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Theory of spin glasses

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Abstract. A new theory of the class of dilute magnetic alloys, called the spin glasses, is proposed which offers a simple explanation of the cusp found experimentally in the susceptibility. The argument is that because the interaction between the spins dissolved in the matrix oscillates in sign according to distance, there will be no mean ferro- or antiferromagnetism, but there will be a ground state with the spins aligned in definite directions, even if these directions appear to be at random. At the critical temperature, the existence of these preferred directions affects the orientation of the spins, leading to a cusp in the susceptibility. This cusp is smoothed by an external field. If the potential between spins on sites i, j is $J_{ij}s_i \cdot s_j$ then it is shown that

$$kT_c = \left(\sum_{ij} \langle \frac{1}{2} J_{ij}^2 \epsilon_{ij} \rangle \right)^{1/2}$$

where ϵ_{ij} is unity or zero according to whether sites i and j are occupied. Although the behaviour at low T needs a quantum mechanical treatment, it is interesting to complete the classical calculations down to $T = 0$. Classically the susceptibility tends to a constant value at $T \rightarrow 0$, and the specific heat to a constant value.

1. Introduction

A dilute solution of say Mn in Cu can be modelled by an array of spins on the Mn arranged at random in the matrix of Cu, interacting with a potential which oscillates as a function of the separation of the spins. To simplify our analysis we consider the spins as classical dipoles pointing in direction s_i , so the interaction energy is $J_{ij}s_i \cdot s_j$. Now if, when the probability of finding a pair at points i, j is ϵ_{ij} , it happens that $\sum J_{ij}\epsilon_{ij} \neq 0$ the system can show residual ferromagnetism or antiferromagnetism at sufficiently low temperatures. If $\sum J_{ij}\epsilon_{ij} = 0$, for the whole alloy, but still has domains in which it is nonzero, one may still construct a theory in which there are thermodynamic consequences, in particular in the susceptibility, a kind of macroscopic antiferromagnet (Adkins and Rivier 1974). In this paper however we argue that there is a much simpler and overriding model, in which it can be assumed that $\sum J_{ij}\epsilon_{ij} = 0$ on any scale, and that the mere existence of a ground state is sufficient to cause a transition and a consequent cusp in the susceptibility, which is found experimentally (Canella and Mydosh 1972). There are many such states each of which is a local minimum and inaccessible from each other. This question is irrelevant to our argument.

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The argument is that there will be some orientation of the spins which gives the minimum of potential energy. This orientation is such that $\langle s_i \rangle = 0$ so the system is neither ferro- nor antiferromagnetic on any scale, nor need it be unique. Nevertheless there comes a critical temperature T_c at which the spins notice the existence of this state, and as $T \rightarrow 0$ the system settles into the state. This physical picture is simple enough, but it requires some new formalism to express. The problem has a resemblance to problems of gellation in polymer science. When a solution of very long molecules becomes dense there comes a density at which the mobility of a molecule falls essentially to zero and the system gels. Such a molecule will still appear as a random coil, but if viewed later will be the *same* random coil. Thus what we must argue is that if on one observation a particular spin is $s_i^{(1)}$ then if it is studied again a long time later, there is a nonvanishing probability that $s_i^{(2)}$ will point in the same direction, ie

$$q = \langle s_i^{(1)} \cdot s_i^{(2)} \rangle \neq 0.$$

Recent observations by A T Fiory and co-workers using μ meson polarization have strikingly confirmed this qualitative change in behaviour. Above T_c there appears to be no mean magnetic field at the site of a stopped μ meson, below T_c there is. At $T = 0$ one expects $q = 1$, at $T \geq T_c$, $q = 0$. The parameter q then takes the role of the mean field of the Curie-Weiss theory and we now construct the theory at the level of accuracy of the Curie-Weiss theory.

2. The mean correlation theory

To illustrate the basis of the phase change we firstly consider a single spin.

