

**Systematic Treatment  
of a Realistic Spin Glass Model**

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**Abstract**

A spin glass is described as a system of spin-bearing particles that are quenched with respect to translational degrees of freedom in continuum space. We use the continuum replica method to develop density expansions for the thermodynamic quantities, and Ornstein-Zernike equations for the two-particle correlation functions.

In this work we provide for the first time an exact, systematic basis for the treatment of a continuum spin glass [1]. This is a non-lattice, configurationally disordered spin system in which the translational degrees of freedom are quenched and the spin degrees of freedom are in thermal equilibrium. Specifically, we consider a system of hard-sphere particles whose positions are quenched in place in a liquid-like state of order. The particles have spins at their centers, and these are free to equilibrate under the influence of a separation-dependent exchange interaction.

In earlier work [11], the spin-fluid version of the model (in which both the positions and spins of particles are in equilibrium) was introduced and solved in the mean-spherical approximation (MSA) and the closely related lowest-order gamma-ordered approximation (LOGA). The spin glass version was subsequently discussed in the same approximation [1]. Various approximate theoretical calculations have been performed on continuum spin liquid models [12]; also, some simulation data is available [13]. However, no systematic theory has been previously published [14].

The replica method we use allows one to extend liquid-state theory to partly quenched systems in which some of the particles are quenched or frozen in place and the rest are annealed or allowed to equilibrate. The method provides an isomorphism between the correlations of such a system and the limiting correlations of a corresponding fully equilibrated system, which we shall call replicated system. This system consists of one replica, or copy, of the annealed species, together with  $n$  replicas of the annealed species, with the potential interactions between particles being exactly those of the partly quenched system, **except** that annealed particles in different replicas don't interact. The properties (e.g., correlation functions) of this system in the replica limit  $n \rightarrow 0$  immediately yield corresponding properties of the partly quenched system as we discuss below [A]. This isomorphism provides Mayer expansions and integral equations for the correlation functions; the latter are the replica Ornstein-Zernike equations. Results for such systems, which overlap our results, have been obtained by Madden and Glandt [17,18]. A very closely related use of the replica

method has been made by Stratt [15,16] to study somewhat different problems.

In this paper, we extend the replica method to treat systems in which the quenched and annealed degrees of freedom refer to the same particles. To do this, we temporarily consider spin-atoms to be a mixture of two species (“atoms” and “spins”), the first quenched and the second annealed (i.e., equilibrated). Spins and atoms are bound together in pairs by a short-range attractive force which can be made arbitrarily strong by tuning a strength parameter that characterizes the spin-atom binding energy.[6] The replica method is used to replace the quenched system of spins with an equilibrated mixture of  $n$  copies of the spins. We then impose the constraint of complete association of spin-atom pairs. This gives an equilibrium system of “spin-molecules”, each of which consists of an atom with  $n$  spins (one from each replica) bound to its center.

We use two equivalent descriptions of the replicated spin glass. Each furnishes a valuable method of dealing with the nontrivial  $n \rightarrow 0$  replica limit. In the first, the “atomic” picture, we use the interaction-site formalism, developed to deal with molecules that contain an unspecified number of particles (a spin-molecule contains  $(n + 1)$  particles with  $n$  variable). We write down the site-site Ornstein-Zernike (SSOZ) equations and show that the symmetries of the Heisenberg interaction enable us to collapse these equations to give one single integral equation for the spin-spin correlation function. We give closures of Percus-Yevick (PY) and hypernetted-chain (HNC) type for this equation. The SSOZ is not “proper”, in the sense that its direct correlation function cannot be expressed as a sum of Mayer-graphs [B], and for this reason PY-type and HNC-type closures cannot be readily improved in a systematic way. One can hope to remedy this situation by introducing “proper” SSOZ equations [B,C], which we do here for our system. Simple closures (of PY and HNC-type) or our proper equations yield no difference between spin-fluid and spin-glass spin-spin correlation functions; we expect that rather sophisticated closures will be necessary to capture these rather subtle differences using the proper SSOZ formalism.

