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Percolation and critical points

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Abstract

The interplay between critical percolating clusters and critical points in physical systems and models is reviewed. The main emphasis is given to systems such as colloids and gels. Much information on the main mechanism leading to percolation in correlated systems can be obtained from the study of the Ising model. It is emphasized that different cluster definitions are necessary for studying different phenomena and that the possibility of experimentally detecting the percolation line is related to the cluster lifetime. Some results on the interplay between critical points and percolating clusters in fluids are also discussed.

1. Introduction

It is a great pleasure to dedicate this paper to Sow-Hsin Chen on the occasion of his 65th birthday. His pioneering contribution to the field encompassing the subject that I am going to address here has been crucial.

I would like to review some experimental results and theoretical ideas related to the interplay between percolation phenomena and critical points, which are manifested in a large variety of models and physical systems such as the Ising model, fluids, colloids and gels.

2. Percolation and critical points in physical systems

To consolidate the ideas involved here, I would like to consider three particular physical systems which could each be thought of as representative of a general situation:

- (a) Microemulsions of water in oil [1].
- (b) Triblock copolymers in unicellular systems [2, 3].
- (c) Gelatin–water–methanol systems [4].

In figures 1, 2, 3 we show respectively the phase diagrams of the systems (a), (b), (c); in each case, the coexistence curve in the temperature–concentration diagram is shown together with ‘percolation lines’.

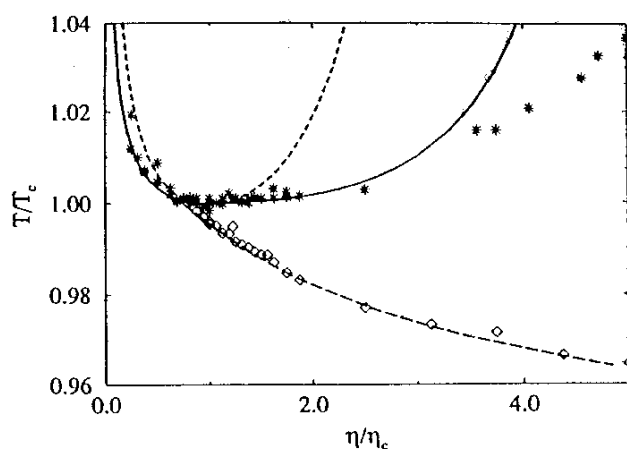


Figure 1. Experimental points on the coexistence curve (stars) in the temperature–volume fraction phase diagram of AOT/water/decane. η denotes the volume fraction of the dispersed phase (AOT plus water) and η_c the critical value at the thermal critical point. The theoretical coexistence curve (solid line) and spinodal line (short-dashed line) were calculated using Baxter’s model. Experimental percolation points (diamonds) where the conductivity exhibits a steep increase have been fitted with Baxter’s model. From reference [1].

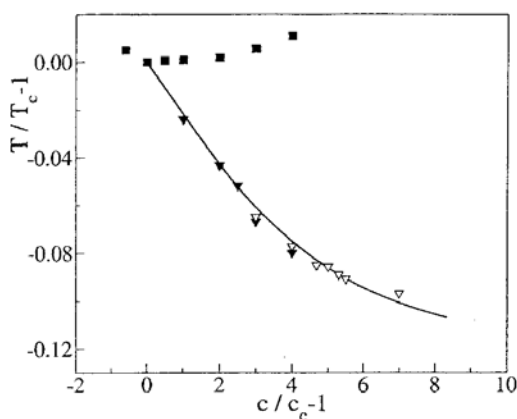


Figure 2. The phase diagram of a triblock copolymer/water system; experimental points on the coexistence curve (squares) and the percolation line, where the viscosity exhibits a steep increase, measured via the viscoelasticity (full triangles) and photon correlation spectroscopy (empty triangles). The percolation line has been fitted with Baxter’s model (solid line). Developed from reference [2].

In (a) the system consists of three components: AOT/water/decane. For the temperatures and concentrations of interest, we can consider the system as made up of small oil droplets surrounded by water and a solvent. The droplets interact via a hard-core potential plus a short-range attractive interaction. Due to the entropic nature of the attractive interaction, the coexistence curve is ‘upside-down’ with the critical point being the minimum instead of a maximum (figure 1). The broken line is characterized by a steep increase of conductivity.

In (b) the system is made up of unicellular triblock copolymers in solution in water; c is the volume fraction of the single cells (figure 2). The line is characterized by a steep increase in the viscosity.