The probability of finding orientation s_i is

$$P(s_i) = \exp [(F - \sum J_{ij} s_i \cdot s_j)/kT]. \quad (2.1)$$

The joint probability of finding $s_i^{(1)}$ at one time and $s_i^{(2)}$ at an infinitely remote time will be

$$P(s_i^{(1)}, s_i^{(2)}) = \exp \{ [2F - \sum J_{ij} (s_i^{(1)} \cdot s_j^{(1)} + s_i^{(2)} \cdot s_j^{(2)})]/kT \}. \quad (2.2)$$

The fields that spins $s_i^{(1)}$ and $s_i^{(2)}$ find themselves in are

$$\xi_i^{(1)} = \sum_j J_{ij} s_j^{(1)} \quad (2.3)$$

and

$$\xi_i^{(2)} = \sum_j J_{ij} s_j^{(2)}. \quad (2.4)$$

If a spin, as a function of position, is completely random,

$$\langle \xi \rangle = 0 \quad (2.5)$$

and

$$\langle \xi_i^{(1)} \cdot \xi_i^{(1)} \rangle = \langle \sum J_{i\alpha} s_\alpha^{(1)} J_{i\beta} s_\beta^{(1)} \rangle \quad (2.6)$$

$$= \sum_\alpha J_{i\alpha}^2 \varepsilon_{i\alpha} = J_0^2 \quad (2.7)$$

where ε is the probability of finding a spin at α given that there is one at i .

Also

$$\langle \xi_i^{(1)} \cdot \xi_j^{(1)} \rangle = \langle \sum J_{ix} s_x^{(1)} J_{j\beta} s_\beta^{(1)} \rangle \quad (2.8)$$

$$= \sum J_{ix} J_{jx} \quad (2.9)$$

$$= 0 \quad i \neq j. \quad (2.10)$$

However if

$$s_i^{(1)} \cdot s_j^{(1)} = q \neq 0 \quad (2.11)$$

$$\begin{aligned} \langle \xi_i^{(1)} \cdot \xi_i^{(2)} \rangle &= q \sum J_{ix}^2 \epsilon_{ix} \\ &= q J_0^2. \end{aligned} \quad (2.12)$$

Now reconsider (2.2) from the point of view of one spin, s_1 , say. Suppose that all the other spins are bundled into the fields ξ , so that

$$P(s_1^{(1)} s_1^{(2)} \xi^{(1)} \xi^{(2)}) = \mathcal{N} \exp \left(-\frac{1}{kT} \xi_1^{(1)} s_1^{(1)} - \frac{1}{kT} \xi_1^{(2)} s_1^{(2)} \right) \mathcal{P}(\xi_j^{(1)} \xi_j^{(2)}). \quad (2.13)$$

where $\mathcal{P}$ is the probability of finding the ξ_i 's independently of any correlation caused by coupling to $s^{(1)}$, which we assume obeys equations (2.10)–(2.12), and $\mathcal{N}$ a normalization. If there are a large number of s 's arranged at random the ξ variables can be expected to have a gaussian distribution so that

$$\begin{aligned} P(s^{(1)}, s^{(2)}) &= \mathcal{N}^* \exp \left[-\frac{1}{(kT)^2} (s_1^{(1)})^2 \langle \xi_1^{(1)2} \rangle - s_1^{(1)2} \langle \xi_1^{(2)2} \rangle - 2s_1^{(1)} \cdot s_1^{(2)} \right. \\ &\quad \left. \times \langle \xi_1^{(1)} \cdot \xi_1^{(2)} \rangle \right]. \end{aligned} \quad (2.14)$$

But $s_1^{(1)2} = s_1^{(2)2} = 1$. Hence

$$P(s_1^{(1)}, s_1^{(2)}) = \tilde{\mathcal{N}} \exp(-s_1^{(1)} \cdot s_1^{(2)} \rho q) \quad (2.15)$$

where

$$\rho = \frac{2J_0^2}{3(kT)^2}. \quad (2.16)$$

Finally, therefore,

$$q = \langle s_1^{(1)} \cdot s_1^{(2)} \rangle \quad (2.17)$$

$$= \int \mu e^{-\mu \rho q} / \int e^{-\mu \rho q} \quad (2.18)$$

$$= \coth \rho q - \frac{1}{\rho q} \quad (2.19)$$

as usual. As $T \rightarrow 0$, $\rho \rightarrow \infty$, $q \rightarrow 1$ correctly. Expanding near $q = 0$