In our second description of the spin glass, the “molecular” description, the replica

method is applied somewhat more directly to the spin degrees of freedom. In this description, we combine the  $n$  replicas of a Heisenberg spin into a single  $3n$ -component spin, then use what we call the "self-avoiding walk (SAW) approximation" to take the  $n \rightarrow 0$  replica limit.

We consider then a system of spin-atoms having their positions quenched but their spins free to equilibrate. We assume the atomic positions to be quenched according to a Gibbs distribution defined by the hard sphere potential  $v_{HS}(x)$ . The interaction  $v_{11}(ij)$  between a pair of spins  $i$  and  $j$ , both constrained to be of unit length, is taken to be a classical Heisenberg interaction

$$v_{11}(ij) = J(x_{ij})(\vec{s}_i \cdot \vec{s}_j) \quad (1)$$

where the dot product between the vector spins located at atoms  $i$  and  $j$  is multiplied by the separation-dependent exchange coupling  $J(x_{ij})$ . In many materials a reasonable form for  $J(x)$  is provided by the sinusoidally modulated coupling

$$J(x) = \frac{\exp[-\kappa x]}{x^p} \sin[\alpha x + \theta] \quad (2)$$

where  $\kappa = 0$  and  $p = 3$  is the case of the usual RKKY interaction.

The fact that the sign of this exchange coupling varies rapidly as the separation between spin-atoms changes gives rise to the competition between spin-spin interactions which is characteristic of the spin-glass state.

The free energy of this system, averaged over quenched degrees of freedom, is

$$-\beta F = \langle \ln Z_1 \rangle = \frac{1}{Z'} \int e^{-\beta H_{00}} \ln Z_1 d\vec{0} \quad (3)$$

with

$$Z' \equiv \int e^{-\beta H_{00}} d\vec{0} \quad (4)$$

and

$$Z_1 \equiv \int e^{-\beta H_{11}} d\vec{1} \quad (5)$$

Here we write  $H_{00}$ , resp.  $H_{11}$ , for the sum of all atom-atom (hard-sphere) interactions, resp., all spin-spin interactions. Also, we write  $d\vec{0}$ ,  $d\vec{1}$ , to represent integration over the translational, resp., spin degrees of freedom. The average in (3) is difficult to treat analytically because of the presence, under the integral sign, of the logarithm. We thus make use of the replica trick, which consists of replacing the logarithm with an exponential by using the identity

$$\ln Z_1 \equiv \lim_{n \rightarrow 0} \frac{1}{n} [Z_1^n - 1] \quad (6)$$

Substituting (6) into (3) gives, for the quenched free energy

$$-\beta F = \lim_{n \rightarrow 0} \frac{1}{n} \frac{1}{Z'} \int \left\{ \exp \left[ -\beta \sum_{i=1}^n H_{11}^{(i)} \right] - 1 \right\} \exp \left[ -\beta H_{00} \right] \{d\vec{1}\} d\vec{0} \quad (7)$$

The spins have been replicated and now appear in  $n$  copies, in accordance with (4). We number these copies, or replicas,  $1, 2, \dots, n$ . The notation  $\{d\vec{1}\}$  indicates an integration over the  $n$  sets of configuration variables corresponding to these particles. Eqn. (7) shows that a spin glass is equivalent to a limiting case of a fully quenched system of spin-molecules, each consisting of a hard-sphere atom with  $n$  spins, one from each replica, located at its center. This system of spin-molecules has the Hamiltonian

$$H = \sum_{\langle i,j \rangle} v_{HS}(i,j) + \sum_{\alpha, \beta=1}^n \sum_{\langle i,j \rangle} J(ij) [s_i^{(\alpha)} \cdot s_j^{(\beta)}] \delta_{\alpha\beta} \quad (8)$$

Here  $\alpha$  and  $\beta$  are dummy indices that label the replicas or copies of the spin variables  $s_i, s_j$ . We note that, according to the Kronecker delta on the RHS of (8), pairs of spins interact only when they belong to the same replica.

