Phase behavior under the averaging over disorder realizations

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Abstract

Effects of the averaging over disorder realizations (samples) on the phase behavior are analyzed in terms of the mean field approximation for the random field Ising model with infinite range interactions. It is found that the averaging is equivalent to a drastic modification in the statistics of the quenched variables. In its turn, this lowers the critical temperature of a second-order phase transition or, depending on the sampling, even suppresses the ordered phase. Possible first order transitions are shown to be softened by the sample averaging. Common issues and differences in the interpretation of these effects in the context of the simulation and experimental studies are discussed.

1 Introduction

An influence of a quenched disorder on the phase behavior is a long-standing problem that has received much interest\cite{1,2}. Various theoretical aspects, such as disorder relevance, Griffiths phenomena, possible lack of self-averaging\cite{3} or disorder-induced rounding are being discussed\cite{4} (see\cite{5} for a recent review). In the case of the so-called weak (or random $T_c$) disorder it is believed\cite{5} that the details of the probability distribution should not be important because the physics is dominated by the long-range properties.

On the other hand, there are systems in which the shape of the probability distribution is important. For instance, the fluid adsorption\cite{6} or the colloid-polymer mixtures separation in random porous media are found\cite{7} to belong to the universality class of the random-field Ising model (RFIM)\cite{8,9}. The latter is just a prototype of a system, where the randomness plays an essential role, the so-called strong disorder\cite{9}. In contrast to the weak disorder case\cite{1,5}, a change in the distribution modifies the degree of frustration, inducing specific fluctuations\cite{10}, which are not present in the pure (bulk) case. The RFIM has been analyzed in the mean field
approximation (MFA) \cite{11, 12, 13} and more recently by computer simulations\cite{10, 16}. The distribution width\cite{11}, asymmetry\cite{12} or bimodality\cite{13, 14, 15} have been shown to induce crucial changes in the phase diagram. Nevertheless, in the context of adsorption studies it becomes questionable \cite{6, 17} that the true equilibrium picture is observed in experiments, revealing a hysteretic behavior instead of sharp steps typical for a two phase coexistence. Moreover, it has been demonstrated \cite{6, 18} that the hysteresis can exist even without an underlying phase transition. This, however, does not discard completely a possibility of the phase behavior in disordered systems, but rather makes one to search for the conditions at which it can be observed.

Another aspect of the randomness is that two quenched systems prepared in the same way are not microscopically identical because only few macroscopic disorder parameters are usually controlled. Therefore, one has to average over different realizations. In the present study we argue that in this class of systems the averaging over disorder realizations in the simulations or appearing in the context of self-averaging hypothesis\cite{1, 2} in the analysis of experiments, is equivalent to crucial changes in the distribution of quenched variables (random fields in the RFIM language). In this way a sample averaged distribution brings up new statistical features which are absent from the statistics of each sample. Consequently, the phase behavior seen on average can be remarkably different from that in a separate sample. In particular, we are going to analyze whether a small difference of realizations can lead to qualitative changes in the phase behavior.

2 Averaging in disordered systems

Let us consider a quenched-annealed system. The annealed subsystem consists of interacting species (e.g. particles or spins) characterized by a set of variables \{s_i\}. The latter are governed by some Hamiltonian \[H[\{s_i\}|\{h_k\}]\] that contains a set of quenched variables (local porosities or magnetic fields) \{h_k\}, distributed according to some probability density \[f(\{h_k\})\]. For simplicity we assume the disorder to be non-correlated \[f(\{h_k\}) = \prod_k f(h_k)\], such that the position label is dropped \[f(h_k) = f(h)\]. In contrast to coupled annealed systems (e.g. an adsorbate-substrate coupling\cite{19}), in quenched-annealed systems the averaging should be taken in two steps. Tracing off the annealed variables one gets a quenched thermodynamic function \[m(h)\] (an order parameter) that is conditional to the state, \(h\), of the quenched counterpart. Then, as usually\cite{1, 2}, one takes an average of \[m(h)|_r\] with the distribution \[f(h)|_r\].