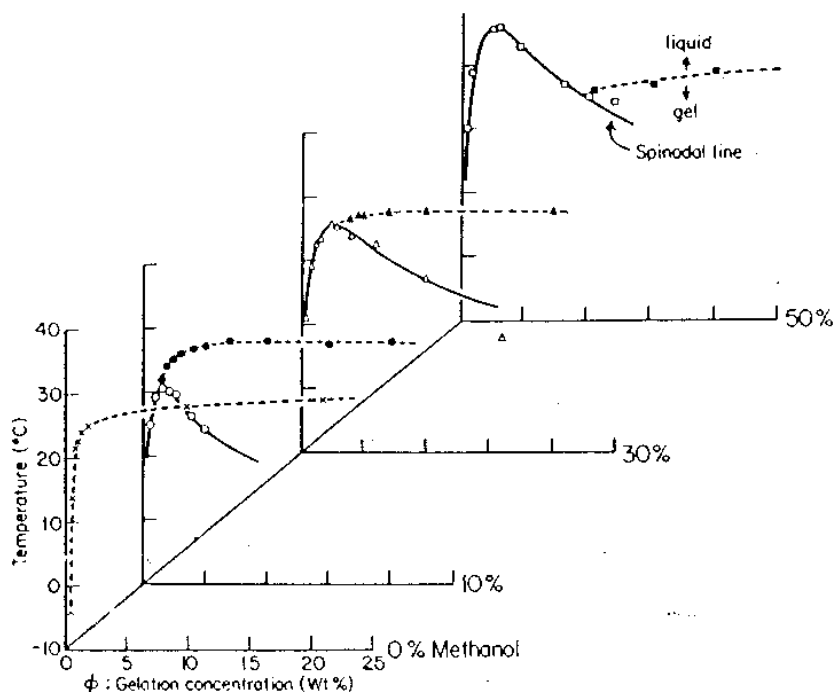


Figure 3. The sol-gel transition temperature (solid symbols) and the spinodal temperature (open symbols) for gelatin-water-methanol mixtures as functions of the gelatin concentration. At the sol-gel transition the viscosity diverges. From reference [4].

In (c) the system is made of gelatin dissolved in water plus methanol; ϕ is the gelatin concentration. The broken lines are characterized by the divergence of the viscosity and correspond to the sol-gel transition. Each line represents a different value of the methanol concentration, which has been chosen in such a way that the line ends at the consolute point or below it in the low- or high-density phase (figure 3).

In all of these experiments the consolute point is characterized by a thermodynamical singularity, where the correlation length and compressibility diverge. The other lines are usually ascribed to a 'percolation' transition. However, it is important to be precise as regards which clusters are the relevant ones in the three different systems. Also we would like to understand why in system (c) the viscosity diverges at the percolation transition, while in (b) it reaches a plateau, and why in (a) and (b) the 'percolation' lines end on the coexistence curve very close to the critical point.

In order to clarify these questions, it may be convenient to review the cluster properties in the Ising or lattice gas model.

3. Clusters in the lattice gas or Ising model

The most convenient model for studying the interplay between the percolation line and critical point is the Ising model, or equivalently the lattice gas model, which is more suitable for comparing with a real fluid. The Hamiltonian of the lattice gas model is given by

$$\mathcal{H} = -\varepsilon \sum_{\langle ij \rangle} n_i n_j - \mu \sum_i n_i \quad (1)$$

where $n_i = 1, 0$ are the occupancy variables, ε is the interaction between two nearest-neighbour (NN) particles and μ is the chemical potential. In the Ising language, the spin variables s_i are related to the lattice gas variable by the relation $s_i = 1 - 2n_i$. We will usually use the lattice gas terminology except in a few cases where it may be more convenient to use the Ising terminology.

From the thermodynamic point of view, the only quantities of interest are those which can be obtained from the free energy, and these were the only quantities that Onsager was concerned with in his famous solution of the 2D Ising model. However, one can look at the lattice gas model from a different perspective by studying the connectivity properties using concepts such as clusters which have been systematically developed in percolation theory [5]. There are two reasons for approaching the problem also from the connectivity point of view.

One reason is that it gives a better understanding of the mechanism of the phase transition [6]. In fact, concepts like universality and scaling have been better understood in terms of geometrical clusters and fractal dimensions [7].

A second reason is that there are physical quantities amenable to experimental observation which are associated with the connectivity properties and cannot be obtained from the free energy. It is very important to note however that the definitions of connectivity and therefore the definitions of the cluster are not always the same, and may depend on the particular observable considered.

In the lattice gas model, for a given configuration of particles it is rather natural to define a cluster as a maximal set of NN particles (figure 4(a)). For some time these clusters were believed to be responsible for the correlations present in the lattice gas model. This idea was also based on numerical results which showed evidence that in two dimensions the mean cluster size diverges at the thermal critical point [8]. However, the idea that the clusters could be used to describe thermal correlations was definitively abandoned when it was shown by numerical simulation in the three-dimensional lattice gas model [9] and by exact solution on the Bethe lattice [10] that the percolation point appeared in the low-density phase on the coexistence curve at a temperature T_p before the critical point T_c was reached ($T_p < T_c$).

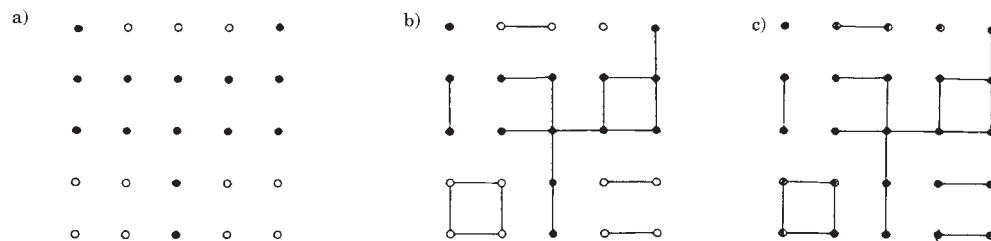


Figure 4. (a) Ising configuration: 'up' spins and 'down' spins are represented respectively by filled and empty circles. (b) Correct clusters obtained from the configuration given in (a) by putting bonds between sites in the same state with probability $p = 1 - e^{-\beta\varepsilon/2}$. (c) The bond configuration after summing over the spin configurations in (b).

