

Gelation and Critical Phenomena

Dedicated to Prof. Manfred Gordon on the occasion of his 65th birthday, who discussed critical phenomena at the gel point as early as in 1974, see Ref. 1.

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For the critical exponents near the sol-gel phase transition, classical theories like those of Flory and Stockmayer predict one set of exponents, whereas scaling theories based on lattice percolation predict different exponents. The two groups of theories differ in their treatment of intramolecular loops, space dimensionality and excluded volume effects. In this article, the differences and similarities between the results of the competing theories are reviewed. For example, a gel fraction like $(p - p_c)^\beta$ vanishes for conversion factors p very close to the gel point p_c , the weight average molecular weight diverges as $(p_c - p)^{-\gamma}$ for p very slightly below p_c , and the radius of macromolecules at the gel point $p = p_c$ varies as the q -th power of the number of monomers in that macromolecule. Classical theories predict $\beta = \gamma = 1$ and $q = 1/4$ whereas the percolation theory gives $\beta \approx 0.45$, $\gamma \approx 1.74$ and $q \approx 0.40$. We also generalize the percolation concept to include interaction effects and concentration fluctuations; in this case the sol-gel phase transition may be connected with a phase separation.

Some experimental results are reviewed to check whether the percolation theory agrees with reality; no clear answer has been found so far, due to experimental difficulties. For instance, for the viscosity a power law $(p_c - p)^{-0.8}$, which agrees with one of the percolation ideas has been established in several experiments; the shear modulus of the gel vanishes roughly as $(p - p_c)^3$ in some experiments, which agrees better with the classical theory.

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A. Introduction

M. Gordon suggested some time ago¹⁾ that the behavior of gels at the sol-gel phase transition should be investigated more closely. And indeed shortly thereafter^{2, 3)} theoretical predictions were published according to which the critical exponents for these phase transitions should differ drastically from those of the widely accepted "classical" theories^{1, 4, 5)}. These speculations^{2, 3)} were based on the analogy with other phase transitions like the liquid-gas critical point, and in particular with the percolation problem and its recent advances.

Thus, this review explains critical exponents and percolation theories and compares these theories, preferred by physicists, with the classical approach (Flory-Stockmayer type theory^{4, 5)}) used by chemists, and summarizes experimental evidence both in favor and against the theoretical predictions. Since most readers are well acquainted with classical theories we emphasize here recent developments of percolation theories. Due to the rapid development of the situation since 1979, some earlier reviews^{6, 7)} are partly outdated now. We hope that the same can be said soon about the present article, too.

B. What are Critical Phenomena

B.I. Preliminary Remarks

In the sol-gel phase transition, an infinitely large macromolecule is formed. Critical phenomena are those which occur exactly in the phase transition or asymptotically close to it. Let us explain this definition in detail (Eq. (10) gives a summary):

We discuss a solution of molecules ("monomers") with functionality $f \geq 3$ (in general); from each molecule may emanate zero to f bonds to neighboring molecules and thus this molecule may participate in the formation of a large cluster which is called a macromolecule. Two monomers in the same cluster or macromolecule are thus connected directly or indirectly (through other monomers in the same cluster) by such bonds whereas two monomers in two different macromolecules are not connected by such bonds. We denote the number of monomers in one macromolecule by s and then call this macromolecule also an s -cluster; an isolated monomer without bonds to its neighbors is thus designated as an 1-cluster with $s = 1$. (For simplicity, we also call s the mass of the macromolecule, i.e. we set the molecular weight of the monomers equal to unity in the theoretical discussions.) Under certain conditions, an "infinite" cluster can be formed, i.e. a network which extends from one end of the sample to the other.

The concept of an infinite cluster makes sense only in the thermodynamic limit of very large samples; otherwise, there is no sharp phase transition. If the mass s of the largest cluster in the sample is proportional to the system size and if the latter goes to infinity we call the cluster infinitely large. For usual system sizes there is either one or no cluster whose mass is much larger than the mass of any other cluster. Such a special cluster is large enough for most scientific considerations.

This infinitely large macromolecule is called a *gel*; a collection of finite clusters is called a *sol*. A gel usually coexists with a sol: the finite clusters are then trapped in the interior of the gel.

Gelation is the phase transition from a state without a gel to a state with a gel, i.e. gelation involves the formation of an infinite network^{4, 6, 9}.

The conversion factor p is the fraction of bonds which have been formed between the monomers of the system, i.e. the ratio of the actual number of bonds at the given moment to the maximally possible number of such bonds. Thus, for $p = 0$, no bonds have been formed and all monomers remain isolated 1-clusters. In the other extreme, $p = 1$, all possible bonds between monomers have been formed and thus all monomers in the system have clustered into one infinite network, with no sol phase left. Thus for small p no gel is present whereas for p close to unity one such network exists. Therefore, there is in general a sharp phase transition at some intermediate critical point $p = p_c$, where an infinite cluster starts to appear: a gel for p above p_c , a sol for p below p_c . This point $p = p_c$ is the gel point and may be the analog of a liquid-gas critical point: For p below p_c only a sol is present just as for T above T_c only a supercritical gas exists. But for p above p_c , sol and gel coexist with each other; similarly for T below T_c vapor and liquid coexist at equilibrium on the vapor pressure curve. Magnetism experts may prefer the analogy with the Curie point: For T above T_c , no spontaneous magnetization exists (corresponding to no gel), whereas below T_c this remanence is non-zero (corresponding to the gel above p_c). However, we do not assert that these thermal phase transitions and gelation have the same critical behavior. Also, in gelation there is no phase separation: Whereas the vapor is above the liquid, the sol is within the gel. The liquid-gas transition is a thermodynamic phase transition whereas gelation deals with geometrical connections (i.e. with bonds). At least in simple gelation models the temperature plays only a minor role compared with its dominating influence on the thermodynamic phase transitions. Such simple gelation theories often make the assumption that the conversion p alone determines the behavior of the gelation process, though p may depend on temperature T , concentration ϕ of monomers, and time t . Sections C.V. and D. will deal with more complicated models where temperature and concentration are more important variables.

This review will emphasize one particular approach to gelation theory, *the percolation model*. It can be explained simply as follows: Monomers are thought to occupy the sites of a periodic lattice, and between two nearest neighbors of lattice sites a bond is formed randomly with probability p . Figure 1 shows the resulting macromolecules at the gel point for the two-dimensional square lattice ($p_c = 1/2$), an example which can be easily produced by a programmable pocket calculator. We will compare the results of this percolation theory with those of the "classical" theories which, in their simplest form⁴, allow the same random process of bond formation to be performed on a tree-like structure, the Bethe lattice or Cayley tree of Fig. 2. Most of our review deals with irreversible gelation, where a bond, once formed, is not easily broken again.

Critical phenomena are phenomena occurring for p very close to or identical with the gel point p_c . Thus the critical behavior happens in "asymptopia" (R. A. Ferrell), i.e. in the limiting region of p asymptotically close to p_c . Of course, any real experiment can never reach this purely mathematical limit, but one can try to come as close as possible to asymptopia. Similarly, social justice is difficult to accomplish completely, but one can try to improve society in that direction. Similarly, chemistry is usually concerned with "pure" materials which do not exist in reality; in experiments one therefore uses "chemically pure" substances, i.e. those which are as clean as possible. As usual in thermodynamics, we deal also in gelation theory with the limit of very large systems, and in some cases with systems in complete thermal equilibrium, two other asymptotic limits which may be

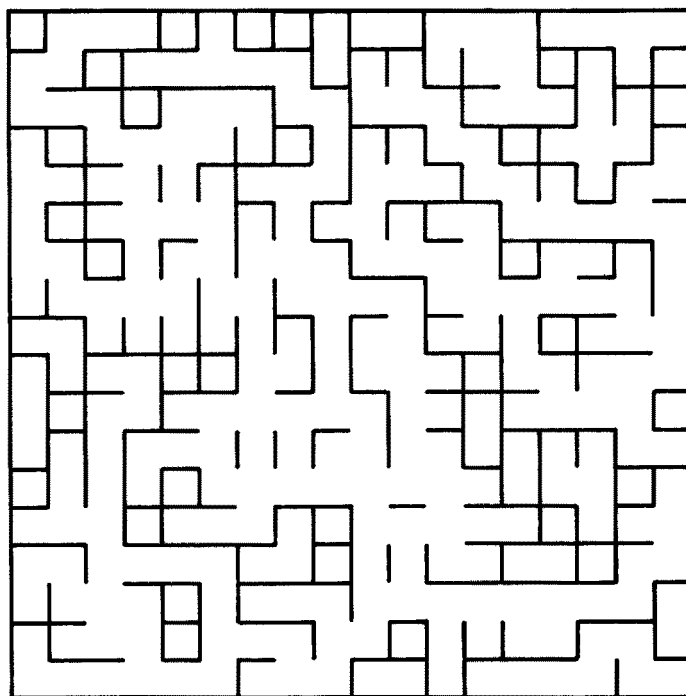


Fig. 1. Example of percolation at the gel point, $p = 1/2$, in a square lattice. Each bond which has been formed is shown as a short line connecting two monomers; the monomers are not shown. One sees some nearly "infinite" macromolecules, where infinite means that they span the whole sample. Each bond is formed with probability p

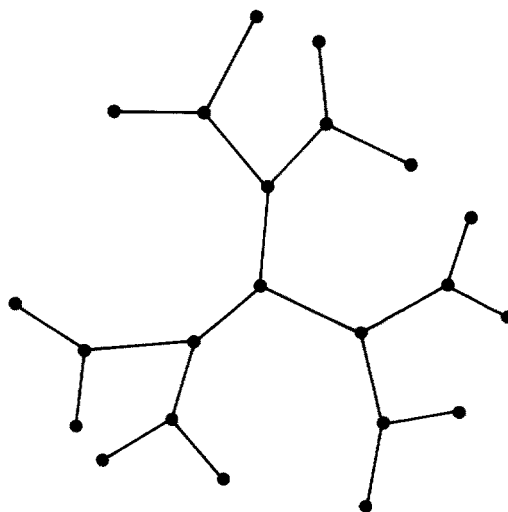


Fig. 2. Structure of the Bethe lattice with $f = 3$ (interior part of the infinite system only). Each possible bond is shown as a line connecting two monomers (dots). The Flory-Stockmayer theory assumes that each actual bond of these possible bonds is formed with probability p

difficult to achieve. (For a critique of asymptopia see Ref. 11.) Thus none of the limits discussed in this article is very special to gelation or percolation theory.

(These two examples also show that for precision experiments one should try to measure data also slightly away from asymptopia even if one wants to know the asymptotic behavior only. In chemistry, it is more suitable to work with several samples differing in a small but well-defined amount of impurities so that one can extrapolate to zero impurities. In thermodynamics it is useful, e.g. in computer simulations, to work with samples of different size in order that one can subtract the surface effects by extrapolating to infinite size. Similarly, knowledge of gelation slightly away from the gel point will increase the precision of the results in the asymptotic regime close to p_c since then extrapolations are possible.)

How can we describe critical phenomena quantitatively? We will be interested mainly in quantities which become either zero or infinite at the gel point $p = p_c$; thus we want to know how they approach these limiting values. For example, since an infinite macromolecule appears for p above p_c but not for p below p_c , it is likely that some average molecular weight or degree of polymerization diverges, if p approaches p_c from below (denoted as $p \rightarrow p_c^-$, in contrast to $p \rightarrow p_c^+$ for the opposite direction). Let us look at the weight average degree of polymerization, DP_w (which corresponds to the weight average molecular weight M_w ; we are mostly interested in proportionalities only). A simple behavior for p slightly below p_c would be

$$DP_w \propto 1/(p_c - p) \quad (p \rightarrow p_c^-),$$

in analogy with the Curie-Weiss law of the paramagnetic susceptibility or the van der Waals result for the compressibility. More generally, one may postulate

$$DP_w \propto (p_c - p)^{-\gamma} \quad (p \rightarrow p_c^-)$$

with a suitable constant γ which is called a critical exponent. The asymptotic proportionality factor C in the equality

$$DP_w = C(p_c - p)^{-\gamma} \quad (p \rightarrow p_c^-)$$

is called a critical amplitude. Only may also measure the degree of polymerization above p_c in the sol coexisting with the gel; then the critical behavior may be described by another (or the same?) critical exponent and critical amplitude:

$$DP_w = C'(p - p_c)^{-\gamma'} \quad (p \rightarrow p_c^+).$$

If very accurate experimental data are available or if one has achieved an exact solution of a theoretical model, one can find out also the leading correction terms like

$$DP_w = C(p_c - p)^{-\gamma} + C_1(p_c - p)^{-\gamma_1} + C_2(p_c - p)^{-\gamma_2} + \dots \quad (p \rightarrow p_c^-) \quad (1)$$

with $\gamma > \gamma_1 > \gamma_2 > \dots$. These relations are not the only possibilities; for example, a quantity may diverge as $\log(p - p_c)$, in which case one may identify the corresponding critical exponent with zero since $\log(p - p_c)$ diverges more slowly than any finite power

of $p - p_c$. Conversely, an infinite exponent may describe an exponential increase, as in $\exp(-\text{const}/(p - p_c))$. A combination of powers and logarithms is also possible, as in $(p_c - p)^{-1}|\log(p_c - p)|^{2.7}$ for DP_w in the six-dimensional percolation theory⁸); at present, there is no reason to believe that these complications occur in the usual three-dimensional gelation. Since all three-dimensional gelation theories known to us are compatible with expansion (1) we assume from now on its validity as a limit; but Ref. 11 pointed out that the form of Eq. (1) in general remained unproven. Exact solutions of theoretical models are presently known for the tree approximation of Fig. 2 and similar "classical" approaches, and for extreme space dimensionalities d like $d = 1$ and $d \geq 6$ ^{8,10}.

In the analysis of experimental data, including Monte Carlo results found by computer simulation, the accuracy in most cases is insufficient to allow a reliable determination of the many parameters of Eq. (1). One still gets useful results by a double logarithmic plot of the measured quantity against $|p - p_c|$. For example, if $DP_w = C(p_c - p)^{-\gamma}$, then $\log(DP_w) = \text{const} - \gamma \cdot \log(p_c - p)$; the slope of the straight line fitting the data gives a critical exponent. Such a log-log plot reveals that data should be particularly accurate near the gel point. In particular, a small shift in p_c results in large shift in the critical exponent. If p_c is not known one may take, as a first approximation, that value which fits best a straight line in the log-log plot. An early example of this kind of analysis was given by Peniche-Covas et al.¹². Preferably, one should have more than one quantity measured in the gelation experiment. Then, one can fix p_c from the best fit of data and use the same p_c for the other properties. If DP_w (or a similar quantity) has been measured on both sides of the phase transition, it is particularly simple and often quite efficient to assume its critical exponent (but not the critical amplitude!) to be the same on both sides. (This symmetry of exponents on both sides of the phase transition is known to be correct in exactly solvable simple models like the two-dimensional Ising model or gelation on the Bethe lattice of Fig. 2 and consistent with numerical evidence in numerous other cases.) Then, one can shift p_c , if not known more reliably from other measurements, until the two straight lines, fitting the log-log plots above and below p_c , have the same slope. This is the best value of p_c ; the method also gives automatically a good estimate for the critical exponent $\gamma = \gamma'$ as the slope, and finally the distance between the two parallel lines of the log-log plot is the logarithm of the ratio C'/C of the two critical amplitudes above and below p_c , which is also of great theoretical interest in the existing models¹³.

These simple methods provide, of course, only an effective critical exponent in the sense that this exponent depends on $p - p_c$. If accurate data give, despite a correct choice for p_c , a clear curvature in the log-log plot, then one tries to extrapolate the slope smoothly to its value at the critical point. Only if experimental data were of infinite accuracy and extended into the region infinitely close to the gel point would a true asymptotic exponent be obtained accurately, as is known from all real experiments. (Theoretically, the exact solution⁹) of gelation on the Bethe lattice of Fig. 2, $DP_w = (1 + p)/(1 - 2p)$, allows the effective critical exponent $\gamma_{\text{eff}} = -d \log(DP_w)/d \log(p_c - p)$ to be determined for all p between 0 and $p_c = 1/2$, with $\gamma_{\text{eff}} = 1.50, 1.07$ and 1.01 at $p = 0, 0.4$ and 0.49 , respectively, as compared with $\gamma = 1.7$ obtained with the percolation theory.) In practice, an accuracy of the order of 10% for an exponent can be reached if experiments have been made to determine this exponent, with moderate relative accuracy for its data points, and if this set of points extends over a decade in distance from p_c . The analysis becomes unreliable if the correction exponent (γ_1 in Eq. (1)) is very close to the leading exponent (γ) or if logarithmic factors occur as discussed above; we assume that in general this is not the case for three-dimensional gelation. The accuracy is also lowered appreciably if one has to reanalyze¹⁴) data read off from published figures and if no tabular data or log-log plots are available. The accuracy is improved when suitable data extend over several decades in $p - p_c$ in order to fit also the correction terms in Eq. (1). Such detailed analysis was first performed ten years ago on the lambda transition of superfluid helium¹⁵). However, for gelation we have not yet reached the same experimental state of art. We can only suggest that in future experiments efforts should be made to get many data near the suggested gel point and to determine the position of this gel point as accurately and consistently as possible.

None of the problems with asymptopia is new since they occur also in thermal phase transitions like the liquid-gas critical point or the magnetic Curie point mentioned above,

only that $p - p_c$ is replaced there by $T_c - T$. Thousands of experimental and theoretical papers on the determination of critical exponents have appeared during the last twenty years; they are summarized in various books¹⁵⁾. For a few models, exact results have become available after numerical investigations had been made before, and usually the deviation of the true result from earlier estimates was of the order of the error bars published with the estimate. The “new” ideas^{2, 3, 7, 14)} suggesting deviations from classical theory in the critical exponents are nothing but applications of experiences from other phase transitions to gelation.

Another type of critical exponents is less commonly used in thermal phase transitions but suitable for gelation theory; experimentally, they are more difficult to measure. These exponents are defined by taking $p = p_c$ and by considering various macromolecules which are found in the system. Each such cluster consists of s monomers where s varies from unity to infinity. Now we study cluster properties *as a function of mass s at fixed $p = p_c$* . For example, the total number N_s of such macromolecules or s -clusters at the critical point, might be written as

$$N_s \propto s^{-\tau} \quad (s \rightarrow \infty), \quad (2)$$

asymptotically for very large but finite mass s . In other words, instead of the limit $p \rightarrow p_c$ we consider the limit $s \rightarrow \infty$. If measured experimentally, as in¹⁶⁾, they serve as a more fundamental test of theories than other quantities derived from averages made over all macromolecules.