For a general spin-spin interaction, the site-site functions of the replicated system satisfy a set of site-site Ornstein-Zernike (SSOZ) equations for the site-site (or intermolecular) correlation functions of a system of spin-molecules

$$h_{ij} = \sum_{k,\ell} \omega_{ik} c_{k\ell} \omega_{\ell j} + \sum_{k,\ell} \omega_{ik} c_{k\ell} h_{\ell j} \quad (9)$$

with the subscripts taking the values 0 (for atoms) and  $1, \dots, n$  for spins in the different replicas. Here  $\omega_{ij}$  is the intramolecular correlation function

$$\omega_{ij} = \lim_{L \rightarrow 0} \left[ \delta_{ij} + \frac{1}{4\pi L^2} (1 - \delta_{ij}) \delta(x - L) \right] \quad (10)$$

and  $L$  is the separation between a spin and an atom. We group together identical terms in eqn. (9) and take the  $n \rightarrow 0$  limit to give the SSOZ equations for a spin glass. It is valuable to separate out from each correlation function its average over spin orientation, denoted by a bar, and the orientation-dependent remainder, denoted by a tilde. Thus, for example  $h_{ij} = \bar{h}_{ij} + \tilde{h}_{ij}$ .

For interactions having the symmetry of the Heisenberg interaction, great simplifications are possible in the  $L \rightarrow 0$  limit, which we take after averaging over orientation. In such cases, we have

$$\tilde{h}_{10} = \tilde{h}_{12} = 0 \quad (11)$$

In the complete-association limit, the positions of atoms and spins must coincide. Thus we have for a general spin-spin interaction

$$\bar{h}_{11} = \bar{h}_{10} = h_{00} \quad (12)$$

where  $h_{00}$  is a hard-sphere correlation function. Using eqns. (10-11) to simplify eqn. (9) gives an Ornstein-Zernike (OZ) equation for  $\tilde{h}_{11}$

$$\tilde{h}_{11} = \tilde{c}_{11} + \rho \tilde{c}_{11} \otimes \tilde{h}_{11} \quad (13)$$

An appropriate HNC closure is

$$\tilde{c}_{11} = \tilde{h}_{11} - \ln \widetilde{g}_{11} \quad (14)$$

where  $f_{11}$  and  $y_{11}$  are defined by  $1 + f = \exp = \beta v_{11}$  and  $g_{11} = (1 + f_{11})y_{11}$ . This constitutes a ‘‘reference’’ HNC closure for the full  $h_{11}$ , since the  $\bar{h}_{11}$  is taken from (12) to

be the exact hard-sphere  $h_{00}$ . The resulting  $\tilde{h}_{11}$  will be different from the HNC result for a spin liquid, despite the similarities of form of the HNC spin-liquid and spin-glass equations for  $\tilde{h}_{11}$ , since  $\bar{h}_{11}$  enters as input in computing  $\ln \widetilde{y}_{11}$ . For the spin-liquid  $\bar{h}_{11}$  is not  $h_{00}$  in either the HNC approximation or an exact assessment. Similar remarks apply to the PY closure

$$\tilde{c}_{11} = f_{11} \widetilde{y}_{11} \quad (15)$$

Because of its linearity in  $v_{11}$ , however, the MSA yields an  $h_{11}$  that is identical in the spin glass and spin liquid, as does the LOGA. This was first surmised (but not demonstrated) in [1].

One approach to going beyond these approximations in a systematic way is to develop a “proper” integral-equation treatment of this system [B,C]. This involves classifying the Mayer graphs that contribute to  $h_{11}$  into four types, according to whether they have neither, one, or both of the root points (representing spins) in such a graph connected directly to type 0 vertices (representing atoms.) The corresponding decomposition of  $h_{11}$  is

$$h_{11} = h_{11}^{00} + h_{11}^{01} + h_{11}^{10} + h_{11}^{11}. \quad (16)$$

The quantities  $\{\tilde{h}_{11}^{ij}\}$  obey a coupled set of OZ equations which generalizes (13) to the form

$$\tilde{h}_{11}^{ij} = \tilde{c}_{11}^{ij} + \sum_{k,\ell} \tilde{c}_{11}^{ik} \otimes \rho^{k\ell} \tilde{h}_{11}^{\ell j}. \quad (17)$$