Later it was suggested on the basis of topological arguments [11] that only in two dimensions does the critical point coincide with the percolation point, and this is not necessarily the case in higher dimensions. The arguments followed two steps, which we report for convenience in the spin language. In the first step it was argued that an infinite cluster of up spins is a necessary condition for having a spontaneous magnetization. This implies a percolation transition of down spins on the coexistence curve $T_p \leq T_c$. In the second step it was argued that for topological reasons in two dimensions it is not possible to have an infinite

cluster of up spins coexisting with an infinite cluster of down spins, which implies that $T_p \geq T_c$. Combining this with the previous inequalities, one obtains in two dimensions $T_p = T_c$.

Later these results were proven rigorously [12, 13] along with many other results relating connectivity quantities and thermodynamic quantities. Here we report some of the main relations. Given an Ising model with NN ferromagnetic interactions in any dimensions the following inequalities hold:

$$\begin{aligned} \rho_\infty &\geq m \\ p_{ij} &\geq g_{ij} \end{aligned} \tag{2}$$

where ρ_∞ is the density of sites in the infinite cluster, m is the magnetization, p_{ij} is the probability that i and j are in the same cluster and g_{ij} is the spin–spin pair correlation function. In the lattice gas terminology the magnetization m is replaced with $m = 1 - 2\phi$, where ϕ is the density of particles.

These relations prove rigorously that the percolation line ends in the low-density region at a temperature $T_p \leq T_c$ [12].

Can we detect these clusters? If the particles are characterized by a conductance much larger than the substrate, the percolation line can be detected by a steep increase from the lower conductivity of the substrate to the larger conductivity of the percolating particles [14]¹.

Can we extend the above inequalities to off-lattice particles? We can argue that this could well be appropriate if the density is not too high. The physical meaning of the relations (2) is that a necessary condition for two particles to be positively correlated is that they are connected by at least one chain of NN particles; that is, a particle can transmit correlations through a chain of particles only if they are in a position where they feel the attractive interaction. This should apply also to off-lattice particles interacting via a potential made essentially of a hard-core plus a short-range attraction, if the density is not too high. In fact in this case the correlation due to the repulsive potential is negligible. We expect then for such systems a percolation line ending below the critical temperature in the low-density region as in the three-dimensional lattice gas model. This is in fact what is found experimentally in the colloidal system (figure 2) and also in an analytical calculation using the Baxter potential [1].

4. Droplets in the lattice gas or Ising model

From section 2 it is clear that the Ising cluster, defined as group of NN particles, has a physical meaning in the context of a binary mixture, in which each species has a different conductance. These clusters however do not have the property of modelling correlated regions corresponding to spin or density fluctuations, as originally expected. In fact even in two dimensions where the thermal critical point coincides with the percolation point the Ising clusters were not suitable for such modelling. Series expansion showed that the mean cluster size diverged with an exponent $\gamma_p = 1.91 \pm 0.001$ rather different from the susceptibility exponent $\gamma = 1.75$ [16]. For a cluster to properly represent a correlated region it must exhibit the same properties as the droplets in Fisher’s droplet model [6]—namely,

- (i) the size of the clusters must diverge at the Ising critical points,
- (ii) the linear dimension of the clusters must diverge with the same exponent as the correlation length exponent and
- (iii) the mean cluster size must diverge as the susceptibility exponent.

¹ Actually the effective percolation line occurs at a lower density, since the clusters move and a charge carrier will percolate even at a lower density before an infinite cluster is formed (stirring percolation) [15].

From the properties mentioned in section 2, it appears that the Ising clusters are too big for modelling the actual droplets. The reason is that there are two contributions to the Ising clusters. One is due to correlations, but there is another contribution, purely geometrical, due to the fact that for a fixed density ρ , two NN sites, even in the absence of correlation, have a probability ρ^2 of being occupied. The latter contribution becomes evident in the limit of infinite temperature and zero external field. In this case the density of particles is $\rho = 0.5$ and there are no correlations, although the cluster size is different from zero, and identical to the cluster size of random percolation at the same density.

By introducing connecting bonds between NN particles with probability p_b , the size of the clusters is reduced (figure 4(b)). The connectivity properties of this model were originally studied using a Hamiltonian formalism [17] based on a dilute-state Potts model. From the properties of the Hamiltonian and using real-space renormalization group arguments, it was possible to show that for the particular choice of the bond probability

$$p_b \equiv p = 1 - e^{-\beta\varepsilon/2} \quad (3)$$

the size of the clusters made up of particles connected by bonds diverges at the Ising critical point with Ising exponents, exhibiting thus the same properties as the droplets in Fisher's model. The clusters of parallel spins connected by bonds with probability p given by (3) were called droplets to distinguish them from the Ising clusters. Later it was shown that the droplets so defined have the same statistics as the clusters introduced by Kasteleyn and Fortuin (KF) (see the appendix for the differences between the CK droplets and the KF clusters) and using the KF formalism it was possible to prove that for zero external field or along the critical isochore [18] the following relations hold:

$$\begin{aligned} \rho_\infty &= m \\ p_{ij} &= g_{ij} \end{aligned} \quad (4)$$

where ρ_∞ is the density of sites in the percolating droplet, m is the magnetization, p_{ij} is the probability that i and j are in the same droplet and g_{ij} is the spin-spin pair correlation function. Equations (4) prove that the droplets lead to a good description of the thermal fluctuations [19].