A third form of exponents should not be called “critical” but is also defined by asymptotic limits. For example, the suitably defined radius R_s of macromolecules consisting of s monomers each may vary as

$$R_s \propto s^{\varrho} \quad (s \rightarrow \infty, p \text{ fixed}) \quad (3)$$

not only at $p = p_c$ but also for fixed p far away from p_c with $\varrho = \varrho(p)$. In particular, the limits $p \rightarrow 1$ and $p \rightarrow 0$ can and have been studied theoretically. There is good reason to believe¹⁷⁾ that the exponent ϱ defined by Eq. (3) assumes in simple models only three different values as a function of p : It has one value at the gel point which is related to the other critical exponents; a second for all p below p_c (i.e. $0 < p < p_c$) which is equal to $1/2$ and a third one equal to $1/3$ for all p above p_c (i.e. $p_c < p < 1$). In the latter two cases, this exponent is not related to the critical exponents at the gel point^{17, 18, 34)}.

We mention the radius, since it forms a bridge to well-studied pseudocritical exponents for *linear* polymer chains, $f = 2$. Numerous experiments (for experimental and theoretical data see Ref. 19) on the radius of gyration R_s of linear polymers in a monodisperse solution as a function of the number s of monomers in the chain have been carried out. A simple random-walk approximation for these chains gives $R_s^2 \propto s$, i.e. $\varrho = 1/2$. According to Flory’s treatment of the excluded volume effects $\varrho = 3/5$ (see Ref. 4) whereas present estimates are close to 0.59 in three dimensions¹⁹⁾. When the chains collapse $\varrho = 1/3$, as for gelation (percolation) above p_c . All these exponents describe the asymptotic limit $s \rightarrow \infty$ only. Thus, the exponents and the relevant problems with asymptopia are nothing new to polymer science. We believe that the classical gelation theory (Flory-Stockmayer theory^{4, 5)} is the analog of the random-walk approximation, relating however only to branched polymers instead of linear ones. Recently, the application of Flory’s idea of the excluded volume effects of chains to gels yielded an exponent ϱ which

is different from that obtained by certain classical theories ($q = 1/4$) but which is in almost perfect agreement with the percolation theory²⁰). Thus, one can use one Flory theory against the other!

B.II. Compilation of Quantities and Their Exponents

After these preliminary remarks, we now discuss the quantities and the corresponding exponents which can be measured near the gel point or which have been studied using theoretical gelation models. (Eq. (10) summarizes these definitions.) First we repeat that the conversion factor p is the number of actual bonds divided by the number of possible bonds. The mass s of an s -cluster is the number of monomers in such a macromolecule. We allow the space dimensionality d to vary, according to $1 < d < 6$, though usually we have $d = 3$.

The average number n_s of s -clusters (normalized as number per f -functional monomer) defines at the gel point the critical exponent τ and the critical amplitude q_0 by

$$n_s(p = p_c) = q_0 s^{-\tau} \quad (s \rightarrow \infty) \quad (4a)$$

Since n_s is the probability that a given monomer is part of an s -cluster, the weight average degree of polymerization DP_w (or weight average molecular weight M_w) is defined as

$$DP_w = \frac{\sum_s s^2 n_s}{\sum_s s n_s} \quad (4b)$$

and must be distinguished from the z -average $DP_z = \frac{\sum_s s^3 n_s}{\sum_s s^2 n_s}$ (from now on Σ denotes the sum over all finite $s = 1, 2, \dots$ but excludes the infinite cluster $s = \infty$). As already mentioned, the exponents γ and γ' with their amplitudes C and C' are defined by

$$DP_w = C(p_c - p)^{-\gamma} \quad (p \rightarrow p_c^-) \quad (4c)$$

$$DP_w = C'(p - p_c)^{-\gamma'} \quad (p \rightarrow p_c^+) \quad (4d)$$

The probability G that an f -functional monomer belongs to the infinite network is equal to the gel fraction and is non-zero only for p above p_c . The exponent β and its amplitude B are defined by

$$G = B(p - p_c)^\beta \quad (p \rightarrow p_c^+) \quad (4e)$$

If one can measure G and DP_w but not $p - p_c$, one may²¹) plot DP_w as a function of G , where both parameters are measured simultaneously during the formation of the gel. Then trivially from Eqs. (4d, e) one can eliminate the undesired $p - p_c$ and write

$$DP_w \propto G^{1-\delta}; \quad \delta = 1 + \gamma/\beta \quad (G \rightarrow 0) \quad (4f)$$

Each monomer must belong to either a finite cluster of size s (including $s = 1$), or to the infinite network with $s = \infty$. Thus the sum over all probabilities equals unity:

$$G + \sum_s n_s s = 1 \quad (4g)$$

The “susceptibility” $\chi \equiv \Sigma s^2 n_s$, i.e. the second moment of the cluster size distribution, diverges with the same exponents and amplitudes as DP_w :

$$\chi = C(p_c - p)^{-\nu} \text{ or } = C'(p - p_c)^{-\nu'} . \quad (4h)$$

Since $G = 0$ at the critical point, $\Sigma n_s(p_c)s = 1$ in the denominator of expression (4 b). (In two dimensions¹⁰⁾, χ seems easier to be analyzed than DP_w .)

The quantities defined so far are purely topological and give no information about length scales. But also such lengths have been studied. The spatial extent of a cluster is conveniently defined by the radius R_s of gyration²²⁾:

$$R_s^2 = \frac{1}{s} \sum_{i=1}^s r_i^2 \propto s^{2\sigma} \quad (s \rightarrow \infty, p \text{ fixed}) \quad (5a)$$

for p above, at and below p_c ; this sum runs over all s monomers in the macromolecule where r_i is the distance of each monomer center from the center-of-mass of the macromolecule. Essam showed²³⁾ that the so-called z -average of the radius, defined by Eq. (5 b), gives the correlation length ξ , i.e. the spatial extent of the connectivity function $g(r)$ ($g(r)$ is the probability that two monomers at distance r belong to the same macromolecule). More precisely, expressed in d dimensions,

$$\int r^2 g(r) d^d r \equiv \xi^2 = \Sigma s^2 n_s R_s^2 / \Sigma s^2 n_s \equiv \langle R_s^2 \rangle_z . \quad (5b)$$

This typical cluster radius ξ diverges at the gel point:

$$\xi = \xi_0(p_c - p)^{-\nu} \text{ or } = \xi'_0(p - p_c)^{-\nu'} \quad (p \rightarrow p_c) . \quad (5c)$$

In the definition of χ and ξ , several sums over all cluster sizes s were used which diverge at the gel point. The terms in these sums like $s^2 n_s R_s^2$ may first increase with increasing s , then reach a maximum, and finally decrease rapidly with rising s for all $p \neq p_c$ in all gelation theories known so far. Thus there exists a typical cluster mass s_ξ (corresponding roughly to the typical cluster radius $\xi \approx R_{s_\xi}$) with the largest contribution to these sums (provided they diverge at p_c). More quantitatively, we define s_ξ as the z -average degree of polymerization, analogously to Eq. (5 b):

$$s_\xi = \Sigma s^3 n_s / \Sigma s^2 n_s \equiv DP_z . \quad (6a)$$

Luckily, all current theories predict that the position of the maximum in these two and all other diverging sums, like $\Sigma s^5 n_s$, is proportional to this s_ξ for $p \rightarrow p_c$. This concept of a typical cluster mass s_ξ is useful for qualitative arguments concerning the critical behavior of various quantities: Sums like $\Sigma s^5 n_s R_s^3$ can be evaluated correctly, apart from proportionality factors, if we replace all its summands by their values at the gel point and then let the sum run from $s = 1$ to $s = s_\xi$ only. While critical amplitudes cannot be estimated reliably by this approximation, the critical exponents are correct if the sum diverges at the gel point. For this purpose, one needs to know how s_ξ diverges:

$$s_\xi \propto |p - p_c|^{-1/\sigma} \quad (p \rightarrow p_c) . \quad (6b)$$

(For simplicity, we assumed the same critical exponent on both sides of the phase transition.) More details are given in Refs. 22, 23. We leave it as a possible exercise to the reader to prove, with the above approximation, that the weight average of the square radius, $\langle R_s^2 \rangle_w$, in contrast to the z -average, diverges with a critical exponent $2\nu - (\tau - 2)/\sigma$ as a function of $|p - p_c|$.

Finally, the exponents ζ and θ can be defined for all $p \neq p_c$, not only close to the gel point, by the asymptotic decay of cluster numbers^{22, 23}:

$$n_s(p) \propto s^{-\theta} \exp(-\text{const} \cdot s^\zeta) \quad (s \rightarrow \infty, p \neq p_c) \quad (6c)$$

where the constant depends on p . (With $p = p_c$, $\text{const} = 0$ and $\theta = \tau$ we recover Eq. (4a).) Similar to q for $p \neq p_c$, these exponents are in the percolation theory not related^{17, 18, 22} to other critical exponents like β , γ or δ and assume one value for all p below p_c and another for all p above p_c , according to the present state of knowledge.

Equation (4a) gives only a result for the cluster numbers n_s at $p = p_c$ and Eq. (6c) does not indicate how the constant in the exponential function depends on $p - p_c$. The reader can derive its critical exponent by assuming that Nature (or mathematics) is kind to us^{22, 23}: Then we have a similarity law for $p \rightarrow p_c$ and $s \rightarrow \infty$ in the sense that the ratio $n_s(p)/n_s(p_c)$ may depend on the ratio s/s_c only, and not on $p - p_c$ and s separately. Since $s/s_c \propto |p - p_c|^{-1/\sigma} \cdot s$, or $(s/s_c)^\sigma \propto \pm (p - p_c)s^\sigma$, one may rewrite this similarity postulate as

$$n_s(p)/n_s(p_c) = f((p - p_c)s^\sigma) \quad (p \rightarrow p_c, s \rightarrow \infty) \quad (6d)$$

with a suitable scaling function $f(z)$, which rapidly becomes zero for the argument $z \rightarrow \pm \infty$. This assumption is valid for all current gelation theories for $d < 6$ and has come historically from a generalization of the Fisher droplet model²⁴ for liquid gas critical points and also from a generalization of the Flory-Stockmayer theory²⁵. This similarity law also is the secret behind the approximation mentioned before in Eq. (6b).

Experimentally, much more obvious than all these microscopic quantities are the macroscopic elasto-hydronechanical properties: the viscosity η of the sol below p_c and the elasticity of the gel above p_c . (For the critical exponent of the viscosity it should not matter much whether in the theory, we use η or the intrinsic viscosity.) These are presently the two most thoroughly studied quantities near the gel point from the experimental point of view whereas the theory is still in bad shape here (see below). Since the gel point is the onset of some kind of solidification, η of the sol and E of the gel should diverge there or vanish, respectively:

$$\eta \propto (p_c - p)^{-k} \quad (p \rightarrow p_c^-) \quad (7a)$$

$$E \propto (p - p_c)^t \quad (p \rightarrow p_c^+) \quad (7b)$$

These definitions refer to the zero-frequency limit only; for oscillatory motions both quantities will depend on the product of oscillation frequency and a characteristic time, which presumably diverges at p_c and about which little is known.

Finally, we always assumed implicitly that the gel is formed continuously, i.e. the gel fraction vanishes continuously at the gel point. In solutions, as a function of chemical potential the gel fraction may also jump to zero discontinuously if the system jumps over the miscibility gap. In the language of phase transition theory, this would be called a first-order transition, and we ignore its properties in this review which deals with continuous transitions for gels (cf. Chap. D.).

This rather long compilation of independent exponents can be shortened appreciably if we assume the similarity equation (6d) to be valid. Then, using Eq. (6b) and the approximation described before, one can express β , γ , γ' and δ in terms of σ and τ , as explained e.g. in reviews^{22, 23}:

$$\beta = (\tau - 2)/\sigma, \gamma = \gamma' = (3 - \tau)/\sigma, \delta = 1/(\tau - 2) \quad (8a)$$

whereas

$$\nu = \nu' = \varrho/\sigma \quad (8b)$$

with ϱ taken at $p = p_c$. The *scaling relations*⁸⁾ are valid for all current gelation theories and have so far not been contradicted by reliable experiments. Then one has to work with only three exponents ϱ , σ , τ near the gel point, in addition to the less well understood mechanical exponents k and t . Assuming “hyperscaling”, the number of free exponents can be reduced further by one

$$\varrho(p = p_c) = (1 + 1/\delta)/d \quad (9a)$$

in d dimensions, or, from Eq. (8):

$$d\nu = 2\beta + \gamma = \beta(\delta + 1) . \quad (9b)$$

Such hyperscaling relations are also known from other phase transitions; a short introduction to scaling in the case of thermal phase transitions is given in the appendix of Ref. 7. In contrast to scaling relations (Eq. (8)), the hyperscaling relation (9) involving the dimensionality d cannot be used in Flory-Stockmayer theories and similar approaches.

Derivation of Eq. (9a): We assert that very large but finite clusters ($s \gg s_g$) have for p above p_c the same internal structure as the gel, and that analogously to assumption (6d) the cluster radius $R_s(p)$, divided by its value $R_s(p_c)$ at the gel point, is for large molecules near p_c a function of s/s_g only. In particular, in the cluster interior of these very large macromolecules the probability of a monomer to be part of the cluster equals the probability G of that monomer to be part of the infinite cluster. Then, in d dimensions that “mass” s of the very large but finite cluster equals the product of the “density” $G \propto (p - p_c)^\beta$ and the cluster volume $\propto R_s^d$. The above similarity assumption allows to apply this equality (apart from a constant factor) even at $s = s_g$:

$$s \propto (p - p_c)^\beta R_s^d \propto (p - p_c)^\beta s^{d\varrho} \propto s^{-\sigma\beta} s^{d\varrho}$$

with $\varrho = \varrho(p_c)$, or $\varrho = (1 + \sigma\beta)/d$, from which Eq. (9a) follows.

The reciprocal of the radius exponent ϱ may be defined as a fractal dimension^{22, 26)} d_f , since the mass s varies with (radius) ^{$1/\varrho$} . According to Eq. (9a), this effective dimension of large but finite macromolecules right at the gel point is thus smaller than the Euclidean dimension d of the space by a factor $1 + 1/\delta$ which varies from 1 to 1.5, depending on the theory and dimensionality used. One may alternatively define the dimension d_f by requiring that for $p = p_c$ in a large but finite cube of length L the number of monomers in the largest cluster (aspiring to become the infinite cluster) varies with L as L^{d_f} ; then, according to the percolation theory^{22, 23)} we have again $d_f = 1/\varrho = d/(1 + 1/\delta)$.

A reader who is not interested in all the theoretical ramifications discussed in this article and merely wants to know what are at present the most important and controversial exponents may restrict himself to β , γ , ν , ϱ , k and t , as summarized through

$$G \propto (p - p_c)^\beta, DP_w \propto M_w \propto |p - p_c|^{-\gamma}, \langle R_s^2 \rangle_z \propto |p - p_c|^{-\nu}, \eta \propto (p_c - p)^{-k}, \quad (10)$$

$$E \propto (p - p_c)^t, R_s(p_c) \propto s^e$$

He should keep in mind that the hyperscaling law of Eq. (9b), which can be rewritten as $d\varrho(p_c) = (2\beta + \gamma)/(\beta + \gamma)$, is valid in the percolation theory but not in the classical theory

of the Flory-Stockmayer type, and that in all theories and experiments these various exponents of Eq. (10) are defined only asymptotically close to p_c , or for asymptotically large s . He may then immediately proceed to Table I with the various predictions for the exponents (Sect. C.I.).

B.III. Universality

Twenty years of research into critical phenomena occurring in thermal phase transitions has given two main results¹⁵⁾: Scaling and universality. The ideas of scaling (including hyperscaling) have just been introduced. The principle of universality states that the critical exponents are independent of many details of the materials and models investigated. In other words, Nature likes its critical exponents so much that once it has invented a set of exponents it is selling it to us over and over again. And this principle is the main reason why critical exponents, as opposed e.g. to the positions p_c of the gel point, are so important.

More precisely:

The many materials and models which exhibit a continuous phase transition can be grouped into a much smaller number of universality classes such that within one such class the critical exponents and other "universal" quantities are the same.

Let us take an example from thermal phase transitions: At a liquid-gas critical point the density difference Δ between liquid and vapor on the coexistence curve, normalized by the density at the critical point, approaches zero continuously, similar to the gel fraction G near the gel point. For temperatures slightly below that critical temperature, we may write

$$\Delta = B(1 - T/T_c)^\beta \quad (11)$$

with a critical exponent β and a critical amplitude B , as in Eq. (4 a). Experiments performed on fluids such as helium, xenon, carbon dioxide, and water have shown according to Ref. 27 that within the experimental accuracy of a few percent the exponent $\beta \approx 0.32$ is the same for all these liquid-gas critical points, and also for the three-dimensional lattice gas (Ising model). (Half a century ago²⁷⁾ β was about ten percent higher for CO_2 ; for a different opinion, cf. Gordon et al.¹¹⁾.) The critical temperature T_c varied from material to material by more than two decades, and also the amplitude B changes appreciably when quantum or polarity effects are important. But the exponent β stayed the same. Moreover, the same β was also found (within small error bars) for different lattices in the lattice gas model (simple cubic, fcc, bcc, . . .).

One may also look, for this example of liquid-gas critical points, at the predictions of the classical van der Waals equation. This approximation allows T_c (and the critical density) to vary arbitrarily but it always gives $\beta = 1/2$, as the universality principle requires. In addition, also the amplitude B of the van der Waals equation is always the same, an effect known as the classical law of corresponding states. Therefore, universality is nothing but a generalization of the law of corresponding states; it also allows the critical amplitudes to be varied and fixes only the critical exponents whereas the law of corresponding states fixes both exponents and amplitudes.

Why is universality valid? Renormalization group methods^{13, 23, 28)} have given since 1970 a theoretical explanation; we confine ourselves here with a qualitative picture: As we saw in Eq. (5c), the average extent ξ of fluctuations (or clusters) diverges at the critical point; this is also the case for thermal phase transitions. Thus, close to the critical point the system averages over a length ξ much larger than the size of a single molecule or the range of its interaction. Therefore, molecular details become unimportant when ξ has become sufficiently large, i.e. near the critical point. This argument makes not only plausible the universality principle but also indicates that exceptions exist if the range of interaction is infinite. We also see from this discussion that universality, critical exponents, etc. should not be applied far away from the critical point where ξ is small.

