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COMMENT

On the possible non-universality of critical behaviour in micellar solutions

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Abstract. We reconsider the renormalisation treatment of the model introduced by Shnidman to explain the observed non-universal behaviour of micellar solutions. We show that his derivation of the recursion relations would introduce non-universality even for a model which obviously belongs to the Ising universality class. This argument casts some doubt on the validity of Shnidman analysis.

The prevalent description of critical phenomena has universality as its major feature: namely, one does not expect that quantities like the critical exponents depend on the details of the system under consideration. Non-universal behaviour—such as the continuous dependence of critical exponents on the parameters of the Hamiltonian—exceptionally appears in some exactly solvable models (Baxter 1982) or in the low-temperature phase of XY systems (Kosterlitz 1980). This appears to be related to the unusually large symmetry enjoyed by these two-dimensional models: the invariance with respect to the conformal transformations of the complex plane, which has an infinite number of generators (Belavin *et al* 1984). It comes therefore as a surprise to observe experimentally a non-universal behaviour in a *three-dimensional* system: micellar binary solutions at their lower consolute point (Corti *et al* 1984, Degiorgio *et al* 1985, Cantu *et al* 1985, Corti and Degiorgio 1985, Degiorgio 1985), a system which at first sight should belong to the Ising universality class.

An explanation of this apparent non-universality has been propounded by Shnidman (1986). It builds on the thermodynamical theory of phase separation in micellar solutions due to Blankschtein *et al* (1985). A generalisation of the Ising model aimed at describing a solution of rodlike micelles is introduced. A parameter H° appears in the Hamiltonian, describing the difference in the chemical potential of amphiphile molecules depending on their environment. It is then argued that this parameter should remain invariant under renormalisation group transformations. Recursion relations of the Migdal-Kadanoff (MK) type (Migdal 1975, Kadanoff 1976) are then derived for a two-dimensional version of the model. These recursion relations exhibit a line of fixed points with continuously varying exponents, depending on the parameter H°. This is taken to represent the dependence of the critical exponents on the nature of the amphiphile.

We wish to expound in this comment a few criticisms of Shnidman's approach, from which we draw the conclusion that the problem of the origin of non-universality in micellar solutions cannot be considered as settled. On a physical basis, the arguments by which Shnidman justifies the lack of renormalisation of the parameter H° are unclear. Even if this is granted, the way the MK recursion relations are derived is incorrect. We define a slight variation on his model, which by Shnidman's method is characterised by the same recursion relations as his model. Nevertheless it is easy to show that this model has Ising-like critical behaviour. We trace the source of the contradiction to an incorrect treatment of the H° term in the Hamiltonian.

The model considered by Shnidman is defined by the Hamiltonian

$$-\beta\mathscr{H} = k\sum_{\langle ij\rangle}\sigma_i\sigma_j + \sum_i H_i^e\sigma_i \tag{1}$$

where the σ are Ising variables, with $\sigma = 1$ corresponding to a site occupied by an amphiphile and $\sigma = -1$ to a site occupied by water. The effective field H_i^e is given by

$$H_i^e = H + H_i^\circ = H + \tfrac{1}{2}n_iH^\circ \tag{2}$$

where H represents the difference in chemical potential between amphiphile and water, H° represents the excess chemical potential due to the environment and n_i is a number which depends on σ_i and on the environment of site i. If $\sigma_i = -1$ the site is occupied by water molecules and $n_i = 0$. If $\sigma_i = 1$ one should distinguish three cases: if the $\sigma_i = 1$ is surrounded by -1 spins, it represents a spherical isolated micelle and $n_i = 0$; if it is surrounded by at least two $+1$ spins, forming a linear configuration with the σ_i spin, it represents a region in the cylindrical part of the micelle, and $n_i = 2$; otherwise it represents one of the globular end caps of the micelle and $n_i = 1$. This represents a complicated many-site interaction which is hard to write down in the Hamiltonian. Shnidman argues that the parameter H° characterises the *states* of the model (in the same way as the value $S = \frac{1}{2}$ of the modulus of the Ising spins) and is not just another parameter characterising the Hamiltonian. As a consequence it should remain invariant under renormalisation group (RG) transformations. He then proceeds to derive such RG transformations by means of a MK approach. It is unclear why H° should be treated differently from the other parameters appearing in the Hamiltonian. This point is crucial, since it appears that his recursion relations are indeed handpicked to keep H° invariant. Their derivation is not explicitly given. We now reconsider the path leading to Shnidman's recursion relations.