One very interesting application based on the droplets idea was produced by Swendsen and Wang [20, 21], who developed a cluster dynamics which drastically reduced the slowing down near the critical point of the Ising and Potts models (see also [22] for further developments).

By applying a renormalization group it was also possible to study the percolation line for different values of p_b for two dimensions and by ε -expansion near six dimensions [23]. The phase diagram for three dimensions has been calculated numerically and it is reported in figure 5 for three different values of p_b (see also [24]). Along the percolation line one finds critical exponents in the universality class of random percolation everywhere except in the case $p_b = p$, where one finds critical exponents of random percolation with a crossover to Ising critical exponents as the Ising critical point is approached. One also finds that there is no singularity in the free energy along the percolation lines except of course at the Ising critical point. This last result is a consequence of the bonds having been defined in a fictitious way. They do not change the interaction energy; they are present only to define the connectivity. As a consequence, the percolation lines can be changed by changing the value of p_b .

Finally, let us note that the droplet definition can be extended to a lattice gas model characterized by an attractive interaction potential $u(r)$ between two particles at a distance r apart. In this case the droplets are made up of occupied sites connected by bonds and the bonds are present between any pair of particles with a probability

$$p(r) = 1 - e^{\beta u(r)/2} \quad (5)$$

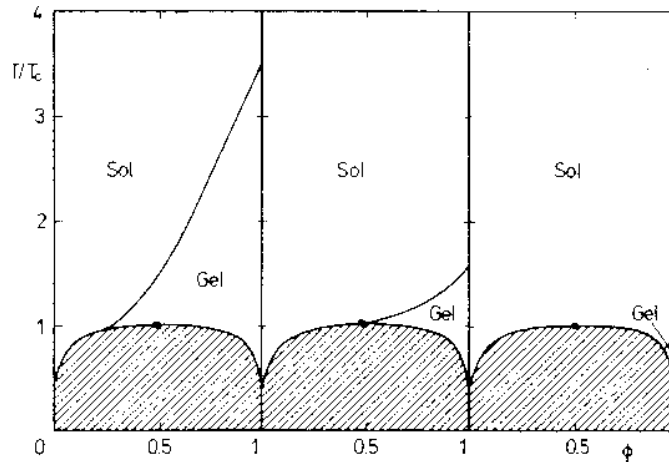


Figure 5. Monte Carlo simulations of the phase diagram of the 3D lattice gas model for three different bond probabilities $p_b = 1 - e^{-c\beta\epsilon/2}$ with the constant $c = 2.25, 1, 0.564$ from left to right. ‘Gel’ and ‘Sol’ indicate the percolating and non-percolating phases. From reference [25].

where r is the distance between the two particles. It can be shown that in this case also the relations (4) between the connectivity and thermal quantities holds.

Besides the definition of droplets which characterizes geometrically the density or spin fluctuation along the critical isochore, one may wonder whether there is a physical meaning also of the percolation line which appears in the phase diagram (figure 5) where we know that there is no singularity in the free energy.

We will discuss this point in the next section, where we will consider two different physical mechanisms leading to the formation of physical clusters in simple fluids, colloids and gels.

5. Hill’s clusters in simple fluids and colloids

Let us first discuss the possibility of extending the definition of droplets to simple fluids. In 1955 Hill introduced the concept of physical clusters in a fluid in an attempt to explain the phenomenon of condensation from a gas to a liquid. In a fluid made of particles interacting via a pair potential $u(r)$, physical clusters are defined as a group of particles bonded pairwise. A pair of particles is bonded if in the reference frame of their centre of mass their total energy is less than zero—that is, their relative kinetic energy plus the potential energy is less than zero. The probability that two particles at distance r are bonded can be calculated [26] and is given by

$$p_H(r) = \frac{4}{\pi} \int_0^{\sqrt{-\beta u(r)}} x^2 e^{-x^2} dx. \quad (6)$$

More recently it was noted [27] that the bond probability (6) calculated for the interaction of the three-dimensional NN lattice gas model is almost coincident with the bond probability p of equation (3). This implies that Hill’s physical clusters for the 3D lattice gas almost coincide with the droplets defined by Coniglio and Klein, and in fact Hill’s clusters percolate along a line almost indistinguishable from the percolation line in the middle of figure 5.

In fact Hill’s bond probability in 3D fits very well with the general bond probability $p(r)$ of equation (5) for any potential whose attractive part is given by $u(r)$. Thus one may

wonder whether Hill's physical clusters in a fluid may be suitable for describing the thermal fluctuations like the droplets in the lattice gas model.

