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LETTER TO THE EDITOR

Singular behaviour of the free energy in the sol–gel transition

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Abstract. The problem whether the sol–gel transition is accompanied by singularities in the free energy is investigated. Two kinds of gels are considered, the weak and the strong gels. In the former case the cross-links are ‘annealed’, while in the latter they are ‘quenched’ or permanent. It is found that the ‘annealed’ free energy has no singularity while the ‘quenched’ free energy has a singularity at the percolation threshold, given by the elasticity critical exponent.

The sol–gel transition, although studied for many years (Flory 1953, de Gennes 1979), is still not fully understood. From the experimental point of view, the sol phase can be characterised by a finite value of the viscosity while the gel phase is characterised by an infinite viscosity (in practice a viscosity larger than a very high value conventionally fixed). A theoretical approach to this problem is by means of percolation concepts (Essam 1980, Stauffer 1979). In this approach, the sol is the phase where only finite molecules are present, and the gel is the phase where a macroscopic molecule infinite in spatial extent coexists with finite molecules. The question of whether or not such transition is accompanied by a singularity in the free energy has not received much attention. The existence and nature of such a singularity will be the main object of this paper. More explicitly, in the usual percolation problem, one considers only the connectivity properties of the clusters. It is usually accepted that the free energy does not have any interesting property at the percolation threshold. In the following, we will consider two different kinds of gelations, where the bonds are respectively annealed or quenched (see below), and see that the free energy is very different for these two cases: whereas it does not show any singularity in the former case, it does in the latter, and this is our central result. On the other hand, the connectivity properties for both cases are the same and are identical to those of the percolation problem, as expected.

Let us briefly review the essential features of the gelation theory (Stauffer 1975, de Gennes 1976a, b). For simplicity, we consider the case of polyfunctional condensation on a system of identical monomers without solvent, each with a functionality $f = 4$ (see figure 1). The monomers are indicated by an open circle and the bonds by wavy lines. The bonds between two nearest-neighbour monomers are randomly distributed. The probability for a given bond to be present is given by p_B . If the probability p_B is low enough, there are only finite clusters made of monomers linked by bonds: this is the sol phase (figure 1(a)). If p_B is high enough, there exists in addition to finite molecules a macroscopic (infinite) cluster: this is interpreted as the gel phase (figure 1(b)).

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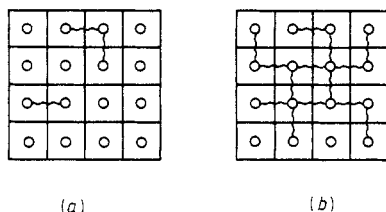


Figure 1. Percolation model for the sol-gel transition: the open circles are the monomers, the wavy lines are the bonds between monomers, which occur with probability p_B : (a) is the sol phase; (b) is the gel phase.

In order to study the free energy, we have to distinguish between two kinds of gels: the weak and the strong gels (de Gennes 1979).

The weak gels are characterised by the fact that the bonds are *not* permanent and they can form and break in thermal equilibrium. If E_B and S_B are the energy and entropy for bound states, E_n and S_n the same quantities for the unbound state, then the bond probability is given by

$$p_B = \frac{\exp[(TS_B - E_B)/kT]}{\exp[(TS_B - E_B)/kT] + \exp[(TS_n - E_n)/kT]} \quad (1)$$

where k is Boltzmann's constant, T the temperature.

The free energy of such a system must be calculated as for an 'annealed' system. To be more precise, given a distribution of bonds one calculates the *partition function* and then averages over all configurations of bonds. For the system described in figure 1 the free energy per particle is

$$F = -kT \lg[p_B \exp(-E_B/kT) + (1 - p_B) \exp(-E_n/kT)] \quad (2)$$

where p_B is given by (1). Such free energy clearly has no singularity at the percolation threshold p_C . This is true even when correlation due to solvent is taken into account (Coniglio *et al* 1979). Therefore there is no phase transition in the ordinary sense at the percolation threshold.

The absence of a singularity in the free energy at the percolation threshold somehow is not surprising. In fact, in the weak gels the appearance of an infinite cluster does not necessarily produce a sharp change in the properties of the system. The viscosity, for example, does not necessarily diverge at p_C although it can become extremely high. In fact, a little ball, as a probe to measure viscosity, will eventually penetrate into the infinite network, due to the properties of the bonds to break and reform in the course of time.

