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SURFACE MAGNETISM: A CONTROVERSIAL POINT

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ABSTRACT: We discuss a controversial point of surface magnetism in semi-infinite three-dimensional systems. More precisely, the thermal evolution of the surface spontaneous magnetization is expected to present, whenever $T_c^{surface} > T_c^{bulk}$, a singularity at $T = T_c^{bulk}$. The nature of this singularity has been, during recent years, subject of controversy on both theoretical and experimental grounds. The point is analysed and (possibly) optimal conditions for its definitive clarification are presented.

Key-words: Surface magnetism; Extraordinary transition; Spontaneuous magnetisation; Semi-infinite Ising model.

Surface magnetism is an interesting phenomenon which, being in some sense a mixture of $d = 2$ and $d = 3$ magnetisms, presents various subtleties. It is a rich problem on both theoretical and experimental grounds, and presents also various applications such us corrosion, catalysis and information storage. For general reviews see Binder 1983 and Kaneyoshi 1990; for theoretical reviews, respectively using real space and reciprocal space renormalization group (RG) approaches, see Tsallis 1986 (as well as Tsallis and Chame 1989) and Diehl 1986.

The theoretical prototype for surface magnetism is the spin 1/2 Ising ferromagnet in semi-infinite simple cubic lattice with a (0,0,1) free surface, the surface and bulk coupling constants being respectively J_S and J_B. The phase diagram is indicated in Fig. 1. Three phases (namely the bulk ferromagnetic (BF), the surface ferromagnetic (SF) and the paramagmetic (P) ones) are separated by three second order critical lines (namely the ordinary transition, the extraordinary transition and the surface transition) which join at a multicritical point (special transition). The ordinary and extraordinary transitions occur at the standard $d = 3$ Ising ferromagnetic critical point $T_c^{bulk} \equiv T_c^{3D}$, whereas the surface transition occurrs at $T_c^{surface} > T_c^{2D}$(≡ critical temperature of the standard $d = 2$ Ising ferromagnet in square lattice). The multicritical point is located at $\Delta \equiv J_S/J_B - 1 = \Delta_c$. In its neighbourhood, it is

$$\frac{T_c^{surface}(\Delta)}{T_c^{3D}} - 1 \sim A\left(\frac{\Delta}{\Delta_c} - 1\right)^{1/\phi} \tag{1}$$

We can consider as good estimates the following values: $\Delta_c \simeq 0.5$, $\phi \simeq 0.6$ and $A \simeq 0.4$. Values available in the literature are: (i) for Δ_c, 0.25 (Mean field; see Binder 1983 and references therein), 0.6 ± 0.1 (series; Binder and Hohenberg 1974), 0.82 (Bethe approximation; Aguilera-Granja et al 1983), 0.5 ± 0.03 (Monte Carlo; Binder and Landau 1984), 0.42 (Effective field; Sarmento et al 1984), 0.74 (simple real space RG; Tsallis and Sarmento 1985), 0.57 (extrapolated RG; Costa et al 1985); 0.52 (Monte Carlo; Binder and Landau 1990);

(ii) for ϕ, 0.68 (ε-expansion; Diehl and Dietrich 1980), 0.56 ± 0.04 (Monte Carlo; Binder and Landau 1984), 0.64 (real space RG; Costa et al 1985); (iii) for A, 0.4 (real space RG; Costa et al 1985).

Let us now focuse the case $\Delta \geq \Delta_c$ (i.e., the SF phase exists). The surface magnetization $M_S(T,\Delta)$ decreases (for fixed Δ) while T increases, is expected to present a singularity at T_c^{3D} (where the bulk magnetization vanishes) and finally vanishes at $T_c^{surface}(\Delta)$; see Fig. 2 (obtained with a diamond hierarchical lattice RG by Tsallis and Chame 1988). The singularity of M_S which is expected to occur at the extraordinary transition is a controversial matter since several years. The present paper is dedicated to the discussion of this controversy. More precisely, the controversy consists on whether the temperature derivative $\partial M_S(T,\Delta)/\partial T|_{T_c^{3D}}$ at T_c^{3D} is discontinuous (as in Fig. 2) or continuous.