MK recursion relations are obtained by a bond-moving transformation, followed by a one-dimensional decimation. In the bond-moving step the two-body interactions are rearranged to obtain a lattice of lower ramification. No prescription is given for one-body interactions. One can choose therefore either to leave them on site, or to distribute them (totally or partially) among the bonds insisting on each site.

In order to recover Shnidman's recursion relations one should distribute H but not H_i°. Then, after bond moving, the one-body potential present at each site to be decimated is given by

$$\tilde{H}_i^e = \frac{2}{z}\tilde{H} + \tfrac{1}{2}n_iH^\circ \tag{3}$$

where z is the coordination number and

$$\tilde{H} = b^{D-1}H. \tag{4}$$

We are considering a D-dimensional space and a length rescaling factor equal to b.

Setting $b=2$ we obtain the renormalised couplings k' and H' after decimation:

$$\exp[k'\sigma\sigma'+\delta H'(\sigma+\sigma')+\delta J]=\sum_{s=\pm 1}\exp(\tilde{k}\sigma s+\tilde{k}s\sigma'+\tilde{H}^{e}_{s}s)$$

$$=\exp[-\tilde{k}(\sigma+\sigma')-\tilde{H}^{e}_{-1}]+\exp[\tilde{k}(\sigma+\sigma')+\tilde{H}^{e}_{+1}] \tag{5}$$

$$H'=\tilde{H}+z\delta H' \tag{6}$$

where $\tilde{k}=2^{D-1}k$, and δJ is a constant contribution to the free energy generated by decimation. The fields $\tilde{H}^{e}_{-1}$, $\tilde{H}^{e}_{+1}$ are obtained from the rule given above, according to the values of the neighbouring spins σ, σ':

$$\tilde{H}^{e}_{-1}=(2/z)\tilde{H} \tag{7}$$

$$\tilde{H}^{e}_{+1}=(2/z)\tilde{H}+\tfrac{1}{2}(1+\sigma+\sigma')H^{\circ}. \tag{8}$$

Equations (4)-(8) lead to the same equations as in Shnidman's paper, which we rewrite as follows:

$$\exp(-4k')=A^2/BC \tag{9}$$

$$\exp(-4H'/z)=C/B \tag{10}$$

where

$$A=\exp(-2\tilde{H}/z)+\exp(2\tilde{H}/z+H^{\circ}/2) \tag{11}$$

$$B=\exp(-2\tilde{k})+\exp(2\tilde{k}+4\tilde{H}/z+H^{\circ}) \tag{12}$$

$$C=\exp(-2\tilde{k})+\exp(2\tilde{k}-4\tilde{H}/z). \tag{13}$$

From these recursion relations one would like to derive the existence of a line of fixed points, with critical exponents which depend continuously on H°.

Let us now consider the following model. Let n_i in (3) be equal to zero if $\sigma_i=-1$, and be equal to the number of nearest neighbours j with $\sigma_j=1$ if $\sigma_i=1$. One can apply to this model the same transformation as in the previous case, and *one obtains the same recursion relations* (9)-(13). This happens because (7) and (8) are still valid. Nevertheless one easily sees that this model has Ising-like critical behaviour. In fact, we may write for this model

$$n_i=\tfrac{1}{4}\sum_j(\sigma_i+\sigma_j+\sigma_i\sigma_j+1) \tag{14}$$

where the sum runs over the nearest neighbours j of the site i. We obtain therefore

$$-\beta\mathcal{H}=J\sum_{\langle ij\rangle}\sigma_i\sigma_j+H_I\sum_i\sigma_i+\text{constant} \tag{15}$$

with suitably defined parameters J and H_I. As a consequence the recursion relations (9)-(13) do not represent the critical behaviour of the model and this is quite independent of whether H° is a marginal parameter or not.

We are thus led to the conclusion that the recursion relations propounded by Shnidman would imply a non-universal behaviour even for a model of the Ising universality class. In fact the complicated many-body interaction represented by n_i cannot be renormalised just as a one-body interaction, as shown in the simple alternative model we have considered. The question of whether the model is sufficient to explain the apparent non-universality of micellar solutions deserves further investigation.

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