$$q = \frac{1}{\rho q} - \frac{1}{\rho q} + \frac{1}{3} q \rho - \frac{1}{45} q^3 \rho^3 \quad (2.20)$$

$$\text{so that } q = 0, \text{ or, writing } \frac{1}{3} \rho^2 = (T_c/T)^2 \quad (2.21)$$

$$\frac{1}{5} q^2 \left(\frac{T_c}{T} \right)^6 = \left(\frac{T_c}{T} \right)^2 - 1 \quad (2.22)$$

$$q^2 = 5 \left[1 - \left(\frac{T}{T_c} \right)^2 \right] \left(\frac{T}{T_c} \right)^4. \quad (2.23)$$

The structure is similar to the standard Curie-Weiss theory, with the proviso that, as $T \rightarrow 0$, $q \rightarrow +1$ not -1 , whereas either root is permitted in ferromagnetism. So far we have considered the life of a single spin, and find an abrupt change in its behaviour at a T_c . Clearly if we considered the single spin on three separate occasions we would get correlation $s^{(1)} \cdot s^{(2)}$, $s^{(2)} \cdot s^{(3)}$, and more complex correlations. So far we have not related these functions to thermodynamics, and it is not clear that the q above is directly related to the free energy. In the next section a development of disordered thermodynamics will be given following the method used in rubber elasticity (Edwards 1970, 1971) which permits the calculation of the free energy. A new definition of q will be given which will be directly related to the thermodynamic functions.

3. The formulation of the thermodynamic functions

Consider a particular spin glass specified by a set of occupation numbers. We can absorb these into the definition of J_{ij} so that there is a probability of finding a particular interaction operative, ie let

$$\mathcal{J}_{ij} = J_{ij} \epsilon_{ij}. \quad (3.1)$$

$P(\mathcal{J})$ is then the probability of finding a $\mathcal{J}$.

A particular spin glass will have a free energy $\mathcal{F}(\mathcal{J})$ defined by

$$\exp[-\mathcal{F}(\mathcal{J})/kT] = \int \exp\left[+\sum \mathcal{J}_{ij} s_i \cdot s_j\right] \Pi(ds_i) \quad (3.2)$$

where the integration allows for the probability of occupation. The ensemble free energy is then

$$F = \int \mathcal{F}(\mathcal{J}) \mathcal{P}(\mathcal{J}) [d\mathcal{J}] \quad (3.3)$$

$$= -kT \int \mathcal{P}(\mathcal{J}) \left[\log \int (\Pi ds) \exp\left(\sum \mathcal{J} ss\right) \right] d\mathcal{J}. \quad (3.4)$$

In order to be able to perform the integrals over $\mathcal{J}$ and s it appears to be essential to be able to alter the order of the integration. A way to do this is to consider m systems and define an $\tilde{F}(m)$ by

$$\exp[-\tilde{F}(m)/kT] = \int \prod_{z=1}^m (\Pi ds^{(z)}) \exp\left(\sum_{i,j} \mathcal{J}_{ij} s_i^{(z)} s_j^{(z)}\right) P(\mathcal{J}) d\mathcal{J} \quad (3.5)$$

$$= \int \exp[-m\mathcal{F}(\mathcal{J})/kT] P(\mathcal{J}) d\mathcal{J}. \quad (3.6)$$

