

# SPIN-GLASS: A NEW CHALLENGE IN STATISTICAL PHYSICS

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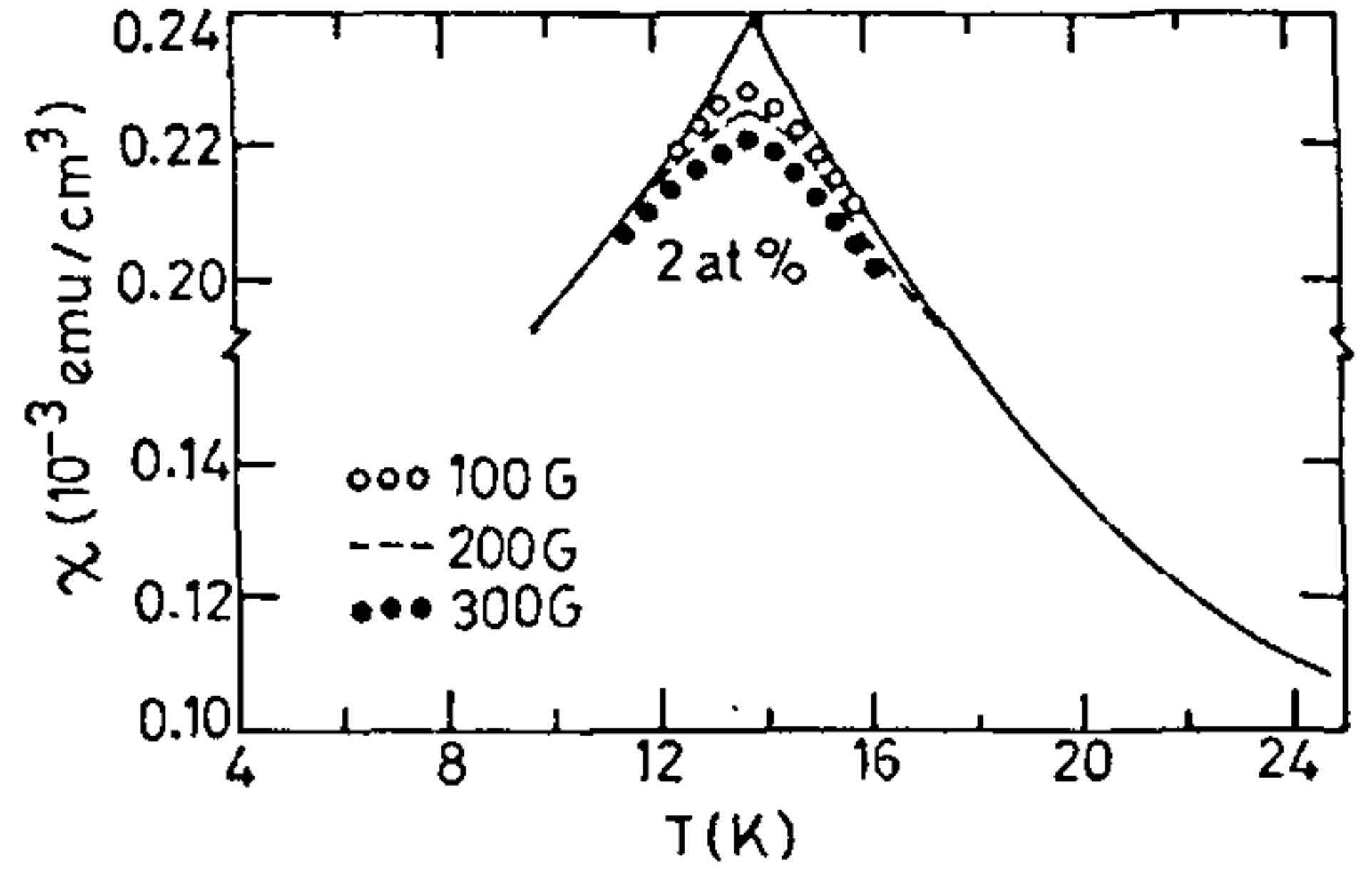
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## 1. INTRODUCTION

THE discovery of the so-called spin-glass (SG) behaviour<sup>1</sup> in certain magnetic alloys in the early seventies has led to a series of very rich and exciting developments in Statistical Physics. These developments have promise of making a far-reaching impact on our theoretical capability to handle new levels of complexity in condensed matter Physics and allied subjects. The purpose of the present article is to provide a survey of the main challenges posed by SG behaviour, key theoretical ideas which have been developed in this context, and their general significance in the study of cooperative behaviour and phase transitions in random systems.

The archetypal SG system contains a low concentration ( $\sim 1\%$ ) of magnetic atoms distributed randomly in a nonmagnetic metallic host. The magnetic coupling between the moments arises due to long-ranged oscillatory RKKY interaction, as a result of which certain pairs of atoms interact ferromagnetically while the others interact antiferromagnetically. The best studied examples of such systems are Cu Mn and Au Fe.<sup>2</sup> There are a variety of other insulating and concentrated substances which exhibit SG behaviour. Thus it seems that the essential properties of magnetic couplings which give rise to SG behaviour are randomness and conflict.

The main characteristic of the SG phenomena is the freezing of magnetic moments in random directions at an apparently sharp temperature. The evidence for this comes from several experimental observations, listed as follows. (i) The foremost signature for this freezing is a cusp in the low field magnetic susceptibility as a function of temperature. This is shown in figure 1. The sharpness of the cusp suggests that freezing sets in rather sharply at  $T_f$ . (ii) Mössbauer spectrum shows a line splitting abruptly below a temperature indicating onset of static hyperfine fields,



**Figure 1.** Susceptibility of Au Fe alloy with 2% Fe, plotted as function of temperature. Full curves refer to zero field.

