The Replica Approach: Spin and Structural Glasses

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December 18, 2008

Abstract

A spin glass is a type of magnetic ordering that can emerge, most transparently, when a system is both frustrated and has quenched disorder. This paper will review some of the basics of such systems, and then touch on some of the experimental results that served as a guide for the theory. In exploring the theory it will focus on one particular framework, the replica approach, that has been used to study such systems, and will briefly examine how that framework is being expanded to look not only at spin but also structural glasses.

1 Introduction

Spin glasses are a fascinating class of magnetic materials with properties quite different from those of familiar ferro- and anit-ferro-magnets. In a spin glass the magnetic moments are frozen into some (apparently) equilibrium orientations, but without any long-range order. This feature, frozen-in orientation without long-range order, makes an instant analogy with structural glasses, which themselves have molecules seemingly in equilibrium positions but without any sort of crystalline ordering. In recent years links between spin-glasses and structural glasses have been made, and the potential for spin glass research to shed light on the theory of structural glasses is one of the exciting developments of the field.

In any event, an early theory of spin glasses was proposed by Edwards and Anderson [1], in which they identified two key features for a successful theory of spin glass: quenched disorder and frustration. Note that, in fact, quenched disorder turns out not to be strictly necessary in some spin glass theories (see, for instance, [2]). Indeed, this is one of the reasons the study of spin glasses has proven useful in answering questions about structural glasses, which do not themselves have quenched disorder. For introductory purposes, though, let us consider only the most basic class of spin glasses and explain the above two properties.

Consider, then, a simple Ising spin model coupled to an external field, h:

$$H = -\sum_i hS_i - \sum_{i,j} J_{ij} S_i S_j. \tag{1}$$

The key feature here is that the coupling strength between spins i and j, J_{ij}, are randomly distributed variables. 'Quenched disorder' refers to the fact that the J_{ij}'s are chosen randomly (hence 'disordered'), but that once chosen the values are fixed for purposes of further calculation (hence 'quenched'). 'Frustration' refers to the fact that spin glasses do not have a unique, non-degenerate ground state, but instead occupy one of a vast number of metastable states, all of approximately the same energy, that are separated by large free energy barriers. This comes about because the disorder in the spin-coupling parameter means that often a single spin will be unable to simultaneously minimize the energy of all its interactions, and hence is 'frustrated' in its attempt to reach a true ground state.

To more clearly see how frustration can arise, even in simple systems, consider the four-spin Ising set-up in the absence of an external field shown in Figure 1. If we take $J_{13} = J_{34} = J_{24} = 1$ and $J_{12} = -1$ we can instantly see the problem: for a given spin direction for Spin 1, Spins 2 and 3 will want to be oppositely aligned from each other to minimize their interaction energy with the first spin. But now Spin 4 (and hence the system) is frustrated, as it simply cannot minimize its energy with respect to be Spin 2 and Spin 3 simultaneously.

The remainder of this paper will be organized as follows. Section 2 will give a brief accounting of some of the experimental results that fueled interest in spin glass phenomena, with particular attention paid to phenomena that reinforce the importance of frustration and quenched disorder for model spin-glass sytems. Section 3 will return to theoretical aspects of the problem, defining an appropriate order parameter for the system and focusing on the replica approach to solving the problem. Section 4 will conclude the paper with a short look at how ideas from spin-glass theory have been generalized to try to answer questions about structural glasses.

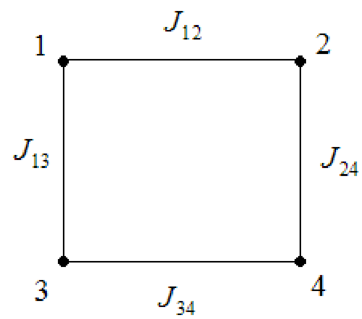

Figure 1: Four Ising spins with individual nearest-neighbor coupling strengths

2 Experimental results

In the seventies and early eighties there was some dispute as to exactly what properties experimentally characterized a spin glass [3], and here we will briefly go over some of what are now accepted as the (near-) universal features of spin-glass systems. As mentioned earlier, by definition there must be no observed periodic long-range order in the magnetization. In addition, the 'frozen-in' magnetic moments of the system leads to the experimental signature of a cusp or peak in the frequency-dependent magnetic susceptibility. Such a cusp was first observed by Cannella and Mydosh in the early seventies [4]. A typical plot is shown in Figure 2, where both the in-phase (χ') and out-of-phase (χ'') components of the complex magnetic susceptibility of a gold-manganese alloy have been measured and shown to be peaked at what the authors identify as the freezing temperature of the system.