Of course, the universality statement in the form of Eq. (11) is more a definition than a law until we have clarified how to determine in practice the universality class. Which parameters are relevant and change the universality class and which details are irrelevant for this classification? Now the universality principle becomes unreliable. Special cases have often been found where, unexpectedly at that time, the exponents suddenly changed. In the Baxter model²⁹⁾, the critical exponents even varied continuously if a suitable parameter changed continuously. But these exceptions are relatively infrequent and occur mostly in rather complicated systems; for a problem as simple as the ordinary liquid-gas critical point all three-dimensional materials and models have the same critical exponents, within some error bars. We hope that ordinary gelation also belongs to the simpler cases where universality holds and will give more complicated examples in Chap. C.V. and D.

Since the hyperscaling Eq. (9) relates critical exponents to the dimensionality d different exponents are obtained for various d : the dimensionality d is a very relevant parameter affecting the universality class provided Eq. (9) is valid. In "classical" theories similar to the Flory-Stockmayer methods hyperscaling cannot be applied and even this dependence on space dimensionality d vanishes: The classical theory is more universal than the scaling (renormalization) theory.

Specifically for gelation, we will discuss in Sect. C.V. various modifications of the simple percolation model of Fig. 1 and check if the exponents change. In most cases, they do not; in particular, the lattice structure (simple cubic, bcc, fcc, spinels^{22, 23, 30, 34)}) is not an important parameter since different lattices of the same dimensionality d give the same exponents within narrow error bars. More importantly, percolation on a continuum without any underlying lattice structure has in two and three dimensions³¹⁾ the same exponents, within the error bars, as lattice percolation. In the classical Flory-Stockmayer theory which does not employ any periodic lattice structure, the critical exponents are completely independent of the functionality f of the monomers or the space dimensionality d . But if the system is not isotropic³²⁾ or if the gel point is coupled with the consolute point of the binary mixture solvent-monomers^{33, 77)}, the exponents may change as discussed in Sect. D.

For practical purposes, we thus regard the simplified universality assertion "exponents are independent of microscopic details" as a 90% principle since it usually works.

Thermal phase transitions show that dynamic properties like transport coefficients or relaxation times may have different exponents for different materials and models even if the static equilibrium properties have the same exponents. Thus the static universality classes are split into smaller dynamic universality groups. Conversely, certain exponent ratios like γ/ν or β/ν may remain constant even if β , γ , and ν are a function of a parameter²⁹⁾. Nothing seems to be known yet about whether or not gelation and percolation exhibit similar effects.

The analogy between gelation and liquid-gas critical points (or Curie point for ferromagnetism) should not be construed as an assertion that gelation belongs to the same universality class as liquid-gas critical phenomena. In fact, all current theories (for $d > 1$) give a gel fraction exponent β different from the corresponding exponent β for the difference between liquid density and vapor density (or for the spontaneous magnetization). Flory⁴⁾, for example, found $\beta = 1$ whereas, according to the van der Waals equation, $\beta = 1/2$.

The exponents are not the only universal quantities. Also certain combinations of critical amplitudes are expected to be universal even though each amplitude separately varies with the material^{13, 35)}. For the present state of the art, in gelation we need here only the ratio C'/C of "susceptibility" amplitudes, i.e. DP_w (or M_w) below p_c divided by DP_w (or M_w) above p_c at the same distance from p_c , within the limit of very small distances. This ratio is universal in all current theories, though its numerical value is controversial. To anticipate further experimental developments, we mention here the more general universality postulate²²⁾ for the cluster numbers of Eq. (6d):

$$n_s(p)/n_s(p_c) = f_u(q_1(p - p_c)s^\sigma) \quad (12)$$

where the function f_u and the exponents σ and τ are the same for all members of the same universality class. Only the amplitudes q_0 and q_1 depend on the material or model (q_0 and τ enter, via Eq. (4a), the $n_s(p_c)$ appearing in Eq. (12)). One may derive from Eq. (12) and the definition of DP_w , Eq. (4b, g), that the parameters q_0 and q_1 cancel from the amplitude ratio C'/C , i.e.

$$C'/C \text{ is universal.} \quad (13)$$

In general^{13, 35)}, whenever a relation between critical exponents exists, due to scaling, one can also form a universal combination of critical amplitudes. For example, the scaling law $\gamma' = \gamma$ corresponds to Eq. (13), and hyperscaling, $d\nu = \gamma + 2\beta$, corresponds to a universal combination of the amplitudes ξ_0^d , C and B^2 ³⁵⁾.

Very important is the fact that the position p_c of the gel point is not universal: Just like the amplitudes alone, p_c is not independent of materials and models. For example, in the Stockmayer theory of f -functional gelation, $p_c = 1/(f - 1)$ obviously depends on f ; considering lattice percolation in two dimensions for the square lattice of Fig. 1 $p_c = 1/2$ whereas for the triangular lattice $p_c = 2 \cdot \sin(\pi/18) \approx 0.34729$ ^{22, 23)}. As a consolation for the lack of exact universality for p_c , one can offer the critical volume fraction³⁶⁾, which is not exactly the same but nearly the same for a broad class of different lattices and models with the same dimensionality.

This universality concept explains why we are interested so much in critical exponents, more than in critical amplitudes, the value of p_c , or the behavior far away from p_c . The latter non-universal quantities depend on microscopic details; thus, if a theory does not fit experimental results for the non-universal quantities one may change some details in the theory until the theoretical curve fits the experimental curve with reasonable accuracy everywhere. Such a good fit does not necessarily mean that this improved theory describes the qualitative essentials of the phase transition mechanism correctly. On the other hand, a more or less elegant and simplified model may describe correctly the essential phase transition mechanism and give the correct critical exponents; however, it would be an accident if it yielded the correct value of p_c or other non-universal quantities. It is the exponent rather than p_c which determines the universality class of the material or model.

The well-known Flory-Stockmayer theory can be used as a simple example: Depending on the value of the functionality f , we can shift p_c over a large interval; for more complicated mixtures we may even give f a fractional value¹²⁾. These changes are important for many aspects of gelation. However, as far as critical phenomena are concerned,

none of them causes a change in the critical exponent β for the gel fraction away from its Flory-Stockmayer value $\beta = 1$. Thus theories for different f , while giving different p_c , still feature the same exponents since they describe the same essential mechanism for the phase transition.

From the experimental point of view, critical exponents offer a scheme to group numerous materials into a few universality classes, just as for example the concept of the functionality f allows to characterize many different molecules by a single parameter. This f does not tell us everything about the structure of the molecule and its technical application but chemistry has always regarded f as an important and useful parameter. We submit that for a classification of critical phenomena occurring in (continuous) phase transitions, critical exponents are an important and useful parameter for the classification of different materials and transition mechanisms. For other types of phase transitions, like in magnets, this search for exponents is widespread, and we suggest to follow this method also for gelation.

The situation may be compared with Kepler's laws for the motion of planets about the sun. If the force between planet and sun varies with (distance) $^{-\alpha}$, then for $\alpha = 2$ the motion is ellipsoidal. For other values of this "critical exponent" α , the motion is different and more complicated. "Non-universal" quantities like the mass and shape of the planet are less important if we are interested only in the motion of the planet as a whole and in Kepler's laws. The crucial quantity is the exponent α . Of course, to predict next week's weather we need much more information, and a reliable theory then becomes extremely difficult. Clearly, Kepler's laws and the exponent α for gravitational force do not tell us everything we want to know about the planetary system; they have played, however, an important role in the development of science. Similarly, critical phenomena and their critical exponents do not tell us everything we want to know about gels, but they may play an important role in our understanding of the phase transition. The position of the critical point is less important for this aspect, just as the mass of a planet is less important for Kepler's laws.

Thus the remainder of this review will concentrate in finding out which theory predicts the best critical exponents relating to critical phenomena, and what type of experiments determining the exponents exist. Further details, in particular gelation outside the region of critical phenomena, are left to other reviews and to future research (apart from some results in Chap. D.).

C. Comparison of Classical and Percolation Theories

C.I. Classical Theory

The Flory-Stockmayer theory^{4,5)} assumes that each bond between two monomers is formed randomly, and it neglects cyclic bonds, excluded volume effects, and steric hindrance. Thus for example, the probability for one of the f bonds emanating from a monomer to be formed is always p , independent of how many of the other $f-1$ bonds have been generated. Since cyclic bonds are excluded, it is not allowed that, say, an active bond connects monomer A with monomer B, another monomer B with monomer C, and

a third bond is formed between C and A, thus closing a loop of three bonds. Because of this randomness and neglect of cyclization the Flory-Stockmayer theory does not take into account that two different molecules cannot be at the same place (excluded volume effects) or are influencing the bond formation probability locally due to the space they are filling. Thus this theory assumes point-like monomers, and the resulting macromolecules are a "graph-like state of matter" in the concept of Gordon and his collaborators¹¹). The dimensionality d is not important in this approximation. (For an inconsistency of this approximation if $d = 3$ see end of Sect. C.III.) Figure 2 shows the bonding possibilities for such a system for the simplest case where $f = 3$: Each line between two points in the figure either represents a bond which has been formed (with probability p) or a bond which is still open (with probability $1 - p$). Neither temperature nor concentration enter this simple model; everything is fixed by f and p .

It is obvious that Fig. 2 represents a drastic simplification of reality for complicated molecules⁹). The merit of this theory is that it gives a good qualitative picture of real gelation, the first indication for the universality principle that complicated molecular details are not very relevant for the main results. Physicists call Fig. 2 a Bethe lattice, and this gelation process is then called percolation on a Bethe lattice³⁷). The macromolecules are also designated as Cayley trees since, like trees in a forest, they have no cyclic links between their branches. Many other problems of theoretical physics, besides percolation, have been studied on Bethe lattices. When critical exponents were found they usually agreed with those obtained by using simple approximations for real lattices like mean field (or molecular field) approximation, Landau ansatz for phase transitions, van der Waals equation, etc. We will thus also denote them as "mean field" approximations.

A warning for experts: A non-negligible fraction of monomers is located on the surface of the Bethe lattice, even within the thermodynamic limit, as one can see already from Fig. 2. We are interested here in the Bethe lattice as an approximation for real three-dimensional space and thus neglect the complications arising from this surface³⁸). This is achieved by considering the central site of Fig. 2 as a representation of all monomers in the real system.

The critical point in the Flory-Stockmayer theory is

$$p_c = 1/(f - 1) \quad (14a)$$

The average cluster number n_s (per monomer) also can be calculated exactly^{4,5,37}) and involves binomial coefficients; if we replace the factorials by Stirling's formula we arrive at^{12,25})

$$n_s \propto s^{-5/2} \exp(-\text{const} \cdot s) \quad (s \rightarrow \infty) \quad (14b)$$

where the proportionality factor and the constant in the exponential depend on p . For $p \rightarrow 1$ and $p \rightarrow 0$, this constant approaches infinity, and it vanishes at the critical point since

$$\text{const}(p) \propto (p - p_c)^2 \quad (p \rightarrow p_c) \quad (14c)$$

We see that near the critical point the Flory-Stockmayer solution Eq. (14 b, c) is a special case of the scaling assumption in Eq. (6 d): With $\tau = 5/2$, $\sigma = 1/2$ and $n_s(p_c) \propto s^{-5/2} = s^{-\tau}$ we take the scaling function $f(z)$ in Eq. (6 d) as $f(z) = \exp(-az^2)$ with a constant a and then get from Eq. (14 b, c)

$$n_s(p)/n_s(p_c) = \exp(-a(p - p_c)^2s) \quad (14d)$$

This is in agreement with Eqs. (14b, c).

Since the Flory-Stockmayer theory is a special case of Eq. (6d) it also obeys all the scaling laws resulting from it, except hyperscaling. Since $\tau = 5/2$ and $\sigma = 1/2$ we get from Eq. (8) immediately

$$\beta = 1, \gamma = \gamma' = 1, \delta = 2, \nu = 2\rho. \quad (14e)$$

Inspection of Eq. (14b) shows directly $\zeta = 1$ and $\theta = 5/2$ independent of p . Because of the symmetric nature of Eq. (14c) one has $C' = C$ for the amplitudes of DP_w .

Using the Flory-Stockmayer approximation, additional calculations give³⁹⁾

$$\rho = 1/4 \quad (14f)$$

This implies that the radius of very large macromolecules varies with the fourth root of their mass, again independent of p . Thus, from Eq. (14e) we obtain $\nu = 1/2$. Finally, the elasticity of the gel vanishes at the gel point with $(p - p_c)^t$ with $t = 3$ according to Dobson and Gordon^{2, 40, 41)}. We now call "classical" all theories whose results are in the same universality class as the Flory-Stockmayer theory, i.e. whose critical exponents agree with Eq. (14e, f). (Future research may make it necessary to distinguish between theories that agree with Eq. (14e) but not with Eq. (14f) and/or not with $t = 3$ but at present that does not seem necessary.) Thus, Table 1 gives, in its "classical" column, a summary of these exponents.

Table 1. Predictions of universal quantities (critical exponents and one amplitude ratio)

| Exponent | Equation | d = 2 Percolation | d = 3 Percolation | Classical | Quantity |
|--------------------|----------|----------------------|----------------------|-----------|------------------|
| β | 4e | 5/36 | 0.45 | 1 | Gel fraction |
| γ | 4c, d | 43/18 | 1.7 ₄ | 1 | DP_w |
| δ | 4f | 91/5 | 4.9 | 2 | $DP_w = DP_w(G)$ |
| ν | 5c | 4/3 | 0.88 | 1/2 | Corr. length |
| k | 7a | ? | ? | ? | Viscosity |
| t | 7b | 4/3? | 1.7? | 3 | Elasticity |
| σ | 6b | 36/91 | 0.46 | 1/2 | Typical size |
| τ | 4a | 187/91 | 2.20 | 5/2 | $n_s(p = p_c)$ |
| $\varrho(p = p_c)$ | 5a | 48/91 | 0.40 | 1/4 | Radius |
| $\varrho(p < p_c)$ | 5a | 0.641 | 1/2 | 1/4 | Radius |
| $\varrho(p > p_c)$ | 5a | 1/2 | 1/3 | 1/4 | Radius |
| $\zeta(p < p_c)$ | 6c | 1 | 1 | 1 | $\log n_s$ |
| $\zeta(p > p_c)$ | 6c | 1/2 | 2/3 | 1 | $\log n_s$ |
| $\theta(p < p_c)$ | 6c | 1 | 3/2 | 5/2 | Prefactor n_s |
| $\theta(p > p_c)$ | 6c | 5/4 | -1/9 | 5/2 | Prefactor n_s |
| C'/C | 13 | 0.005 | 0.1 | 1 | DP_w ratio |

For percolation, scaling and hyperscaling is used whenever it determines an exponent more accurately than direct data. Rational numbers indicate (presumably) exact results, numbers with a decimal point are numerical extrapolations with an estimated error typically of the order of one unit in the last digit given. Data from earlier reviews^{22, 23)} and recent research^{10, 18, 49, 51, 52, 56, 58, 65, 131)}. Question marks are explained in Sect. C.IV

Readers familiar with thermal phase transitions like the liquid-gas critical point will not be surprised about $\gamma = 1$ in a classical theory. Quite generally, Bethe-lattice approaches¹⁵⁾ give simple critical exponents like integers or $1/2$. It is important to note that $\beta = 1$ for gels, in contrast to $\beta = 1/2$ according to the "classical" theories of thermal phase transitions. However, one can already see from Eq. (7) of Flory's second paper²⁾ that, close to p_c , the gel fraction vanishes linearly with $p - p_c$, i.e. $\beta = 1$. Table 2 summarizes these analogies between thermal phase transitions and Table 3 compares, also for the classical case, the critical exponents. We see that the analogy is somewhat loose since the critical exponents are not the same: Gelation does not belong to the same universality class as liquid-gas phase transitions. However, the general structure of the theory is similar, and the scaling laws relating the various exponents, i.e. Eq. (8), are the same.

Many modifications of the Flory-Stockmayer theory, e.g. the cascade formalism^{11, 12)}, have been published. To some extent they allow for loops in the bond formation process. Refs. 1, 9, 11 give more references and details on theories which are based on an improved simple Flory-Stockmayer theory. The position of the gel point then shifts away from $p_c = 1/(f - 1)$, i.e. the gel point is not universal. In general, however, the exponents remain the same. For exceptions see Refs. 42, 43; for example, in a solution at thermal equilibrium, when the critical consolute point is also a gel point the degree of polymerization DP_w may vary with $(T - T_c)^{-1}$ above is critical temperature but with $(T_c - T)^{-1/2}$

Table 2. Analogies between gelation, liquid-gas critical points, and ferromagnetic-paramagnetic transitions

| Gelation | Critical Fluid | Curie Point |
|-----------|----------------|-------------|
| DP_w | κ | χ |
| G | Δ | M_0 |
| ξ | ξ | ξ |
| $p - p_c$ | $T_c - T$ | $T_c - T$ |

Δ is the relative density difference between the liquid and its vapor, M_0 the spontaneous magnetization, κ the isothermal compressibility, χ the susceptibility and ξ the correlation length. These analogies do not mean that the numerical values of corresponding critical exponents are the same

Table 3. Comparison of gelation (percolation) exponents (left part) with exponents in thermal phase transitions (right part) for both classical and "modern" theories

| | random-percolation model | | | Ising-magnet or lattice-gas model | | |
|----------|--------------------------|------------------|-----------|-----------------------------------|-------|-----------|
| | d = 2 | d = 3 | classical | d = 2 | d = 3 | classical |
| β | 5/36 | 0.45 | 1 | 1/8 | 0.32 | 1/2 |
| γ | 43/18 | 1.7 ₄ | 1 | 7/4 | 1.24 | 1 |
| ν | 4/3 | 0.88 | 1/2 | 1 | 0.63 | 1/2 |

Numbers with decimal points are numerical estimates, fractions are (presumably) exact. As explained in Eq. (16) and on p. 126, classical exponents are exact for dimensionalities above 6 (left part) and above 4 (right part)

below is temperature, even in a Bethe-lattice approximation⁴³). Burchard⁴²) reported results obtained by the application of a cascade theory to heterogeneous systems which lead to $\gamma = 2$, $\nu = 1/2$. (For simplicity, we ignore these few exceptions when dealing with classical or similar theories.) Nearly all these theories in terms of the Flory-Stockmayer theory seem to fall into the “classical” universality class with $\beta = \gamma = 1$, etc. Let us cite just two examples which dealt explicitly with critical exponents: Fisher and Essam³⁷) took into account the possibility of the formation of small cycles in bond formation by investigating the so-called Bethe cactus. Many features turned out to be different now but the critical exponents, which still could be calculated exactly, remained exactly the same. Recently, Burchard and collaborators⁴⁴) found that local heterogeneities cause important changes but the asymptotic exponent γ , which could be calculated exactly, was again exactly unity. Thus, Table I seems to give in its “classical” column a reasonable summary of the critical exponents found during the past 40 years in most of the research on gelation theory.