The chronological story is more or less as follows. As discussed in detail by Binder 1983 the above derivative is continuous within a Mean Field Approximation (MFA), but it is of course well known that the MFA criticality is not reliable at $d < 4$ for the Ising model. Then various calculations appeared (e.g., Effective Field Approximation (see Kaneyoshi 1990 and references therein); also Selzer and Majlis 1983) which exhibit discontinuous derivatives. These discontinuities should however be considered as mathematical artifacts of the approaches. Indeed, in such treatments, an infinite set of equations appear, relating the magnetizations associated with neighbouring layers further and further away from the free surface. The infinite set of equations being not solvable, one is obliged to truncate it at a certain depth of the bulk. The discontinuities are expected to disappear when the depth tends to infinity. The point is illustrated in Moran-Lopez and Sanchez 1989. In fact, we believe it should be so for any approach whose basic criticality is the MFA one.

Then a careful electron-spin polarization experiment is done in 1987 by Rau and Robert on Gd: they find continuous slope. Let us make a few comments: (i) Gd is a conductor, hence important long-range spin interactions can be induced by the electronic gas; consequently the criticality could well be the MFA one (we recall the model we are analyzing here is a <u>first-neighbouring</u> coupling one); (ii) the bulk interactions in Gd are commonly assumed to be close to the (isotropic) Heisenberg ones (we recall the model we are analyzing here is the Ising one for <u>both</u> surface and bulk); (iii) for Gd, $T_c^{3D} \simeq 292$ K and $T_c^{surface} \simeq 306$ K (from Rau 1982) hence $(T_c^{surface} - T_c^{3D})/T_c^{3D} \simeq 0.05$; this value roughly suggests, <u>if</u> an Ising model was assumed, $[J_S/J_B - (1 + \Delta_c)]/(1 + \Delta_c) \simeq 0.5$, and consequently (by using Fig. 2 and the associated calculations) $J_S/J_B \simeq 1.8$, which is a value particularly hard for experimentally detecting any possible discontinuity in the derivative. Summarizing, because of points (i) and (ii), it is not obvious that the experimental result of Rau and Robert 1987 is directly relevant for the present discussion; moreover, even if it was directly comparable with the present model, the actual coupling constants of Gd would make this substance an inconvenient one for checking possible discontinuities in the derivative we are interested in.

Still in 1987, Burkhardt and Cardy present (essentially heuristic) scaling arguments which are basically consistent with Bray and Moore 1987 and which also suggest a <u>continuous</u> derivative.

One year later, in 1988, for the first time (as far as we know) a non-MFA-like calculation of $M_S(T,\Delta)$ was published covering the entire range of temperatures and arbitrary Δ (Tsallis and Chame 1988, from which the present Fig. 2 was taken), and <u>discontinuous</u> derivatives were exhibited which intend to be <u>not</u> a mathematical artifact (the truncation difficulty mentioned before is herein naturally overcome through the successive iterations which generate the hierarchical lattice). However, this calculation cannot be considered as the final word on the problem because (i) real space RG's can sometimes be misleading since their degree of approximation is, generally speaking, mathematically uncontrolled; (ii) in the present RG, where two-body correlations are exactly preserved, the Bravais lattice is replaced by an hierarchical one, a fact which might introduce undesirable differences; and (iii) although everything appears plausible for almost arbitrary values of J_S/J_B, a weakness of the calculation is detected in the region $J_S/J_B << 1$; more precisely, an unphysical inversion of monotonicity of M_S with respect to J_S/J_B is observed in that region (surprise about this result was first expressed in Tsallis and Chame 1988 and 1989; this feature was also pointed by Moran-Lopez and Sanchez 1989; contradiction between this result and the exact Griffiths inequalities was pointed by a japanese physicist in the audience of the Workshop on "New Methods and Applications to Phase Transitions" (Kyoto, 1988), and was discussed in Payandeh and Robert 1990).

One year later, in 1989, Ohno and Okabe present an ε-expansion ($\varepsilon \equiv 4 - d$) which, being a reciprocal space RG, is mathematically controlled. They confirm the <u>discontinuous</u> derivatives found in Tsallis and Chame 1988. Furthermore, as in Tsallis and Chame 1988 , they find (for $\varepsilon \neq 0$) $\left|[\partial M_S(T,\Delta)/\partial T]_{T\to T_c^{3D}-0}\right| > \left|[\partial M_S(T,\Delta)/\partial T]_{T\to T_c^{3D}+0}\right|$: we shall come back onto this point later on. As expected, Ohno and Okabe recover a <u>continuous</u> derivative for ε=0 since at d=4 the MFA starts being correct. Unfortunately, even this calculation cannot be considered the last word on the controversy because one can argue that ε=1 (i.e., d=3) is too far away from ε→0 (where the expansion is strictly valid).