Other striking experimental signatures of spin-glass systems are those of remanence and hysteresis. Put simply, remanence in the case of spin glasses just means that, after a field-induced magnetization has been created in the spin-glass system and the external field switched off, there remains a remanent magnetic field with a very slow decay time (i.e. a remanent field is still observable after a macroscopic amount of time is allowed to pass). A linked but perhaps even more vivid effect is the dependence of the magnetization on the 'magnetic history' of the sample. One common way to study this is to consider two different phase-space paths. In the first path

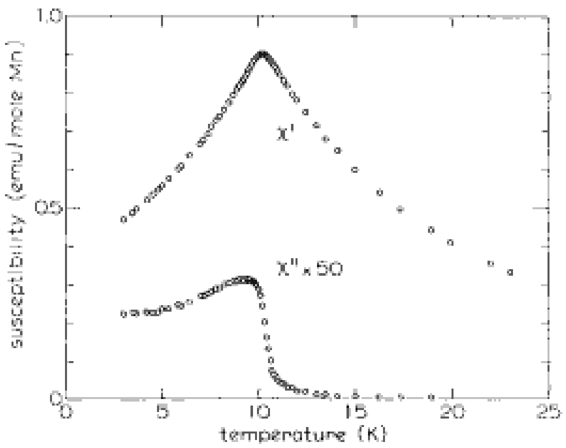

Figure 2: Temperature dependence of the susceptibility χ' and χ'' for AuMn in zero static external field. From reference [5]

the sample is cooled in the absence of an external field to below the freezing temperature, and then the response of the system to a particular external field is studied. Alternately, the system can be studied by starting above the freezing temperature, cooling it down in the presence of an external field to well below the freezing temperature, switching off the external field, and then studying the response of the system to another particular external field.

Figure 2 gives a clear illustration of these phenomena: there is a remanent magnetization of the system (made clear by the different starting values of the system magnetization depending on whether the system was cooled in the presense of a magnetic field or not), and the hysteresis seen makes the importance of the 'magnetic history' of the spin glass equally apparent.

There are many other experimental features of spin-glass systems that deserve mention and are of interest - deviation from the Curie-Weiss law even far above the freezing temperature, broadening of the peak of the specific heat curve above the freezing temperature, the lack of a singularity in the zero-field specific heat even at the freezing temperature (important in that this is in direct contrast with the predictions of mean-field theoretic predictions) - but these must be passed over in the interest of brevity. But, the importance of the observation of these effects for the theoretic development of spin glasses is clear: the cusp in the frequency-dependent susceptibility leads to putting

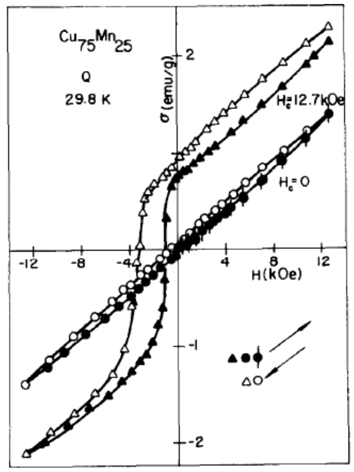

Figure 3: Magnetization, σ, vs. applied field, H, for quenched $Cu_{75}Mn_{25}$ at 30 K after zero-field cooling (circles) and after $H_c = 12.7$ kOe (triangles). Filled symbols represent data taken in ascending fields, and empty symbols represent data taken in descending fields. From reference [6]

quenched disorder into the models, and the remanence and history-dependent effects calls to mind a situation where there are many minima in the free energy landscape for the system to settle into, but with the minima separated by rather large barriers. Thus, we see the importance of adding frustration to any spin-glass model.

3 Theory: the replica approach

Above we saw the importance of including quenched disorder in a model of a spin-glass system, but in many ways this is also the source of much of the theoretical difficulty of the problem. Put simply, we know from our experience with statistical mechanics that in problems with randomness we want to perform an average over that randomness as soon as permissible. However, since for quenched disorder (and, for definiteness, we'll keep in mind the Hamiltonian of Equation 1) we randomize the interactions at the outset and fix them thermodynamically, we can only perform the average on physical observables (the free energy, for example) instead of on the partition function - and, of course, averaging the log of Z is a much thornier problem than just averaging Z itself.