C.II. Random Percolation

The percolation theory (or more precisely, random bond percolation on nearest-neighbor lattices) assumes that each bond between two nearest-neighbor sites on an infinite periodic lattice is formed randomly with probability p . Detailed reviews, which are partially outdated, are available^{22, 23}), and even a movie about percolation has been made⁴⁵). Its possible applications range from quark matter in high-energy physics and the extraction of crude oil from porous media^{46, 47}) to, perhaps, gelation!

The critical exponents of the two- and three-dimensional percolation are listed in Table 1. They have been found by using a variety of methods which are generally also applied in thermal phase transitions, and are listed in increasing order of accuracy but with decreasing versatility:

- a) Monte Carlo simulations²²) with the help of random numbers, as in Fig. 1 or our Appendix, give the amplitude ratio C'/C with an accuracy of about 20%; lattices containing up to 10^8 sites (and more) have been investigated, giving e.g. the two-dimensional ν with an accuracy of about 2%^{10, 48}).
- b) In series expansions²³), the properties of small clusters are exactly determined (s up to 20) and suitable extrapolations by means of ratio methods, Padé approximants etc. are made. The three-dimensional $\beta \approx 0.45 \pm 0.02$ is an example⁵⁸). Also, the first non-classical percolation exponent, $\gamma = 19/8 \pm 0.03$, was determined by Sykes and Essam⁵³) in 1964; it agrees within 0.014 with the ratio 43/18 in Table 1.
- c) In phenomenological renormalization (or finite size scaling or Nightingale renormalization) the properties of narrow strips in two dimensions are studied and extrapolated to infinite lattices. Thus, it was confirmed that $\nu = 4/3$ with an accuracy of 0.2%⁴⁹). Three-dimensional results can be hoped for in the future (B. Derrida, priv. comm.).
- d) Exact results beyond classical theory include inequalities⁵⁰) ($\zeta = 1$ above and $\zeta = 1 - 1/d$ below p_c). Correspondence with other exactly solved phase transitions gave^{18, 51}) θ and ϱ in two and three dimensions ($\varrho = 1/d$ above p_c from Ref. 17).

While methods c, d and, to some extent, also b are mainly suitable for the determination of the asymptotic behavior close to the gel point, the Monte Carlo method is a computer simulation similar to a real experiment and can, in principle, be applied to all

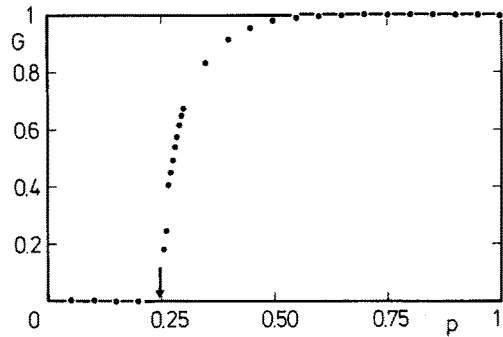


Fig. 3. Dependence of gel fraction on bond formation probability p . Results of a test run with the program given in the Appendix, in a simple cubic lattice of size 50^3 . The arrow indicates the gel point $p_c = 0.248 \pm 0.001$ for infinite lattices. For better results in larger systems see e.g. Ref. 10

cases; it is, however, difficult to use it close to the gel point. Figure 3 shows a simple test performed with a CDC Cyber 76 computer which took only about half a minute; as in a real experiment it shows the gel fraction G as a function of p over the whole range of interest, i.e. from $p = p_c (= 0.248 \pm 0.001$ from (65)) to $p = 1$. As explained in Sect. B.III. this behavior over the whole interval of p is not universal; if we had used a different three-dimensional lattice, we would have obtained a somewhat different curve. Only the critical exponent β , which is difficult to get from Fig. 3, would have been the same within its error bars. (Using more suitable data on a larger lattice, Nakanishi and Stanley found by means of the same method $\beta = 0.42 \pm 0.02$.) For log-log plots of such Monte Carlo “experiments” see e.g. Refs. 22, 56.

Between method c and d is the den Nijs-Pearson-Nienhuis et al. conjecture about the Potts model in two dimensions (which includes percolation and the lattice gas as special cases)⁵²). It assumes a simple form for the variation of the exponents and fits its parameters for exactly solved models. Since

- (i) one exponent predicted by this formulation of the model agreed exactly with an exact solution found later,
- (ii) the other exponents agreed generally within 0.2% with the numerical results obtained later by Blöte et al.⁴⁹), and
- (iii) theoretical arguments (no rigorous proof) can be given for this approach (Nienhuis⁵²), this conjecture is now widely believed to be exact.

The two-dimensional β , γ , δ , ν , σ , τ , and $\rho(p_c)$ given in Table 1 are based on this assumption (and scaling and hyperscaling). These are not the first “exact but not rigorous” results obtained by use of the percolation theory. Already in 1964, Sykes and Essam⁵³) found $p_c = 1/2$ for the square lattice of Fig. 1 but only in 1980 was Kesten’s mathematically rigorous and complete proof published⁵⁴). It may also be time-consuming to prove (or disprove?) $\nu = 4/3$ for the same problem. (For the explanation of the question marks in Table 1 see Sect. C.IV.) In Table 1 the majority of the percolation values are listed as (presumably) exact; only a minority is based solely on numerical extrapolations or computer experiments, with all their dangers menacing us from the dark of asymptopia¹¹). Table 3 merely repeats the most important exponents to compare them with the lattice gas (Ising model) for $d = 2$ (rigorous exact solution) and $d = 3$ (numerical extrapolation from Borel transforms of renormalization group results⁵⁵).

Comparing the results in Table 1, we see that the classical exponents typically differ from three-dimensional percolation exponents by a factor of about two. Even experiments of moderate accuracy may distinguish between two such drastically different pre-

dictions. We draw the reader's attention particularly to the amplitude ratio C'/C for DP_w , which is about 1/8 or 1/11 in the three-dimensional percolation^{10, 56} but unity in the classical theory. Since other alternatives to the classical theory are less developed at present, the three-dimensional percolation theory is now leading the field of challengers against the classical theory.

We mentioned already in Sect. B.III. that continuum percolation³¹) without a lattice structure gives, within narrow error bars, the same exponents as lattice percolation. Thus, if we place circles or spheres randomly into a two- or three-dimensional space, the resulting overlaps denote a bond formation: this continuum percolation problem seems to fall into the same universality class as the above mentioned random percolation on lattices. The reason seems to be that for bonds between nearest, next nearest, third-nearest neighbors etc. on a lattice the critical exponents are presumed to be independent of this maximum bond length. In the limit of very large maximum bond lengths ("long-range interaction") for percolation, in contrast to the phase transitions, we may have the same exponents⁵⁷); but now the lattice structure has become irrelevant and we arrived at continuum percolation. This is not very surprising: The lattice structure is also irrelevant for liquid-gas transitions (e.g. real xenon behaves very similarly to a lattice gas²⁷) and for linear polymers for which self-avoiding walks on a lattice, computer simulations of chains in a continuum, and experiments all gave the same excluded volume exponent within a tolerance of about 1%¹⁹). However, the amplitudes (front factors) are different for lattice and continuum percolation since they are not universal quantities.

How Close is Close to the Critical Point?, asks the title of a recent review on thermal critical phenomena⁶⁴). The same question is also asked for percolation. Is it likely that classical exponents are valid close but not extremely close to the gel point, and then in an extremely small region about p_c percolation exponents are found, analogous to the situation in the superconducting phase transition or for long-range interactions in Ising magnets. At present, no material or model is known so far for which experiments or numerical data like Monte Carlo simulations or exact solutions give a clear evidence for such a crossover from classical exponents (moderately close to p_c) to percolation exponents (extremely close to p_c). It would be interesting, of course, to study systems where, as a function of a continuously varying parameter, one can go smoothly from the Bethe lattice limit to, say, square lattice percolation, and where one should expect that as a result of this variation the width (in $1 - p/p_c$) of the true critical region increases from zero (Bethe lattice) to about 0.1 (square lattice). It has been suggested^{3, 59}) that the concentration in dilute solutions, or the length of the primary chains in vulcanization (crosslinking) are such suitable parameters. While these theories⁵⁹) may be correct they have not yet been confirmed directly. However, a very simple model was recently reduced exactly by Ord and Whittington⁶²) to random percolation; they *proved* that the width of the critical region approaches zero if the average length of the primary chains involved in crosslinking tends to infinity. Monte Carlo simulations on usual lattices have given exponents in the range $10^{-2} < |1 - p/p_c| < 10^{-1}$ which agreed with those obtained from other methods. No Monte Carlo experiment is known so far which allows classical gelation exponents.

We see that the percolation theory is only a generalization of the classical gelation theory using lattices other than the Bethe lattice, with other critical exponents, and concerning applications other than polymers. Thus, one should not ask who first applied the percolation theory to gelation, since the Flory-Stockmayer theory was simply the first example of what was called later percolation theory⁶¹). Later additional works on critical exponents, starting with the publication from London in 1964⁵³), led to the assertions^{2, 3}) that the application of the Flory-Stockmayer or classical gelation theory results in a wrong description of the critical behavior.

C.III. Isaacson-Lubensky-Flory Approximation

In order to demonstrate that the percolation theory has at least some relevance for branched macromolecules, we now discuss the Isaacson-Lubensky theory²⁰). These

authors, by using a suggestion of de Gennes²⁰⁾, applied Flory's ideas⁴⁾ of the excluded volume effects of linear polymers to the excluded volume effects of branched polymers; the agreement with the lattice percolation theory is excellent. Also, this method shows the importance of the dimensionality d .

We denote by

$$R_{s0} \propto s^{\varrho_0} \quad (s \rightarrow \infty)$$

the radius of gyration in a theory which neglects excluded volume effects. Thus, $\varrho_0 = 1/2$ for linear polymers (random walks, chains at the theta point⁴⁾) and $\varrho_0 = 1/4$ for branched polymers (classical gelation theory, Eq. (14f)). Now we look at a dilute solution of macromolecules which are no longer approximated by points; this limit corresponds to p below p_c in gelation and to conditions far from the collapse transition for chains. The influence of the excluded volume is found by minimizing, with respect to the polymer radius R_s , the sum of the elastic energy E_e , which attempts to make R_s equal to R_{s0} , and the repulsive "excluded volume" energy E_r which tries to stretch the molecule as far as possible:

$$E_e \propto ((R_s - R_{s0})/R_{s0})^2; \quad E_r \propto s(s-1)/R_s^d \quad (15a)$$

in d dimensions. The expression for E_r comes from the approximation that each of the s monomers in the macromolecule feels an average interaction from all the other $s-1$ molecules, which are spread over a volume $\propto R_s^d$. Minimization of the total energy

$$E_{\text{tot}} = E_r + E_e \propto R_s^2/R_{s0}^2 + \text{const} \cdot s^2/R_s^d \quad (s \rightarrow \infty) \quad (15b)$$

gives

$$R_s \propto (s^2 R_{s0}^2)^{1/(d+2)}, \quad \text{or} \quad \varrho = (2 + 2\varrho_0)/(d+2) \quad (15c)$$

For linear polymers, $\varrho_0 = 1/2$ leads to the well-known Flory formula $\varrho = 3/(d+2)$ ($= 0.6$ in three dimensions). For branched polymers (sol below the gel point, Ref. 34), we have $\varrho_0 = 1/4$; then Eq. (15c) gives the main result:

$$\varrho = 5/(2d+4). \quad (15d)$$

This result agrees exactly with the three-dimensional percolation¹⁸⁾ theory, $\varrho = 1/2$ for all p below p_c , and differs only by 0.016 from the latest numerical estimate in two dimensions, $\varrho = 0.6408 \pm 0.0003$ (Derrida and de Seze, Ref. 131).

Moreover, we see that for d larger than some upper critical dimension d_c the repulsive term vanishes for $s \rightarrow \infty$, thus the elastic term dominating asymptotically. Then, R_s/R_{s0} approaches unity, and $\varrho = \varrho_0$, i.e. there is no excluded volume effect in the exponent. This happens whenever R_{s0}^d in the repulsive energy term increases more rapidly than s^2 with mass s , i.e. if $d > d_c \equiv 2/\varrho_0$. Therefore, the limiting dimension is

$$d_c = 4 \text{ (linear)} \quad \text{and} \quad d_c = 8 \text{ (branched, } p < p_c) \quad (16)$$

Thus for linear polymers, the classical theory gives correct exponents if $d > 4$, just as in usual thermal phase transitions. For dilute branched polymers, however, i.e. $p < p_c$, classical exponents are correct for $d > 8$ only.

In the more concentrated solutions of branched molecules right at the gel point, a screening factor $\propto s^{-1/2}$ is introduced²⁰⁾ into the repulsive energy, giving $d_c = 3/2 \varrho_0 = 6$ in a completely analogous calculation; ϱ now equals $(3/2 + 2\varrho_0)/(d + 2) = 2/(d + 2)$ which is in excellent agreement with three-dimensional percolation but slightly too small in two-dimensional percolation, and in strong contrast to the classical $\varrho = 1/4$. It should be noted that the "upper critical dimension" d_c can also be determined, with the same result $d_c = 6$, as that dimension where classical theory and hyperscaling are compatible, i.e. where $d\nu = \gamma + 2\beta$ classically. Below this d_c , hyperscaling is valid whereas above it classical exponents hold.

With additional assumptions this result leads to good estimates for other exponents or exponent ratios at the three-dimensional gel point. Let us assume the validity of the (hyper-)scaling relations (Eq. (9)) which are based on similarity assumptions valid also in the classical theory and on the assertion that the interior of a very large cluster has the same structure as the infinite network. Then, with $\varrho(p_c) = 3/5$, Eq. (9 a) gives $\delta = 5$ in three dimensions. Thus, from Eq. (9 b) we obtain $\gamma = 4\beta$ and $d\nu = 3\nu = 6\beta = 3/2\gamma$. The resulting $\gamma/\nu = 2$, which means $DP_w \propto \langle R_s^2 \rangle_z$, is exact in classical theory and a good approximation for random three-dimensional percolation; the other ratio $\gamma/\beta = 4$ is compatible with percolation but four times larger than the classical ratio.

Clearly, the result $\varrho = 1/4$ of the classical theory cannot be true (de Gennes³⁹⁾) for real three-dimensional gels; it shows that the classical theory does not take into account correctly the excluded volume effects in polymerization. With the definition of R_s one can generally show that at least half of all cluster points are contained within a sphere of radius $\sqrt{2}R_s$ surrounding the center of mass. (It should be noted that the cluster density profile in random percolation is not Gaussian^{22, 63)}.) Thus, the average number of monomers per cm^3 , the density, in the interior of the cluster is at least $\text{const} \cdot s/R_s^d \propto s^{1-3\varrho}$ for $s \rightarrow \infty$. This density cannot diverge in reality, which means that the true exponent ϱ has to be at least $1/3$ (or $1/d$ in d dimensions). The classical theory is therefore internally inconsistent, independent of all experimental problems, as far as the asymptotic radius exponent is concerned. For very dilute solutions this inconsistency might show up only for extremely large clusters, but finally for $s \rightarrow \infty$ deviations from the classical result *must* occur, *even for p far away from p_c*.

For future applications we mention some Monte Carlo results on cluster radii in the simple cubic lattice. Let R_g be the radius of gyration, R'_g the average distance of a monomer from the cluster center, R''_g the inverse of the average inverse distance between two molecules in the cluster, and L_s the average spanning length (averaged over the three-lattice directions). Table 4 compiles unpublished (site) percolation results at intermediate cluster sizes. We see that the effective exponent, if the data are plotted double-logarithmically, is larger than the theoretical prediction $\varrho = 0.4$ at the three-dimensional percolation threshold. Using a more efficient computer program and extending the data to larger clusters, Holl⁶³⁾ found a curvature in his $\log R_s$ versus $\log s$ plot and an effective exponent ϱ decreasing with increasing cluster size, as shown in Fig. 4 for $p = p_c$ and $p \rightarrow 0$. These Monte Carlo experiments give the reader an impression of the quality of such numerical data since the theoretical result $\varrho(p = 0) = 1/2$ was found only after these simulations.

Table 4. Comparison of various definitions for cluster radii (see text) at intermediate mass s in simple-cubic site percolation at $p = p_c = 0.31$. (Similar results were also obtained for $p \rightarrow 0$.)

| s | R_s | R'_s | R''_s | L_s |
|-----|-------|--------|---------|-------|
| 10 | 1.39 | 1.30 | 1.63 | 2.32 |
| 20 | 1.95 | 1.82 | 2.08 | 3.77 |
| 30 | 2.39 | 2.22 | 2.43 | 4.86 |
| 40 | 2.79 | 2.58 | 2.74 | 5.81 |
| 50 | 3.04 | 2.82 | 2.97 | 6.55 |
| 60 | 3.28 | 3.04 | 3.18 | 7.15 |

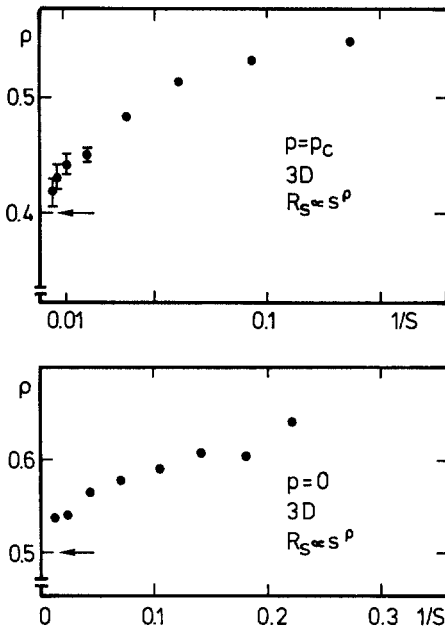


Fig. 4. Dependence of the effective radius exponent $\rho \equiv d \log(R_s)/d \log s$ on reciprocal cluster mass s (Holl⁶³). The arrows indicate exact or presumed asymptotic values for $s \rightarrow \infty$. The upper part corresponds to the three-dimensional gel point, the lower to the three-dimensional limit of very dilute solutions

C.IV. Viscosity and Elasticity Problems

We now explain why we used only question marks into Table 1 for the critical exponent k of the sol viscosity, $\eta \propto (p_c - p)^{-k}$; if not stated otherwise, our discussion refers to three dimensions. (For polydisperse samples near the gel point, the concept of the ratio of the intrinsic viscosities of a branched and a linear polymer is somewhat impractical for the calculation of the viscosity exponent k . We express the viscosity contribution of each cluster size in terms of cluster radius R_s , cluster mass s , and cluster number n_s (normalized as number per monomer). Note that $n_s s$ is the fraction of mass contained in

macromolecules having the degree of polymerization s ; their volume fraction is denoted by ϕ_s .)