(iii) Muon-spin rotation experiments also show a rotational dephasing abruptly below the freezing temperature indicating the presence of static local fields, (iv) Neutron scattering experiments show an onset of incoherent elastic part around the freezing temperature, which is again indicative of the freezing of the motion of the atomic magnetic moments.

More precisely, these experiments suggest that at least over the time scale of the order of the probe time of the experiment (*e.g.*, the probe time of neutron scattering is  $10^{-11}$  sec, while that for Mössbauer experiment is  $10^{-7}$  sec) the moments are frozen. Coupling this set of observations with the fact that such systems show no net equilibrium magnetisation or any other kind of magnetic long range order as ascertained from neutron scattering measurements, leads us to believe that magnetic moments freeze in random directions rather sharply as a function of temperature.

To investigate the nature of this freezing, the SG systems have been subjected to several other measurements, like measurements of specific heat, resistivity, magneto-resistance, ultrasound attenuation, NMR, ESR, frequency dependent sus-

ceptibility, M-H curves, various types of remnant magnetisations and their relaxation, various kinds of neutron scattering measurements etc<sup>3</sup>. A discussion of all these measurements and their contribution to our present understanding of the SG state and the freezing process is beyond the scope of this article. We content ourselves by mentioning a few important observations (a) The magnetic specific heat shows no anomaly at  $T_f$ , and there is significant contribution at temperatures well above  $T_f$ . Quantitatively it seems roughly 70% of the total entropy develops above  $T_f$ , implying strong short-ranged magnetic correlations, (b) Below  $T_f$  there is remnant magnetisation which decays rather slowly with time. This relaxation is distinctly non-exponential and occurs over time scales ranging from minutes to hours. The value of the remnant magnetisation depends upon whether the system is cooled below  $T_f$  in the presence of the field or the field is applied and removed after cooling. Several SGs, show rather narrow but displaced hysteresis loops, characteristic of unidirectional anisotropy (c) The SG state is rather sensitive to external magnetic field. The sharp cusp seen in susceptibility measurements is broadened considerably by the application of a field as low as 100 G. This can be seen in figure 1. (d). Anomalies which occur in other properties at the usual phase transition point are not seen in the SG transition. For example, temperature derivative of resistivity, ultrasound attenuation and specific heat show no anomaly unlike other transitions.

All this points to the fact that if SG transition is at all a thermodynamic, cooperative transition, it is an unusual one. Another dominant view that finds considerable favour is that SG freezing is a viscous freezing, in which single moments first develop strong, short range order to form super paramagnetic clusters, whose free rotations are blocked by anisotropy energy barriers. The relaxation time of such a cluster to tunnel from one favourable orientation to another is given by Neel's formula

$$\tau = \tau_0 \exp(E_a/k_B T) \quad (1.1)$$

where  $E_a$  is the anisotropy energy barrier. As  $T$  decreases  $\tau$  becomes large very rapidly and the

cluster appears frozen in any experiment whose measurement time  $\tau_m$  is less than  $\tau$ . This clearly implies that freezing temperature  $T_f$  should be a function of probe time. The experimental support for such a view comes from two classes of experiments. For certain SG the a.c. susceptibility measurements do show a dependence of freezing temperature on frequency<sup>4</sup>. In neutron scattering measurements on AuFe, Murani<sup>3</sup> has found definite evidence to conclude that the onset of freezing, as indicated by the onset of diffuse elastic scattering, occurs at different temperatures, dependent upon the energy resolution. This is indicative of the fact that the system dynamics contains processes whose relaxation times cover a wide range. Thus as the energy window, is increased more and more, such processes are included in the elastic part and the freezing appears to set in at higher temperatures.

The major challenge posed before SG theories is to understand phase transition or sharp viscous freezing in a system where the effects of disorders are very strong and nontrivial. In the traditional theories of phase transition, the mutual interaction between the degrees of freedom have a tendency to produce order i.e. an alignment of some sort, which competes against disorder favouring thermal energy entering through entropy. At high temperatures, the statistical weight shifts towards states with large disorder while at lower temperatures the states with high alignment or order dominate the statistical sum, leading to the ordered phase. The interactions in the SG, do not produce any spatial order even when they dominate at low temperatures and it is not clear in what precise way, they compete against thermal disorder. Since the spin glass freezing is not accompanied by any spatial long range order, a time dependent description for freezing seems more natural. However, such a time dependent description is not easy to incorporate within the usual statistical mechanics for systems which contain a wide range of time scales.

In the next section we discuss the Hamiltonian, its low energy properties and possible choice of the order parameter which can describe the SG phase. We also present in some detail, the

understanding obtained from numerical calculations on small samples. In the third section, we review the statistical mechanical theories, which have been developed to describe the SG transition. In the last section, we briefly describe the dynamical theory for the transition and some other ideas which have been found useful.

## 2. THEORETICAL MODELS: LOW TEMPERATURE PROPERTIES.

Let us now turn our attention to the basic theoretical models which are used to understand SG magnetism. As in the other types of magnetism, the basic model used is the random version of Heisenberg model and its simplified cousin, the Ising model. Edwards and Anderson (EA) were the first to introduce the following Hamiltonian<sup>5</sup>

$$H = \frac{1}{2} \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j \quad (2.1)$$

where the spin  $\vec{S}_i$ 's lie on a regular lattice whose sites are denoted by  $i$  and  $J_{ij}$ 's are random variables which are non-zero for nearest neighbours and have a common probability distribution  $P([J_{ij}])$  for all pairs. EA took the probability distribution to be gaussian, so that the Hamiltonian contains only two coupling parameters

$$P(J_{ij}) = (2\pi\bar{J}^2)^{-1/2} \exp\left[-\frac{(J_{ij}-J_0)^2}{2\bar{J}^2}\right] \quad (2.2)$$

In the original EA model  $J_0 = 0$ . The idea behind, these abstractions is that the important elements of the SG physics are randomness and conflicting interactions, the particular form of randomness, the form of interaction *e.g.* whether it is RKKY or direct exchange, being irrelevant for general properties, whose understanding should be the first goal of the theory.