So, initially, we can think of the replica approach as a formal mathematical trick to get around this problem of averaging the log of Z. To do so, we note that the taylor expansion of the function x^n near $n = 0$ is given by

$$x^n = 1 + n \log x + \mathcal{O}(x^2), \tag{2}$$

so, taking the partition function as x above, we can write

$$\log Z = \lim_{n \to 0} \frac{Z^n - 1}{n}. \tag{3}$$

We will think of Z^n as being the product $Z^n = \prod_{a=1}^{n} Z_a$, where a is a label denoting n identical 'replicas' of the system, and our problem of averaging $\log Z$ has been replaced by averaging Z^n, albeit in the somewhat unintuitive limit where the number of replicas goes to zero.

The effect of averaging over Z^n is to introduce interactions between the replicas a when n is an integer, an effect which was exploited by Sherrington and Kirkpatrick (S-K) in [7] for the case of a Hamiltonian like Equation 1 where the interaction strengths J_{ij} were distributed as a gaussian. They were able to derive an expression for the free energy per spin using two addition mathematical maneuvers: the interchange of the order of the thermodynamic ($N \to \infty$) and replica ($n \to 0$) limits, followed by the analytic continuation of the results of an integral that could be evaluated for integer $n \geq 2$ to the case for real $n \to 0$.

Both of these moves seem less than fully justified, but the authors were able to derive the following expression:

$$f = kT \left((\frac{\overline{J}_0 m^2}{2kT} - \frac{\overline{J}^2 (1 - q^2)}{(2kT)^2} - \frac{1}{\sqrt{2\pi}} \int dz e^{-z^2/2} \log(2 \cosh \Xi) \right), \tag{4}$$

where $\overline{J}_0$ and $\overline{J}$ are related to the cumulant expansion of the distribution of the J_{ij}, Ξ is related to those cumulants, m, q, and the external field, and (most importantly for us) $m = \langle \langle S_i \rangle \rangle_d$ and $q = \langle \langle S_i^2 \rangle \rangle_d$ (here unadorned angled brackets indicate a thermal average, and those with a d subscript indicate an average over the spatial disorder). We see in m and q, then, our order parameter: if both m and q are nonzero the system is in a ferromagnetic phase, and if $q \neq 0$ while m vanishes we see the emergence of a spin-glass phase (whereas if both are zero the system is in a paramagnetic state). We pause here to note an interesting feature of the transition between zero and non-zero values of the order parameter: while the phase transition itself is second order in a thermodynamic sense (having a continuous change in the free energy and a jump in the specific heat), the order parameter itself jumps *discontinuously* from zero to some non-zero value upon entering the spin-glass phase [8].

The theory outlined here (the reader is invited to see [7] for the derivation and a much more thorough discussion) performs fairly well when compared to experiment for high temperatures, and in fact also predicts the freezing temperature in good agreement with experiment. At low temperatures, though, serious problems emerge; as just one example, in the zero-external-field, zero-temperature limit this theory actually predicts a negative entropy. Clearly something has gone wrong! In addition to the technical mathematical issues (the two maneuvers mentioned above) that lead to such results, there is also something a bit unsatisfying about the above presentation: viewing the replicas as a mathematical trick instead of reflecting some sort of more physical idea feels not very compelling. Or, viewed through the lens of what was discussed in class this semester, we know that ordered states are typically the result of a broken symmetry, but here it is not at all clear what (if any!) symmetry we have broken to arrive in the ordered spin glass phase from the ferromagnetic phase. To make the idea of broken symmetry more apparent, we have to, at least briefly, look at Parisi's version of the replica approach.

To begin, we will have to define a new order parameter, albeit one a bit more abstract than the q we defined above. Loosely following Parisi in [9], we consider the $n \times n$ matrix $Q_i^{\alpha,\beta} = \langle \sigma_i^\alpha \sigma_i^\beta \rangle$. That is, the average of the product of the spins on the same site but across different replicas. In our earlier discussion, where all the replicas were identical, this is not a terribly interesting matrix, as all of its elements would be identical, enforcing $Q^{\alpha\beta} = q$ independently of α and β. At this point it is a purely trivial statement to say that, in such a case, the matrix Q is symmetric under a relabeling of the replicas (or, equivalently, under a permutation of the replicas).

