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METASTABILITY AND LANDAU THEORY FOR RANDOM FIELDS AND DEMIXING IN POROUS MEDIA

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I. INTRODUCTION

In recent years there was a big increase in experiments on physical systems that are realizations of random fields. Just to name a few these include diluted antiferromagnets in a magnetic field, charge density waves pinned by impurities, hydrogen in binary metallic alloys and quite recently also binary liquid mixtures in gels. In all these systems there are annealed degrees of freedom (spin like) and a source of quenched disorder (impurities, random structure, etc) that effectively creates a random field which is coupled to the order parameter. In this article we will concentrate on random field systems where the order parameter is a scalar and the random field is coupled linearly to it (i.e. the random field Ising model - RFIM).

Theoretically, much effort has been made to study critical behavior and the lower critical dimension (d_ℓ) of this model.[1] (d_ℓ is the dimension below which there is no long-range order). Using a simple domain argument Imry and Ma predicted[2] $d_\ell = 2$ whereas other works claimed $d_\ell = 3$.[1] The current belief that indeed $d_\ell = 2$ is based on a refined domain argument[1,3] that takes into account domain wall roughening, some numerical investigations,[4] as well as a rigorous proof[5] on the existence of long-range order at T = 0 for the d = 3 RFIM. At first glance this theoretical prediction of $d_\ell = 2$ seems to be contradictory with neutron scattering experiments[6] on diluted antiferromagnets. Domains (thus lack of long-range order) are seen as the sample is cooled down in presence of a constant magnetic field (field cooling). To resolve this discrepancy, Villain[7] considered the domains as metastable states pinned by the random field. Hence although the long-range order state has the lowest energy, the system gets stuck (or has very long relaxation times) in one of these domain states since it cannot jump over all the energy barriers during the field cooling procedure. Other theories using similar ideas about non equilibrium states also exist.[8]

The purpose of the present work is two-fold : (i) we would like to emphasize the connection between the RFIM investigated so far mostly by its

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magnetic realization and between recent experiments on binary liquid mixtures[9] in presence of random structures such as gels or porous solids. (ii) We propose a Landau theory that takes into account the possibility of metastable domain states and which leads to an explanation of the opalescence seen in the A/B + gel systems close to the demixing curve of the pure A/B mixture.[9] In addition the theory can provide a *possible* explanation of recent neutron scattering experiments[10] on diluted antiferromagnets where an abrupt transition from history-independent to history-dependent behavior occurs. Our theory is also in agreement with recent numerical investigations of the RFIM on finite lattices.[11]

II . BINARY MIXTURES IN GELS AND POROUS MEDIA : RANDOM FIELD SYSTEMS

Recent experiments[9] showed that phase separation and critical behavior of binary liquid mixtures with a well defined demixing curve changes drastically as a gel is immersed in the liquid mixture. One of the most striking phenomena seen in the A/B + gel system (water-lutidine or water-isobutyric acid are chosen as the binary mixtures and agorose or polyacrylamide as the gels) is the appearance of opalescence which follows closely the demixing curve of the pure A/B mixture. The onset of opalescence is not sharp but rather gradual on a range of a few degrees and even well inside the pure two-phase region it persists for long times. This opalescence should be distinguished from critical opalescence usually seen in pure A/B mixtures but only in a range of a few mK^{o} around the consolute point. Nevertheless the fact that the onset of opalescence follows the pure demixing curve is a strong indication that it has to do mainly with the liquid-liquid fluctuations rather than with the gel fluctuations.

Pure A/B liquid mixtures are usually described by lattice gas models ; we would like to extend these models to binary liquid mixtures in a gel. The gel always has an heterogeneous chemical structure. We focus here on rigid gels which thus act on the liquid mixture as a source of quenched disorder (the same assumption is correct for porous solids). In the opposite limit of flexible gels, thermal fluctuations become important and one should consider the binary mixture in the gel as a ternary system. The main effect of the gel on the A/B mixture is a preferential adsorption[12] of one of the liquid components (in our case the water-component A). The gel + A/B system has two characteristic lengths : one is the mesh size of the gel (L) and the other is the bare fluid-fluid correlation length (ξ). The behavior is determined by a comparison between these two lengths. We will describe the system in the regime $L < \xi$ (tight gels or temperatures close to the consolute point). Since ξ is large, the system can be divided into blocks of size L (coarse graining) ; in each block there is an effective random field h(r) proportional to the average gel concentration in the block. The average of h(r), $< h(r) >$, expresses the total preference of the gel plus a contribution from the concentration difference between the liquid inside the gel in the A/B reservoir into which the gel is immersed. The order parameter of the system (analogous to the magnetization in magnetic systems) may be defined as $M = (C_A - C_B)/(C_A + C_B)$ where C_A (C_B) is the number density of A (B). The strength of the random field is characterized by the r.m.s. deviation H.