For a monodisperse suspension of solid spheres occupying a volume fraction ϕ in a liquid of viscosity η_0 , Einstein showed in 1905 that the total viscosity is

$$\eta = \eta_0 \left(1 + \frac{5}{2} \phi + \dots \right) \quad (17a)$$

for small concentrations ϕ . In the case of gelation, we have a polydisperse suspension of clusters with the volume $\propto R_s^3$ which fill a volume fraction $\phi_s \propto R_s^3 n_s$ of the sample. If we approximate the viscosity by a linear superposition of the viscosities of each single cluster, neglecting cluster-cluster interactions, and if we apply the Einstein formula considering the cluster as a solid sphere (“excluded volume limit”) then we simply have to replace ϕ in Eq. (17 a) by $\Sigma \phi_s \propto \Sigma R_s^3 n_s$

$$\eta/\eta_0 = 1 + \text{const} \cdot \Sigma R_s^3 n_s . \quad (17b)$$

In both the classical and random percolation theory, $R_s^3 n_s$ varies as $s^{3\rho - \tau \bar{f}} ((p_c - p)s^\sigma)$ with a scaling function \bar{f} decaying rapidly for large arguments (see Eq. (6 d)). In the classical theory, the radius exponent ρ is 1/4 and the number exponent τ is 5/2 whereas $3\rho = \tau - 1$ in percolation according to Eqs. (9 b, 8 a). Then, for large s the s -power in front of the function \bar{f} varies for $R_s^3 n_s$ with s^{-1} in the percolation theory and with $s^{-7/4}$ in the classical theory. Therefore, in the classical theory the contribution of large clusters to the viscosity is small even at the gel point, and the viscosity remains finite there, as mentioned already by Dobson and Gordon³⁹). In the percolation theory the sum diverges logarithmically at the gel point. Thus,

$$\eta \propto \log(p_c - p) \text{ (percolation)} ; \quad \eta \rightarrow \text{const} \text{ (classical)} ; \quad (17c)$$

the exponent k is zero in both cases for this excluded volume approximation in the (unrealistic) dilute limit. More details are found in Ref. 66.

Is this result (17 c) reliable? For this purpose, we estimate the next, quadratic term in the “virial expansion” of Eq. (17 b). From Batchelor’s work⁶⁸), we find for moderately concentrated suspensions

$$\eta/\eta_0 = 1 + \frac{5}{2} \Sigma \phi_s + \Sigma \Sigma K_{s's'} \phi_s \phi_{s'} + \dots \quad (17d)$$

where the double sum runs over the two cluster sizes s and s' . Presumably one may approximate the interaction function $K_{s's'}$ by a constant of the order of unity:

$$\eta/\eta_0 = 1 + \frac{5}{2} \Sigma \phi_s + (\Sigma \phi_s)^2 \cdot \text{const} . \quad (17e)$$

Now, we see that in the classical theory the quadratic term is as important as the linear term, and for the percolation theory the quadratic term even diverges more strongly ($\propto \log^2(p_c - p)$) than the linear term. Therefore, the whole “virial expansion” in powers

of the concentrations ϕ seems to break down near the gel point; since the macromolecules interact with each other too strongly (entanglement etc.) the above approximation becomes unreliable.

In another theory⁶⁷⁾ the contribution of an s-custer to the viscosity varies with R_s^2 instead of R_s^3 ("Rouse approximation"). Thus,

$$\eta/\eta_0 = 1 + \text{const} \cdot \sum R_s^2 n_s + \dots \quad (17f)$$

a sum which diverges close to the gel point with $(p_c - p)^{\beta-2\nu}$ as one can see, using the trick described on p. 112. Thus, the viscosity exponent k is about 1.3 in the percolation and zero (logarithmic divergence of η) in the classical theory. However, for very large macromolecules dominating very close to the gel point, this Rouse limit seems to be more deleterious than the excluded volume limit of Eq. (17b) according to Sievers⁶⁶⁾, in agreement with a remark made by Zimm and Stockmayer³⁹⁾. Moreover, the problem of cluster-cluster interactions also remains unsolved, in this approximation. (If one measures the intrinsic viscosity by diluting the sol, the disturbing influence of cluster-cluster interactions is weakened.)

A completely different and perhaps better approach⁶⁷⁾ is based on an analogy of viscosity with elasticity, resistor networks, and superconductors. The viscosity below p_c is the counterpart of the elasticity above p_c . According to the proponents of both the percolation^{2,3)} and the classical⁴¹⁾ theory, the elastic constant of the gel varies with the conductivity of a random mixture of conductors (fraction p) and insulators (fraction $1 - p$). This conductivity or elasticity has the exponent $t = 3$ according to the classical and $t \approx 1.7$ according to the percolation theory. (For two-dimensional percolation perhaps $t = \nu = 4/3$.) (All conductivities are defined by the current flowing between two large plates. The current flowing out of a single wire tip depends on whether the tip points to a conductor which is part of the infinite conducting network or only to a finite cluster of conductors; thus, the conductivity for such point measurements varies with $(p - p_c)^{t-\beta}$, corresponding to $(p - p_c)^2$ in the Bethe lattice.) Thus, it seems plausible that the viscosity of the sol, i.e. the counterpart of the elasticity of the gel, varies with the conductivity in a random mixture of superconductors (fraction p) and normal conductors (fraction $1 - p$); surely, it is infinite in the gel, corresponding to infinite conductivity in the presence of an infinite network of superconducting links. According to the percolation theory this conductivity varies with $(p_c - p)^{-S}$ where S coincides with t in two and is about 0.7 in three dimensions; the classical exponent is presumably zero. (For more information on conductivities see Refs. 22, 23.) Thus, in this theory, the viscosity diverges as

$$\eta \propto (p_c - p)^{-0.7} \quad (18)$$

for the three-dimensional percolation.

However, the picture is hardly an exact theory; moreover, it was recently questioned whether the elasticity of the gel really varies with the conductivity of random resistor networks¹⁰⁷⁾; instead, the elasticity exponent was defined as $\gamma + 2\beta$ (which happens to be again 3 in the classical theory, but is about 2.6 in the percolation theory). Then, also the identification of viscosity with superconductor mixtures may be questionable. Even if this is not the case, entanglement effects may lead to a change in the viscosity exponent as compared to the conductivity exponent. Therefore, we use question marks instead of giving numerical predictions for k in Table 1. But Table 5 summarizes, with increasing order of reliability, the viscosity exponents determined by means of these three approximations, for both the percolation and classical theory.

Table 5. Results of various approaches to the sol viscosity exponent k

| Approximation | Percolation | Classical |
|---------------|-------------|-----------|
| Rouse | 1.3 | $0'$ |
| Zimm | $0'$ | 0 |
| Supercond. | 0.7 | $0'?$ |

Zero corresponds to a finite limit of the viscosity, zero with a prime to its logarithmic divergence. The first least reliable line refers to the Rouse approximation, Eq. (17f), the second line to the excluded volume (Zimm) approximation, Eq. (17b), the last and most reliable line to the superconductor analogy of Eq. (18)

In the paragraph preceding Eq. (18) we already mentioned the widely accepted idea^{3,41)} that the elasticity of the gel has a critical exponent of the conductivity for resistor-insulator mixtures, and we listed these exponents. A theory which relates this exponent to the others, say ν or σ , and to the dimensionality d is still lacking^{22, 23)}, at least for general d . Table 1 lists the presently known exponents for this conductivity; since the conductivity-elasticity analogy was recently questioned¹⁰⁷⁾ we added question marks to the percolation prediction.

C.V. Variations of Percolation

Other types of percolation which differ from the random-bond percolation described above, will be discussed briefly with respect to their critical exponents. These variants may have no direct relevance to gelation but may be a guide for the efficiency of other models which may be developed in the future for gelation and which are at least similar to one of the models reviewed here. In most cases, the critical exponents are not changed unless drastic modifications, which influence the system in its long-range behaviour, are introduced.

C.V.1. Random-Site Percolation

This is a variant of the random-bond percolation described in Sect. C.II. It is not directly relevant to gelation but is often used, particularly in Monte Carlo simulations, to calculate critical exponents more easily or with higher precision. Sites on an infinite lattice in this model are supposed to be randomly occupied by particles with probability p and pairs of nearest-neighbor particles are considered to be bound.

Therefore, while in bond percolation the sites are always occupied and bonds between them may or may not be formed, in site percolation the sites may or may not be occupied whereas bonds between them always exist. For a given lattice it is not possible to express random-site percolation in terms of random-bond percolation, except in the Bethe lattice³⁷⁾. Nevertheless, it is commonly believed on the basis of quite accurate numerical evidence that site and bond percolation belong to the same universality class. (For details see Refs. 23 and Nakanishi and Reynolds¹⁰⁶⁾.)

C.V.2. *Random-Random Percolation*

In the usual random percolation, the bonds or sites are regularly located on a lattice, and the only randomness is connected with the question whether or not this bond (site) is formed (occupied). Additional randomness is introduced if the sites are no longer placed on a lattice but arbitrarily in space. Then we have “continuum” percolation and, since this problem is of particular value for gelation, we have already mentioned in Sect. C.II. that it belongs to the same universality class as random percolation³¹⁾. In that case, for two dimensions circles of a fixed radius are placed randomly on a plane and are supposed to form a bond if they overlap. A further degree of randomness has been introduced by allowing the radius of these circles to vary randomly, a model which might be relevant for mixtures of monomers with different functionalities. Even then, the critical exponents are compatible with those of ordinary percolation⁶⁹⁾ as expected⁷⁰⁾.

C.V.3. *Correlated Percolation*

This variant of random-site percolation considers the more general case in which the particles, instead of being randomly distributed, are correlated due to interactions between them. The most studied case is percolation in the lattice gas (Ising model) where the particles interact via an attractive nearest-neighbor force and are distributed in thermal equilibrium^{65, 71-76)}. For any temperature T there is a density percolation threshold $p_c(T)$. (Since in this model p is the density of occupied sites and not the probability of bond formation, it is of no direct relevance to gelation but represents an intermediate step in the more complicated model which is discussed in Chapter D.) In the limit $T \rightarrow \infty$ (or zero interaction) the particles are distributed randomly, and $p_c(\infty)$ is thus the random-site percolation threshold. When T decreases, attractive interactions facilitate the formation of clusters; therefore, $p_c(T)$ decreases with falling T while the clusters become more compact^{79, 80)}.

In two dimensions an interesting case occurs in which the line of percolation points $p_c(T)$ ends at the critical point of the lattice gas^{77, 82)}, as shown in Fig. 5 a. This special point is a multicritical point where both density fluctuations (critical opalescence) and connectivity properties (average molecular weight) become critical. For $d \geq 3$ ^{65, 74, 82)} and for the Bethe lattice^{72, 75, 76)}, the percolation line starts from the random limit $p_c(T = \infty) < 1/2$ and ends at an even lower density on the coexistence curve below T_c , as shown in Fig. 5 b. Since site percolation is not directly relevant to gelation we shift the discussion of the coexistence curve to the site-bond problems presented in Chapter D. We regard Fig. 5 as an indication that interactions in site percolation do not change its behavior drastically as a function of p , i.e. T is unimportant.

Along the whole percolation line $p_c(T)$ the critical exponents are the same as for random percolation, according to theory and the Monte Carlo experiment^{33, 77, 78, 83, 84)}, except for the special point $p = 1/2$, $T = T_c$ in two dimensions, where percolation and critical point coincide. At this point, the following inequalities between percolation exponents and lattice gas exponents have been proved⁸²⁾:

$$\nu^* \geq \bar{\nu}, \gamma^* \geq \bar{\gamma}, \beta^* \leq \bar{\beta}$$

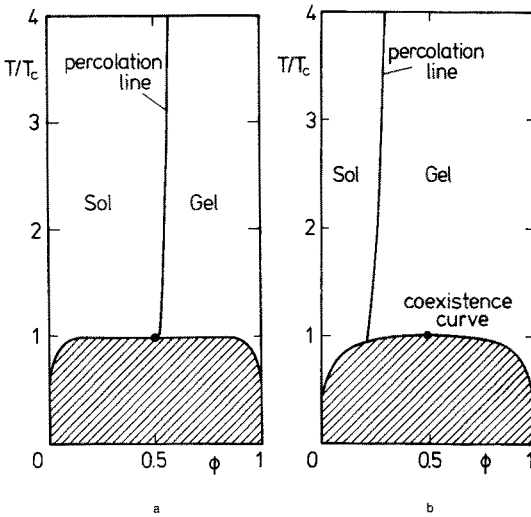


Fig. 5 a, b Monte Carlo results of the phase diagram in correlated percolation on square (5 a, Ref. 71) and simple cubic (5 b, Ref. 65) lattices. The shadowed region indicates phase separation. (T = temperature; ϕ = monomer mol fraction.)

where the symbols with asterisks refer to the percolation exponent at that point, and the tilde marks to the ordinary lattice gas exponent of Table 3. In agreement with such inequalities, series expansions⁸⁵⁾ give $\nu^* = 1.91 \pm 0.01$, which is larger than the exact lattice-gas susceptibility exponent $\tilde{\nu} = 1.75$, but perhaps related to the latter⁸⁶⁾. The renormalization group method⁷⁷⁾ confirms with 1% accuracy this series value, and also predicts that the correlation length exponents for percolation and lattice gas agree here, $\nu^* = \tilde{\nu} = 1$. (The crossover exponent, which describes the change of the critical behavior from this special point to random percolation behavior is given by the lattice gas “gap” exponent $\tilde{\beta} + \tilde{\nu} = 15/8$.)

Percolation in the two-dimensional lattice gas is very instructive in connection with the universality concept: If percolation occurs at finite lattice-gas correlation length, the critical exponents are the same as for random percolation. This can be easily understood if one takes into account that near the percolation threshold the lattice-gas correlation length $\tilde{\xi}$ is much smaller than the typical cluster radius ξ^* ; thus, the large clusters average over the effects of correlation. This argument breaks down only at the critical point of the two-dimensional lattice-gas where both ξ^* and $\tilde{\xi}$ vary simultaneously; in fact, we have seen that at this point some exponents do change.

A warning: According to Stoll and Domb³³⁾, a supposedly ratio of universal amplitudes, determining the shape of the scaling function in Eq. (6d), depends on T even at temperatures above T_c .

The reason why in two dimensions the transition line (Fig. 5 a), does not end below T_c as is the case with higher dimensions (Fig. 5 b) is due to topological properties of all two-dimensional systems. For $d = 2$, the probability that an infinite cluster of occupied sites coexists with an infinite cluster of empty sites is zero^{81, 82)} whereas in three dimensions this coexistence is possible. A phase diagram of the type of Fig. 5 b, would necessarily contain a large region in which such a coexistence occurs, for example above T_c in the interval $p_c(T) < p < 1 - p_c(T)$.

In percolation occurring in a lattice gas, care must be taken to differentiate between the critical behavior of percolation and that of the lattice gas. While there is an entire line $p_c(T)$ of percolation

points where the cluster size becomes infinite, there is only one critical point of the lattice gas ($T = T_c$, $p = 1/2$) where thermal properties like the compressibility become singular.

The reason why the divergence of the cluster size does not necessarily induce critical density fluctuations (critical opalescence) is that clusters are composed of two contributions: one is due to density correlations while the other is purely geometrical. For a given density p of occupied sites, these particles are joined to clusters not only because they attract each other but also because they are constrained to a given volume. For $T = \infty$, the attraction becomes negligible and the density correlations vanish; nevertheless, the mean cluster size DP_w is different from unity and may even diverge, as discussed in Sect. C.II.

For other questions related to these lattice-gas clusters besides percolation see also Ref. 88, in particular for the dynamics.

C.V.4. Antiferromagnetically Correlated Percolation

Repulsive lattice-gas interactions have also been studied^{33, 71, 72, 78, 87, 89}. The main feature is that repulsive interactions inhibit cluster formation and $p_c(T)$ increases from the random percolation threshold $p_c(T = \infty)$ to higher values. In this case, even in two dimensions the lattice-gas critical point is not a percolation point, and the critical exponents never change along the whole percolation line⁸⁹.

C.V.5. Potts'-Correlated Percolation

This is a generalization of the lattice-gas correlated percolation. In the lattice gas every site can be either occupied or empty; in the Q-state of the Potts model⁹⁰, every site can be occupied by one of Q different sorts of particles, having e.g. different colors. The particles interact via nearest-neighbor attractive interactions which assume a value J, if they have the same color and otherwise a value zero. This model has the interesting property that for any dimensionality d there exists a value $Q = Q_c$ such that the model exhibits second-order transitions for Q below Q_c and first-order transitions above Q_c . The value of this critical Q_c decreases from 4 in two dimensions⁹¹ to 2 for $d \geq 4$ ⁹².

Thus, a cluster distribution of all these colored particles gives a "polychromatic" correlated percolation problem, which in the limit of infinitely high temperatures degenerates to a random polychromatic percolation⁹³. (A different polychromatic correlated percolation model⁹⁴ for supercooled water will be discussed later.)

Potts'-correlated percolation was recently studied in two dimensions by the renormalization group⁹⁵. For any color there is a percolation critical density which ends at the Potts critical point where all colors percolate at the same time. For Q below Q_c , at this Potts critical point (similar to the critical point of the lattice gas) the exponent ν^* of the typical cluster radius coincides with the exponent $\tilde{\nu}$ of the Potts correlation length while the exponent γ^* of the weight-average cluster size is larger than the $\tilde{\gamma}$ value of the Potts susceptibility. For Q above Q_c , a first-order percolation transition is found at the same Potts critical point where also the thermal transition becomes first order.

C.V.6. Multiple-Coordinated Percolation

Recently, another type of correlated percolation has been introduced in connection with the unusual properties of supercooled water^{94, 96}. Consider a lattice with coordination

number z in which a fraction p of bonds are formed randomly. The sites can be partitioned into $z + 1$ separate species (colors again, if you wish) according to the numbers $i = 0, 1, \dots, z$ of bonds emanating from each site of the species concerned. Though bonds are distributed randomly, the sites are correlated in this model. For example, if all z nearest neighbors of a given site belong to the species $i = z$, then this site itself also belongs to that species $i = z$. In this sense, this model is a type of polychromatic correlated percolation.