The insight allowing further progress with the replica approach, though, is the recognition that the free energy (and other observables) can be obtained under different assumptions about the structure of Q. We can define, for instance, an iterative procedure for constructing the matrix Q, whereby (now using the conventions from the cosmetically different version of the theory presented in [10]) at each iteration blocks of ever-smaller size on the diagonal have their elements replaced by a different value of q, while the off-diagonal blocks are left untouched. A particularly simple example showing two such steps is shown in Figure 3. Each iteration of this proceedure is refered to as a level (the k^{th}-level after k steps) of replica symmetry breaking, as each iteration further reduces the set of permutations we can still make to the replicas while leaving the matrix Q invariant. And indeed, as the name suggests, this is precisely the symmetry that is broken in entering the ordered spin-glass phase.

$$\begin{pmatrix} q_0 & q_0 & q_0 & q_0 \\ q_0 & q_0 & q_0 & q_0 \\ q_0 & q_0 & q_0 & q_0 \\ q_0 & q_0 & q_0 & q_0 \end{pmatrix} \rightarrow \begin{pmatrix} q_1 & q_1 & q_0 & q_0 \\ q_1 & q_1 & q_0 & q_0 \\ q_0 & q_0 & q_1 & q_1 \\ q_0 & q_0 & q_1 & q_1 \end{pmatrix} \rightarrow \begin{pmatrix} q_2 & q_1 & q_0 & q_0 \\ q_1 & q_2 & q_0 & q_0 \\ q_0 & q_0 & q_2 & q_1 \\ q_0 & q_0 & q_1 & q_2 \end{pmatrix}$$

Figure 4: Illustration of two levels of replica symmetry breaking for $n = 4$

Now, this proceedure still has its fair share of mathematical subtleties. For instance, the proceedure outlined above makes perfect sense for integer n and finite k, but in the final version of the theory we not only make an analytic continuation to the $n \to 0$ limit, but simultaneously let $k \to \infty$. The result of this analytic continuation is to end with not a single order parameter as in the S-K theory, but rather an order parameter $Q(x)$ that is a continuous function on the domain $[0, 1]$ (although we note that $Q(x)$ cannot be computed exactly except quite close to the freezing temperature; in other temperature regimes it must be approximately studied). Our earlier order parameter q (or, rather, a simple variation of it), corresponding to the $k = 0$, fully permutation-symmetric version of this proceedure, can be shown to be related to this new order parameter quite simply: $q = Q(1)$.

In terms of comparing the results with those of S-K replica theory, it is more that the two approaches are complementary (in a sense). In the high-temperature regime the predictions of S-K are still valid, and indeed for such temperatures replica-permutation symmetry is not broken, so the system is S-K solution is a stable one. Below a certain temperature (one that depends on the external field), though, this generalized replica approach predicts that the replica-symmetric solution is unstable to replica-symmetry-breaking solutions. It turns out that this more general theory corrects for many of the low-temperature shortcomings of the S-K theory; for instance, it correctly predicts a zero instead of negative entropy at zero temperature.

4 Conclusion

The various applications and predictions of the replica approach are so varied that in a paper of this length there is hardly time to do it any justice, let alone properly address the large class of other approaches to the spin glass problem. So, for this conclusion I would like to focus on just one particularly exciting way the replica approach has been extended and talk about its relation to structural glasses.

A structural glass results when a fluid is cooled sufficiently quickly, and the glassy state is characterized by a freezing-in of local structures that prohibit easy movement of the particles, breaking the ergodicity of the system. An intuitive, physical order parameter (like q, and not the matrix Q, in the preceeding section) can be thought of as follows: let us define the 'cage length' to be a length scale related to the amount of space a given particle can explore in some appropriately chosen time scale. At high temperatures, when the system is in a liquid state, the particles are not constrained and can effectively explore the entire space of the system, but as the temperature is lowered and local 'cage' structures emerge, the amount of space explored ceases to scale with the volume of the system. So, we can define a physical order parameter by the inverse of the cage length: it is zero for the liquid, and takes a non-zero value in the glassy state. As it turns out, the transition to the glassy state shares a common feature with the transition to the spin-glass state, in that it is thermodynamically a second-order transtion, but this physical order parameter jumps discontinuously to some finite value at the transition [11]. This observation, along with other similarities (for instance, the fact that glassy systems exhibit the same frustrated state of affairs, with many equivalent free energy minima separated by high barriers), helped fuel interest in using the replica approach from mean-field spin glasses and applying it to structural glasses.