The element of conflict can easily be understood if we consider a plaquette of four spins as shown in figure 2, interacting via the Hamiltonian of Eq. (2.1). If the signs of interactions are as shown, it is easy to convince oneself, that no spin configuration is possible in which all bonds have the smallest energy. For example if

we keep all the spins up the bond 2-3 remains in its higher state, while if we make spin 2 or 3 down, one of the ferromagnetic bonds remains unsatisfied. One refers to this situation by saying that the plaquette is frustrated<sup>6</sup>. When we consider the complete lattice, the frustration of plaquettes makes the problem of determination of ground state configuration and ground state energy extremely difficult, an impossibility for a macroscopically large system. This underlies the basic difficulty in describing the low temperature or frozen phase of spin-glasses. The randomness and *frustration* makes it very difficult to find a single or a few parameters which characterise the SG state even in a statistical manner. Yet for a theoretical description of the type we are familiar with, a condensed phase is described in terms of one of a few order parameters. The first noteworthy attempt in this direction, which really generated most of the later developments in this field was due to Edwards and Anderson who introduced the order parameter  $q$ ,

$$q = \overline{\langle \vec{S}_i \rangle \cdot \langle \vec{S}_i \rangle} \quad (2.3)$$

where the brackets  $\langle \rangle$  denotes thermal average for a fixed configuration of  $J_{ij}$ 's and the bar denotes the configurational average. When there is no special direction or a spatial pattern for spin ordering,  $q$  which is the magnitude of the spin vector in the frozen state is perhaps the most natural choice. Another definition which adds

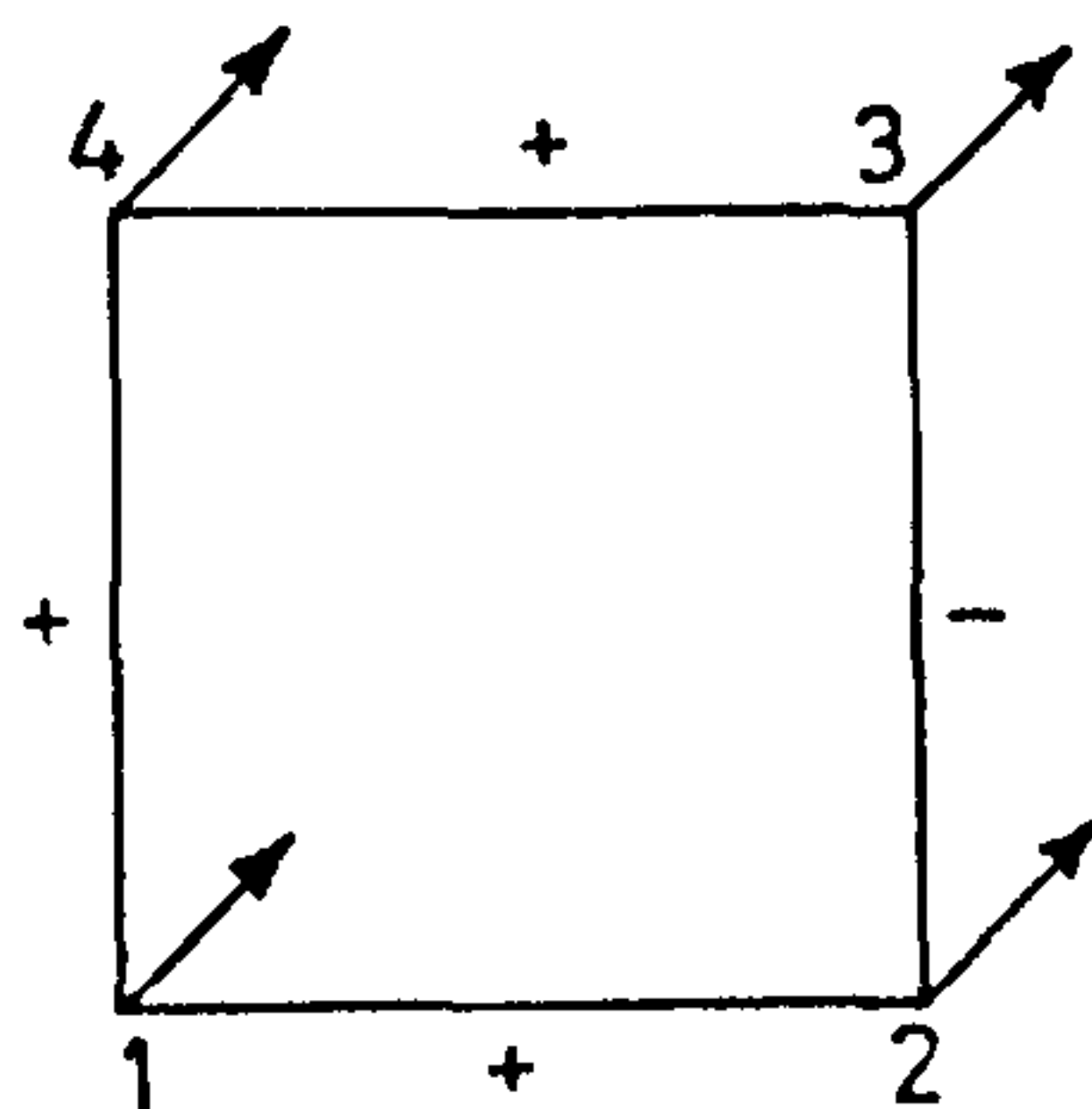


Figure 2. A plaquette of four spins illustrating the concept of frustration.

some physical insight to  $q$ , is to regard it as the infinite time limit of<sup>5</sup>

$$q = \lim_{t \rightarrow \infty} q(t) = \lim_{t \rightarrow \infty} \langle \vec{S}_i(t) \cdot \vec{S}_i(0) \rangle. \quad (2.4)$$

This is essentially a measure of time persistence of the direction of the spin vector in the frozen state. Note how these definitions enable one to distinguish between the frozen state and the paramagnetic state. If we took a snap shot of the paramagnetic state, it would be very much like that of a frozen SG state. However, the snap shots of the paramagnetic state, at two fairly different times would show little correlation whereas for the SG state, we should see a pronounced correlation even when the two times are far apart.