The main difference between this model and the one described in Sect. C.V.5 is that in the previous case the length describing the correlations between different sites diverges (with exponent $\bar{\nu}$) at the Potts critical point whereas in the present case the correlations extend over at most one lattice spacing. Accordingly, one would expect that this type of polychromatic percolation belongs always to the same universality class as random percolation, and Monte Carlo calculations⁹⁶⁾ as well as renormalization group methods⁹⁷⁾ have confirmed this expectation.

(The exponents also seem to be the same in a variant where sites are occupied randomly and one looks only at those sites surrounded by at least i occupied neighbors, $i = 1, 2, \dots, z$ ⁹⁸⁾.)

C.V.7. Chain Percolation

A percolation model, that has been introduced in connection with vulcanization of chains^{62, 99, 100, 103)}, is the case in which two different species of bonds, say A and B, are placed on a lattice with concentrations C_A and C_B , respectively. Species A has the same properties as the usual bonds in random percolation whereas on species B is imposed the restriction that no more than two bonds of the same species B can be formed on the same site. Thus, species B forms polymer chains while species A acts as a crosslink. In the limit $C_A = 0, C_B \neq 0$, the system reduces to self-avoiding chains, described by exponents¹⁹⁾ different from percolation. The opposite limit, $C_A \neq 0, C_B = 0$, is the usual random-bond percolation. In the intermediate case, it was found^{62, 99)} that percolation in which clusters are composed of sites connected by bonds of either species belongs to the same universality class as random percolation, unless the particular situation is realized in which percolation occurs when the typical size of chains made out of B bonds only diverges. In this case, there is a crossover from random percolation exponents to self-avoiding walk exponents¹⁹⁾, similar to the situation in lattice-gas correlated percolation. (These chains of B atoms must be distinguished from the sometimes chain-like structures formed randomly in the usual percolation process.)

C.V.8. Restricted Valence Percolation

To describe steric hindrance effects in gelation one may study percolation on a lattice in which bonds are restricted in a way that no more than v bonds can emanate from the same site, or no site may have more than v nearest neighbors¹⁰¹⁾. Similarly, valence saturation may occur for the monomers in the gelation process. The case $v = 2$ is similar to self-avoiding walks¹⁹⁾, while for larger v one expects random percolation exponents, as confirmed by the Monte Carlo methods¹⁰¹⁾ in two and three dimensions. Then, on a large

scale, a large cluster looks like a monomer with multiple valencies, and the restricted valence at the monomer length scale does not affect the critical behavior.

C.V.9. Bootstrap Percolation

Similarly to the case described in Sect. C.V.6, for bootstrap (or environmental) percolation one considers only those sites as occupied which are surrounded by at least i particles. But now all lattice sites are first occupied randomly with probability p and then all those sites having less than i occupied neighbors are made unoccupied. This process is repeated until the lattice is completely empty or every remaining occupied site has at least i occupied remaining neighbor sites. ($i = 0$ corresponds to random site percolation.) The solution of this problem on the Bethe lattice and Monte Carlo simulation in two and three dimensions give either the same universality class as random percolation (low i), or different critical exponents (intermediate i), or even a first-order phase transition, where the gel fraction jumps from zero to a finite value¹⁰²). The physical reason for such jumps is based on the fact that after the coalescence of two clusters suddenly many more of their originally occupied sites can remain occupied in the ensuing reduction process, i.e. they are stabilized. Therefore, when an infinite cluster appears, this positive feedback may stabilize so many new sites that the infinite cluster, instead of being born “tiny” with zero density at $p = p_c$, is born already large with a non-zero density at p_c . (The limit $i = z =$ coordination number is trivial¹⁰²): For $p = 1$, all sites of the lattice are and remain occupied; for all p below unity, all sites will be removed in the “culling” process.)

C.V.10. Oriented Percolation

Broadbent and Hammersley⁶¹) proposed a percolation model in which neighboring sites may be joined randomly by two directed bonds; one transmitting in one direction, the other in the opposite direction. A limit on the square lattice is reached when randomly occupied bonds may transmit only upwardly or to the right. This model has exponents differing from those of random percolation^{32, 104}); applications to gelation are missing at present. More general models which describe a distribution of diodes and resistors have also been introduced¹⁰⁵). (In the literature oriented percolation is also called directed percolation.)

A summary of these ten examples shows how the random percolation problem can be modified: The critical exponents change only if the modification introduced can be seen on a scale which may become infinitely large, as in particular at the critical consolute point of phase separation. Otherwise, the modification concerns only “inessential” details and does not change the critical exponents. In some sense, the correlated site-bond percolation model described in Chapter D is only a further generalization of modifications 1 and 2 above providing similar results for the critical exponents.

D. Solvent Effects

D.I. Site-Bond Percolation

The theory of random-bond percolation in Sect. C.II. assumes that every site is occupied by a monomer, and bonds between monomers are formed randomly. In a real gel, besides the f -functional monomers, also solvent molecules are usually present. In order to take this solvent into account in a first approximation, one can allow the sites to be occupied by a monomer with a probability ϕ (mol fraction) and to be occupied by a solvent molecule otherwise, with probability $1 - \phi$. Two nearest-neighbor monomers may form a bond with probability p whereas no bonds emanate from or lead to the solvent molecules. The original random-bond percolation model is thus transformed into a random site-bond percolation¹⁰⁶⁾ in which the clusters consist of randomly distributed monomers connected by random bonds.

As Fig. 6 shows, for any concentration ϕ of monomers above the site percolation threshold (which is 0.312 in the simple cubic lattice, as opposed to the bond percolation threshold $p_c = 0.248$), there is a percolation threshold $p_c(\phi)$ for the bond formation probability: For p above $p_c(\phi)$, an infinite network of bonds between monomers exists. Thus, one has a whole percolation line in a $\phi - p$ diagram, which ends for $p = 1$ at the site-percolation threshold for ϕ , and ends for $\phi = 1$ at the bond-percolation threshold for p . There is strong evidence that the whole percolation line is described by the usual random-percolation exponents¹⁰⁶⁾. Note that even for $p = 1$ not all f bonds of all monomers are formed since the solvent molecules remain inert and may isolate the monomers.

D.II. Correlated Site-Bond Percolation

If we assume that the monomers of the site-bond problem described above are no longer distributed randomly but instead are distributed as in a lattice gas (interactions between nearest neighbors) in thermal equilibrium at temperature T , then we obtain Ising-correlated site-bond percolation^{43, 65, 77, 83, 84)}, the most general percolation problem discussed

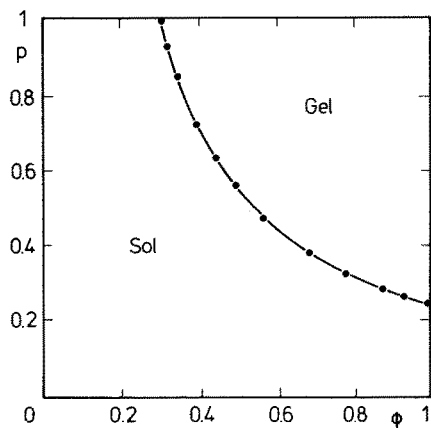


Fig. 6. Phase diagram of random site-bond percolation in the simple cubic lattice. (Monte Carlo simulation⁶⁵⁾)

so far in detail. From the point of view of pure theory, or of Monte Carlo simulations, it is practical⁶⁵⁾ to regard temperature T , bond probability p , and monomer concentration ϕ as three independent variables and to study phase transition surfaces in this $T - p - \phi$ space. (The special plane $p = 1$ corresponds to Fig. 5 above, the limit $T = \infty$ to Fig. 6.) At a fixed temperature T above the critical consolute temperature T_c , i.e. in the one-phase region one has curves similar to the $T = \infty$ limit of Fig. 6; only the end point at $p = 1$ is shifted slightly to lower concentrations ϕ if the temperature is diminished. Reference⁶⁶⁾ gives the quantitative results for these percolation line in the simple cubic lattice on the basis of Monte Carlo simulations. (At temperatures appreciably below the phase separation temperature T_c , the system is separated into one phase with very few monomers where even for $p = 1$ no gelation is possible, and another phase with very few solvent molecules where the system is approximated well by random-bond percolation, $\phi = 1$.)

What is the meaning of the coexistence curve discussed here and earlier (Fig. 5)? In our models first f -functional monomers and inert solvent molecules are distributed as if no chemical bonds are formed at all. At temperatures below the consolute temperature T_c , the system is then separated into two phases: In one phase nearly all molecules are solvent molecules, preventing any gelation to happen there later; in the other phase, nearly all molecules are f -functional monomer molecules, arranged nearly as on a periodic lattice, with only a few holes (solvent molecules) between them. Then, after equilibrium between these various molecules without chemical bonds has been established, we assume that, due to a very quick reaction, chemical bonds are formed with probability p before the molecules have changed appreciably their position. Then, the gel curve, i.e. the phase transition line separating the region of finite macromolecules from that of infinite macromolecules, simply gives the critical concentration p_c where *for the given distribution of monomers and solvent molecules* an infinite network is formed from neighboring monomers. The model does not take into account that, subsequent to the chemical reaction, the motion of monomers and solvent molecules is changed and that therefore also the coexistence curve and the critical temperature will be shifted by chemical reactions. In the special case of correlated site percolation (Fig. 5) where $p = 1$ *all* bonds between neighboring monomers are defined as being formed very quickly before the molecules can move appreciably. This special case is not directly relevant to gelation but important as a simpler special case of the more general models discussed in the following.

To apply these theories to gelation we have to distinguish between two types of gels, reversible and covalent gels. For simplicity, we call the reversible gels "weak" and the irreversible or covalent gels "strong"¹⁰⁷⁾.

D.II.1. Reversible Gels

In "weak" or reversible gels the bonds may form and break in thermal equilibrium ("annealed bonds"). The probability p for two monomers at nearest-neighbor distance to form a bond depends on the other two variables temperature and concentration (or even on other variables if they exist):

$$p = p(T, \phi) \text{ or } p = p(T)$$

This model was solved analytically for the Bethe lattice⁴³⁾, and with the simple approximation $p = 1 - \exp(-\text{const}/T)$ one can determine its behavior on the simple cubic lattice from Ref. 65. These Monte Carlo results are shown in Fig. 7. They agree qualitatively with the phase diagram in the Bethe lattice⁴³⁾ and also with the experimental data of Tanaka et al.¹⁰⁸⁾ using a gelatin-methanol water system. As already found for correlated

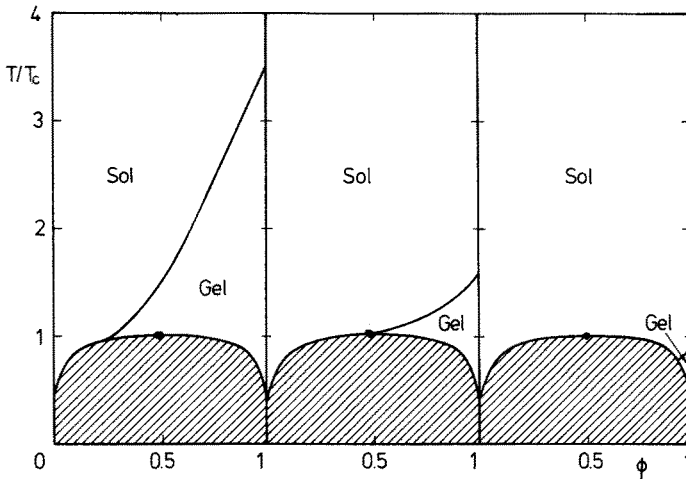


Fig. 7 Phase diagram of a monomer-solvent binary mixture, of weak gels and three different solvents chosen such that the consolute point is in the gel (*left*), on the gelation line (*center*) and in the sol (*right*). Taken from Monte Carlo simulations in the simple cubic lattice⁶⁵ together with the approximation $p = 1 - \exp(-\text{const} \cdot T_c/T)$, and $\text{const} = 1, 0.443$ and 0.25 respectively from left to right

site percolation in Fig. 5, we have two phase transition lines: First, a line of percolation thresholds separates the high-temperature region of the sol only from the low-temperature region where a gel exists; second, a phase-separation curve, topped by the consolute critical point, indicates where the system starts to split into a monomer-rich and a monomer-poor phase. A feature common to the experiment¹⁰⁸, the Bethe lattice solution⁴³, and the Monte Carlo simulation on the simple cubic lattice⁶⁵ is the existence of a maximum temperature at the concentration $\phi = 1$ for the percolation line: Above this maximum temperature, gel formation is impossible. If p is below the percolation threshold p_c for random-bond percolation (i.e. if T is too high), then even at the maximum monomer concentration ($\phi = 1$) the number of bonds is insufficient for the formation of an infinite network. This maximum temperature can be found by solving $p = p(T, \phi = 1)$ with $p = p_c$ from random-bond percolation. (At low temperatures we have a gel in the monomer-rich phase and a sol only in the solvent-rich phase.)

By adjusting the parameters of the function $p = p(T)$ or $p = p(T, \phi)$, which corresponds experimentally to a change in the solvent, an interesting situation described by the central part of Fig. 7 results, where the sol-gel boundary meets the phase separation curve exactly at the critical consolute point. In this case, the Bethe lattice theory⁴³, which corresponds to the Flory-Stockmayer model, gives classical exponents for random-bond percolation along the whole sol-gel boundary. This is true even for the special case where the critical consolute point and the end point of the gelation line coincide; then, one has to use the concentration ϕ and not the temperature T as a variable to define critical exponents.

In contrast, different forms of the renormalization group theory^{77, 83} show that random-percolation exponents are obtained along the entire gelation line except at the critical consolute point, if the latter is also the end point of the gelation line. In the latter case, the critical exponents are given by the lattice-gas exponents, i.e. the weight average

degree of polymerization diverges as the lattice-gas compressibility $\propto (T - T_c)^{-1.24}$, and the z-average radius of macromolecules varies with the lattice-gas correlation length $\propto (T - T_c)^{-0.63}$ (where we used the numerical values for the exponents in three dimensions).

The free energy reveals no singularity along the whole sol-gel transition line except at the critical consolute point (if this line meets this point at all). Therefore, at these gel point we have no phase transitions in the ordinary, thermal sense; only the connectivity properties become critical. This absence of singularities in the free energy or in its derivatives reflects⁽¹⁰⁷⁾ the fact that in a weak gel the appearance of an infinitely large but reversible macromolecule does not necessarily produce a dramatic change in the system. For example, the viscosity does not necessarily diverge: A small sphere will eventually penetrate into and through the infinite network, due to the ability of the reversible bonds to break and form again in the course of time.

In weak gels, the gel resembles a highly viscous liquid⁽⁶⁾. Instead of interpreting the percolation threshold as a sharp critical point of the sol-gel transition, it is more appropriate, e.g. for the viscosity, to consider it as the center of a transient region in which one passes smoothly from the fluid (sol) to the viscous (gel) phase. Of course, in the highly viscous region, the relaxation time required to reach equilibrium is very long. Only for times much longer than this relaxation time can the bonds be considered as fully reversible (annealed). For times much shorter than this relaxation time such gels behave more like strong gels⁽¹⁰⁷⁾.

As a consequence, the consolute monomer density ϕ_c is much smaller than that calculated for an annealed gel⁽¹⁰⁹⁾, due to the presence of large molecules with a long lifetimes ($\phi_c \propto M^{-1/2}$ where M is the typical molecular weight of a molecule).

We repeat that the position of the gel point is not a universal quantity. Therefore, the phase diagrams shown in Figs. 5–8 should not be regarded as quantitative predictions from which one can judge the validity of the classical or percolation theory. It is the exponents defined at or near these phase transition lines which are universal and which allow a clear distinction and classification of competing theories. However, a complete and correct theory must predict both the correct exponents and the correct phase diagram.

D.II.2. Irreversible Gels

In strong or covalent gels the bonds are permanent. These gels are obtained by quenching the system at a given quenching temperature T . While monomers and solvent are in thermal equilibrium-controlled by their interaction forces, a fraction p of chemical bonds may be formed quickly and randomly, at least in a Gedanken experiment. Once these bonds have been created, the system no longer consists of single monomers but of permanent clusters (monomers, dimers, trimers, ...) possibly including an infinite permanent network. Later, the temperature T may change, inducing even first-order transitions⁽¹¹⁰⁾ (gel collapse), but the cluster distribution will always be the same independent of the varying thermodynamic temperature. It can be obtained from the correlated site-bond percolation model described above, using for T the temperature at which quenching (the bond formation) took place.

We stress here the main difference: Weak gels are determined by one equilibrium temperature T . By changing this temperature, the bond probability p , the free energy and the cluster distribution change. In strong gels there is a quenching temperature which, together with p and ϕ , determines the cluster distribution; it may differ from the thermodynamic temperature, which changes the free energy after the macromolecules have been formed permanently, but does not influence p .

While in weak gels p depends on T , in strong gels it is an independent variable. Therefore, in weak gels (Fig. 7), we can change the point where the gelation line and the

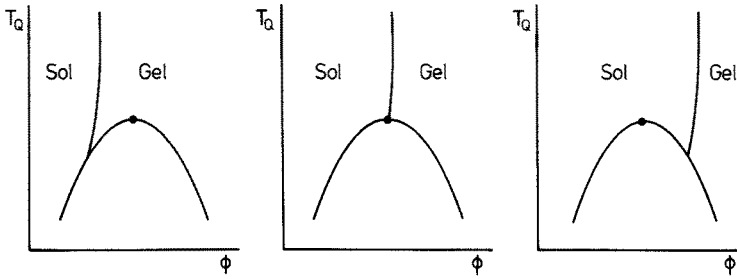


Fig. 8 Schematic phase diagram of a monomer-solvent binary mixture, of strong gels and three different bond formation probabilities p chosen such that the consolute point is in the gel (*left*, $p > p^*$), on the gelation line (*center*, $p = p^*$) and in the sol (*right*, $p < p^*$). p^* is for the nearest-neighbor lattice gas defined on p. 65. The “quenching” temperature at which the bonds are formed is shown; later T may change. Moreover, also the consolute point and the shape of the coexistence curve (shown here as a parabola) may change after bonding has taken place, due to the presence of large macromolecules

phase separation line meet only by changing the solvent. In a strong gel, this meeting point can be shifted also for a given solvent by choosing a suitable and fixed value for the bond formation probability p , as in Fig. 8. It has been shown^{65, 77, 83} that this point, where the two lines meet, coincides with the critical consolute point if

$$p = 1 - \exp(-W/2kT_c) \equiv p^*$$

where W is the effective lattice-gas interaction energy and T_c the critical consolute temperature. (An energy $W/2$ is needed to replace in a pair of monomer neighbors, surrounded everywhere by solvent molecules, one of the monomers by a solvent. In the simple cubic lattice, $W/kT_c = 0.8867$ and thus $p^* = 0.358$.) This p^* value also holds for weak gels, p being however a function of the other variables; thus, different solvents are necessary to obtain $p = p^*$. Another difference is that strong gels, in contrast to weak gels, do not have a maximum temperature for the gelation line; this sol-gel transition line may extend up to an infinite temperature (which simply means a random distribution of monomers and solvent molecules).