In order to calculate percolation quantities in a fluid, in references [28] the authors developed a theory based on Mayer's expansion. In particular, using this theory they calculated analytically, for a potential made up of a hard-core plus an attractive interaction, the percolation line of Hill's physical clusters in a crude mean-field approximation and compared with the liquid-gas coexistence curve. They found that the percolation line ended just below the critical point in the low-density phase but not exactly at the critical point.

Very recently, Campi *et al* [29], using molecular dynamics, have calculated the percolation line of Hill's physical clusters for a Lennard-Jones potential. The results showed a percolation line ending close to or at the critical point (figure 6), suggesting that Hill's clusters are good candidates for providing a description of the density fluctuations, like the droplets in the lattice gas model, although there is no proof of relations analogous to those valid for the droplets in the lattice gas such as equation (4), which would prove that their size would diverge exactly at the critical point with thermal exponents.

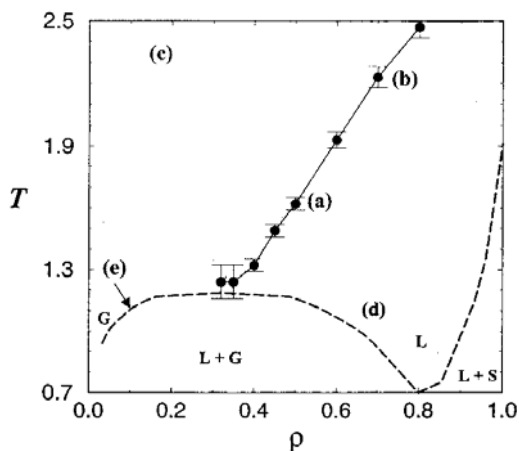


Figure 6. The phase diagram of the Lennard-Jones fluid obtained using molecular dynamics. The full line corresponds to percolation of a cluster following Hill's definition. From reference [27].

Although Hill's clusters may lead to critical fluctuation near the critical point, we may wonder whether they have a physical manifestation away from the critical point. In particular, we may wonder whether we can detect experimentally the percolation line in the phase diagram. For a Lennard-Jones fluid, molecular dynamics shows that quantities such as the viscosity and the diffusion coefficient do not seem to exhibit any anomalous behaviour through the percolation line [29]. In some colloids, the percolation line is detected instead through a steep increase of the viscosity. What could the difference between the two cases be? The difference may rely on their lifetime. The possibility of detecting the percolation line of these clusters is expected to depend on the lifetime of the clusters, which in turn depends on the bond lifetime. The larger the cluster lifetime, the larger the increase of the viscosity, and the easier it is to detect the percolation line. In section 6 we will discuss the behaviour of the viscosity as a function of the lifetime of the clusters.

6. Clusters in weak and strong gels

In the previous section we have described the case in which the probability of having a bond between two particles coincides with the probability that the two particles form a bound state defined according to Hill's criterion. Now we want to describe another mechanism leading

to the formation of bound states, which is more appropriate to gels. The importance of connectivity in gels was first emphasized by Flory [30]. The application of percolation theory to gels was later suggested by de Gennes [31] and Stauffer [32, 33]. Here we consider a system made up of monomers in a solvent. Following reference [34] we shall assume that the monomers can interact with each other in two ways. One is by the usual van der Waals interaction, and the other is by a directional interaction that leads to a chemical bond. A simple model for such a system is a lattice gas model where an occupied site represents a monomer and an empty site a solvent. For simplicity we can put the monomer–solvent interaction and the solvent–solvent interaction equal to zero and include such interactions in an effective monomer–monomer interaction. The monomer–monomer interaction ε_{ij} can be approximated reasonably well by a nearest-neighbour interaction:

$$\varepsilon_{ij} = \begin{cases} -W \\ -E \end{cases} \quad (7)$$

where $-W$ is the van der Waals type of attraction and $-E$ is the bonding energy. Of course, this second interaction which is the chemical interaction only occurs when the monomers are in particular configurations. For simplicity we can suppose that there is one configuration which corresponds to the interaction of strength E and that there are Ω configurations which correspond to the interaction of strength W . We expect $E \gg W$ and $\Omega \gg 1$. It can be easily established by calculation [34] that such a system is equivalent to a lattice gas model with an effective NN interaction $-\varepsilon$ given by

$$e^{\beta\varepsilon} = e^{\beta E} + \Omega e^{\beta W}. \quad (8)$$

Therefore from the static point of view the system exhibits a coexistence curve and a critical temperature which characterize the thermodynamics of the system. However, the system behaves microscopically rather differently to a standard lattice gas. In fact, in a configuration in which two monomers are NN, in a standard lattice gas they feel one interaction, while in the system considered here with some probability p_b they feel a strong chemical interaction $-E$ and with probability $1 - p_b$ they feel a much smaller interaction $-W$. The probability p_b can be easily calculated and is given by

$$p_b = \frac{e^{\beta E}}{e^{\beta E} + \Omega e^{\beta W}}. \quad (9)$$

In conclusion, the system from the static point of view is equivalent to a lattice gas with interaction ε given by (8). However, we can also study the percolation line of the clusters made up of monomers connected by chemical bonds. This can be done by introducing bonds between NN particles in the lattice gas with NN interactions, the bonds being present with the probability p_b given by (9). On changing the solvent, the effective interaction W changes and one can realize three cases topologically similar to those of figure 5, where the percolation line ends at the critical point or below the critical point in the low-density or high-density phase (for more details see [34]).