We consider that (3.6) can truly be evaluated for all m and continue the integral to a small m value and expand it

$$\exp[-\tilde{F}(m)/kT] = 1 - \frac{mF}{kT} + O(m^2). \quad (3.7)$$

Hence

$$\tilde{F}(m) = mF + O(m^2). \quad (3.8)$$

If, then, one can evaluate the $3mN$ dimensional integral (3.5) one can obtain the free energy of the system. The integral can be evaluated by the method of the previous section. Firstly, we note that whereas in the $s^{(1)}, s^{(2)}$ discussion above one had $s_i^{(1)2} = s_i^{(2)2} = 1$, $\langle s_i^{(1)} \cdot s_i^{(2)} \rangle = q$ and the argument works at the level of approximation in which $s_i \cdot s_j = 0$. We now will have

$$s_i^{(\alpha)2} = 1 \quad \langle s_i^{(\alpha)} \cdot s_i^{(\beta)} \rangle = q \quad \alpha \neq \beta$$

when we now employ the same symbol q , but it will follow a different definition. We take the simplest possible probability distribution for the $\mathcal{J}_{ij}^2$, ie

$$P(\mathcal{J}_{ij}) = \exp(-\mathcal{J}_{ij}^2/2J^2\rho_0^2) \quad (3.9)$$

where $J^2 = \sum_{ij} J_{ij}^2$ and ρ_0 is the density of occupation.

Then

$$\int \exp\left(\sum_{ij\alpha} \mathcal{J}_{ij} s_i^{(\alpha)} \cdot s_j^{(\alpha)}\right) = \exp\left[+\frac{3}{2} \frac{\rho}{\rho_0} \sum_{\alpha\beta ij} (s_i^{(\alpha)} \cdot s_j^{(\alpha)} s_i^{(\beta)} \cdot s_j^{(\beta)})\right] \quad (3.10)$$

where

$$\rho = \frac{2}{3} J^2 \rho_0^2 / (kT)^2. \quad (3.11)$$

To do the integral over the s we have to resort to a variational principle of the Feynman type, replacing the quartic form by a best quadratic. The replacement is then to write

$$\exp\left\{+\frac{1}{2} \sum_{i,\alpha \neq \beta} \eta s_i^\alpha \cdot s_i^\beta + C - \left[\frac{1}{2} \eta \sum_{i,\alpha \neq \beta} s_i^\alpha \cdot s_i^\beta + C - \frac{3}{2}(\rho/\rho_0) \sum s_i^\alpha s_j^\alpha s_i^\beta s_j^\beta\right]\right\} \quad (3.12)$$

$$> \exp\left\{+\frac{1}{2} \sum_{\alpha \neq \beta} \eta s_i^\alpha \cdot s_i^\beta + C\right\} (1 + [\text{as above}]). \quad (3.13)$$

So one chooses C so that

$$\int \Pi ds \exp\left(+\frac{1}{2} \sum \eta ss + C\right) \left[\frac{1}{2} \eta \sum ss - C - \frac{3}{2}(\rho/\rho_0) \sum s_i^\alpha s_j^\alpha s_i^\beta s_j^\beta\right] = 0. \quad (3.14)$$

Thereupon one performs the final integral over s_i^α and minimizes

$$\int \Pi ds \exp\left(-\frac{1}{2} \sum \eta ss + C\right),$$

to determine η .

Note that a term in $s_i^\alpha \cdot s_i^\alpha$ is not required since it is unity, and terms in $s_i \cdot s_j$ need not be included to the order of accuracy of this paper and without, of course, violating the extremal property of the solution. To evaluate we note that

$$\sum_{\alpha \neq \beta} s_i^\alpha \cdot s_i^\beta = \left(\sum s_i^\alpha\right) \cdot \left(\sum s_i^\alpha\right) - m \quad (3.15)$$

and that

$$\exp\left[\left(\sum s_i^\alpha\right)^2 \eta/2\right] = \frac{1}{(2\pi)^{3/2}} \int \exp\left[\eta^{1/2} \left(\sum s_i^\alpha \cdot \mathbf{r}\right) - \frac{1}{2} r^2\right] d^2 r. \quad (3.16)$$

Thus

$$\int \Pi(ds) \exp\left(\frac{1}{2}\eta \sum_{z \neq \beta} s_i^z s_i^\beta\right) = e^{-m\eta/2} \left(\frac{1}{2\pi}\right)^{3/2} \int \left(\frac{\sinh r\eta^{1/2}}{r\eta^{1/2}}\right)^m e^{-1/2r^2} d^3r. \quad (3.17)$$

