Extended abstract.

De Gennes met percolation first almost when the concept appeared ; his first two contribution, with Lafore and Millot date from 1959, and they point out clustering effects. They also refer to the work of Kasteleyn and Fortuin.
He then spent a long period without considering percolation, until the middle of the 70's.

Let me remind that gelation takes place when one lets multifunctional units react in a vessel. One then observes that one gets a solution that is more and more viscous, indicating that the mass of the polymers being synthesised becomes larger and larger. This is the "sol" phase. Above a threshold, in time in this experiment, one gets an elastic solid, even though its modulus is very low close to the threshold. (this is in addition to the sol).
This special "liquid-to- solid" transition was described on a purely geometrical basis by Flory, Stockmayer and Zimm, among others, within a mean field approximation: they worked on a Cayley tree, where no loops are possible, and without interactions. Any two points on a branched polymer are related by one single linear path, and the problem is to some extent one dimensional, and soluble exactly (slide 4).
They found a very large distribution of masses, that may not be reduced to a single mass: the weight and z average masses do not diverge the same way near the threshold. The variations of various quantities (slide 5) such as masses or distances as a function of the distance ε from the threshold were determined. Note that the characteristic distance ξ is either the radius of the largest polymers, or the size of the "node to node distance" for a gel. If one eliminates ε, one finds that the radius of gyration of the polymers varies with mass with an exponent ¼. Such exponent is too low, and it implies, in the three dimensional case, that the density inside the sphere that contains the polymer grows with mass, and eventually diverges. Therefore something had to be done.
Note also that the Cayley tree cannot be embedded in a space with finite dimension, because the number of elements grows exponentially. Therefore the "classical " result corresponds to infinite dimension, and is the mean field limit, which was shown to be valid for space dimension above 6.
In the general case, the solution was brought by de Gennes and Stauffer in 1976, who showed the equivalence between the sol- gel and the percolation transitions. The example shown in slide 6 is bond percolation on a square lattice in two dimensions. Very generally, it is found again that there is a very broad distribution of masses, characterized by two diverging masses and not a single one, the weight average and largest masses for instance. The distribution function decreases as a power law when mass increases, with an exponent τ that depends on the dimension of space. For very large masses, above a "largest mass", the distribution decreases exponentially. The exponent τ may be related to the fractal dimension of the polymers in the reaction bath, that is to the fractal dimension of percolation. This relation was discussed by Cates, who showed that it corresponds to a C* situation for a given value of N: each class of polymers with given N is at C*. Because they are fractal, much space is left, which is occupied by smaller polymers, still at C* for each mass. The resulting monomer concentration is unity at every point.
This variation of the distribution was checked experimentally by several groups (Leibler et al, Rubinstein and Colby, Schaefer, Martin et al., Lapp), who measured the value of τ , which they found roughly equal to 2.2 (slide 7). What is important is that the various groups used various methods for synthesis (cross-linking by irradiation, end-linking, ..), showing that the " details" of the chemistry are not important, as long as the main assumptions are fulfilled. These are that chemistry dominates, and that diffusion is not important. The latter becomes important when the reaction bath is a dilute solution.

The difference between percolation clusters and animals was considered by de Gennes in 1980. We recall that animals are obtained by considering all the possible configurations with N units, with same weight for each of the configurations. This is the first difference with percolation clusters, where an occupied site has probability p, and a vacant one a probability (1-p). A second difference comes from the evaluation of the fractal dimensions in both cases. This was done in a Flory approximation, which was also used by Lubensky and Isaacson.

For animals, one writes down a Flory free energy that has two contributions (slide 8). The first one is an entropic contribution, where the denominator is the square of the ideal radius, and the second one the classical interaction term, where the 2 monomer interaction only is kept because we consider a good solvent.

Minimization of this free energy leads to an exponent equal to ½ for d = 3. Note also that the critical dimension, where the exponent equals the mean field value is 8.

A Flory free energy may also be written for a sol near the gelation threshold (slide 9). It has the same form as for the animas, with one important difference: because the reaction bath is concentrated, the interaction term is screened. This corresponds to the Edwards screening for linear chains. Here, because of the polydispersity , the interaction term is divided by the weight average molecular weight. This leads to a larger value, 2.5 for the fractal dimension of the branched polymers in the reaction bath. Note also that the critical dimension is 6 instead of 8 for animals.