III. LANDAU THEORY FOR RANDOM FIELDS

Making the analogy between the A/B + gel system and random fields, we proceed by obtaining a description of the former via a Landau theory for the latter. We make a Landau expansion of the free energy (always using the magnetic terminology : magnetization, random fields, etc) in terms of

the local order parameter M(r). The expansion includes even terms in M(r) up to fourth order, a gradient term related to the short-range character of the interactions and a linear term which describes the coupling to the random field h(r):

$$F = \int \left[\frac{1}{2} (\nabla M)^2 + \frac{1}{2} \varepsilon M^2 + \frac{1}{4} u M^4 - h(r)\, M(r) \right] d\vec{r}, \qquad (1)$$

$\varepsilon = a\,(T - T_c^o)$ is proportional to the distance from the pure critical temperature T_c^o and $u > 0$ is a constant. We restrict the following discussion to the symmetric case $\langle h(r) \rangle = 0$, eventhough for the A/B + gel, $\langle h(r) \rangle = h \neq 0$ can be controlled by changing the concentration in the reservoir around the gel.[12-14] For the diluted antiferromagnets, $\langle h(r) \rangle = h = 0$; a non zero h would correspond to a staggered field (which is not realizable).

Minimizing the free energy functional (1) with respect to M(r) we get an equation for the order parameter M(r)

$$\frac{\delta F}{\delta M(r)} = -\nabla^2 M + \varepsilon M + u M^3 - h(r) = 0 \qquad (2)$$

In order to solve (2) which is non linear and has a random source h(r), we split M(r) into two terms : $M(r) = M_0 + \delta M(r)$, where M_0 is the average magnetization of the system, $M_0 = \langle M(r) \rangle = V^{-1} \int M(r) d\vec{r}$ and $\delta M(r)$ is the local fluctuation, $\langle \delta M(r) \rangle = 0$. The equation for the average magnetization M_0 is obtained by averaging (2), thus yielding

$$M_0 \left(\varepsilon + 3u \langle \delta M^2 \rangle \right) + u M_0^3 = 0 \qquad (3)$$

where $\langle \delta M^2 \rangle$ is the r.m.s. magnetization fluctuation (the average of odd powers of $\delta M(r)$ vanishes). Subtracting (3) from (2) we get an equation for $\delta M(r)$

$$\nabla^2 \delta M + h(r) = (\varepsilon + 3u M_0^2) \delta M + 3 M_0 u \left[\delta M^2 - \langle \delta M^2 \rangle \right] + u \delta M^3. \qquad (4)$$

Linearizing (4), we neglect the term $\delta M^2 - \langle \delta M^2 \rangle$ and using a decoupling scheme the last term δM^3 is written as $3 \langle \delta M^2 \rangle \delta M$.* Within this decoupling approximation we get in Fourier space a linear relation between $\delta M(q)$ and $h(q)$

$$\delta M(q) = \frac{h(q)}{q^2 + K^2} \quad \text{where} \qquad (5)$$

$$K^2 = \varepsilon + 3u M_0^2 + 3u \langle \delta M^2 \rangle \qquad (6)$$

and K^{-1} is the correlation length of the magnetization $\delta M(r)$. Hence the contribution to the structure factor from the field fluctuations is a Lorentzian square :

$$S(q) = \langle \delta M^2(q) \rangle \simeq \frac{H^2}{(q^2 + K^2)^2} \qquad (7)$$

In position space (5)-(6) implies

$$\delta M(r) = \text{const.} \int d\vec{r}' \left[\exp(-K \left| \vec{r} - \vec{r}' \right|) / \left| \vec{r} - \vec{r}' \right|^{d-2} \right] h(r'). \qquad (8)$$

The three physical quantities M_0, K and $\langle \delta M^2 \rangle$ which we want to determine as functions of the reduced temperature ε and the strength of the random field $H = \langle h^2 \rangle^{1/2}$, are linked by the three equations (3), (6) and (8).