A surprise arises one year later, in 1990, through a Monte Carlo calculation by Landau and Binder. In this calculation they find a <u>continuous</u> slope for the d=3 model. This fact reopens the discussion. Indeed, in spite of their calculation being a very careful one, the Monte Carlo technique is not exempted from criticism. Furthermore, they run a case ($J_S/J_B = 1.7$ with $\Delta_c \simeq 0.52$, hence $[J_S/J_B-(1+\Delta_c)]/(1+\Delta_c)\simeq 0.1$) which, as can be checked in Fig. 2, is not particularly confortable for detecting possible slight discontinuities.

Recently, Payandeh and Robert 1990 claim that they (exactly) prove that the derivative is <u>continuous</u>. This claim would by itself be astonishing since the relevance of the three-dimensionality of the Ising model in this discussion is well known. In fact, by reading the paper we could not find anywhere the proof claimed in its Abstract (we found instead conjectural arguments based in analogies with the semi-infinite d=2 Ising problem whose free edge presents no critical phenomenon at any finite temperature); furthermore, the authors seem to be not aware of the result obtained by Ohno and Okabe 1989.

The recent Monte Carlo calculation by Binder and Landau suggesting continuity of the derivative stimulated further analysis of the type of real space RG approach of Tsallis and Chame 1988. Branco and Chame 1991 used the same method to study surface and bulk magnetizations in various Sierpinski-like sponges. They obtained in these systems, continuous temperature derivatives of M_S at T_c^{bulk}. Therefore, this RG technique is capable of leading to both results, continuous or discontinuous derivatives. Consequently, if discontinuity is obtained for the semi-infinite d=3 Ising model there might be a good reason for that. What could be this "good reason"? Let us make a few speculative comments along this line.

At $T<T_c^{3D}$, the bulk spontaneous magnetization M_B enhances, by acting as a favourable external field, that of the surface. This contribution disappears a $T \geq T_c^{3D}$. However, surprisingly enough, both RG calculations (real space by Tsallis and Chame 1988, and reciprocal space by Ohno and Okabe 1989) yield $\left|[\partial M_S(T,\Delta)/\partial T]_{T\to T_c^{3D}-0}\right| > \left|[\partial M_S(T,\Delta)/\partial T]_{T\to T_{c+0}^{3D}}\right|$. What could be the cause of that? At T_c^{3D}, the bulk susceptibility diverges, hence a favourable feed-back mechanism might become very efficient for $T \gtrsim T_c^{3D}$. More precisely, the nonvanishing surface magnetization M_S might induce relatively short time magnetization at the bulk (because of its high susceptibility), not enough to create spontaneous magnetization deep inside the bulk, but enough to reinforce M_S. The bulk susceptibility being stronger in its paramagnetic phase than in its ferromagnetic one, this effect could compensate with profit the disappearence of M_B at T_c^{3D}. The fact that, within the MFA and for $T \simeq T_c^{3D}$, the paramagnetic susceptibility is precisely the double of the ferromagnetic one could be one of the elements explaining the MFA continuity of the derivative we are discussing here.

Let us now summarize the present status of the controversy as we understand it. The Gd experiment should be regarded, unless otherwise proved, as possibly not relevant for the semi-infinite d = 3 Ising model. On theoretical grounds for the precise model under discussion, we can say that there are two quite strong indications (Tsallis and Chame 1988 and Ohno and Okabe 1989) favouring discontinuous derivative and at least one strong indication (Binder and Landau 1990) against it. What to do next? Let us mention a few ways which would give interesting hints:

(i) The generalization of the Tsallis and Chame 1988 RG calculation to a model with surface and bulk anisotropic Heisenberg interactions. This is now possible by following along the lines of the recent calculation by Chame 1991 of the spontaneous magnetization of the $d = 2$ anisotropic Heisenberg ferromagnet. The discrepancy between the left and right derivatives of M_S will certainly depend on the surface and bulk degrees of anisotropy. This could even enlighten the discussion of the Gd experiment;

(ii) It should be interesting to run Monte Carlo calculations (e.g., like that of Binder and Landau 1990) for more favourable values of J_S/J_B, say in the interval [2,2.5];

(iii) It should be interesting to perform experiments (e.g., electron-spin polarization like that of Rau and Robert 1987 or maybe magnetic x-ray dichroism like that discussed in Baudelet 1991) on substances which are insulators or at least bad conductors (in order to avoid long range interactions), which tend to present an Ising-like free surface on a more or less anisotropic Heisenberg (to enlarge the SF phase: see Mariz et al 1987) and which could even have a slightly diluted bulk (in order to decrease T_c^{bulk} in such a way to have a convenient ratio $T_c^{surface}/T_c^{bulk}$: see Tsallis et al 1986).