The reliable checks about this sort of frozen state and its description in terms of EA order parameter can only be done by computer calculations on some finite spin-systems. The Hamiltonian (2.1), particularly its Ising version has been subjected to a number of Monte-Carlo studies in dimensions two to five<sup>7-9</sup>. There have also been exact calculations of the partition function of small systems,<sup>10-11</sup> which have shed considerable light on the nature of low energy states and the kind of ordering which is implied by Eq. (2.1). The Monte-Carlo (MC) calculations on Ising systems show features very much like experiments, *i.e.* a cusp in susceptibility, a broad maxima in specific heat, a non-zero value of the EA order parameter below the freezing temperature  $T_f$  and a very slow power law relaxation below  $T_f$ . Results for Ising systems are similar for all dimensions between two to five. However, the slow relaxation and some later exact numerical calculations lead us to believe that the MC results do not correspond to equilibrium. Bray *et al*<sup>12</sup> had made this suggestion initially by looking at longer Monte-Carlo runs. The matter was however confirmed by Binder and Morgenstern<sup>10</sup>, who performed exact calculations for small samples of two dimensional Ising model. By extrapolating their results to  $N \rightarrow \infty$  ( $N$  denotes the number of spins in the sample) they concluded that the equilibrium statistical mechanical averages do not show any transition in two dimensions and the various features of the MC calcu-

lations are non-equilibrium effects. Recently, Young and Kirkpatrick<sup>11</sup> have chosen to do exact statistical calculations on small samples of the infinite-ranged model, for which various theoretical calculations have established that a transition must occur. They do notice the transition but also find that the characterisation of the low temperature phase is far from adequate.

The picture of the low temperature phase which has emerged from MC and other numerical calculations is the following.<sup>9, 13</sup> The first point is that the Hamiltonian of Eq. (2.1) has a very large number of metastable states of order  $\exp(\alpha N)$ . The metastable states themselves are grouped in valleys in phase space. The phase space between different valleys and the ground state of respective valleys are quite orthogonal to each other, the overlap between such ground states being of the order  $N^{-1/2}$ . The metastable states within a given valley require reversals of a small number of spins, whereas the ground states of different valleys are separated by large energy barriers and require turning of a very large number of spins. A pictorial understanding of the situation can be obtained in terms of figure 3. Here we plot constant energy surfaces as the function of a typical phase space coordinate. One sees that at higher energies, the energy surface is continuous and well spread over the entire phase space. On the other hand, at lower energies, constant energy surfaces are divided into small pockets in phase space. In terms of this picture, one visualises the low temperature properties of the system as follows. As the energy of the system is lowered, the system falls into one of the valleys in phase