However, in reality, the situation is not so straightforward. In experimental or simulation studies only few disorder parameters (e.g. mean porosity, average field or site activity) are usually controlled during the quenching. Therefore, one has to deal with sample-to-sample fluctuations in different realizations \(r\). Thus, for a given sample the distribution implicitly depends on the realization \[f(h)|_r\]. Consequently, the disorder averages are also realization dependent

\[
m(r) = \overline{m(h)} = \int dh f(h|r) m(h) \tag{1}
\]

In order to find a "representative" result in the simulations one could generate an ensemble of samples corresponding to different realizations which appear with a probability density \(\varphi(r)\). Such a procedure has recently been reported\cite{20}. Then an average over realizations is taken

\[
m = \int dr \varphi(r) m(r) = \int dr \varphi(r) \int dh f(h|r) m(h) \tag{2}
\]
If the sampling $\varphi(r)$ does not depend on the $h$-disorder, we may change the order of integration, defining the realization-averaged (or sample-averaged) distribution
\[ \Psi(h) = \int dr \varphi(r)f(h|r). \] (3)

Then the order parameter should be calculated from
\[ m = \int dh \Psi(h)m(h). \] (4)

On the other hand, an experimentalist is usually working with a single system (or with few systems). This rises a question on a representability of a single experiment for a given class of materials. This leads to the concept of self-averaging\cite{1, 2, 3, 5}. Namely, it is assumed that an experimental system is large enough, such that it may be viewed as a composition of a large number of macroscopic subsystems (samples). Each of them corresponds to a different realization of the quenched disorder. In this way a measurement corresponds to an average over the subsystems, thus we arrive at the same representation (3), (4). This mathematical similarity enables one to compare the simulation and the experimental results. Note that the averaging over realizations (3) is formally equivalent to creating some "representative" or "typical"\cite{1} sample with a distribution $\Psi(h)$ that is thought to incorporate the generic features, independent of the system preparation procedure. However, in the context of experimental studies, invoking the self-averaging concept, this system is (or is believed to be) a real object, while in the simulation, where each realization can be tested independently, it is artificial.

Therefore, despite its logical transparency, the averaging (3) is not a trivial procedure. It leaves some important questions, such as how the final result (4) depends on the sampling $\varphi(r)$ and on the quenching in each sample $f(h|r)$? Indeed, from eq. (3) we may expect that, depending on these ingredients, the resulting distribution $\Psi(h)$ could be remarkably different from that in a separate sample. From a quite general point of view this issue has been analyzed within the superstatistical approach\cite{21}. It has been demonstrated how an exponential distribution (e.g. of Boltzmann type) transforms into a power-law as a result of a fluctuating environment\cite{21, 22} or a constraint\cite{23} restricting the phase space. In its turn, such a modification in the statistics of the quenched variables (namely, an enhancement of "rare" events \cite{1, 5, 9}) might lead to non-trivial consequences for the thermodynamics, especially near a phase transition point. In what follows we analyze this issue in more details.

### 3 Phase behavior

Realizations of the quenched subsystem are usually obtained by repeating some preparation procedure (e.g. sol-gel technique in experiments, or diffusion-limited aggregation in the simulation studies). Therefore, it is reasonable to accept that in all samples the distribution $f(h|r)$ has the same functional form. For analytical purposes let it be gaussian
\[ f(h|r) = \left[\sqrt{2\pi r^2}\right]^{-1} \exp\left(-h^2/2r^2\right) \] (5)

with zero mean $\overline{h} = 0$ and dispersity $r$ that may vary from sample to sample. As is discussed above, this variation is governed by the sampling $\varphi(r)$. One may argue that taking a gaussian distribution with varying dispersity is not realistic because the latter can also be controlled and then all realizations would be identical. In this respect it should be noted that real (e.g. pore

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size) distributions are usually more complex than gaussian. Therefore, even if the first two moments are fixed, the other parameters (asymmetry, multimodality, etc.) are not controlled. Thus, our choice (5) is just the simplest way of modeling such a situation.