In weak gels, the gel phase is more similar to a highly viscous liquid (de Gennes 1979), and therefore it is not convenient to consider the percolation threshold as the critical point in the sol-gel transition. Instead, as in the glass transition, it is more appropriate to consider a transient region Δp_C in which one goes from the fluid (sol) phase to the viscous (gel) phase. Of course, in the highly viscous regime, the time τ required to reach the equilibrium is very large. Only for times involved much larger than τ is the 'annealed' free energy adequate to describe such a system. For time scales much shorter than τ such a gel behaves more like a strong gel. A better description will be given by a 'quenched' free energy. Such a situation is now described.

In the strong gels an infinite energy is associated with a cross-link. Such cross-links are therefore permanent and randomly distributed. The strong gels must then be treated as a quenched systems. Let us make it clear that only the cross-links are quenched. Once they are formed they cannot break (chemical as opposed to Van der Waals cross-links for instance). But the motions of the molecules are otherwise completely free (see below).

We want now to write formally the free energy of such a quenched system. We always refer to the simple case depicted in figure 1. Any realisation of bonds generates a distribution of different species of molecules. Any species is characterised by the number of monomers s and its topology t (see figure 2). We indicate this distribution by

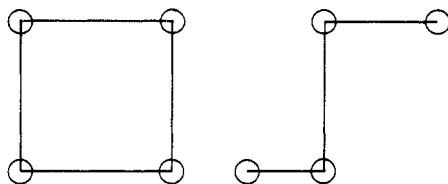


Figure 2. Example of two molecules made of four monomers with different topologies.

$n = \{n_{st}\}$, a set of numbers specifying the numbers of molecules belonging to the various species s and t . In order to calculate the free energy of such a quenched system, we first calculate the free energy for a given realisation of bonds $\{C\}$ and then average over all possible realisations of bonds. For a given realisation of bonds $\{C\}$, the free energy $F\{C\}$ is

$$F\{C\} = \lg Z\{n\} \quad (3)$$

where $Z\{n\}$ is the number of configurations compatible with the distribution of molecules n generated by the realisation of bonds $\{C\}$. By averaging equation (3) over all bond realisations, we obtain the quenched free energy \bar{F} ,

$$\bar{F} = \langle \lg Z\{n\} \rangle,$$

where the brackets stand for the average over the bond realisations.

If we suppose that the bonds are randomly distributed, the probability $P\{C\}$ for a given realisation $\{C\}$ of bonds is given by

$$P\{C\} = p_B^n (1 - p_B)^{N-n} \quad (4)$$

where n is the number of bonds in the configuration $\{C\}$ and N the total number of bonds in the lattice[†].

Now we want to estimate the free energy (3). We first make a rough evaluation of it for $p \leq p_C$; later we will discuss the behaviour of the free energy in more detail below and above p_C .

If w is the average degeneracy of a finite molecule, the partition function $Z\{n\}$ can be written

$$Z\{n\} = w^{N_C} \quad (5)$$

[†] This random distribution of bonds may be valid in many cases of gel formation. One example is when the bonds are formed by radiation. On the other hand, when the bonds are formed in the process of a chemical reaction, the kinetics may play an important role and the bond distribution may not be the same as given by (4) (see for instance Manneville and de Sèze 1981).

where N_C is the number of molecules, and from (4)

$$\bar{F} = \langle N_C \rangle \lg w \quad (6)$$

which is proportional to the average number of clusters. Therefore it has the same critical behaviour as the average number of clusters in the usual random percolation problem, namely

$$\bar{F} \sim \varepsilon^{2-\alpha} \quad (7)$$

where

$$\varepsilon = \left| \frac{p_B - p_C}{p_C} \right| \ll 1. \quad (8)$$

The presence of such a singularity in the free energy shows that there is a phase transition in the ordinary sense at the percolation threshold.

Note that this singularity appears when the density of chemical bonds p_B is used as a variable. Since the bonds are permanent, they cannot be varied with the temperature and therefore the singularity cannot be seen in a specific heat measurement, for instance.