The lifetimes of the bonds are of the order of $e^{\beta E}$. Since E is very large, the lifetime could be very large. For an infinite bond lifetime the bonded clusters are permanent and the viscosity diverges as the mean cluster size diverges (see for example [33]), and the percolation line can be easily detected as in Tanaka's experiment.

7. Scaling behaviour of the viscosity

If the lifetime of the chemical bonds is infinite, the viscosity exhibits a divergence at the percolation threshold as recently shown in various models [35–37]:

$$\eta \sim \xi^{\bar{k}} \quad (10)$$

where ξ is the linear dimension of the critical cluster which diverges at the percolation threshold with the exponent ν .

For a probe of radius R much larger than ξ , the diffusion coefficient $D(R)$ is given by the Stokes–Einstein relation:

$$D(R) \sim \frac{1}{R\eta}. \quad (11)$$

It has been proposed (reference [38]) that if we consider as a probe a cluster of radius R smaller than ξ , the viscosity will depend also on R in such a way as to satisfy a generalized Stokes–Einstein relation (11) with $\eta = \eta(R)$. When $R = \xi$ the viscosity $\eta(\xi) = \eta$, and from (11) one obtains the following scaling behaviour for R :

$$D(R) \sim R^{-(1+\bar{k})}. \quad (12)$$

Therefore the relaxation time $\tau(R)$ for a cluster of radius R is

$$\tau(R) \sim R^{1+\bar{k}}. \quad (13)$$

If τ is the lifetime of a typical cluster, then a cluster of radius R will contribute to the viscosity if $\tau(R) < \tau$, and therefore

$$\eta \sim \xi^{\bar{k}} f\left(\frac{\tau}{\xi^{1+\bar{k}}}\right) \sim \begin{cases} \xi^{\bar{k}} & \tau > \xi^{1+\bar{k}} \\ \tau^{\bar{k}/(1+\bar{k})} & \tau < \xi^{1+\bar{k}} \end{cases} \quad (14)$$

which implies that the viscosity will exhibit a steep increase followed by a plateau. The higher τ , the higher the plateau.

The viscosity data on microemulsions show such a plateau in fact, suggesting that the mechanism for the appearance of the plateau is linked to the bond lifetime which in turn is related to the cluster relaxation time.

8. Conclusions

In conclusion, we have discussed the interplay between the percolation line and the critical point in systems where thermal correlations play an important role. For each phenomenon it is very important to define the appropriate cluster. In the conductivity experiment on microemulsions the appropriate clusters are made up of ‘touching’ spheres similar to nearest-neighbour particles in a lattice gas model. From the cluster properties of the lattice gas model, we expect the percolation line to end up just below the critical point in the low-density region, as observed in the experiments.

The viscoelastic properties of microemulsions may be more suitably described using clusters made up of spheres bonded pairwise. These clusters along the critical isochore seem to be closely related to the droplets which give rise to a description of the critical fluctuations. As a result, the percolation line ends very close to the critical point.

In weakly reversible gelatin the clusters are made up of monomers (or polymers) bonded by a strong interaction which leads to chemical bonding. In this case the bond probability can be changed by changing the solvent, and therefore the percolation line—on properly choosing the solvent—can end on the coexistence curve at or below the critical point.

The viscosity in the gel experiments diverges at the percolation point, while it reaches a plateau in colloids, because the lifetime of the bonds is much longer in the first system than in the second. The percolation line of clusters bonded pairwise can also be defined in fluids, but due to the negligible lifetime such lines are very difficult to detect.

Appendix. The cluster approach to spin Hamiltonians: the KF dilution method and the CK approach

The idea of describing the Ising system in terms of a purely percolative model was introduced by Kasteleyn and Fortuin in 1969 [39] (KF). Subsequently Coniglio and Klein [17] (CK) independently used a different approach with the aim of defining correct clusters in the Ising model. It was only later that it was realized that the two approaches were related, although ‘clusters’ has different meanings in the two approaches. We will discuss these two approaches here, pointing out that the clusters are different, although their statistical properties are the same.

A.1. The KF dilution method

Let us consider an Ising system of spins $S_i = \pm 1$ on a lattice with nearest-neighbour interactions and, when needed, let us assume periodic boundary conditions in both directions. All interactions have strength J and the Hamiltonian is

$$\mathcal{H}(\{S_i\}) = - \sum_{\langle i,j \rangle} J(S_i S_j - 1) \quad (\text{A.1})$$

where $\{S_i\}$ represents a spin configuration and the sum is over NN spins. The main point in the KF approach is the replacement of the original Ising Hamiltonian with an annealed diluted Hamiltonian

$$\mathcal{H}'(\{S_i\}) = - \sum_{\langle i,j \rangle} J'_{ij}(S_i S_j - 1) \quad (\text{A.2})$$

where

$$J'_{ij} = \begin{cases} J' & \text{with probability } p \\ 0 & \text{with probability } 1 - p. \end{cases} \quad (\text{A.3})$$