3.1 Discrete sampling

One of the simplest non-trivial samplings is a discrete bimodal $\varphi(r) = \varphi_d(r)$

$$\varphi_d(r) = c\delta(r - a) + (1 - c)\delta(r - a - \Delta),$$

where we have two sample populations, one with $r = a$ and concentration $c$, the other with $r = a + \Delta$ and concentration $1 - c$. From eq. (3) we get

$$\Psi_d(h) = cf(h|a) + (1 - c)f(h|a + \Delta).$$

This function is displayed in Fig. 1 in comparison with a gaussian distribution of the same width (i.e. $\overline{r^2}$ is the same). It is seen that $\Psi_d(h)$ has a pronounced non-gaussian shape with a central peak (around $h = 0$) and the tail that favors higher $h$ values. In order to estimate the effect of this distribution on the criticality we consider the RFIM [1, 8] with infinite-range interactions [11, 12, 13]. This is a generic toy model exhibiting a second-order phase transition between the ferromagnetic ($m \neq 0$) and "frozen" ($m = 0$) or independent spin [11, 12, 13] phases. We are focusing on the very existence of the transition, without discussing its universality class (critical exponents, etc.). For this reason we deal the MFA which is sufficient for a qualitative estimation. In addition it is expected [11, 12] to be exact for the infinite-range interactions. Therefore, we have to solve

$$m = \int dh\Psi_d(h) \tanh[\beta(qJm + h)],$$

where $q$ is the lattice coordination number, $J$ is the interaction constant and $\beta = 1/kT$ is the inverse temperature. It is well-known [11, 13] that for a single gaussian field distribution with dispersity $r = \delta$ the critical temperature $T_c$ decreases with increasing $\delta$, reaching $T_c = 0$ for $\delta = \delta_c$ such that $qJ/\delta_c = \sqrt{\pi/2}$. For $\delta > \delta_c$ the system remains non-critical ($m = 0$) at all temperatures. For an arbitrary field distribution $\Psi(h)$ the condition for such a zero $T_c$ point is given by [13]

$$2qJ\Psi(h = 0) = 1$$

In the case of the sample averaged distribution $\Psi_d(h)$ (7) from the condition (9) we have found the following relation for the threshold width $a = a_c$ corresponding to the zero-temperature critical point

$$a_c/\delta_c = c + (1 - c)/(1 + \Delta/a_c) = \frac{1 + c\Delta/a_c}{1 + \Delta/a_c}$$

which implies $a_c < \delta_c$ suggesting that the zero-temperature critical point is shifted towards the region of a weaker field disorder. The phase diagram is given in Fig. 1 (the inset). It is seen that $T_c$ decreases with increasing distance $\Delta - a$ between the two sample groups. Even if we take a population with $a \ll \delta_c$, such that all these samples are critical (two phases are detectable), then the result seen on average depends on the population (magnitude of $c$ and $\Delta$) of non-critical ($m = 0$) samples. Therefore, even a small heterogeneity in the realizations suppresses the tendency towards the ferromagnetic ordering. We would like to emphasize the difference
in the interpretation of this result from the simulation/theoretical and the experimental points of view. If the simulation samples are generated as distinct realizations, then testing each sample (e.g. by decreasing temperature and recording the magnetization) one would detect the criticality or not. Then the critical and non-critical samples could be considered as qualitatively different and taking an average over this group of dissimilar objects might seem to make little sense. Nevertheless, in order to mimic the behavior of a real self-averaging system (in the experimental sense) one has to perform such a realization averaging. On the other hand, if the realizations are thought to be macroscopic subsystems of a single sample, then they cannot be tested separately and the observed response is a superposition given by eqs. (3), (4). In that case an experimentalist would conclude that the system is critical or not depending on the preparation details \((a, \Delta, c)\). But, as we have already seen, the conditions for observing the criticality are quite strict. Small inhomogeneities in the realizations shift the transition to low temperatures, which might be difficult to reach.

### 3.2 Continuous sampling

In practice it is difficult to expect that the realizations will fall into a finite number of distinct groups. A more realistic sampling should involve a quasi-continuous sample distribution in some interval. In this context we consider a continuous step-wise distribution \(\varphi_c(r) = \varphi(r)\)

\[
\varphi_c(r) = H(r) H(\Delta - r) / \Delta,
\]

where \(H(r)\) is the Heaviside step function. In this way we have a set of samples with the gaussian field distribution \(f(h|r)\) \([5]\), whose dispersity is distributed between \(r = 0\) and \(r = \Delta\) with equal probability. According to \([3]\) the average over this set is given by

\[
\Psi_c(h) = \frac{1}{\sqrt{8\pi\Delta^2}} E_1 \left( \frac{h^2}{2\Delta^2} \right),
\]

where \(E_1(x)\) is the exponential integral\([24]\).