In the following, we want to discuss in more detail the critical behaviour of the free energy both above and below p_C in the vicinity of the threshold p_C for the quenched system. We first consider the contribution to the free energy above p_C due to the infinite cluster. For simplicity, let us consider the usual model in which the infinite cluster is considered as a network made of nodes connected by large chains (de Gennes 1976a, b, Skal and Shklovskii 1974, 1975). The node to node distance is of the order of the pair connectedness length ξ in the percolation problem.

The elastic free energy per unit volume, F_{el} , can be written as (de Gennes 1976a, b)

$$F_{el} = \sum_{\text{nodes}} K (\mathbf{R}_i - \mathbf{R}_j)^2 \quad (9)$$

where the sum is restricted to nodes in the unit volume, $|\mathbf{R}_i - \mathbf{R}_j| = \xi$ is the distance between two nearest-neighbour nodes and K is the effective elastic constant of the chain connecting i to j . Since in a volume ξ^d there is only one node, the elastic free energy per unit volume is

$$F_{el} \sim \xi^{-d} K \xi^2 \sim \varepsilon^\mu \quad (10)$$

where μ is the elasticity exponent. It has been suggested that $K \sim \varepsilon^\zeta$ where ζ is the conductivity exponent of the chain connecting i to j (de Gennes 1976a, b, Harris and Kirkpatrick 1977), leading to

$$\mu = (d-2)\nu + \zeta \quad (11a)$$

which coincides with the conductivity exponent. More recently, we suggested that $K \sim \xi^{-2}$, leading to

$$\mu = \nu d = 2 - \alpha \quad (11b)$$

where ν and α are the usual percolation exponents.

We now evaluate the contribution to the free energy F_f due to the finite clusters, both below and above p_C . If n_{st} is the number per unit volume of molecular species (s, t) we can write

$$F_f = \sum_{s,t} n_{st} [f_T(s, t) + f_R(s, t) + f_{el}(s, t)] \quad (12)$$

where $f_T(s, t) = \lg sn_{s,t}$ is the contribution due to the translational degrees of freedom and is the same as in a mixture of gases of different species (s, t) (see for example Sommerfeld (1973)). $f_{el}(s, t)$ corresponds to those internal degrees of freedom of the finite clusters which are the analogue of the elastic term in the infinite cluster, so that we call this contribution a 'local elastic' term by analogy. We note that this term does not contribute to the macroscopic elasticity, but it contributes to the entropy. By $f_R(s, t)$ we denote the contribution coming from other internal degrees of freedom such as rotation

The contribution to the critical behaviour in (12) comes from those terms in the sum corresponding to clusters of linear dimensions $\xi \sim \varepsilon^{-\nu}$. In a volume ξ^d there is one such cluster. Therefore

$$F_t \sim \xi^{-d} (f_T + f_R + f_{el})$$

where f_T , f_R and f_{el} are the contributions from such critical clusters. $f_T \sim \lg s \xi^{-d}$ and $s \sim \xi^{d_f}$ (where d_f is the fractal dimensionality of the cluster). Therefore f_T does not add any contribution to the leading singularity $\varepsilon^{-\nu d}$, except from logarithmic corrections. We also suppose that there is no other contribution from f_R .

It is plausible to assume that $f_{el} = K \xi^2$ as in the infinite network. Therefore

$$\xi^{-d} f_{el} \sim \varepsilon^\mu. \quad (13)$$

Summing all these contributions, the singular part of the free energy both below and above p_C can be written as

$$F \sim A \varepsilon^{2-\alpha} + B \varepsilon^\mu \quad (14)$$

where A and B are numerical constants.

We note that in mean field theory ($d = 6$), $\mu = 3$ and both contributions in (14) are of the same order. For $d = 3$, (11a) leads to an approximate value for μ between 1.6 and 2.0 (Straley 1977, Harris and Kirkpatrick 1977) which would be dominant compared with $2 - \alpha \approx 2.6$. On the other hand, if we accept (11b) then $\mu = 2 - \alpha$ in any dimension.

We will not enter in the discussion of the value for the exponent, our main point here being just to show that there is a singularity in the free energy at the percolation threshold.

In conclusion, we have considered the question of whether or not the sol-gel transition is accompanied by a singularity in the free energy as in ordinary phase transitions. Two very different cases were studied: the strong and weak gels where the cross-links are respectively quenched or annealed. While in the first case there is a singularity in the free energy, meaning a phase transition, no such singularity is found in the latter case.

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