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Model calculation for a liquid ferromagnet

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It is demonstrated that a model which has been proposed by Honda and Kato shows that a liquid can be ferromagnetic. The melting temperature and Curie temperature of a system of spins are calculated in the mean-field approximation. The possible correlation between the magnetization and translation order parameter was included, but was not found to be too significant. It is shown that one must choose certain solutions for the magnetization and translation order parameter to minimize the free energy.

I. INTRODUCTION

The possibility of a liquid ferromagnet has been investigated by several authors.[1-8] The controversial experimental investigations[1-4] have led to theoretical analyses in terms of very crude models.[5-8] The complexity of the problem makes it necessary to use very simple models and even these simple models can only be solved approximately. We examine the possibility of ferromagnetism in liquids by using a model which was proposed by Honda and Kato[5] and based on a model due to Nakano.[9] Using their model, Honda and Kato made some mean-field theory calculations and concluded that a ferromagnetic liquid state is unlikely. We will show in this paper that the model does exhibit liquid ferromagnetism if one includes some terms which are neglected by Honda and Kato and considers the minimization of the free energy in choosing the solutions of the equations for the magnetization and translational order parameter. We have also included the possibility of correlations between the spin variable σ_i and the variable associated with the translational order parameter ρ_i.

II. MODEL

Following Honda and Kato, we consider a system of N atoms in a volume V. The system is divided into N unit cells of volume $v = V/N$, which each contain one atom. Each cell is divided into a central region of volume v', centered about the lattice site, and an outskirt region of volume $v - v'$. The atoms each possess a spin σ_i, capable of taking the values ± 1 (the Ising model is assumed). The interaction between the i th and j th atoms is assumed to have the form $-U(r_{ij}) - J(r_{ij})\sigma_i\sigma_j$, where r_{ij} is the distance between the i th and j th atoms. Then the Hamiltonian of the system will be given by

$$H = -\sum_{\langle ij\rangle} [U(r_{ij}) + J(r_{ij})\sigma_i\sigma_j] \;, \tag{1}$$

where the sum is over all nearest-neighbor pairs of atoms. We assume that there is an interaction only between nearest neighbors. To simplify the calculation, the interactions $U(r_{ij})$ and $J(r_{ij})$ are approximated by averaged values for various ranges of interparticle separation, r_{ij}. If the i th and j th atoms are both in central regions, the interactions $U(r_{ij})$ and $J(r_{ij})$ are approximated by $4U_1$ and $4J_1$, respectively. If the i th and j th atoms are in different regions, the interactions are approximated by $4U_2$ and $4J_2$. Finally, if the i th and j th atoms are both in outskirt regions, the interactions are approximated by $4U_3$ and $4J_3$. We define the variable ρ_i to be $+1$ when the i th atom is in a central region and -1 when the atom is in an outskirt region. Then Hamiltonian given by Eq. (1) can be written

$$\begin{aligned} H = -\sum_{\langle ij\rangle}[&(U_1+2U_2+U_3) + (U_1-2U_2+U_3)\rho_i\rho_j + (U_1-U_3)(\rho_i+\rho_j) \\ &+ (J_1+2J_2+J_3)\sigma_i\sigma_j + (J_1-2J_2+J_3)\sigma_i\sigma_j\rho_i\rho_j + (J_1-J_3)\sigma_i\sigma_j(\rho_i+\rho_j)] \;. \end{aligned} \tag{2}$$

III. CALCULATION

We will now calculate the averages of σ_i, ρ_i, and $\sigma_i\rho_i$ in the above system. To simplify the calculations, we use the mean-field approximation. To do this, we focus our attention on the i th atom, which interacts with its neighbors via the single-particle Hamiltonian

$$H_i=-\sum_{j=1}^{\gamma}[\,(U_1+2U_2+U_3)+(U_1-2U_2+U_3)\rho_i\rho_j+(U_1-U_3)(\rho_i+\rho_j)$$
$$+(J_1+2J_2+J_3)\sigma_i\sigma_j+(J_1-2J_2+J_3)\sigma_i\sigma_j\rho_i\rho_j+(J_1+J_3)\sigma_i\sigma_j(\rho_i+\rho_j)]\;. \tag{3}$$