An interesting aspect of strong gels, which has not received much attention experimentally, is that quenching and bond formation occur exactly at the critical consolute point. In this case, the resulting size distribution of macromolecules keeps up *permanently* with the highly correlated distribution of monomers in the solution (although the consolute point may be shifted after the bonds have been formed, due to the presence of large molecules) In particular, if an infinite network is formed, it should exhibit unusual elastic properties about which little is known at present.

What are the critical exponents of gelation? Similarly to weak gels, along the whole sol-gel transition we expect^{77, 83, 84} random-percolation exponents, except for $p = 1 - e^{-W/2kT}$ on the coexistence curve where lattice-gas exponents dominate. A third set of exponents is found by approaching the point $p = p^*$, $T = T_c$ and $\phi = \phi_c$ (critical consolute point) through variation of p and keeping fixed T and ϕ at their critical values T_c and ϕ_c . Then, the typical cluster radius varies as

$$\xi \propto |p^* - p|^{-\nu_B} \quad (p \rightarrow p^*)$$

and the weight average degree of polymerization as

$$DP_w \propto |p^* - p|^{-\gamma_B} \quad (p \rightarrow p^*)$$

Renormalization methods gave in two dimensions⁷⁷⁾ $\nu_B \approx 2.02$ and $\gamma_B \approx 3.54$ whereas⁸³⁾ $\gamma_B = 2\nu_B = 4/(d - 2)$ near $d = 6$ dimensions; the latter result is believed to be true for $4 \leq d \leq 6$. For details of the cluster size distribution we refer to the original papers⁸⁴⁾.

A further difference between weak and strong gels: While in weak gels the free energy does not reveal any singularity at the percolation threshold, in strong gels it seems to exhibit such a singularity¹⁰⁷⁾, showing that in this case the sol-gel phase transition can also be considered as a thermal phase transition, with a non-analytic free energy. The permanent nature of the "strong" bonds makes the phase transition more obvious than the temporary nature of the "weak" bonds.

E. Critique of Theory

The structure of a monomer is clearly more complicated than assumed in the first parts of Chap. C., where a monomer was simply considered as a point with f arms both in the classical and lattice percolation theory. In reality, the interactions between atoms will influence the probability of bond formation. Then, gelation occurs no longer randomly, and correlations between various bonds exist. We have reviewed in Chap. C. V. and D. existing theories of non-random percolation; a simplified summary shows that purely geometric restrictions to and thermal correlations between the bonds do not change the critical exponents whereas phase separation does. Thus, one may expect sometimes different but in most cases the same exponents if more realistic gelation models are investigated instead of random-bond percolation on a lattice.

We have already mentioned that the lattice structure, while used for most percolation studies, is not really necessary³¹⁾ and that even without the help of a lattice the critical exponents seem to have invariable lattice values. According to the simple classical theory this is not the case since the radius of trees on a periodic lattice (with excluded volume effects) increase for large cluster masses s at least with $s^{1/d}$ (in d dimensions) whereas in the classical theory on a continuum a Cayley tree has a radius varying asymptotically with $s^{1/4}$, independent of d .

An important ingredient of gelation reality, namely dynamics, is missing in these classical and percolation theories we have reviewed here. The probability of a bond to be formed is not necessarily random but may depend on the history of the sample. In particular, the role of molecular mobility has been ignored in our description. Let us discuss here two extreme cases: zero mobility and infinite mobility of macromolecules. In the first case, the monomers can be assumed to be fixed on the sites of a lattice, and we have the same situation as discussed in Sect. C.II. In the opposite limit of infinite mobility it seems reasonable to assume that every macromolecule of mass s can form a bond with every other molecule of mass s' within the sample, and that the rate at which such coagulation occurs is $K_{ss'}n_s n_{s'}$. (K is a coagulation constant and n the number of clusters.) In this case, the solutions of the resulting coagulation equations^{16, 111)} show that the cluster size distribution n_s in the course of time may be different from both the classical and percolation theory and depends strongly on the form of the coagulation coefficient $K_{ss'}$. More work in this direction with emphasis on critical phenomena would be desirable.

Reality is presumably between the two limits of zero and infinite mobility. If two neighboring macromolecules are joined together, then near that place no other coagulation is likely to occur for some time. A numerical study of time-dependent correlation effects would be useful. (Some percolation models^{112, 113}) which were not intended for gelation indicate that exponents resulting from a growth process may differ from those of a random process. Grassberger's dynamical model¹³²) seems to give random percolation exponents for long times.)

An important though incomplete step in this direction of dynamical percolation for gels was the Monte Carlo simulation of Manneville and de Seze¹¹⁴) for additive copolymerization initiated by radicals. Two-functional and four-functional monomers were mixed randomly on a cubic lattice and fixed there, with a small concentration of mobile free-radical activation centers. The result of this simulation was that the critical exponent ν for this chemical process agreed with that of random percolation for intermediate concentrations of 4-functional monomers, but was slightly (significantly?) higher for lower concentrations. We regard this work¹¹⁴) as the most realistic of all existing computer studies on gelation and urge that it be improved further. And rather generally, we believe that the dynamic aspects of percolation should be investigated in detail for gelation and other applications.

Summarizing these theoretical sections of our review, we can say that many percolation models belong to the universality class of random-bond percolation on a periodic lattice which is different from the universality class of the classical Flory-Stockmayer theory. (A literature review of the critical exponents relating to modifications of the Flory-Stockmayer theory is still lacking; we have only given some examples.) However, exceptions do exist. Therefore, it is possible that for certain gels both competing theories (simple classical and simple percolation theory) are wrong as far as critical exponents are concerned. In this case we believe that the more general scaling idea still remains valid, i.e. the exponents are related to one another as in Eqs. (8, 9):

$$d\rho/\sigma = d\nu = \gamma + 2\beta = (\tau - 1)/\sigma$$

though the exponents do not have the values listed in Table 1. For example, the statement $\tau - 1 = d\rho$ in d dimensions relates the radius exponent ρ to the cluster-number exponent τ and is valid much more generally than the specific (not exactly determined) prediction $\rho = 0.4$ in three dimensions. It is the scaling laws like Eqs. (8, 9) and not the specific exponent values for definite models which can be regarded as the most general result of modern phase transition research¹⁵).

Let us see now if experiments can decide which theory is right and which is wrong.

F. Experimental Determination of Exponents Near the Gel Point

It was shown in the preceding sections that most three-dimensional versions of the percolation theory have the same critical exponents. They differ only if phase separation occurs during the percolation process. Thus, if gelation can be described by the percolation theory, the exponent values must be independent of the chemical system studied.

This is a theoretical result but what is the experimental situation? In this section, we will try to answer this question but we do not intend to give a complete review of experimental results obtained on gelation systems. We will systematically take no account of experimental results which are intimately tied to a theory in order to verify it. In fact, we will try to point out the physical quantities which can be measured, how we can measure them and what are the experimental difficulties.

We will divide this section into 2 parts. The first one will deal with measurements performed on samples of a given p called "quenched samples" in which the chemical reaction was stopped and the system dissolved; the second group of measurements, called "in situ", has been performed in a reaction bath without any chemical manipulation.

F.1. Experiments Performed on "Quenched Samples"

In this section we consider quantities which necessitate chemical manipulations preceding the experimental determination. The chemical reaction must be stopped by freezing or deactivation of the reacting groups. (For details on chemical procedures see following references and Refs. 1, 39.) The sample is then dissolved in a known quantity of solvent the cluster distribution remaining unaffected. The swelling of clusters occurring during dissolution of the sample in good solvent may increase the radius of gyration. Consequently, the experimental R_g value will be higher than that predicted by Eqs. (5 b) and (5 c). Beyond the gelation threshold, the gel fraction must be extracted whereas the finite clusters, which are trapped in the holes of the gel, should not. The gel fraction must not be broken into small pieces. The separation of sol and gel is sometimes very difficult to achieve experimentally.

Let us, first of all, review the measurable quantities.

F.1.1. Measurable Quantities

From Section B.II. we know that the system is highly polydisperse and the number of clusters n_s having s units can be approximated by:

$$n_s \propto s^{-\tau} \quad \tau = \frac{2\gamma + 3\beta}{\gamma + \beta} = 2 + \frac{1}{\delta}.$$

In this approximation s has two extreme values, as explained above (Eq. (6 b)): $s = 1$ (monomer) and $s = s_g =$ number of units in the largest finite cluster of the system; this number varies for small $\Delta p \equiv |p - p_c|$ according to

$$s_g \propto \Delta p^{-(\gamma+\beta)}, \quad (\text{Eqs. (6 a) and (6 b)})$$

In this section, we will derive proportionalities for the mean molecular weights that can be determined experimentally, using the corresponding average degrees of polymerization. We will replace the discrete sum used in the preceding sections by an integral because near p_c , $s_g \gg 1$.

By definition, the *number average molecular weight* is:

$$M_n \propto \frac{\int_1^{s_g} s n_s ds}{\int_1^{s_g} n_s ds},$$

M_n is finite for $\Delta p \rightarrow 0$. Thus, the osmotic pressure, which depends on M_n , does not exhibit any discontinuity near the gelation threshold p_c .

The *weight average molecular weight*, which is defined by

$$M_w \propto \frac{\int_1^{s_g} s^2 n_s ds}{\int_1^{s_g} s n_s ds} \propto \Delta p^{-\gamma}, \quad (19)$$

is determined by light scattering measurements, M_w diverges as $\Delta p \rightarrow 0$.

Using the same method, we can measure the *z average radius of gyration*:

$$\langle R^2 \rangle_z \propto \frac{\int_1^{s_g} s^2 n_s R_s^2 ds}{\int_1^{s_g} s^2 n_s ds}$$

where R_s^2 is the radius of gyration of an s cluster in the reaction bath,

$$R_s^2 \propto s^{2\varrho} \text{ with } \varrho = \frac{\nu}{\gamma + \beta} \text{ at } p = p_c$$

$$\text{thus } \langle R^2 \rangle_z \propto \Delta p^{-2\varrho(\gamma+\beta)}$$

$$\text{and } \langle R^2 \rangle_z \propto \Delta p^{-2\nu} \quad (20)$$

The radius of gyration ξ of the largest cluster s_g is given by $\xi^2 \propto \Delta p^{-2\nu}$ (Eq. (5c)); therefore, $\langle R^2 \rangle_z \propto \xi^2$ (Ref. 23).

The *intrinsic viscosity*,

$$\lim_{c \rightarrow 0} [\eta] = \frac{\eta - \eta_0}{\eta_0 c},$$

is difficult to calculate (c is the concentration). It can be approximated by:

$$[\eta] \propto \frac{\int_1^{s_g} s n_s \frac{R_s^z}{s} ds}{\int_1^{s_g} s n_s ds},$$

where $z = 3$ if we assume total hydrodynamic interactions inside clusters (Zimm clusters) and $z = 1/\nu + 2$ if we assume no hydrodynamic interaction (Rouse clusters).

In the case of Zimm clusters, the intrinsic viscosity is $[\eta] \propto \Delta p^{-(3\nu - (\nu + 2\beta))}$; therefore, $[\eta] \propto \log \Delta p$, if hyperscaling (Eq. (9 b)) is used. Then, we have

$$[\eta] \propto \log(M_w). \tag{21}$$

In the case of Rouse clusters, the resulting intrinsic viscosity $[\eta] \propto \Delta p^{\beta - 2\nu}$ varies strongly at $p_c^{66, 67}$. Using values for β and ν as listed in Table 1, we find:

$$\begin{aligned} [\eta] &\propto \Delta p^{-1.3} \\ [\eta] &\propto M_w^{0.75}. \end{aligned} \tag{22}$$

Expression (22) corresponds accidentally to $[\eta]$ of linear polymers in good solvents where hydrodynamic interactions occur.

Beyond the gelation threshold, the *gel fraction* G , obtained after extraction

$$G \propto \Delta p^\beta,$$

is measured by weighing.

Static quantities such as $\langle R^2 \rangle_z$, M_w , and G can be calculated by using the percolation or mean field theory. To predict the dynamic quantity $[\eta]$, we must know the static one and the type of the hydrodynamic interaction.

F.I.2. Light Scattering Results

Light scattering is measured as function of a momentum transfer k defined by:

$$k = \frac{4\pi}{\lambda} \sin \frac{\theta}{2},$$

where λ is the wavelength of the incident beam in the medium, θ the scattering angle (a typical value of k is $1.8 \times 10^{-3} \text{ \AA}^{-1}$ for $\lambda = 5000 \text{ \AA}$ and $\theta = 90^\circ$).

Assuming monodisperse molecules with radius of gyration R_g and molecular weight M , one has¹¹⁶⁾ for the scattered light intensity I :

$$cI_{\rightarrow 0}^{-1} \propto \frac{1}{M} \left(1 + \frac{k^2 R_g^2}{3} \right), \text{ if } k^2 R^2 \leq 1;$$

here, c is the monomer concentration. For a polydisperse sample (cf. Sect. F.I.5.), if $k^2 R^2 \leq 1$, the curve $cI_{c \rightarrow 0}^{-1} = f(k^2)$ has a slope proportional to $\langle R^2 \rangle_z / M_w$ and an intercept at $k = 0$ proportional to $1/M_w$, if $k^2 R^2 \gg 1$, the curve $cI_{c \rightarrow 0}^{-1} = f(k^2)$ has an intercept at $k = 0$ proportional to $1/2M_n$.

Light scattering experiments should be performed in dilute solution. Since the size of the clusters may increase during dissolution due to swelling, it is not evident that the radius measured can be compared with expression (20). The same difficulty is encountered in intrinsic viscosity measurements.

Light scattering experiments were essentially performed on three kinds of samples:

- Polycondensates of decamethylene glycol/benzene-1,3,5-triacetic acid (DMG/BTA). The reaction was stopped by neutralization of the carboxy and hydroxy groups^{117, 119}.
- Copolymers of methyl methacrylate with other methacrylates where the reaction was terminated by quenching; then, precipitation occurred¹¹⁸.
- Styrene-divinylbenzene copolymers at complete conversion²¹. In these experiments, the concentration of initiator was changed whereas the concentration of DVB and styrene remained constant; thus, a series of samples at varying distance from the gel point was obtained by considering $\Delta p \propto \Delta X/X_c$ where $X = [\text{DVB}]/[\text{initiator}]$.

In Refs. 21, 117–119 the weight average molecular weights and the z -average radii of gyration are discussed; it was found that on both sides of the gel point $\langle R^2 \rangle_z \propto M_w$, in agreement with both existing theories. Using expressions (19) and (20), we obtain indeed

$$\langle R^2 \rangle_z \propto M_w^{2\nu/\gamma}, \quad \text{where } \frac{2\nu}{\gamma} \approx 1.$$

However, this result does not mean that the conformation of a cluster is Gaussian. If a linear polymer has a Gaussian conformation, the law $R^2 \propto M$ is valid at any scale and for any pair of the mean values considered ($R_n^2 \propto M_n$, $R_w^2 \propto M_w$, $R_z^2 \propto M_z$). For solutions of non-Gaussian clusters, this relation holds only if the z -average radius of gyration is compared with the weight average molecular weight. For example, one can show that

$$\langle R^2 \rangle_w \propto M_w^{(2\nu - \beta)/\gamma}.$$

This exponent is different from $2\nu/\gamma \approx 1$.

Variations of $\langle R^2 \rangle_z$ and M_w as a function of Δp are analyzed in Refs. 118, 21, Figs. 6 or 5 and 6, respectively. No exponent value is given by the authors because the two quantities cannot be expressed by any simple power law within the range of Δp studied. This may be due to a high inaccuracy in the determination of p_c .

As noted by the authors themselves¹¹⁸ (p. 881): "The flattening off of the curve at large M_w is caused by the inaccuracy in the determination of the gel point ... The maximum value for the exponent in Fig. 6 is 1.5" (this corresponds to the exponent $\gamma = 1.7$ in Table 1). Actually, one must realize that the precision of p_c must be much higher than the range of Δp on which measurements are performed. It is evident that, if p_c is known with a 10^{-2} precision and Δp is of the order of 10^{-2} , the error of Δp is 100%. Thus, direct determination of γ and ν will be possible only if the precision in the determination of p_c is improved.

F.I.3. Comparison Between Gel Fraction and Light Scattering Measurements

One way to overcome the lack of precision in $\Delta\rho$ is to compare the different quantities, M_w , $\langle R^2 \rangle_z$ and G . Using the expressions (19, 20, 22) one obtains

$$\langle R^2 \rangle_z^{1/2} \propto G^{-\nu/\beta}$$

and

$$M_w \propto G^{-\gamma/\beta}$$

In Ref. 21, the z-average radius of gyration and the weight average molecular weight are plotted, on a log-log scale, as a function of the gel fraction (Fig. 10, Ref. 21).

The value of the exponent $\gamma/\beta = 4.5$, determined by the authors, is in good agreement with the percolation model (4) and clearly differs from the mean field value (1). The authors give two values for the exponent ν/β : 1.65 near gel point and 3.3 far from gel point. These two exponents, although inaccurate, are closer to the percolation value (2) than to the classical value (0.5).

However, the two difficulties mentioned above must be taken into account: gel extraction may be achieved only incompletely, and the radius of the clusters may increase by dissolution of the sample. These two facts will increase the experimental values of the exponents ν/β and γ/β . Another problem results from light scattering analysis of high molecular weight polydisperse samples (see Chap. 5).

F.I.4. Intrinsic Viscosity Results

In Ref. 118 (Fig. 8), the intrinsic viscosity $[\eta]$ is compared with the weight average molecular weight. It was found that the absolute value of $[\eta]$ and the slope of the curve (on the log-log scale) are much lower for solutions of branched than of linear polymers. This experimental result, together with the percolation expressions for the intrinsic viscosity (Eqs. (21, 22)) confirm that clusters undergo hydrodynamic interactions. In fact, the molecular weight exponent value of $[\eta]$ is much lower with than without hydrodynamic interactions. This result implies that a calculation of the viscosity of the reaction bath is correct only if hydrodynamic interactions are taken into account.