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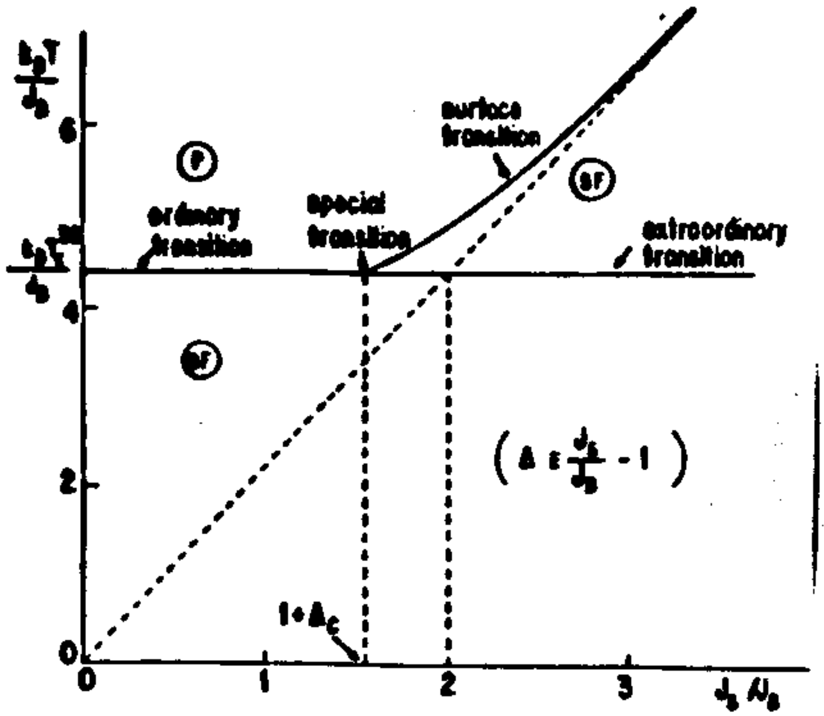

Fig. 1 - Phase diagram for the spin 1/2 Ising ferromagnet in the semi-infinite simple cubic lattice with a (0,0,1) free surface.

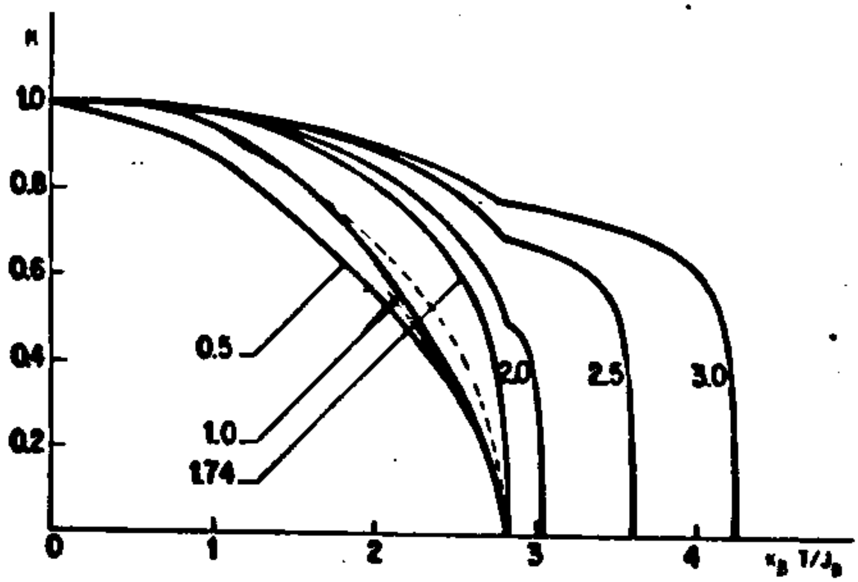

Fig. 2 - RG surface spontaneous magnetization M_S as a function of the temperature for the Ising ferromagnet with a free surface (0,0,1); $J_s/J_B \simeq 1.74$ corresponds to $\Delta = \Delta_c$. The dashed line indicates the bulk spontaneous magnetization M_B.

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