Let us first analyze the statistical features associated with different realizations. The distribution \(\Psi_c(h)\) is displayed in Fig. 2 together with a gaussian distribution of the same width. It is seen that \(\Psi_c(h)\) has a non-gaussian shape with a logarithmic singularity at \(h = 0\) and a well-pronounced tail favoring stronger fields \(h\) (see the inset) with higher probability than it was in the case of the bimodal sampling. The striking difference in the sample and the sample-averaged statistics is worth of being emphasized. Namely, in each sample the field fluctuation is determined by a quenching path \(\bar{h}^2 - \bar{h}^2 = r^2\) (the average is taken with \(f(h|r)\), eq. (5)). The sample-averaged fluctuations (given by \(\Psi_c(h)\)) are controlled by the sampling procedure \(\bar{h}^2 - \bar{h}^2 = \Delta^2/3\). Moreover, the sample-averaged field fluctuations are coupled to the sample dispersity fluctuations

\[
\bar{h}^2 - \bar{h}^2 = 4[\bar{r}^2 - \bar{r}^2] = \Delta^2/3,
\]

where the correspondent averages are taken with the distributions \(\Psi_c(h)\) and \(\varphi_c(r)\). Therefore, the sample averaging induces specific fluctuations, which do not take place in separate samples. This reflects a superposition of different realizations contributing to the overall result.

To see how does this affect the criticality we consider a uniform sampling distribution with the gaussian width distributed between \(r = a\) and \(r = \Delta\), \((\Delta > a)\).

\[
\varphi(r) = \frac{1}{\Delta - a} H(r - a) H(\Delta - r)
\]

(13)
In this way we avoid the counting of the "pure" states with \( r = 0 \), for which \( f(h| r = 0) = \delta(h) \) and there is no field disorder. Then the realization averaged field distribution is given by

\[
\Psi(h) = \frac{1}{\sqrt{8\pi(\Delta - a)^2}} \left[ E_1 \left( \frac{h^2}{2\Delta^2} \right) - E_1 \left( \frac{h^2}{2a^2} \right) \right]
\]  

From the condition (9) for the \( T_c = 0 \) critical point we obtain

\[
a_c \delta_c = \ln \left( \frac{\Delta}{a_c} \right) \frac{\Delta}{a_c} - 1
\]  

where, as before, \( \delta_c \) is the threshold width of a single gaussian distribution. Therefore, as in the case of the discrete sampling, \( a_c/\delta_c \leq 1 \). This implies that the lower border \( a \) should be below the gaussian threshold \( \delta_c \) at a "right" distance determined by the maximal width \( \Delta \). In other words, the transition is shifted towards the region of weaker disorder. In order to study the phase behavior at non-zero temperatures we have again analyzed the MFA (8) with \( \Psi_d(h) \) being replaced by \( \Psi(h) \). Our numerical analysis reveals that the phase diagram is qualitatively similar to that obtained for the discrete sampling (the inset in Fig. 1). Therefore, the ordered phase \( (m \neq 0) \) appears only if the realization parameters \( a \) and \( \Delta \) are chosen in a proper way with respect to \( \delta_c \). Thus, changing the system composition with a small fraction of impurities may completely "eliminate" the ordered phase. Note that quite recent experiments [25] on lamellar ordering transitions in doped block copolymers reveal that a very small concentration \( (\approx 1\%) \) of the doping agent suppresses the ordered phase.