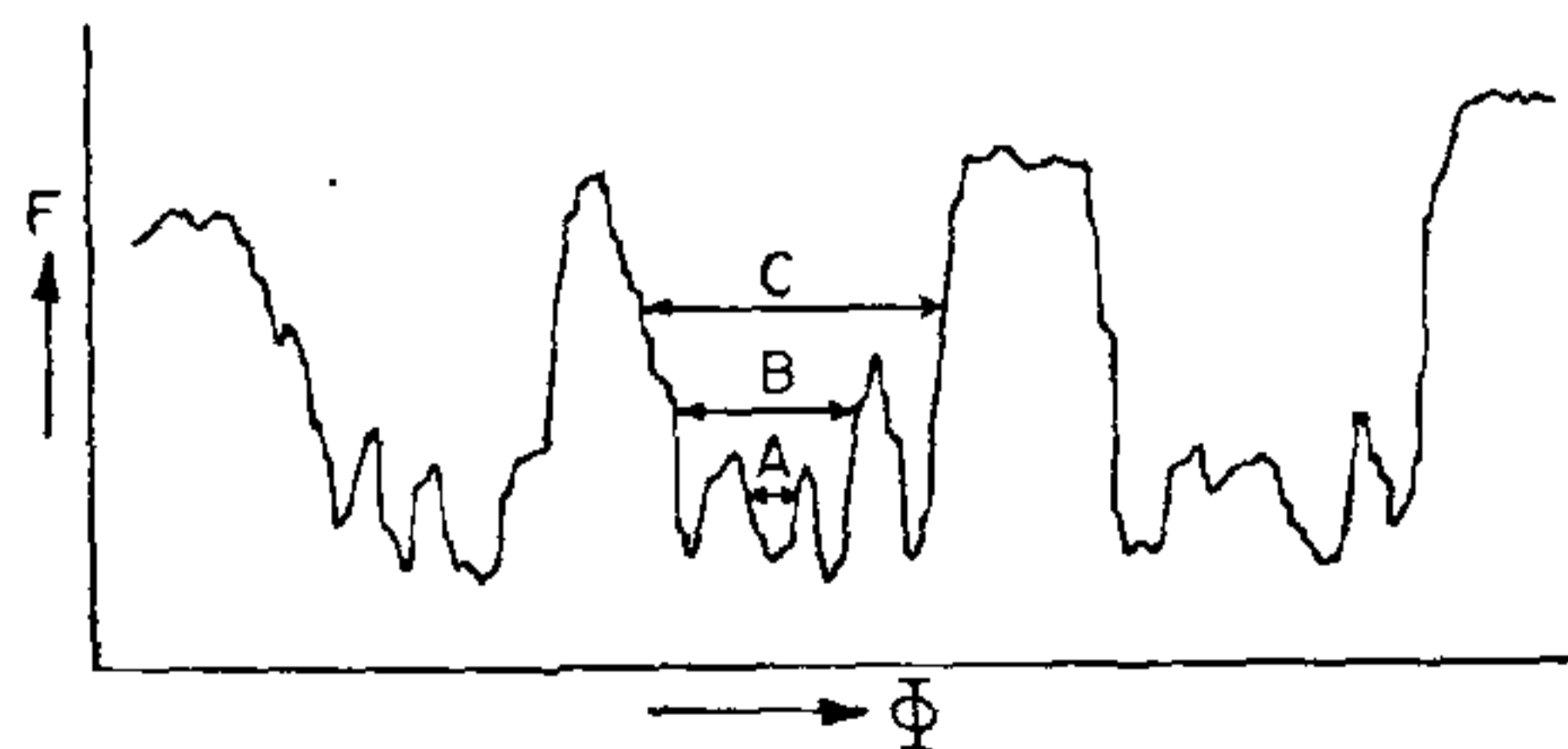


Figure 3. A schematic diagram of free energy plotted against a typical variable of phase space.

space and at some stage, other parts of the phase space become inaccessible to it on the time scales of the experiment. In low temperature MC calculations, the system is probing the energy surface in one valley only, because to jump to equal energy states of other valleys requires reversals of very large number of spins. For Ising spins the cause of slow relaxation within a given valley is the presence of a large number of metastable configurations, which can be escaped by reversal of a few spins only. (For vector spins, such metastable configurations are less likely due to the additional degrees of freedom. Walstedt and Walker<sup>13</sup>, instead find that the bottoms of the valleys have very small curvature in certain directions.) One might ask at this stage as to why should one expect a sharp and unique freezing temperature in this picture. The reason seems to be that the ground states of various valleys have nearly the same energy, and there is a rather well defined energy below which migration, between energy wells ceases on time scales of the simulation. Walker and Walstedt<sup>13</sup>, working in micro-economical ensemble, have identified the freezing temperature with this energy, in reasonable accord with experiments on Cu-Mn.

On the basis of this picture the cause for discrepancy between Monte-Carlo results and the results based on Statistical Mechanics becomes quite clear. In Statistical Mechanics, one sums over states from the entire phase space, including states which are quite inaccessible to the system at low temperatures. In fact, it is quite straight-forward to see that for the symmetric Hamiltonian of Eq. (2.1), the thermal average  $\langle \vec{S}_i \rangle$  is strictly zero in the absence of an external field. The situation is quite analogous to a ferromagnet, where due to the degeneracy of the ground state, the statistical mechanical average  $\vec{S}_i$  is again zero. The well known prescription to discuss low temperature properties, is to put on, an infinitesimal external field of the order  $(1/N)$ , which restricts the statistical sum to states in the neighbourhood of one of the ground states. More precisely, though

$$\lim_{N \rightarrow \infty} \frac{1}{N} \sum_i \langle \vec{S}_i \rangle_{h \rightarrow 0} = 0 \quad (2.5)$$

the average

$$\lim_{h \rightarrow 0} \lim_{N \rightarrow \infty} \sum_i \langle \vec{S}_i \rangle_h \neq 0. \quad (2.6)$$

Can one not do something similar for sgs too? The first point to note is that the various ground states in this case are not selected by any symmetry. Secondly, there is no simple field by which one can select a particular ground state (For small systems one can calculate such a staggered field, but a knowledge of such staggered field for various ground states of a macroscopic system is clearly impossible.) Young and Kirkpatrick<sup>11</sup> point out that in the presence of a uniform field or a random staggered field, both of which are equivalent, as far as their coupling to a particular ground state is concerned, the order parameter  $q$  is non-zero, but is not equal to that obtained from time-averaging as in MC calculations, *i.e.*,

$$q_{TA} = \overline{\left( \frac{1}{T} \int_0^T S_i(t) dt \right)^2} \quad (2.7)$$

$$q = \lim_{h \rightarrow 0} \lim_{N \rightarrow \infty} \frac{1}{N} \sum_i \langle S_i \rangle_h \neq 0 \quad (2.8)$$

$$\neq q_{TA} \quad (2.9)$$

The last inequality follows from the fact, that since the uniform field has a projection on a ground state which is of the order  $N^{1/2}$  only, it does not restrict the statistical sum to states in the neighbourhood of one ground state only.

### 3. SPIN-GLASS TRANSITION: MEAN FIELD THEORY

Having seen the difficulties in finding a suitable order parameter for the sg state, let us now consider the theory of transition, first proposed by Edwards and Anderson (EA)<sup>5</sup>. The main difficulty which occurs in the calculations of the statistical mechanics of random systems is the calculation of the free energy averaged over random configurations *i.e.*

$$F = -k_B T \langle \log Z \{ J_{ij} \} \rangle \quad (3.1)$$

$$Z \{ J_{ij} \} = Tr \exp [ -\beta H \{ J_{ij} \} ] \quad (3.2)$$

where  $\beta = (k_B T)^{-1}$ . Configuration averaging of

$\log Z$ , even in the simplest approximation, presents considerable difficulties. On the other hand, the configuration averaging of  $Z\{J_{ij}\}$  is not difficult. EA dealt with this problem by the following mathematical trick, which has come to be known as 'Replica Trick'. We can write

$$\overline{\log Z} = \lim_{n \rightarrow 0} \frac{1}{n} (\overline{Z^n} - 1) \quad (3.3)$$