Here we have  $\rho^{00} = \rho^{01} = \rho^{10} = \rho$  and  $\rho^{11} = 0$ . Systematic closures for the  $\{c_{11}^{ik}\}$  can be developed on the basis of formally exact cluster expansions for these functions that we have derived. In order to explore the differences between the Heisenberg spin glass and spin fluid using (20) one must invoke closures relating  $\tilde{h}_{11}^{ij}$  and  $\tilde{c}_{11}^{ij}$  that include the “elementary” Mayer graphs that contribute to correlation functions; the usual closures of HNC and PY form, which do not include such graphs, yield spin-glass and spin-fluid results for  $\tilde{h}_{11}$  that are identical. This is in contrast to the use of such closures in the context

of the simple SSOZ equation. The necessity of going beyond such closures for “proper” equations in the case of simple molecular models was already clear from the results of [C]. More recently [D] one of us has identified an intrinsic source of difficulty with such closures to be associated with substantial core interpenetrability or core nonadditivity, which are features of our modelling here.

An alternative approximation scheme we have developed is based on mapping spin glass models into interacting self-avoiding walk (SAW) models. This scheme offers a direct method for handling the replica limit  $n \rightarrow 0$ , yielding liquid-state theory for spin-atoms in which the spin-spin correlation function obeys an Ornstein-Zernike equation. To do this, we consider the  $n$  replica spins on a single spin-molecule to form a single  $3n$ -component spin vector  $s_i = (s_i^{(1)} \cdots s_i^{(n)})$ . The SAW approximation consists of setting all moments of this spin vector higher than the second equal to zero. We call this scheme the SAW approximation because it consists of mapping spin-glass models onto interacting models of self-avoiding chains. The relation between the  $n \rightarrow 0$  limit of the  $n$ -vector model and the SAW was originally shown by de Gennes[19]; it is readily seen by examining the Mayer diagram content of this approximation. The Mayer bond for the interaction of two spin-atoms in the corresponding spin liquid can be written

$$f(12) = f_{HS} + e_{HS} \cdot \sum_{k=1}^{\infty} \Phi^k(12) \quad (18)$$

where  $\Phi(12) = -\beta\phi(12)$ , with  $\phi(12) \equiv -\beta J(x)(s_1 \cdot s_2)$ . Using this decomposition, the Mayer series for the correlation function of a spin liquid is given by the sum of all doubly connected graphs with  $\rho$ -vertices, some or no  $f_{HS}$ -bonds, and some or no  $\Phi$ -bonds, with at most one  $f_{HS}$ -bond, but any number of  $\Phi$ -bonds joining any pair of vertices. The Mayer series for the pair correlation function of the corresponding spin glass, in the SAW approximation, is given by that subset of these graphs obeying the further constraint that the  $\Phi$ -bonds form one or more non-intersecting chains, each of which begins and ends at a root vertex.



By extending the argument of de Gennes [19] we can show that the SAW approximation is exact for some spin-glass models; we suggest it is a good approximation for many others. For example, this ansatz can be shown to be exact for the Gaussian spin glass with Hamiltonian

$$\sum_{\langle i,j \rangle} v_{HS}(ij) + \sum_{\langle i,j \rangle} J(ij)(s_i \cdot s_j) - \alpha \sum_i (s_i \cdot s_i) \quad (19)$$

Here the third term generates a Gaussian distribution of spin lengths to replace the Heisenberg-model constraint of constant spin length.

The SAW approximate is also exact when applied to a quantum-mechanical tight-binding model calculation of the density of states of an electron in a liquid. Xu and Stratt[15] showed that the SAW approximation for this problem is a consequence of using the mean-spherical approximation (MSA). However, in certain studies, e.g., of the conductivity of liquids, it is valuable to have the SAW approximation without being forced to use linear approximations like the MSA. We also note that the SAW approximation permits a precise liquid-state formulation of an isomorphism hinted at by Edwards[20] between the localization transition of a randomly hopping electron and the collapse transition of the corresponding SAW.