The mean-field approximation consists of replacing the spin operators on the neighboring sites j by their average values. We thus replace σ_j by $\langle\sigma_j\rangle$, ρ_j by $\langle\rho_j\rangle$, and $\sigma_j\rho_j$ by $\langle\sigma_j\rho_j\rangle$. Since these averages are independent of the lattice site j, we will drop the subscript and write them as $\langle\sigma\rangle$, $\langle\rho\rangle$, and $\langle\sigma\rho\rangle$, in order to simplify the notation. Then the approximate single-particle Hamiltonian becomes

$$H_i=-\gamma[\,(U_1+2U_2+U_3)+(U_1-2U_2+U_3)\rho_i\langle\rho\rangle+(U_1-U_3)(\rho_i+\langle\rho\rangle)+(J_1+2J_2+J_3)\sigma_i\langle\sigma\rangle$$
$$+(J_1-2J_2+J_3)\sigma_i\rho_i\langle\sigma\rho\rangle+(J_1-J_3)\sigma_i\rho_i\langle\sigma\rangle+(J_1-J_3)\sigma_i\langle\sigma\rho\rangle]\;. \tag{4}$$

Now $\langle\sigma\rangle$ can be calculated from the expression

$$\langle\sigma\rangle=\sum_{\sigma_i=\pm1}\;\sum_{\rho_i=\pm1}P_i(\rho_i)\sigma_i e^{-\beta H_i}\Big/\sum_{\sigma_i=\pm1}\;\sum_{\rho_i=\pm1}P_i(\rho_i)e^{-\beta H_i}\;, \tag{5}$$

where $\beta=1/kT$ and

$$P_i(\rho_i)=\begin{cases}p & \text{if } \rho_i=1,\\ q & \text{if } \rho_i=-1\end{cases} \tag{6}$$

and $p=v/v'$ and $q=1-p$. This factor is necessary because the central and outskirt regions have different volumes.

If we define the quantities A, B, C, and D by

$$A=\beta\gamma[(U_1+2U_2+U_3)+(U_1-U_3)\langle\rho\rangle]\;, \tag{7}$$

$$B=\beta\gamma[(U_1-2U_2+U_3)\langle\rho\rangle+(U_1-U_3)]\;, \tag{8}$$

$$C=\beta\gamma[(J_1+2J_2+J_3)\langle\sigma\rangle+(J_1-J_3)\langle\sigma\rho\rangle]\;, \tag{9}$$

and

$$D=\beta\gamma[(J_1-2J_2+J_3)\langle\sigma\rho\rangle+(J_1-J_3)\langle\sigma\rangle]\;; \tag{10}$$

then H_i can be written

$$H_i=-\beta^{-1}|A+B\rho_i+C\sigma_i+D\sigma_i\rho_i|\;. \tag{11}$$

Equation (5) for $\langle\sigma\rangle$ becomes

$$\langle\sigma\rangle=\sum_{\sigma_i}\sum_{\rho_i}P_i(\rho_i)\sigma_i e^{A+B\rho_i+C\sigma_i+D\sigma_i\rho_i}$$
$$\times\left(\sum_{\sigma_i}\sum_{\rho_i}P_i(\rho_i)e^{A+B\rho_i+C\sigma_i+D\rho_i\sigma_i}\right)^{-1}\;. \tag{12}$$

Performing the sums over σ_i and ρ_i, we find

$$\langle\sigma\rangle=\frac{pe^{B}\sinh(C+D)+qe^{-B}\sinh(C-D)}{pe^{B}\cosh(C+D)+qe^{-B}\cosh(C-D)} \tag{13}$$

which may be rewritten as

$$\langle\sigma\rangle=\frac{\tanh C+\tanh(B+\frac{1}{2}\ln p/q)\tanh D}{1+\tanh(B+\frac{1}{2}\ln p/q)\tanh C\tanh D}\;. \tag{14}$$