However, the lack of quenched disorder in structural glasses - where the randomness caused by local packing arrangements is clearly not a thermodynamically fixed quantity - was for a long time an impediment to using the replica approach [8]. As we saw earlier the entire purpose of introducing the replica formalism was to try to deal with averaging the log of the partition function, but with no quenched disorder there seems to be no a priori reason to delay averaging over the randomness of the glass phase sooner than at the level of physical observables. The heart of the issue, though, is that it is hard to describe the amorphous structures of glass as anything other than out-of-equilibrium effects, which would preclude the transition to the glassy state from being viewed as a legitimate phase transition. Thus, replicas (often called 'clones' in this context) are introduced not as a way to deal with quenched disorder but rather as a way to describe the glass state as a true equilibrium state [12].

To get a sense of the clone or replica formalism for this problem, I will sketch some of the barest details leading to the order parameter used in calculation (just as in Parisi's version of the replica approach, where the order parameter Q that he considered was substantially different from but still able to be related to the physical order parameter q, there is similarly a connection between what I will soon describe and the 'inverse-cage-length' order parameter mentioned above). So, following [13] in the remainder of this paragraph, we look at the case where we have two clones of the system. The hamiltonian we use will be

$$H = \sum_{i \leq i \leq j \leq N} (v(x_i - x_j) + v(y_i - y_j)) + \epsilon \sum i, j w(x_i - y_i). \tag{5}$$

So, we have two copies of the system, with particle coordinates x_i and y_i, where the particles have some potential interactions (typically a hard sphere or a Lennard-Jones potential), and there is some weak short-ranged attractive potential, w, *between* the two clones. The exact form of the potential is not terribly relevant, as we will ultimately take the $\epsilon \to 0$ limit. With this as our starting point, we can define a new order parameter g that, like Q, is a continuous function, by

$$g_{xy}(r) = \lim_{\epsilon \to 0} \lim_{n \to \infty} \frac{1}{\rho N} \sum_{i,j} \langle \delta(x_i - y_j - r) \rangle, \tag{6}$$

for ρ the density of particles and N the number of particles. This order parameter has the feature that for the liquid state it is uniformly one, but in the glassy state it discontinuously acquires more intricate structure. We can again ask what symmetry is broken in the new ordered phase, just as for the spin glass system. Well, in the $\epsilon \to 0$ limit and assuming periodic boundary conditions, $g_{xy}(r)$ is invariant with respect to a global translation of the x particles relative to the y for the high-temperature liquid phase, but this symmetry is not present in the glassy state [8].

This cloning proceedure can be intuitively extended to any integer number m of clones, and then to get predictions of the theory the results are analytically continued to $m \to 1$. Remember, since we are not using the clones to compute a quenched-disorder average, there is no need to analytically continue to the zero-clone limit. Instead, the idea is that the weak attraction we put in between the clones encourages the clones to be in the same equilibrium amorphous state, and that when the temperature is low enough and the theory predicts the emergence of the glassy state, such a lining up of the clones exists even in the $\epsilon \to 0$ limit, that is, in the absence of coupling between the clones.

In this paper we have seen the power of the replica approach in dealing with frustrated systems in the presence of quenched disorder, and we have briefly looked at an extension of the approach to systems without quenched disorder. It has been speculated (e.g. in [14]) that this replica/clone generalization might apply to a wide class of 'entropy crisis' models of spin and structural glasses - so called after a seeming paradox uncovered by Kauzman in [15] where there seems to be a finite, non-zero temperature where a measure of the configurational entropy of a glassy system drops below that of a perfect crystal at zero temperature (slightly reminiscent but, I think, only superficially connected with the negative entropy that arises at zero temperature in the S-K model). However, neither this statement nor the whole model of an entropy-crisis-driven approach to the problem of structural glasses is without controversy, and indeed the field remains an area of active research.

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