One way to check both polydispersity and the value of the fractal dimension for animals is by neutron scattering. Bouchaud et al. considered a solution where the branched polymers were first synthesized. Then the sol was heavily diluted, the distribution of masses being quenched. Two experiments were performed, on the distribution, and on a fraction of it. The curves, plotted in log- log plots, obtained in Saclay, show a clear difference between the slopes for both cases. The experiments (slide 11) on the fraction lead to a value 2 for the fractal dimension, in good agreement with the above discussion. The slope 1.7 for the polydisperse sample leads to an effective value for the fractal dimension (slide 10), implying both the fractal dimension of the polymers and the exponent τ of the distribution. This leads to a value for τ in good agreement with the previous one.

So far, we considered the simple case when the units that are reacting are small multifunctional units. What if one cross links linear chains in a melt? This is called Vulcanization, and was considered by de Gennes in 1977 (slide 12). A simple way to consider this is again to write down a Flory free energy. In order to do this, one has to carefully separate what is coming from gelation and from the fact that units are now long linear chains, made of Z monomers, and radius $Z^{1/2}$.

One finds the relation that is on slide 12, and shows that contributions from gelation and linear chains compete if we consider the interaction term. Clearly the contribution coming from ε diverges, whereas that from Z vanishes. In order to observe critical exponents, the interaction term should be large. If it is not, mean field, Flory- Stockmayer- Zimm exponents are observed. This defines the width of the critical region (and is equivalent to the Ginzburg criterion in critical phenomena). Comparing the two contributions, one finds that the critical region is very small for large Z. Thus mean field exponents should be observable. This seems to be in contradiction with the large density argument that was mentioned above. But it is not: In vulcanization, one has indeed a very large density of objects, but each of these is a fractal with very small density, $Z^{-1/2}$. Therefore, one may, to some extent, increase the density and compensate. This was checked experimentally by Colby and Lusignan.

So far, we considered the static properties, and there seems to be a consensus that such properties are, to a large extent, understood. The situation, as usual, is more delicate foe the dynamic and rheological properties. These are characterized by the exponents s for the viscosity, and t for the modulus (slide 3). Both of them were considered by de Gennes.

The viscosity exponent s was considered within a Rouse approximation (slide 13), where no hydrodynamic interaction is present. In this case, de Gennes considered a sol in a longitudinal flow, and calculated its dissipation rate. He showed that this may be related to the weight average radius of gyration, leading to a value $s = d\nu - \beta$. This is in agreement with a calculation by Stephen for a mixture of normal and superconducting links. Other relations were suggested, assuming some hydrodynamic interactions.

Similarly, he also evaluated the exponent t for the modulus (slide 14). He used an analogy with a random array of conductances, present with probability p. The modulus is equivalent to the conductance.In order to evaluate the flux through a sphere with radius ξ, he introduced the notion of active path between nodes, leading to a first approximation for the exponent t. Later, it was recognized that the active path does not diverge in the simple way that was initially assumed, and de Gennes' result was generalized. A challenging relation was suggested by Coniglio et al., who assumed that the modulus is merely related to the density of nodes, leading to $t = d\nu$. Experimentally, the situation is not as clear as for the static properties, because of the difficulty for direct measurements.

The frequency dependent modulus, however was measured by several groups. This may be written in a scaled form (slide 15), implying a longest time. For large frequencies, it behaves as a power law with an exponent that depends on both s and t. The experimental value (slide 16) that was found, approximately 2/3, however could not discriminate between the various assumptions that were made, and the problem is still rather open to a fresh idea or experiment.

A final idea that I discuss concerns the incoherent scattering by a dilute system of labelled monomers (slide 18). Here each branched polymer is ideally labelled by one of its monomers, and one looks at the motion of these labelled monomers over large distances. Then the scattered intensity may be approximated, for small q, by a Gaussian, with a diffusion coefficient D that depends on the viscosity. The distances that are considered here are large compared to the size of a monomer, but small compared to that of a branched polymer. This led de Gennes to assume that for these intermediate distances, the viscosity is local, and depends on distance. He introduced, also for the first time, an interpolation relation between distances on the order of the monomer, where he assumed the viscosity to be that of a "solvent", therefore finite, and distances on the order of the largest polymers, where viscosity diverges with the exponent s. this allows him to find a diffusion coefficient that depends on the size of each polymer. Averaging over the distribution leads to an intensity that varies as a power law of both frequency and q, with exponents that depend again on s and t. (and the exponent β for the gel fraction).