Likewise

$$\begin{aligned} \int \exp\left(\frac{1}{2}\eta \sum s^z s^\beta\right) \left(\sum_{z,\beta} s_i^z \cdot s_j^z s_i^\beta \cdot s_j^\beta\right) &= \frac{e^{-m\eta}}{(2\pi)^{3/2}} \int \exp\left[\eta^{1/2} \left(\sum s_i^z \cdot r\right)\right] \\ &\times \left(\sum s_i^z \cdot s_j^z s_i^\beta \cdot s_j^\beta\right) e^{-r^2/2} d^3r \Pi(ds). \end{aligned} \quad (3.18)$$

Let

$$\mathcal{E}(m, n) = \int \exp\left(\frac{1}{2}\eta \sum_{i,z \neq \beta} s_i^{(z)} \cdot s_i^{(\beta)}\right) \Pi(ds) \quad (3.19)$$

$$= e^{-m\eta/2} \frac{1}{(2\pi)^{3/2}} \int \left(\frac{\sinh r\eta^{1/2}}{r\eta^{1/2}}\right)^m e^{-r^2/2} d^3r. \quad (3.20)$$

Then

$$\langle \sum s_i^z \cdot s_j^z s_i^\beta \cdot s_j^\beta \rangle = \frac{1}{3} \langle \sum s_i^z \cdot s_i^\beta s_j^z \cdot s_j^\beta \rangle \quad (3.21)$$

$$= \frac{1}{3} \langle \sum s_i^z \cdot s_i^\beta \times \sum s_j^z s_j^\beta \rangle \quad (3.22)$$

$$= \frac{m}{3} + \frac{1}{3} \sum_{z \neq \beta} \langle s_i^z \cdot s_i^\beta \rangle \sum \langle s_j^z \cdot s_j^\beta \rangle \quad (3.23)$$

$$= \frac{m}{3} + \frac{1}{3} \left(\frac{2}{\varepsilon} \frac{\partial \mathcal{E}}{\partial \eta} \right)^2 \frac{1}{m(m-1)}. \quad (3.24)$$

If q is now defined to be $\langle s_i^{(z)} \cdot s_i^{(\beta)} \rangle$ then

$$m(m-1)q = (2/\mathcal{E})(\partial \mathcal{E}/\partial \eta) \quad (3.25)$$

and

$$\sum \langle s_i \cdot s_i s_j \cdot s_j \rangle = \frac{m}{3} [1 - q^2(1-m)]. \quad (3.26)$$

Collecting the terms together

$$-\frac{\tilde{F}}{kT} = \log \mathcal{E} - \frac{\eta}{\varepsilon} \frac{\partial \mathcal{E}}{\partial \eta} + \frac{1}{2} \rho/\rho_0 [1 - q^2(1-m)]. \quad (3.27)$$

$\tilde{F}$ will be a minimum with respect to variations in η and since q is defined solely in terms of η , it follows that

$$\frac{1}{m} \frac{\partial \tilde{F}}{\partial \eta} = 0 = 2\eta \frac{\partial q}{\partial \eta} - 2 \left(\frac{\rho}{\rho_0} \right) q \frac{\partial q}{\partial \eta} \quad (3.28)$$

or

$$\eta = \left(\frac{\rho}{\rho_0} \right) q \quad (3.29)$$

where higher order terms in m have now been neglected. The definition of q in terms of η now yields (again keeping only terms in m)

$$1 - q = \int \frac{r}{[(\rho/\rho_0)q]^{1/2}} (\coth\{[(\rho/\rho_0)q]^{1/2} r\} - [(\rho_0/\rho)q]^{1/2} r^{-1}) e^{-r^2/2} \frac{d^3r}{(2\pi)^{3/2}}. \quad (3.30)$$

$$-\frac{F}{kT} = -\frac{\tilde{F}}{mkT} = + \int \log \left\{ \frac{\sinh r[(\rho/\rho_0)q]^{1/2}}{r[(\rho/\rho_0)q]^{1/2}} \right\} e^{-r^2/2} \frac{d^3r}{(2\pi)^{3/2}}. \quad (3.31)$$

