text{eff}}/kT)^3 + \dots = (zJ/kT)M + H/kT - \frac{1}{3}(zJ/kT)^3 M^3 + \dots \quad (\text{A4b})$$

With the abbreviations $T_c = zJ/k$ and $\epsilon = 1 - T_c/T$ we get for small ϵ :

$$H/kT = \epsilon M + \frac{1}{3} M^3 \quad (\text{A4c})$$

The spontaneous magnetization $M_0 = M(H=0, T > T_c)$ is $M_0 = \sqrt{-3\epsilon}$; the susceptibility $\chi_0 = dM/dH$ at zero field for T above T_c is $\chi_0 = 1/\epsilon kT$, which is known as the Curie-Weiss law; and the critical isotherm $H(T=T_c)$ is given by $H/kT_c = (1/3)M^3$.

If we define generally the critical exponents β, γ, δ by $M_0 \propto (-\epsilon)^\beta$, $\chi_0 \propto \epsilon^{-\gamma}$, and $H(T_c) \propto M^\delta$ we thus have found the classical exponents of table 2:

$$\beta = 1/2, \quad \gamma = 1, \quad \delta = 3 \quad (\text{A5})$$

These exponents are not changed if we generalize Eq. (A4c) to the Landau expansion

$$H/kT = a\epsilon M + bM^3, \quad \text{or: Free energy} = \int M dH = F_0 + \frac{1}{2} a\epsilon M^2 + \frac{1}{4} bM^4 \quad (\text{A6})$$

with two constants a and b fitted on experiment.

Since these exponents are known to be wrong we try to generalize these classical results. Obviously we can write Eq. (A6) as

$$H/kT = M^3 f(\epsilon/M^2), \quad f(x) = ax + b$$

or

$$H/kT = M^\delta f(\epsilon/M^{1/\beta}) \quad (A7)$$

since $\delta=3$ and $\beta=1/2$ classically. The scaling assumption now simply asserts that Eq. (A7) is valid with general exponents β and δ , and with a general scaling function f , to be fitted on experiment. Just as the classical result (A6) this scaling assumption is supposed to be valid only asymptotically for small H , small M and small ϵ .

Eq. (A7) is just one of many cases where a quantity Q depends on two variables x and y and is assumed asymptotically to have the form

$$Q = x^\alpha f(y/x^{\alpha'}) \quad (A8)$$

with two free exponents α and α' . For example, our Eq. (6a) for the numbers of macromolecules is such a case, and the radius R_S may vary as

$$R_S = s^\rho \phi(\epsilon s^\sigma),$$

or the correlation function g (which for gelation is the probability that two monomers at distance r belong to the same macromolecule) is

$$g(r) = r^{-2\beta/\nu} \phi(\epsilon r^{1/\nu}).$$

As an exercise we now derive Eq. (5): The inverse susceptibility $1/\chi_0$ varies as ϵ^γ by definition and equals dH/dM ; it is finite for $M \rightarrow 0$ and T above T_C . Thus the scaling function f in Eq. (A7) must behave for very large arguments in such a way that $H \propto M$. This is the case if $f(x \rightarrow \infty) \propto x^{\beta\delta - \beta}$ since then $H \propto M^\delta (\epsilon/M^{1/\beta})^{\beta\delta - \beta}$, or $1/\chi \propto \epsilon^\beta \delta^{-\beta}$. Thus $\gamma = \beta(\delta - 1)$, as required.

Universality is a generalization of the Landau ansatz (A6) with its two free prefactors a and b . It asserts that different materials can be grouped into few universality classes such that within one class the scaling assumption (A7) takes the form

$$H/kT = aM^\delta f(b\epsilon/M^{1/\beta}) \quad (A9)$$

where only the factors a and b , not the exponents and the function f , depend on the particular material.

Analogies between the magnetic language used here and other phase transitions can be seen from table 1. For percolation, Stauffer (5) gives an introduction to the scaling theory of clusters.

We see that scaling and universality can be presented as a simple phenomenological generalization of classical theory, with unknown exponents to be determined experimentally.

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