The parameter p is chosen such that the Boltzmann factor associated with an Ising configuration of the original model coincides with the weight associated with a spin configuration of the diluted Ising model:

$$e^{-\beta \mathcal{H}(\{S_i\})} \equiv \prod_{\langle i,j \rangle} e^{\beta J(S_i S_j - 1)} = \prod_{\langle i,j \rangle} (p e^{\beta J'(S_i S_j - 1)} + (1 - p)) \quad (\text{A.4})$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant and T is the temperature. In order to satisfy (A.4) we must have

$$e^{\beta J(S_1 S_2 - 1)} = p e^{\beta J'(S_1 S_2 - 1)} + (1 - p). \quad (\text{A.5})$$

We now take the limit $J' \mapsto \infty$. In such a case, $e^{\beta J'(S_1 S_2 - 1)}$ equals the Kronecker delta $\delta_{S_1 S_2}$, and from (A.5), p is given by

$$p = 1 - e^{-2\beta J}. \quad (\text{A.6})$$

From (A.4), by performing the products we can write

$$e^{-\beta \mathcal{H}(\{S_i\})} = \sum_C W_{KF}(\{S_i\}, C) \quad (\text{A.7})$$

where

$$W_{KF}(\{S_i\}, C) = p^{|C|}(1-p)^{|A|} \prod_{(i,j) \in C} \delta_{S_i S_j}. \quad (\text{A.8})$$

Here C is a configuration of interactions of strength $J' = \infty$ in which $|C|$ is the number of interactions of strength $J' = \infty$ and $|A|$ is the number of interactions of strength 0. $|C| + |A| = \mathcal{N}$, where \mathcal{N} is the total number of edges in the lattice.

$W_{KF}(\{S_i\}, C)$ is the statistical weight associated (a) with a spin configuration $\{S_i\}$ and (b) with a set of interactions in the diluted model in which a subset of edges C have infinite-strength interactions while all the other edges have zero-strength interaction. The Kronecker delta indicates that two spins connected by an infinite-strength interaction must be in the same state. Therefore the configuration C can be decomposed into clusters of parallel spins connected by infinite-strength interactions.

Finally, the partition function of the Ising model, Z , is obtained by summing the Boltzmann factor (A.7) over all the spin configurations. Since each cluster in the configuration C gives a contribution of 2, we obtain

$$Z = \sum_C p^{|C|}(1-p)^{|A|} 2^{N_C} \quad (\text{A.9})$$

where N_C is the number of clusters in the configuration C .

In conclusion, in the KF formalism the partition function (A.9) is equivalent to the partition function of a correlated bond percolation model [39, 40] where the weight of each bond configuration C is given by

$$W(C) = \sum_{\{S_i\}} W_{KF}(\{S_i\}, C) = p^{|C|}(1-p)^{|A|} 2^{N_C} \quad (\text{A.10})$$

which coincides with the weight of the random percolation except for the extra factor 2^{N_C} . Clearly all percolation quantities in this correlated bond model weighted according to equation (A.10) coincide with the corresponding percolation quantities of the KF clusters made up of parallel spins connected by infinite-strength interaction, whose statistical weight is given by (A.8).

When in (A.4) the limit $J' \rightarrow \infty$ is not taken, it is possible to show that the partition function Z may be written as

$$Z = \sum_C p^{|C|}(1-p)^{|A|} Z(C, J') \quad (\text{A.11})$$

where $Z(C, J')$ is the partition function of a sublattice C of NN spins interacting via J' , and

$$p = (1 - e^{2\beta J}) / (1 - e^{-2\beta J'}). \quad (\text{A.12})$$

A.2. The CK approach

In the approach followed by Coniglio and Klein [17], given a configuration of spins, one introduces at random connecting bonds between NN parallel spins with probability p_B ; antiparallel spins are not connected, with probability 1. Clusters are defined as maximal sets of parallel spins connected by bonds. The bonds here are fictitious; they are introduced only to define the clusters and do not modify the interaction energy as in the FK approach. For a given realization of bonds we distinguish the subsets C and B of NN parallel spins respectively connected and not connected by bonds and the subset D of NN antiparallel spins. The union of C , B and D coincides with the total number of NN pairs of spins E . The statistical weight of a configuration of spins and bonds is [18, 43]

$$W_{CK}(\{S_i\}, C) = p_B^{|C|}(1-p_B)^{|B|} e^{-\beta \mathcal{H}(\{S_i\})} \quad (\text{A.13})$$

where $|C|$ and $|B|$ are the number of NN pairs of parallel spins respectively in the subsets C and B not connected by bonds.