$$-(\rho/\rho_0)q(1 - q) + \frac{1}{2}(\rho/\rho_0)(1 - q^2) = \int \log(\text{as above}) e^{-r^2/2} \frac{d^3r}{(2\pi)^{3/2}} \\ + \frac{1}{2} \left(\frac{\rho}{\rho_0} \right) (1 - 2q + \dots) \quad (3.32)$$

$$-\frac{F}{kT} = \frac{1}{2} \left(\frac{\rho}{\rho_0} \right) (1 - q)^2 + \int \log(\text{as above}) e^{-r^2/2} \frac{d^3r}{(2\pi)^{3/2}}. \quad (3.33)$$

Note that $\partial F/\partial q = 0$ from the definition of q , and in accordance with the variational property of F .

The equation for q and hence for F is not simple but we can solve it in the limits $T \rightarrow T_c$ and $T \rightarrow 0$. For $T \rightarrow T_c$, one has since

$$\coth x = \frac{1}{x} - \frac{x}{3} + \frac{x^3}{45} - \frac{2x^5}{945} + \dots \quad (3.34)$$

firstly the identity at $q = 0$ of

$$1 = \frac{1}{(2\pi)^{3/2}} \int \frac{r^2}{3} e^{-r^2/2} d^3r \quad (3.35)$$

and then

$$q = \frac{1}{(2\pi)^{3/2}} \int \frac{r^4}{45} e^{-r^2/2} \left(\frac{\rho}{\rho_0} \right) d^3r \quad (3.36)$$

ie T_c is where $\rho_0 = \frac{1}{3}\rho$, $T_c^2 = 2J_0^2/9k^2$ as before. Near $T = T_c$, for $T < T_c$

$$[1 - (T_c/T)^2] + 2q = 0. \quad (3.37)$$

Near $T = 0$, putting $q = 1 - \epsilon$

$$\left(\frac{\rho q}{\rho_0} \right)^{1/2} (1 - q) = 2 \left(\frac{2}{\pi} \right)^{1/2} \quad (3.38)$$

$$\epsilon = \left(\frac{8}{3\pi} \right)^{1/2} \left(\frac{T}{T_c} \right). \quad (3.39)$$

From these results we can now calculate the specific heat and susceptibility.

4. The specific heat

The free energy has the form $F = -Tf$, so the internal energy is

$$E = T^2 \frac{\partial f}{\partial T}. \quad (4.1)$$

Since F is stationary with respect to ξ ie q , only ρ_0 need be differentiated in f to yield

$$E = -T^2 \frac{2}{T} \frac{1}{2} \left(\frac{\rho}{\rho_0} \right) (1 - q^2) \quad (4.2)$$

$$= -T(\rho/\rho_0)(1 - q^2). \quad (4.3)$$

$$C_v = \frac{\partial E}{\partial T} = - \left(\frac{\rho}{\rho_0} \right) (1 - q^2) - T \frac{\partial}{\partial T} \left[\left(\frac{\rho}{\rho_0} \right) (1 - q^2) \right]. \quad (4.4)$$

Putting

$$(\rho/\rho_0) = \lambda \quad (4.5)$$

we have

$$C_v = -(1 - q^2)\lambda - T \frac{\partial \lambda}{\partial T} \frac{\partial}{\partial \lambda} [\lambda(1 - q^2)] \quad (4.6)$$

$$= -\lambda(1 - q^2) + 2\lambda \frac{\partial}{\partial \lambda} [\lambda(1 - q^2)] \quad (4.7)$$

$$= +\lambda(1 - q^2) - 4\lambda^2 q \frac{\partial q}{\partial \lambda}. \quad (4.8)$$

This implies a cusp in C_v . There is a little experimental data which neither excludes nor entirely supports this (de Nobel and du Chatenier 1959, Zimmerman and Hoare 1960, Zimmerman and Crane 1961).