One might argue that the quenched variable distributions used in the simulation or theoretical studies are already given as averaged over realizations \( \Psi(h) \). Such that one works with a "representative" sample, trying to find general features, independent of the preparation details. This, however, rises a question on how to get it in practice (both in experiments and simulations). In other words, what should be the sample distributions \( f(h|r) \) that, after the averaging with some \( \varphi(r) \), leads to a given functional form for \( \Psi(h) \). Let us assume that the sample average distribution \( \Psi(h) = \Psi_s(h|\sigma) \) is gaussian with zero mean and dispersity \( \sigma \), and that the sampling is again continuous - eq. (11). Then, following eq. (3) we have to solve

\[
\Psi_g(h|\sigma) = \frac{1}{\sigma} \int_0^\sigma dr f(h|r)
\]  

with respect to \( f(h|r) \). The solution is

\[
f(h|r) = \left( \frac{h}{r} \right)^2 \Psi_g(h|\sigma = r).
\]  

It is clear that in each sample, \( r \), the field disorder is bimodal with \( f(h|r) \) having a minimum at \( h = 0 \) and two maxima at \( h_m = \pm r \sqrt{2} \). It has been reported [13] that the bimodality (or more precisely, a minimum at \( h = 0 \)) is a prerequisite of a tri-critical behavior. If the maxima are separated enough (with increasing \( h_m \)), then in (at least) some fraction of the realizations a first-order transition is observable [26]. Obviously, this effect is lost after the sample averaging. As is discussed above, with the gaussian \( \Psi_g(h|\sigma) \) a second-order transition is observable depending on the magnitude of \( \sigma \). A quite similar softening of a first-order transition has been detected both experimentally [27] and theoretically [28].
It should be noted that the smearing of the singularities discussed here is not a peculiarity of the chosen model or probability distributions. Let us assume that for a given realization $r$ the disorder-averaged quantity of interest $q(x|x_0)$ makes a step at $x = x_0 = x_0(r)$. In the vicinity of the step we can approximate $q(x|x_0) = q_0H(x - x_0(r))$, where $H(x)$ is again the Heaviside step function. In different realizations (samples) the steps occur at different $x_0(r)$. This can be translated into a probability density $g(x_0|s)$ to find the realization with a given $x_0$, where $s$ is a parameter related to the sampling procedure. In particular, for the uniform sampling $\langle \rangle$ we can identify $s$ with $\Delta$. The realization averaging leads to

$$q(x|s) = \int_{-\infty}^{+\infty} dx_0 g(x_0|s)q(x|x_0) = q_0 \int_{-\infty}^{x} dx_0 g(x_0|s)$$ (18)

Since $g(x_0|s)$ is a probability density, then the last integral in the equation above is (by definition) a probability to find a given value of $x$. Therefore, unless $g(x_0|s)$ is singular, $q(x|s)$ varies smoothly in between 0 and $q_0$. The same arguments apply also to divergent functions. For instance, $dq(x|x_0)/dx = q_0\delta(x - x_0(r))$. Its realization average

$$\frac{dq(x|s)}{dx} = q_0g(x|s)$$ (19)

is not singular for any smooth realization (sample) distribution $g(x|s)$.

4 Conclusion

We have found that the averaging over disorder realizations in the simulations or appearing in the context of the self-averaging hypothesis $\langle \rangle$ in experiments, is equivalent to crucial changes in the distribution of quenched variables. In this way a sample averaged distribution brings up new statistical features which are absent from the statistics of each sample. Consequently, the phase behavior seen on average could be remarkably different from that in a separate sample. It is found that the realizations need not be very different in order to induce qualitative differences in the phase behavior. In particular, the sample averaging has a tendency to suppress both first- and second-order transitions, unless the ensemble preparation is done under "right" conditions (e.g. eqs. (10), (15) in the context of the present study). Based on this we may argue that the absence of reliable evidences of a sharp phase behavior in the experiments$^{[25, 27]}$ with disordered systems can be explained by their self-averaging nature, involving a superposition of different disorder realizations. In this respect a development of methods$^{[29]}$ which are not based on the criticality could be quite promising for the characterization of disordered media (e.g. porous or amorphous materials).

References

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This has been shown within a mean-field analysis which is believed to be exact for the infinite range interactions. In the case of nearest neighbor interactions a more refined analysis involving computer simulation techniques does not give a definite answer.
Figure 1: Bimodal gaussian $\Psi_d(h)$ (solid) and a gaussian (dashed) distributions of the same width. The inset displays the phase diagram for different distances between the gaussian populations, where $\delta_c$ is the threshold disorder width for a single gaussian (see text).

Figure 2: Continuous $\Psi_c(h)$ (solid) and a gaussian (dashed) distributions of the same width. The inset displays $\log_{10} \times 10^{-2}$ of these distributions (the tails).