No exponent was determined by the authors but if we use their experimental values given in Table 3 of Ref. 118, we find: $[\eta] \propto M_w^{0.17}$, an exponent value which is not far from the percolation value taking into account hydrodynamic interactions ($\log M_w$). However, it is also not far from the logarithmic divergence (or finite limit) of the viscosity according to the classical theory (Table 5 above).

F.I.5. Difficulties Encountered in Light Scattering Experiments on Polydisperse Samples with High kR Values

It was shown in Sect. F.I.1. that M_n is roughly a constant and M_w diverges as $\Delta p^{-\gamma}$. Thus, the index of polydispersity, i.e. the ratio M_w/M_n , diverges as $\Delta p^{-\gamma}$. It can be shown that $\langle R \rangle_n$ is also a constant near the gel point. For convenience, let us consider an index of polydispersity equal to 2 at $\Delta p \approx 0.1$.

For a polydisperse linear polymer obeying Gaussian statistic, the scattering function is¹²⁰:

$$\lim_{c \rightarrow 0} cI^{-1} \propto \frac{1}{M_w} \frac{1}{\bar{p}(\theta)}$$

where $\bar{p}(\theta)$ is the z average of the scattering function of each species s :

$$\bar{p}(\theta) = \frac{\int_1^{s_g} s^2 n_s p_s(\theta) ds}{\int_1^{s_g} s^2 n_s ds}$$

$$\text{with } p_s(\theta) = \frac{2}{(k^2 R_s^2)^2} [e^{-k^2 R_s^2} + k^2 R_s^2 - 1]$$

if $k^2 \langle R^2 \rangle_z < A$, where A is a constant whose value, 4, has been found experimentally:

$$\lim_{c \rightarrow 0} cI^{-1} \propto \frac{1}{M_w} \left(1 + \frac{k^2 \langle R^2 \rangle_z}{3} \right)$$

if $k^2 \langle R^2 \rangle_z \gg A$,

$$\lim_{c \rightarrow 0} cI^{-1} \propto \frac{1}{2M_n} (1 + k^2 \langle R^2 \rangle_n).$$

Thus, if $k^2 \langle R^2 \rangle_z$ is smaller than 4, we obtain from the inverse of the scattering intensity, extrapolated to $k = 0$, the weight average molecular weight and from the slope of the curve $cI^{-1} = f(k^2)$ the z average of the square of the radius of gyration.

If $k^2 \langle R^2 \rangle_z$ is larger than 4 and if the index of polydispersity is high ($M_w/M_n > 2$), then the extrapolated value of cI^{-1} at $k = 0$ gives a molecular weight average between M_w and M_n . The slope also provides an intermediate value of the average squared radius:

$$\langle R^2 \rangle_n < \bar{R}^2 < \langle R^2 \rangle_z.$$

The expressions derived above can be extended in the first approximation to cluster solutions. The straight line obtained from the plot of c/I versus k^2 , using a sample

of polydispersity M_w/M_n near 2, lies above the curve for a sample of high polydispersity, $M_w/M_n > 2$, which corresponds, in our case, to $\Delta p < 0.1$.

Therefore, analyzing the results of a light scattering experiment, one must keep in mind that the sample is very polydisperse. If one wants to determine $\langle R^2 \rangle_z$ and M_w , one must work at small $k^2 \langle R^2 \rangle_z$ values and be sure that experimental points do not lie below the extrapolated line.

F.II. Experiments Performed “in Situ”

Three quantities were measured, in the reaction bath: shear viscosity η , shear modulus E and ultrasonic absorption. These quantities are easy to measure since no chemical manipulation is necessary; thus, there is no danger that the system studied is modified. Other difficulties are also much easier to overcome. However, the interpretation with respect to the percolation or classical theory is more difficult than that of the geometrical quantities $\langle R^2 \rangle_z$, M_w , or G .

F.II.1. Measurable Quantities

In Section C.I.V, it was shown that, below the gel point, the *viscosity* diverges as $\eta \propto \Delta p^{-k}$. Using the percolation theory, the exponent $k = 0.7$ if an analogy is made between gelation viscosity and electric conductance of a random network of superconductors and normal conductors⁶⁷⁾.

Above the gel point, the system becomes elastic and the *shear modulus* E increases as $E \propto \Delta p^t$, where $t = 1.7$, according to the percolation theory where an analogy is made between E and the electric conductance of a random resistor network²⁾.

The mean field approximation yields

$$k = 0^{121)} \text{ and } t = 3^{9, 41)}$$

the viscosity having a logarithmic divergence at the threshold.

Above the gel point, the *ultrasonic absorption* is proportional to the square of the gel fraction divided by the friction of the solvent passing through the polymer network. Since the measurements are made at a very high frequency, phonons are absorbed by small molecules and f is considered to be constant¹²²⁾. There is no theoretical justification for this assumption.

F.II.2. Viscosity Measurements

On the one hand many viscosity measurements were performed¹²³⁾ in the reaction bath but only few of them were stimulated by the desire to measure critical exponents.

On the other hand some of the viscosity measurements were performed by authors interested in critical exponents but having no access to p , i.e. the conversion of the reaction. In this case, Δp is assumed to be proportional to $(T - T_c)/T_c$ where T is either the reaction time or the temperature (T_c being the threshold value).

In Ref. 124 the viscosity is measured by rotational relaxation of ferromagnetic particles ($0.1 \mu - 10 \mu$) embedded in gelation solution. The exponent k is found to be $k = 0.95 \pm 0.1$.

In Refs. 125, 126 the viscosity is measured with a magnetic sphere rheometer at decreasing shear rate (its lowest value is 10^{-4} s^{-1}) in different polymeric systems: free-radical copolymerization of styrene-meta-divinylbenzene with solvent and polycondensation of hexamethyl diisocyanate with polyoxypropylene with and without solvent. These experiments yield $k = 0.79$ in both systems. The standard deviation of experiments performed at different shear rates at the gel points is 0.07 in k . Since η and E are measured in Ref. 126 using the same apparatus and the same sample, T_c is determined as the time where η^{-1} and E are equal to zero, the precision in T_c being higher than $10^{-2}\%$.

In Ref. 127 the viscosity of the polycondensation system DMG/BTA is measured with a Weissenberg rheogoniometer at constant shear rate not exceeding 85 s^{-1} . The exponent k is found to be 1.03 with a standard deviation of $\sigma = 0.05$. In these experiments the gel time is determined such that the log-log plot of η versus ΔT becomes linear.

In Ref. 118 the viscosity is measured during the freeradical copolymerization of methyl methacrylate by determining the fall rate of a steel sphere (without shear rate control). k is determined to be 0.5.

Thus, the exponent k , defined through $\eta \propto \Delta p^{-k}$, where η is the zero shear rate viscosity, lies between 0.5 and 1.

We will see later that zero shear rate viscosity is difficult to measure near the gelation threshold.

F.II.3. Measurements of the Elastic Modulus

In the measurements of the elastic shear modulus E and its exponent t ($E \propto \Delta p^t$), two types of polymerization with different extent of cyclization (Dušek⁹) were studied: polycondensation and free-radical copolymerization.

For BTA/DMG polycondensation $t = 3.11$ is found¹¹), using a Weissenberg rheogoniometer (lowest frequency 0.1 s^{-1}), and for the polycondensation of polyurethanes prepared from hexamethylene diisocyanate and a polyoxypropylenetriol (with and without solvent and using a magnetic sphere rheometer with a frequency near $2 \times 10^{-2} \text{ s}^{-1}$) the exponent $t = 3.3 \pm 0.3$ was obtained¹²⁶). Therefore, it seems that the exponent t for the shear modulus of polycondensation samples is very close to the classical exponent value of 3.

For the free-radical copolymerization of mono- and bisacrylamide samples¹²⁸) performed and with a magnetic sphere rheometer, $t = 2.05 \pm 0.2$ and for the free-radical copolymerization of styrene and divinylbenzene¹²⁶), using the same type of apparatus, $t = 2.1 \pm 0.3$. These exponents are higher than the value of 1.7 predicted by percolation for an alternative theory see however Ref. 107 and smaller than the classical exponent $t = 3$.

F.II.4. Ultrasonic Wave Attenuation

In Ref. 124, attenuation $\Delta\alpha$ of ultrasonic waves at 790 MHz in gelatin gel was measured as a function of temperature T , and in polyacrylamide gel as a function of reaction time T . It was found that the attenuation increased linearly with rising ΔT for $T > T_c$.

It is shown that $\Delta\alpha \propto G^2/f$, where G is the gel fraction and f the frictional coefficient between the solvent and the polymeric network. Assuming that f remains finite for $\Delta T \rightarrow 0$, it was concluded that $G \propto (\Delta T)^{1/2}$, an exponent value which is not too far from $\beta = 0.4$.

F.II.5. Difficulties of Mechanical Measurements

We are interested in viscosity and elastic modulus which are stationary quantities. Let us call T_r the longest relaxation time of the polymeric system. In order to measure zero shear viscosity and stationary elastic modulus, the experiment must be performed at $\sigma T_R \ll 1$ and $\omega T_R < 1$, where σ is the shear rate and ω the frequency.

This relaxation time is the time needed for the largest cluster to reorient itself¹²⁹:

$$T_R \approx \frac{\bar{\eta}}{kT} \xi^3 \propto \frac{\eta_0}{kT} \Delta p^{-(k+3\nu)}$$

where $\bar{\eta}$ is the macroscopic viscosity.

Thus, as we approach p_c , the relaxation time T_R diverges, and σ must be reduced to maintain $\sigma T_R < 1$.

If $\sigma T_R > 1$, the viscosity measured will be smaller than the stationary viscosity, the effective gel time, where $1/\eta$ approaches zero, will be longer than the real gel time and the k exponent so determined smaller than the "true" exponent. Therefore, a viscosity experiment requires several runs to be made on the same material (each one at a different shear rate) to ensure that k is independent of this shear rate.

This real difficulty of measuring zero shear viscosity near the gel point was taken into consideration by Gordon and Roberts¹²⁷. In this work (p. 686), the T_c value obtained by extrapolation of the modulus and the one obtained by extrapolation of the viscosity are compared: T_c "from back-extrapolation of the modulus is generally lower than the value from viscosity. This small discrepancy is significant and intelligible because shear rate effects will raise the viscometric gel point but lower the gel point from modulus data"¹²⁷.

It should be noted that this "shear rate effect on p_c " not only influences the k exponent but also all exponent values when p_c is determined through non-zero shear viscosity measurements. Actually, we have to point out the predominant effect of the precision of p_c on the determination of exponents.

Effects of mechanical deformations on the destruction of the gel structure and on chemical kinetics are difficult to evaluate. From the agreement of the experimental exponent values ($t = 2.2$ or 3.1) obtained by different authors it may be concluded that gel structure is not modified by measurements.

F.III. Experimental Conclusions

In this section, we have reviewed the difficulties that can be encountered in carrying out experiments which may allow us to answer the question: Does percolation describe gelation close to its threshold? The reader might think that it is impossible to give an answer to this question. In fact, the determination of the exponent would necessitate an improved precision of p_c .

Fortunately, the determination of exponent ratios ν/β and γ/β can be performed without any precise knowledge of p_c and, moreover, exponent values given by each theory are so different that one cannot be misled (roughly, 2 and 4, instead of 0.5 and 1). In Sect. F. I. 3 the experimental tests²¹⁾ of this prediction are mentioned. The experimental values obtained ($1.65 < \nu/\beta < 3.3$ and $\gamma/\beta \approx 4.5$) reveal that the description of the gel structure given by percolation is adequate. But more experiments must be performed to confirm ν/β and γ/β values.

On the other hand, "in situ" experiments do not give an answer to the question. First, because experimental exponent values are scattered. Second, because we do not know, exactly what value of the exponent we expect from the mean field or percolation theories (is k really equal to zero in the classical theory, Table 5?). Another problem that must be solved by theoreticians is the extent (in Δp) of the critical domain where exponents can be determined experimentally.

The problem of exponents just begins to be seriously studied by few experimentators (always loudly criticized by others) and there needs a lot of experimental work to be done to find out whether percolations models are applicable to gelation and, whether there are restrictions to this model. In experiments performed near the gelation threshold many difficulties arise. However, similar difficulties have been overcome by experimentators studying liquid-gas phase transitions and will certainly be overcome by those working on gelation.

G. Summary

Since only shorter reviews were published before^{6, 7, 21)} this review is rather detailed. In Eq. (10), the reader finds the basic definitions, in Table 1 the competing predictions, and in Table 2 the qualitative analogy with thermal phase transitions. Scaling and universality are nothing new for gelation theory: The classical theory, e.g. of the Flory-Stockmayer type, is even more universal than the percolation theory; moreover, it fulfills all scaling laws except those where the dimensionality d enters explicitly ("hyperscaling"). Since both the classical and percolation theory are oversimplifications, they could both be wrong, leaving only relations between the critical exponents intact, as in Eq. (9). In particular, complications like in correlated site-bond percolation can occur, due to solvent effects. The percolation theory, even in that complicated form, still involves simplifications compared with real materials; but it does take into account excluded volume effects and loop formation over large distances. Thus, it removes the inconsistency of the classical theory, where radius $\propto (\text{mass } s)^{1/4}$ cannot be valid for $s \rightarrow \infty$. One may hope that simplifications of the percolation theory on a molecular level do not affect the universal-

ity class, i.e. while they are important e.g. for the value of the gel point p_c , they do not affect the asymptotic critical exponents.

Present experimental evidence is somewhat inconclusive, except for elasticity where the classical theory works reasonably well in the majority of cases, and for viscosity where existing theories are unsatisfactory on both the classical and the percolation level. The exponent $k = 0.8$ determined for the divergence of the viscosity seems to be the most accurately known exponent of gelation at present.

At present, we do not know which theory is more suitable for which materials. Once percolation exponents (or another set of scaling exponents differing from classical values) have been reasonably established as being valid asymptotically, one should embark on Gordon's program¹¹⁾: Improve percolation theory step by step in extending it to the region farther away from p_c and improve classical theory step by step in extending it closer to the gel point.

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H. Appendix: A Percolation Computer Program

To make clear what we mean by Monte Carlo simulation of random percolation and to facilitate future percolation research by polymer chemists, we now give a complete Fortran program which calculates how many sites of a simple cubic lattice belong to the infinite cluster in a random-bond percolation system of size $L \times L \times L$. No large computer is needed: This program works for L up to 24 on a small PDP 11/34 computer and needs about 10 minutes to cover the whole range $p = 0.05, p = 0.10, p = 0.15, \dots, p = 0.95$. It also gives, for masses $s = 1$ to 12, the numbers N_s of clusters observed. (ACCEPT means that the computer is waiting until the user types in the size L he wants to work with. And RAN(IR, JR) gives a random number equally distributed between zero and unity).

The program is not understandable directly. For an explanation of the method, the interested reader is referred to the original paper of Hoshen and Kopelman¹³⁰⁾. The present version is based on a program written by J. Kertész. Figure 3 shows the variation of the gel fraction with p , as calculated from this program for $L = 50$.

```

PROGRAM KERTESZ
C   BOND PERCOLATION IN SIMPLE CUBIC LATTICE
    DIMENSION LEVEL (25,25), N(14000),NS(12)
    LOGICAL TOP,LEFT,BACK
    COMMON /NUMBER/ N
    ACCEPT 9,L
    DATA N/14000*0/,NS/12*0/

```

```

9  FORMAT(12)
   DO 7 IP = 1,19
   P = 1. - IP*0.05
   MAX = 14000
   IR=0
   JR=0
   LP1=L+1
   IF(LP1.GT.25) STOP 1
   INDEX=0
   DO 1 I=1,LP1
   DO 1 J=1,LP1
1  LEVEL(I,J)=MAX
   DO 3 K=2,LP1
   DO 3 J=2, LP1
   DO 3 I=2,LP1
   MOLD = MAX
   MBACK=MAX
   MLEFT=MAX
   LIJ = LEVEL(I,J)
   LIJM1=LEVEL(I,J-1)
   LIM1J=LEVEL(I-1,J)
   TOP = RAN(IR,JR).LT.P.AND.LIJ.LT.MAX
   BACK=RAN(IR,JR).LT.P.AND.LIJM1.LT.MAX
   LEFT=RAN(IR,JR).LT.P.AND.LIM1J.LT.MAX
   IF(.NOT.(LEFT.OR.TOP.OR.BACK)) GOTO 4
   IF(TOP) MOLD = KLASS(LIJ )
   IF(BACK) MBACK=KLASS(LIJM1)
   IF(LEFT) MLEFT=KLASS(LIM1J)
   MNEW = MIN0(MOLD,MBACK,MLEFT)
   LEVEL(I,J)=MNEW
   ICI = 1
   IF(TOP) ICI=ICI+N(MOLD)
   IF(LEFT.AND.MOLD.NE.MLEFT) ICI=ICI+N(MLEFT)
   IF(BACK.AND.MOLD.NE.MBACK.AND.MLEFT.NE.MBACK)
1  ICI=ICI+N(MBACK)
   N(MNEW)=ICI
   IF(TOP.AND.MOLD.NE.MNEW) N(MOLD)=-MNEW
   IF(BACK.AND.MBACK.NE.MNEW) N(MBACK)=-MNEW
   IF(LEFT.AND.MLEFT.NE.MNEW) N(MLEFT)=-MNEW
   GOTO 3
4  INDEX=INDEX+1
   LEVEL(I,J)=INDEX
   IF(INDEX.GE.14000)STOP 2
   N(INDEX)=1
3  CONTINUE
   INF=0
   DO 6 IS=1,INDEX

```

```

      NIS=N(IS)
      IF(NIS.LE.12.AND.NIS.GT.0) NS(NIS)=NS(NIS)+1
      INF=MAX0(INF,NIS)
6     N(IS)=0
      WRITE(5,5) P,L,INDEX,INF,(NS(IS),IS=1,12)
5     FORMAT(1X,F6.3,I3,3I7,11I4)
      DO 8 IS=1,12
8     NS(IS)=0
7     CONTINUE
      STOP
      END

      FUNCTION KCLASS(LEV)
      DIMENSION N(14000)
      COMMON /NUMBER/ N
      MS=N(LEV)
      IF(MS.LT.0) GOTO 1
      KCLASS=LEV
      RETURN
1     KCLASS=-MS
      MS=N(KCLASS)
      IF(MS.LT.0) GOTO 1
      N(LEV)=-KCLASS
      RETURN
      END

```

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