Similarly, we may calculate $\langle\rho\rangle$ and $\langle\sigma\rho\rangle$ as follows:

$$\langle\rho\rangle=\sum_{\sigma_i=\pm1}\;\sum_{\rho_i=\pm1}P(\rho_i)\rho_i e^{-\beta H_i}$$
$$\times\left(\sum_{\sigma_i=\pm1}\;\sum_{\rho_i=\pm1}P(\rho_i)e^{-\beta H_i}\right)^{-1}\;. \tag{15}$$

The calculation is exactly like that for $\langle\sigma\rangle$ and yields

$$\langle\rho\rangle=\frac{\tanh(B+\frac{1}{2}\ln p/q)+\tanh C\tanh D}{1+\tanh(B+\frac{1}{2}\ln p/q)\tanh C\tanh D}\;. \tag{16}$$

Finally, we obtain $\langle\sigma\rho\rangle$ as

$$\langle\sigma\rho\rangle=\frac{\tanh(B+\frac{1}{2}\ln p/q)\tanh C+\tanh D}{1+\tanh(B+\frac{1}{2}\ln p/q)\tanh C\tanh D}\;. \tag{17}$$

Since the three quantities $\langle\sigma\rangle$, $\langle\rho\rangle$, and $\langle\sigma\rho\rangle$ are coupled we must solve the three equations (14), (16), and (17) self-consistently. In general these equations have more than one solution, the physically stable solution being the set of numbers for $\langle\sigma\rangle$, $\langle\rho\rangle$, and $\langle\sigma\rho\rangle$ which minimize the free energy.

The free energy may be calculated from the partition function Z, defined by

$$Z=\sum_{\{\sigma_i\}}\sum_{\{\rho_i\}}P(\{\rho_i\})e^{-\beta H}\;, \tag{18}$$

where the summations are over all possible configurations of σ_i and ρ_i. The function $P(\{\rho_i\})$ is simply a product of N factors of p or q and depends on the configuration of ρ_i. When $\rho_i=1$, we include a factor of p and when $\rho_i=-1$, we include a factor of q.

Using the mean-field approximation, replacing σ_j by $\langle\sigma\rangle$, ρ_j by $\langle\rho\rangle$, and $\sigma_j\rho_j$ by $\langle\sigma\rho\rangle$, the Hamiltonian of Eq. (2) becomes

$$H=-\frac{\gamma}{2}\sum_{i=1}^{N}[(U_1+2J_2-U_3)+(U_1-2U_2+U_3)\rho_i\langle\rho\rangle+(U_1-U_3)(\rho_i+\langle\rho\rangle)+(J_1+2J_2+J_3)\sigma_i\langle\sigma\rangle$$
$$+(J_1-2J_2+J_3)\sigma_i\rho_i\langle\sigma\rho\rangle+(J_1-J_3)\langle\sigma\rangle\sigma_i\rho_i+(J_1-J_3)\sigma_i\langle\sigma\rho\rangle]\ , \tag{19}$$

which may be written

$$H=-\frac{\beta^{-1}}{2}\left[NA+B\sum_{i=1}^{N}\rho_i+C\sum_{i=1}^{N}\sigma_i+D\sum_{i=1}^{N}\sigma_i\rho_i\right]\ , \tag{20}$$

where A, B, C, and D are defined in Eqs. (7)–(10). Now we may write the partition function as

$$Z=e^{NA/2}\sum_{\{\sigma_i\}}\sum_{\{\rho_i\}}P(\{\rho_i\})\prod_{i=1}^{N}\exp[\tfrac{1}{2}(B\rho_i+C\sigma_i+D\rho_i\sigma_i)]\ . \tag{21}$$