Now  $Z^n$  can be calculated for integral values of  $n$  by noting that it is the partition function of  $n$  non-interacting and identical replicas of the system, with the same set of  $\{J_{ij}\}$ . Thus

$$Z^n = \left[ \int \prod_{i=1}^n d\vec{S}_i \exp \left\{ -\frac{\beta}{2} \sum_{i,j} \vec{S}_i \cdot \vec{S}_j \cdot J_{ij} + \beta h \sum_i S_{zi} \right\} \right]^n \quad (3.4)$$

$$= \int \prod_{i=1}^N \prod_{\alpha=1}^n d\vec{S}_i^\alpha \exp \left\{ -\frac{\beta}{2} \sum_{\alpha} \sum_{ij} J_{ij} \cdot \vec{S}_i^\alpha \cdot \vec{S}_j^\alpha + \beta h \sum_i S_{zi}^\alpha \right\}. \quad (3.5)$$

One can now perform the configuration averaging on Eq. (3.5). Using the distribution of Eq. (2.3) we have

$$\begin{aligned} \overline{Z^n} &= \int \prod_{(lm)} dJ_{lm} (2\pi J^2)^{-1/2} \\ &\times \exp \left[ -\frac{(J_{lm} - J_0)^2}{2\tilde{J}^2} \right] Z^n \\ &= \int \prod_{i=1}^N \prod_{\alpha=1}^n d\vec{S}_i^\alpha \exp \left\{ -\frac{\beta}{2} \sum_{\alpha=1}^n \sum'_{ij} J_0 \vec{S}_i^\alpha \cdot \vec{S}_j^\alpha \right. \\ &\quad \left. + \beta h \sum_i S_{zi}^\alpha + \frac{\beta^2 \tilde{J}^2}{2} \sum'_{i,j} \left( \sum_{\alpha=1}^n \vec{S}_i^\alpha \cdot \vec{S}_j^\alpha \right)^2 \right\} \quad (3.6) \end{aligned}$$

where the prime on summation implies that the double sum goes over nearest neighbours only.

Let us now look at the effect of these mathematical operations. We have performed the configuration averaging and obtained an expression in which one has to calculate the partition function of a uniform system. The price paid is (a) the number of integration variables has been raised from  $N\vec{S}_i$  variables to  $nN\vec{S}_i^\alpha$  variables.

There are additional 4-spin interaction terms, in which spin variable of one replica interact with variables of the other replicas (b) at the end of the calculation implied in Eq. (3.6), one has to treat  $n$  as a continuous variable and take the limit  $n \rightarrow 0$ .

The first point here seems akin to the usual difficulties that are encountered in any general problem of statistical mechanics, and the natural way to proceed would be to formulate a mean field approximation. However, for this purpose, one needs to define an order parameter. The definition of an order parameter is quite straight forward for systems where one knows how the symmetry of the high temperature phase, which is the same as that of the Hamiltonian, is broken when the system undergoes the transition. The SG situation forces us to examine afresh this natural procedure. The reason is that definition of the order parameter and its non-zero values contain implicit information about the broken symmetry of the low temperature phase. Below transition temperature, the system can occur in a number of different phases which are related to each other, in ordinary systems, by simple symmetry operations. In order to describe a single condensed phase one must break the ergodicity i.e. restrict the usual canonical sum over states to a particular neighbourhood in phase space dictated by the order parameter. For a ferromagnet, application of a small magnetic field achieves this. The difficulties in the description of the SG state arise because we have no simple way to describe the symmetry breaking in condensed phase and no simple procedure for restricting the canonical sum so that it runs over states of one phase only.

To clarify these points further, let us follow the historical development of the subject by describing the mean field theory of EA. To restrict mathematical complexity, we consider only Ising spins and take  $J_0 = 0$ . Then from (3.6)

$$\begin{aligned} \overline{Z^n} &= \sum_{\{S_i^\alpha\}} \exp \left[ \beta h \sum_{i,\alpha} S_i^\alpha + \beta^2 \tilde{J}^2 \left\{ \sum_{(\alpha\beta)} \sum_{ij} \right. \right. \\ &\quad \left. \left. \times \Delta_{ij} (S_i^\alpha S_i^\beta) (S_j^\alpha S_j^\beta) + \frac{Nz}{2} n \right\} \right] \quad (3.7) \end{aligned}$$

where  $(\alpha\beta)$  indicate all the distinct pairs in which  $\alpha \neq \beta$ , the matrix  $\Delta_{ij} = 1$ , if  $i$  and  $j$  are nearest neighbours and zero otherwise, and  $Z$  is the number of nearest neighbours. We shall use another form of  $\Delta_{ij}$  later. To do the single site mean field approximation, we reexpress the quartic interaction by an integral transformation.

$$\begin{aligned} & \exp \left\{ \sum_{ij} \Delta_{ij} (S_i^\alpha S_i^\beta) (S_j^\alpha S_j^\beta) \right\} \\ &= C \left\{ \prod_i dy_i^{\alpha\beta} \exp \left[ -\frac{1}{4} \sum_{ij} y_i^{\alpha\beta} \Delta_{ij}^{-1} y_j^{\alpha\beta} \right. \right. \\ & \quad \left. \left. + \beta \tilde{J} \sum_i y_i^{\alpha\beta} S_i^\alpha S_i^\beta \right] \right\} \end{aligned}$$

which gives

$$\begin{aligned} \overline{Z^n} = C & \left\{ \prod_{(\alpha\beta)} \prod_i dy_i^{\alpha\beta} \exp \left[ -\frac{1}{4} \sum_{(\alpha\beta)} \sum_{ij} y_i^{\alpha\beta} \right. \right. \\ & \quad \times \Delta_{ij}^{-1} y_j^{\alpha\beta} + \sum_i \log \sum_{\{S^a\}} \\ & \quad \left. \left. \times \exp \left( \beta h \sum_a S^a + \beta \tilde{J} \sum_{(\alpha\beta)} y_i^{\alpha\beta} S^a S^b \right) \right] \right\} \end{aligned} \quad (3.8)$$