We are specially interested near $T \sim 0$ where

$$1 - q = \frac{\gamma}{(q\lambda)^{1/2}} \quad \gamma = \int r e^{-r^2/2} \frac{d^3r}{(2\pi)^{3/2}}. \quad (4.9)$$

Using this form one gets

$$C_v/k = \lambda \left[-\frac{(1 - q)^3 + (1 + 3q^2)/2\lambda q}{3q - 1 + 1/2\lambda q} \right] \quad (4.10)$$

which tends to a constant as $T \rightarrow 0$. This is of course a classical result.

We are grateful to Dr K Fischer for pointing out an error in the first calculation of (4.10).

Dynamics near $T = 0$ always are of the utmost importance and this region cannot really be properly discussed in the present theory. A possible description is given by Anderson (1973).

5. The susceptibility

The argument is again straightforward, and if χ_c is the normal paramagnetic susceptibility, one finds by adding the magnetic field to the energy and differentiating F in the usual way:

$$\chi = \chi_c(1 - q). \quad (5.1)$$

Thus $\chi = \chi_c$ above $T = T_c$. Below $T = T_c$ one finds, since

$$q = -\frac{1}{2} \left[1 - \left(\frac{T_c}{T} \right)^2 \right] \quad (5.2)$$

and

$$\chi_c = \frac{a}{T} \quad a = \text{usual Curie constant} \quad (5.3)$$

that

$$\chi = \frac{a}{T_c} \left[1 - \left(\frac{T_c - T}{T_c} \right) \right] \left\{ 1 + \frac{1}{2} \left[1 - 1 + 2 \left(\frac{T_c - T}{T_c} \right) \right] + O(T_c - T)^2 \right\} \quad (5.4)$$

$$\chi = \frac{a}{T_c} - O(T_c - T)^2. \quad (5.5)$$

The cusp is thus linear on one side but quadratic on the lower T side. From one's experience with the Bragg-Williams theory one can expect this lack of symmetry on either side of the cusp to be an artifact of the molecular field approximation employed here. The true structure will probably be more symmetric.

At low temperatures one has from (3.38)

$$q = 1 - \left(\frac{2}{3\pi} \right)^{1/2} \left(\frac{T}{T_c} \right) \quad (5.6)$$

so

$$\chi = \frac{a}{T} \left(\frac{2}{3\pi} \right)^{1/2} \left(\frac{T}{T_c} \right) \quad (5.7)$$

and is therefore independent of T as $T \rightarrow 0$.

Note that the cusp at $T = T_c$ is destroyed by an external magnetic field. This has the effect of altering r in $\sinh r [(\rho/\rho_0)q]^{1/2} [(\rho/\rho_0)q]^{1/2} r]^{-1}$ to $|r\eta + \mu\mathbf{B}|$ where $\mu =$ dipole moment/ kT . This ensures that $q > 0$ for all T , being of order B^2/T^2 as $T \rightarrow \infty$. However since the cusp has a strong theory dependent shape we do not pursue the algebra of the cusp form as B increases.

It will be noted that the cusp as calculated here is not symmetric unlike the experimental finding. This situation is analogous to the use of the mean field theory with thermodynamics of ordering in alloys (or the Ising model) after Bragg and Williams. The simple 'on or off' theories give an asymmetry. Improvements like the Bethe-Peierls or Rushbrooke expansions redress the asymmetry to a certain extent, but exact theories find exact symmetry at the critical point. The purpose of this paper is simply to uncover the effect however and we do not attempt to apply the well known improvements to the mean field type of theory.

6. Conclusion

In this paper we have applied the simplest theory available to elucidate a new effect in disordered system physics. There are, apart from the obvious improvements required and possible in the present treatment of the phase change, several new avenues of study opened up. Firstly the methods should be made quantum mechanical in order to give a reliable treatment near $T = 0$. Also, just as the mean field theory has many applications in ordered physics, the present theory will have many other applications in disordered state physics. One has already been mentioned, that of rubber elasticity which antedates

the present work. But more generally the present approach permits the use of second quantization methods in problems which have hitherto been studied only as first quantization problems. It is hoped to return to these questions in later papers.

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