A more detailed publication that includes derivations and proofs of the results given here is in preparation. We note in passing that our treatment, which has been explicitly carried out for the Heisenberg model, generalizes to a model in which the spins are  $D$ -dimensional vectors. This includes the important case,  $D = 1$ , of Ising spins, for which  $\bar{f}$  and  $\tilde{f}$  for any correlation function  $f$  can be usefully re-expressed as the “sum” and “difference” functions  $f^S$  and  $f^D$ , resp., with  $f^S = (f_{++} + f_{+-})/2$ ,  $f^D = (f_{++} - f_{+-})/2$ , where  $+$  denotes an up spin and  $-$  denotes a down spin. This notation is especially natural when one breaks spin-up, spin-down symmetry with an infinitesimal magnetic field, so that  $\rho_+ \neq \rho_-$ . It is also natural when the  $J(x_{ij})$  of Eq. (1) is a Coulomb interaction. The equations developed here then give a description of a system with quenched ionic

impurities.

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### References

- [1] P.T. Cummings and G. Stell, *Mol. Phys.* **43**, 1267 (1981). See Section 4.
- [2] J. Given, *Phys. Rev. A* **45**, 816 (1992); J. Given, *J. Chem. Phys.* **96**, 2287 (1992)
- [3] G. Stell and J.A. Given, to appear in Vol. 8 of the Condensed Matter Theories Series (Plenum Press, N.Y., 1993).
- [4] J.A. Given and G. Stell, to be published
- [5] G. Stell, "Correlation Functions and Their Generating Functionals", in *Statistical Mechanics and Critical Phenomena*, Vol. 5B C. Domb and M.S. Green, eds.
- [6] H.C. Andersen, *J. Chem. Phys.* **59**, 4714 (1973)
- [7] D. Chandler, H.C. Andersen, *J. Chem. Phys.* **57**, 1930 (1972)
- [8] D. Chandler and L.R. Pratt, *J. Chem. Phys.* **69**, 2925 (1976)
- [10] M.S. Wertheim, *J. Stat. Phys.* **35**, 19, 35 (1984); loc. cit. **42**, 459, 477 (1986); *J. Chem. Phys.* **88**, 1145 (1988)
- [11] J.S. Høye and G. Stell, *Phys. Rev. Lett* **36**, 1569 (1976)
- [12] E. Martina and G. Stell, *J. Stat. Phys.* **27**, 407 (1982); S.L. Carnie and G. Stell, *Phys. Rev. B* **26**, 1389 (1982)
- [13] A. Chakrabarti and C. Dasgupta, *Phys. Rev. Lett.* **56**, 1404 (1986)
- [14] For a review that focuses on lattice models, see K. Binder and A.P. Young, *Rev. Mod. Phys.* **58**, 801 (1986)
- [15] B.C. Xu and R.M. Stratt, *J. Chem. Phys.* **91**, 5613 (1989)
- [16] R.M. Stratt, *J. Chem. Phys.* **80**, 5764 (1984); RM Stratt, in "The Electronic Structure

- of Liquids”, in *Ann. Rev. Phys. Chem.* **41**:175-205 (1990)
- [17] W.A. Madden and E.D. Glandt, *J. Stat. Phys.* **51**, 537 (1988)
- [18] W.G. Madden, *J. Chem. Phys.* **96**, 5422 (1992)
- [19] P.G. de Gennes, *Scaling Concepts in Polymer Physics*, (Cornell Univ, Ithaca, 1988)
- [20] R.A. Abram and S.F. Edwards, *J. Phys.* **C5**, 1183 (1972)
- 
- [A] To avoid confusion we note here that the replicated system itself does **not** simply become the partly quenched system of interest in the replica limit. The isomorphism is rather one that allows us to express, through a mathematical identity, the free energy (and its functional derivations) of the partly quenched system in terms of the limiting free energy (and derivations) of the replicated system. See Eq. (7).
- [B] D. Chandler, R. Silby, and B.M. Ladanyi, *Mol. Phys.* **46**, 1335 (1982).
- [C] P.J. Rossky and R.A. Chiles, *Mol. Phys.* **51**, 661 (1984).
- [D] G. Stell (to be published). In this connection the simple closures share the same deficiency as a closely related first-order thermodynamic perturbation theory for simple models of chemical association. See Y. Zhou and G. Stell, *J. Chem. Phys.* **96**, 1507 (1992).