For a given spin configuration, using the Newton binomial rule, we have the following sum rule:

$$\sum_C p_B^{|C|} (1 - p_B)^{|B|} = 1. \quad (\text{A.14})$$

From equation (A.14) it follows that the Ising partition function, Z , may be obtained by summing (A.13) over all bond configurations and then over all spin configurations:

$$Z = \sum_{\{S_i\}} \sum_C W_{CK}(\{S_i\}, C) = \sum_{\{S_i\}} e^{-\beta \mathcal{H}(\{S_i\})}. \quad (\text{A.15})$$

The partition function of course does not depend on the value of p_B , which controls the bond density. By tuning p_B instead, it is possible to tune the size of the clusters. For example, on taking $p_B = 1$ the clusters would coincide with nearest-neighbour parallel spins, while for $p_B = 0$ the clusters are reduced to single spins. By choosing $p_B = 1 - e^{-2\beta J} \equiv p$ (identical to (A.6)) and observing that $e^{-\beta \mathcal{H}(\{S_i\})} = e^{-2\beta J |D|}$, where $|D|$ is the number of antiparallel pairs of spins, the weight (A.13) simplifies and becomes

$$W_{CK}(\{S_i\}, C) = p^{|C|} (1 - p)^{|A|} \quad (\text{A.16})$$

where $|A| = |B| + |D| = |E| - |C|$. We will see [17] that with this particular choice of the bond probability, the clusters, which have been called ‘droplets’, percolate at the Ising critical point with Ising critical exponents.

From (A.16) we can calculate the weight $W(C)$ that a given configuration of connecting bonds C between NN parallel spins occurs (figure 4(c)). This configuration C can occur in many spin configurations. So we have to sum over all spin configurations compatible with the bond configuration C ; that is,

$$W(C) = \sum_{\{S_i\}} W_{CK}(\{S_i\}, C) \prod_{(i,j) \in C} \delta_{S_i, S_j} \quad (\text{A.17})$$

where, due to the product of the Kronecker deltas, the sum is over all spin configurations compatible with the bond configuration C . From (A.16) and (A.17) we have

$$W(C) = \sum_{\{S_i\}} p^{|C|} (1 - p)^{|A|} \prod_{(i,j) \in C} \delta_{S_i, S_j} = p^{|C|} (1 - p)^{|A|} 2^{N_C}. \quad (\text{A.18})$$

Consequently in (A.15), by taking the sum over all bond configurations, the partition function Z can be written as in the KF formalism (A.9):

$$Z = \sum_C p^{|C|} (1 - p)^{|A|} 2^{N_C}. \quad (\text{A.19})$$

In spite of the strong analogies, the CK clusters and the KF clusters have different meanings. In the CK formalism the clusters are defined directly in the Ising model as parallel spins connected by fictitious bonds, while in the KF formalism clusters are defined in the equivalent diluted model as parallel spins connected by infinite-strength interactions. However, due to the equality of the weights (A.16) and (A.8), the statistical properties of the two clusters are identical [18] and, due to the relations between (A.8) and (A.10), they coincide with those of the correlated bond percolation whose weight is given by (A.10). More precisely, any percolation quantity $g(C)$ which depends only on the bond configuration has the same average:

$$\langle g(C) \rangle_{KF} = \langle g(C) \rangle_{CK} = \langle g(C) \rangle_W \quad (\text{A.20})$$

where $\langle \dots \rangle_{KF}$, $\langle \dots \rangle_{CK}$ are the averages over spin and bond configurations with weights given by (A.8) and (A.16) respectively and $\langle \dots \rangle_W$ is the average over bond configurations in the bond-correlated percolation with weights given by (A.10). We end this section by noting that in order to generate an equilibrium CK cluster configuration in a computer simulation, it is enough to equilibrate a spin configuration of the Ising model and then introduce at random fictitious bonds between parallel spins with a probability given by (A.6).

A.3. Connection with percolation

In this section we relate the percolation properties associated with the KF–CK clusters to the corresponding thermodynamic quantities of the Ising model. In particular, Kasteleyn and Fortuin have proved that [39]

$$|\langle S_i \rangle| = \langle \gamma_i^\infty \rangle_W \quad (\text{A.21})$$

and

$$\langle S_i S_j \rangle = \langle \gamma_{ij} \rangle_W \quad (\text{A.22})$$

where $\langle \dots \rangle$ is the Boltzmann average. Here $\gamma_i^\infty(C)$ is equal to 1 if the spin at i belongs to the spanning cluster, and equal to 0 otherwise; $\gamma_{ij}(C)$ is equal to 1 if the spins at sites i and j belong to the same cluster, and equal to 0 otherwise. In view of (A.20) it follows [18] that

$$|\langle S_i \rangle| = \langle \gamma_i^\infty \rangle_{CK} \quad (\text{A.23})$$

and

$$\langle S_i S_j \rangle = \langle \gamma_{ij} \rangle_{CK}. \quad (\text{A.24})$$

From equations (A.23), (A.24) it follows that the CK clusters coincide with regions of correlated spins and behave as the droplets in Fisher's droplet model [6]. Specifically, these equalities show that it is possible, in a simple way, to construct clusters which become critical at the Ising critical point with Ising critical exponents, i.e. their percolation point T_p is exactly equal to the thermodynamical critical point T_c and their percolation exponents coincide with Ising exponents (at least for dimensions less than 4) [18].

The above formalism can be extended to any ferromagnetic interaction J_{ij} . In this case the CK clusters are defined as sets of parallel spins connected by bonds present with probability $P_{ij} = 1 - \exp[-2\beta J_{ij}]$. In the presence of a magnetic field the formalism can be generalized [18, 20, 39, 42] by treating the field as a new interaction between each spin and a ghost site. Finally, all the results can also be generalized to the ferromagnetic Potts model [17, 39].

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