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* The numerical factor is chosen as the number of ways to do the decoupling. Here it is three.

The other solution $M_0 \neq 0$ exists only for low temperatures such that $\varepsilon < \varepsilon_c$

$$K^2 = 2uM_0^2 = -2\varepsilon - 6u/(\ell^2 K) \qquad (17)$$

and it has two branches (Fig.1). As will be discussed later the lower branch has always a higher free energy than the upper one which behaves at low temperatures as in the pure case : $K \simeq M_0 \simeq (-\varepsilon)^{1/2}$, thus has an increasing magnetization and a decreasing correlation length as the temperature is reduced.

Having obtained the two solutions $M_0 = 0$ and $M_0 \neq 0$, the next step is to compare the free energy of the two solutions in order to see which one is more stable. Due to lack of space we discuss here only the results and the full calculation will be presented elsewhere.[16] Substituting back into the free energy functional (1), the various solutions (9), (16)-(17) and using the decoupling scheme to estimate $\langle \delta M^4 \rangle \simeq 3 \langle \delta M^2 \rangle^2$, the evaluation of (1) for the different solutions is straight forward but tedious. It leads us to two conclusions : (i) The upper branch of the $M_0 \neq 0$ solution is always more stable than the lower one in agreement with what is expected physically. (ii) In the interval $\varepsilon^* < \varepsilon < \varepsilon_c$, the $M_0 = 0$ solution is more stable than the $M_0 \neq 0$ solution, whereas for lower temperatures, $\varepsilon < \varepsilon^*$, the latter is more stable. The value of ε^* was found to be $1.085\ \varepsilon_c$.

IV. DISCUSSION AND COMPARISON WITH EXPERIMENT AND SIMULATIONS

The Landau theory discussed in the previous sections is relevant to magnetic realizations of the RFIM as well as to binary liquid mixtures in random structure such as gels and porous media under the conditions discussed in section II ; namely that the random structures are rigid and $\xi > L$. The advantage of the present theory is that it is giving the correlation length K^{-1} as function of T and H even in the critical region whereas all previous theories[7-8,13] assumed a rapid quench from high to low temperatures thus not following the experimental procedure. We also would like to note the strong resemblance between our Fig.1 and Fig.3 of ref 10. Starting at high temperature and doing a field cooling we expect the system to stay on the $M_0 = 0$ solution which we interpret to be the domain state at low temperature. Similar dependence of K on T was seen in ref 10 as the system was field cooled. The explanation why the system get stuck in the domain state, although for $\varepsilon < \varepsilon^*$ the long-range order has lower energy, is similar to the explanation of spinodal decomposition using a mean-field approach. As for the zero field cooled procedure, our theory predict a first-order transition. This could be related to an abrupt, apparently discontinuous transition that was observed experimentally.[10] Although the similarity of our predictions and the neutron scattering data of ref 10 are quite appealing, we would like to emphasize that our theory neglected critical fluctuations and we still do not fully understand the effects of our decoupling approximation. One encouraging support of our theory comes from the numerical solutions of mean-field equation for finite lattices.[11] From these simulations, the existence of (i) history independent region in the T-H plane (only a paramagnetic solution) (ii) history dependent region where the domain state has lower energy than the ferromagnetic state, (iii) history dependent region where the ferromagnetic state has the lowest energy although the domain state also exists was found. These finding are in agreement with our three regions : $\varepsilon > \varepsilon_c$, $\varepsilon^* < \varepsilon < \varepsilon_c$, and $\varepsilon < \varepsilon^*$.

As for the A/B + gel systems, since the opalescence in those systems persists for very long times we believe that it is caused by "freezing" of the system in a domain state, thus K^{-1} is the domains size and is related to the solution with $M_0 = 0$ (Fig.1) even for low temperatures ($\varepsilon < \varepsilon^*$).

As for the other solution with $M_0 \neq 0$, unfortunately a procedure analogue to the zero-field cooling is not possible for the gel (this would mean changing in a controlled way the concentration fluctuations of the gel). However an additional external parameter which is available here is the analogue of a constant magnetic field, and phase separation (the equivalent of long-range order) can be induced by changing the relative concentration of the A/B mixture in the reservoir around the gel. Some initial predictions of the influence of such non zero average field are available[13] and could be tested experimentally.

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