where  $C$  is an unimportant constant. In the single site approximation, the functional integral of (3.8) is evaluated by the method of steepest descent and finding a maxima in the subspace in which  $y_i^{\alpha\beta}$  is independent of  $i$ . Thus the problem reduces to finding the maximum of the expression

$$\begin{aligned} & -N \left[ \frac{1}{4Z} \sum_{(\alpha\beta)} (y^{\alpha\beta})^2 \right] - \log \sum_{\{S^a\}} \exp \left[ \beta \left\{ h \sum_a S^a \right. \right. \\ & \quad \left. \left. + \tilde{J} \sum_{(\alpha\beta)} y^{\alpha\beta} S^a S^b \right\} \right] \end{aligned} \quad (3.9)$$

with respect to  $n(n-1)/2$  variables,  $y^{\alpha\beta}$ . The minimisation equation reads,

$$y^{\alpha\beta}/2 = \beta J \langle S^\alpha S^\beta \rangle_{H_1} \quad (3.10)$$

where the averaging is performed with respect to the single site Hamiltonian  $H_1$ ,

$$H_1 = -h \sum_a S^a - \tilde{J} \sum_{(\alpha\beta)} y^{\alpha\beta} S^\alpha S^\beta \quad (3.11)$$

To obtain the self-consistent solution for (3.10) EA made the simplest possible assumption of taking all  $y^{\alpha\beta}$  to be equal, which really seems to be reasonable in view of the fact that all replicas are identical.

Denoting  $\langle S^\alpha S^\beta \rangle$  by  $q$ , one finds that  $q$  obeys the self consistent equation ( $n \rightarrow 0$  limit is taken at this state)

$$q = \int \exp(-x^2/2) \tanh^2 \left[ (Zq)^{1/2} \beta \tilde{J} x + \beta h \right] \frac{dx}{\sqrt{2\pi}} \quad (3.12)$$

Eq. (3.12) implies that  $q = 0$  if the temperature  $T$  is above  $T_f$ , given by

$$T_f = \tilde{J} Z^{1/2} / k_B \quad (3.13)$$

For  $T < T_f$ ,  $q$  takes on, non-zero values, becoming unity at  $T = 0$ . For  $T \leq T_f$

$$q = \frac{1}{2} (1 - T^2/T_f^2) \quad (3.14)$$

Thus the SG phase is characterised by a non-zero value of  $q$ , which EA argued is equivalent to the definition in Eq. (2.3). The corresponding free energy in this approximation comes out to be

$$\begin{aligned} F/N = -k_B T & \left[ Z \beta^2 \tilde{J}^2 (1-q)^2 / 2 + \frac{1}{\sqrt{2\pi}} \int dx \right. \\ & \quad \left. \times \exp(-x^2/2) \log 2 \cosh \beta (h + \tilde{J} (Zq)^{1/2} x) \right] \end{aligned} \quad (3.15)$$

From Eq. (3.15) the expression for susceptibility follows to be

$$\chi = \beta(1-q) \quad (3.16)$$

This expression exhibits cusp at  $T_f$ . For  $T > T_f$ , it has a Curie like behaviour, but as temperature is decreased below  $T_f$ , it starts decreasing abruptly due to development of non-zero values of  $q$ . Qualitative agreement with experiments is remarkable.

The difficulties of this elegant scheme showed up, when Sherrington and Kirkpatrick (SK)<sup>14</sup> realised that the above equations are exact for the infinite ranged model for which  $z \rightarrow N$  and

$J^2 \rightarrow 0$  such that  $nJ^2$  has the finite limit  $J_1^2$ . If the above solution is exact, it should hold at all temperatures. But it was found that at low temperatures, the solution gives negative entropy, which is an unphysical result. Tracing of this difficulty, led to the finding that the replica symmetric extremum of (3.9) as chosen by EA is not a true maxima, but rather a saddle point<sup>15</sup>. This implies an apparently strange consequence that the values of  $y^{x\beta}$  giving the minimum free energy break symmetry with respect to replicas. There is no physical reason to treat different replicas differently as they are introduced simply to calculate  $Z^n$ .

Thus the strange problem at hand is to find the proper extremum point, which makes a distinction among equivalent replicas, and yields reasonable final answer when the  $n \rightarrow 0$  limit is taken. One can immediately see that there are any number of ways to break replica symmetry and search for extrema for a general  $n$  would be very difficult. Any practical scheme has to parameterise the matrix  $y^{x\beta}$  in terms of a few variables and search for extrema in this limited space.

The problem was first tackled by increasing the number of order parameters to two, which led to improvements but did not eliminate the difficulty. Parisi<sup>16</sup> invented a scheme to break replica symmetry in a way which allowed introduction of successively increasing number of order parameters. He was then able to obtain a very reasonable solution by introducing an infinity of order parameters  $q(x)$  labelled by a continuous variable  $x$  defined in the interval  $(0, 1)$ . This is certainly an odd resolution, because the number of order parameters is supposed to be small and related to the symmetry breaking of the condensed phase. But as noted in the previous section, the description of condensed phase in terms of a few order parameters is not known, due to our ignorance of the nature of symmetry breaking in the SG transition.