We conclude by noting that he had an extraordinary contribution to the understanding of the sol- gel transition. Only some aspects were developed above, and others, some of which are as important, were not considered here, but led to experimental realizations. Many aspects are still open, even though de Gennes opened the way.

A list of the corresponding publications is given below, showing the variety of his work in this area. I apologize if this is not complete. I tried to track his publications the best I could, but I might have missed some. The following list should however hopefully give some ideas during some time..

Publications.

Sur un phénomène de propagation dans un milieu désordonné
  (avec P. Lafore et J.P. Millot)
  J. Phys. Rad. <u>20</u>, 624 (1959)

 Amas accidentels dans les solutions solides désordonnées
  (avec P. Lafore et J.P. Millot)
  J. of Phys. and Chem. of Solids <u>11</u>, 105 (1959)

Possibilités offertes par la réticulation de polymères en présence d'un cristal liquide
  Phys. Lett. <u>28A</u>, 725 (1969)

Remarks on entanglements and rubber elasticity
  J. de Phys. <u>35</u>, L-133 (1974)

Critical dimensionality for a special percolation problem
  J. of Phys. <u>36,</u> 1049 (1975)

On a relation between percolation theory and the elasticity of gels
  J. de Phys. Letters <u>37,</u> L-1 (1976)

La notion de percolation
  La Recherche n° <u>72,</u> 919 (1976)

Critical behaviour for vulcanization processes
  J. de Phys. <u>38,</u> L-355 (1977)

Viscosité près d'une transition sol-gel
  C.R. Acad. Sci. (Paris) <u>286,</u> 131 (1978)

  Effects of cross-links on a mixture of polymers
    J. Physique Lett. <u>40,</u> L-69 (1979)

  Incoherent scattering near a sol-gel transition
    J. Physique <u>40,</u> L-197 (1979)

Percolation : quelques systèmes nouveaux
  J. de Physique, Colloque C3, supplément au n° 4,<u> 41,</u> C 3-17 (1980)

Amas sur des réseaux : sur la différence entre la percolation et la statistique des "animaux"
  C.R. Acad. Sci. (Paris) <u>291,</u> 17 (1980)

Transfert d'excitation dans un milieu aléatoire
  C.R. Acad. Sci. (Paris) <u>295,</u> 1061 (1982)

Capture d'une "fourmi" par des pièges sur un amas de percolation
  C.R. Acad. Sci. (Paris) 296, 881 (1983)

Conjectures on the transport of a melt through a gel
  Macromolecules 19, 1245 (1986)

Conducting polymers in solution : scaling laws for charge transport
  Physica 138A, 206-219 (1986)

Fracture d'un adhésif faiblement réticulé
  C.R. Acad. Sci. (Paris) 307, 1949 (1988)

Weak adhesive junctions
  J. Physique 50, 2551 (1989)

 Sur la fracture des adhésifs caoutchoutiques
  (avec S. Troian)
  C.R. Acad. Sci. (Paris) 311, 389 (1990)

Rubber-rubber adhesion with connector molecules
  (avec E. Raphaël)
  J. Phys. Chem. 96, 4002-4007 (1992)

Aggregation of flexible-rigid-flexible triblock copolymers
  (avec E. Raphaël)
  Makromol. Chem., Macromol. Symp. 62, 1-17 (1992)

 Glissement d'un caoutchouc sur un solide greffé
  (avec M. Rubinstein, A. Ajdari, L. Leibler, F. Brochard-Wyart)
  C.R. Acad. Sci. (Paris) 316, 317-320 (1993)

Croissance d'une fissure dans un gel en rétraction
  C.R. Acad. Sci. (Paris) 317, 1165-1168 (1993)
  + Erratum, C.R. Acad. Sci. (Paris) 317, 1683 (1993)

Démouillage entre un solide poreux et un caoutchouc
  C.R. Acad. Sci. (Paris) 318, 1033-1037 (1994)

Adhésion spontanée caoutchouc/solide nu
C. R. Acad. Sci. (Paris) 320, 193-197 (1995)

Adhesion between a rubber and a grafted surface
Il Nuovo Cimento 16D (7), 637-640 (1994)

The adhesion between elastomers (avec E. Raphaël) in
"Soft Order in Physical Systems" edited by Y. Rabin and R. Bruinsma, New York: Plenum Press p. 57-71 (1994)

Adhesion between rubbers and grafted solids
(avec F. Brochard-Wyart)
J. Adhes. <u>57,</u> 21 (1996)