Recently Parisi<sup>17</sup> has offered a very nice physical interpretation to the continuum of order parameters introduced above. The canonical prescription to calculate the statistical expectation value is

$$\langle O[S_i] \rangle = \frac{\sum_{[S_i]} O([S_i]) \exp[-\beta H]}{\sum_{[S_i]} \exp[-\beta H]} \quad (3.17)$$

where  $O([S_i])$  denotes an observable. This equation is not valid below a symmetry breaking transition, because it does not describe a single thermodynamic phase of the system, but rather a mixture of all possible condensed phases. We can decompose this sum as the sum of pure equilibrium states (i.e. states of single phase)

$$\langle \dots \rangle = \sum_{\alpha=1}^M P_{\alpha} \langle \dots \rangle_{\alpha}, \quad \sum_{\alpha} P_{\alpha} = 1 \quad (3.18)$$

where  $\alpha$  denotes a pure thermodynamic phase and  $P_{\alpha}$  is a probabilistic weight given to the phase  $\alpha$ . The results of Monte-Carlo calculation show clearly that for spin-glasses, the configuration space consists of many valleys separated by high mountains whose height goes to infinity in the thermodynamic limit. Since for all practical purposes, the system will not jump from one valley to another, each of these valleys can be regarded as configuration space, belonging to a single condensed phase. We can characterise a phase by the value of the magnetisation in each site:

$$m_i^{\alpha} = \langle S_i \rangle_{\alpha} \quad (3.19)$$

For each phase, we can construct an EA order parameter

$$q_{EA}^{\alpha} = \frac{1}{N} \sum_{i=1}^N \langle S_i \rangle_{\alpha}^2 \quad (3.20)$$

It is quite reasonable that in the infinite volume limit all states have the same value of  $q_{EA}^{\alpha}$ . A disadvantage with the definition of  $q_{EA}$  is that it is different from zero also for normal ferromagnetic or antiferromagnetic systems. Something which characterises a spin glass, or a glassy state in general, can be obtained by studying the overlap of magnetisations between two different phases:

$$q^{x\beta} = \sum_{i=1}^N m_i^x m_i^{\beta} / N. \quad (3.21)$$



$$P(q) = \sum_{\alpha, \beta} P_{\alpha} P_{\beta} \delta(q - q^{\alpha\beta}) \quad (3.22)$$

where  $P(q)$  is clearly the probability distribution of  $q^{\alpha\beta}$ . Parisi<sup>17</sup> now introduces the function  $x(q)$  where

$$x(q) = \int_{-\infty}^q dq P(q) \quad (3.23)$$

which is monotonic and is obviously defined in the interval 0-1. Now the inverse function  $q(x)$  has the following significance. If we have only pure phases which do not differ macroscopically, the function  $q(x)$  is a constant. If the function  $q(x)$  is not a constant, macroscopically different pure phases exist. Thus a variable  $q(x)$  is an essential characteristic of the glassy phase. Parisi has given an explicit demonstration of the equivalence between  $q(x)$  defined in (3.23) and the one obtained in his replica theory. With this, it becomes clear that the mysterious breaking of replica symmetry is just the mathematical transcription of the existence of infinitely many macroscopically distinct pure thermodynamic states. Use of single order parameter would ignore the fact that the condensed phase is not unique.

#### 4. TIME DEPENDENT PROPERTIES

The time dependent behaviour of spin glasses also presents several complexities, foremost among them being, very slow magnetic relaxation, and strong dependence of the behaviour on magnetic history, including hysteresis. As discussed in Sec. 2, much of this behaviour can be understood on the basis of figure 2, which shows that the free energy contains several deep valleys in phase space, and each valley itself contains smaller hills and valleys. In a situation like this, the system has to tunnel through several metastable states successively (or parts of it tunnel through barriers of different heights) which lead to slow power law like decays to equilibrium. The reason for hysteresis also becomes apparent when one realises that there is no one-to-one correspondence between states of different valleys, once the magnetic field is switched on. For example, if the lowest free energy state in the

presence of the field is in one valley, while that in the absence of the field is in another valley, the system would naturally get trapped, in a metastable state, when the field is switched on or off from the equilibrium state, and there would be hysteresis.

The role of observation time in such a situation has been strongly emphasised by Palmer<sup>18</sup>. Referring to figure 2, note that for a small observation time (or temperature) the system may be stuck in the phase region denoted as A, but for longer times, it may cross smaller barriers and be confined to a bigger valley C. Thus the statistical sums used to calculate average properties will depend upon the observation time. More and more states have to be included as the observation time becomes bigger. Though it is not often realised or explicitly stated, this is something which is practised in almost any calculation. Depending upon the time scale of the process, one limits the degrees of freedom to be included in the calculation. A nice example provided by Palmer<sup>18</sup> is that of adding milk to an uncovered cup of hot coffee. Three processes occur with varying time scales. First there is mixing which occurs in seconds, then there is cooling to the room temperature which occurs over minutes and finally there is evaporation which occurs over a period of hours. Since the time scale of the three processes are fairly separated, the statistical mechanical description for each process can be given in terms of a Hamiltonian which involves certain relevant degrees of freedom. For instance, to describe mixing, one can ignore the degrees of freedom for evaporation and introduce a heat bath to inhibit cooling. Working with this restricted set of degrees of freedom, usual methods of statistical mechanics can be employed which amount to taking observation time to infinity. Such simplification in the above example is possible only because the time scales of different processes are well separated. Another way to view the difficulties of SG physics is the presence of a wide continuum of relaxation times and lack of our ability in selecting fast degrees of freedom from the slower ones.

The infinite ranged model for which maximum theoretical progress has been achieved shows such a continuum of relaxation times. Sompolinsky<sup>20</sup> has associated the  $x$ -parameter of Parisi with the various time scale  $t_x$  in the problem;  $t_x$  corresponds to tunnelling between valleys, with  $x$  being a measure of distance between valleys in the configuration space. Sompolinsky<sup>21</sup> has developed a time dependent mean field theory which uses the correlation function  $q(t)$  of Eq. (2.4) as the order parameter. His calculation brings out very clearly how the randomness induces time-persistent correlation which gives rise to SG freezing.

17 March 1984

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