We may separate Eq. (21) into a product of N one-particle partition functions and the partition function becomes

$$Z=e^{NA/2}\left[\sum_{\sigma_1=\pm1}\sum_{\rho_1=\pm1}P_1(\rho_1)\exp[\tfrac{1}{2}(B\rho_1+C\sigma_1+D\sigma_1\rho_1)]\right]^N\ . \tag{22}$$

Evaluating Eq. (22) yields

$$Z=2^N[pe^{(A+B)/2}\cosh\tfrac{1}{2}(C+D)+qe^{(A-B)/2}\cosh\tfrac{1}{2}(C-D)]^N\ . \tag{23}$$

Substituting the expressions for A, B, C, and D in Eq. (23), we obtain

$$Z=2^N\left[p\exp\left(\frac{\gamma U_1}{kT}(1+\langle\rho\rangle)+\frac{\gamma U_2}{kT}(1-\langle\rho\rangle)\right]\cosh\left(\frac{\gamma J_1}{kT}\ (\langle\sigma\rangle+\langle\sigma\rho\rangle)+\frac{\gamma J_2}{kT}(\langle\sigma\rangle-\langle\sigma\rho\rangle)\right]$$
$$+q\exp\left(\frac{\gamma U_2}{kT}(1+\langle\rho\rangle)+\frac{\gamma U_3}{kT}(1-\langle\rho\rangle)\right]\cosh\left(\frac{\gamma J_2}{kT}(\langle\sigma\rangle+\langle\sigma\rho\rangle)\frac{\gamma J_3}{kT}(\langle\sigma\rangle-\langle\sigma\rho\rangle)\right]\Bigg]^N\ . \tag{24}$$

The free energy F may be calculated from the partition function,

$$F=-kT\ln Z\ . \tag{25}$$

We obtain

$$F=-NkT\ln2-NkT\ln\left[p\exp\frac{\gamma U_1}{kT}(1+\langle\rho\rangle)+\frac{\gamma U_2}{kT}(1-\langle\rho\rangle)\cosh\left(\frac{\gamma J_1}{kT}(\langle\sigma\rangle+\langle\sigma\rho\rangle)+\frac{\gamma J_2}{kT}(\langle\sigma\rangle-\langle\sigma\rho\rangle)\right]\right.$$
$$\left.+q\exp\left(\frac{\gamma U_2}{kT}(1+\langle\rho\rangle)+\frac{\gamma U_3}{kT}(1-\langle\rho\rangle)\right]\cosh\left(\frac{\gamma J_2}{kT}(\langle\sigma\rangle+\langle\sigma\rho\rangle)+\frac{\gamma J_3}{kT}(\langle\sigma\rangle-\langle\sigma\rho\rangle)\right]\right]\ . \tag{26}$$

We assume that the materials which we are considering have a stable, ferromagnetic solid phase at low temperatures. Then $U_3 < U_2$ and $U_2 < U_1$. The energy U_1 corresponds to the binding energy, which is of the order of 1 eV. The exchange energy is usually of the order of 10^{-2} eV. The parameter p represents the fraction of the volume available to an atom just before melting and thus corresponds to X_m^3 in the Lindemann melting formula.[10] Here X_m^3 is the ratio of the root-mean-square displacement of an atom from equilibrium at the melting temperature to the mean radius of a unit cell. In most materials, $0.2 < X_m < 0.25$ so p will be in the range from 0.008 to 0.016. Under these conditions, it is easily seen that the free energy is a decreasing function of $\langle\sigma\rangle$, $\langle\rho\rangle$, and $\langle\sigma\rho\rangle$. (We use the non-negative solution for $\langle\sigma\rangle$.) Thus, the stable solutions for $\langle\sigma\rangle$, $\langle\rho\rangle$, and $\langle\sigma\rho\rangle$ are the largest solutions, for these will yield the lowest free energy.

IV. DISCUSSION

We can now solve the coupled equations for $\langle\sigma\rangle$, $\langle\rho\rangle$, and $\langle\sigma\rho\rangle$ numerically to obtain their temperature dependence. Choosing the largest solutions (those which minimize the free energy, as described above), we obtain the results shown in Figs. 1 and 2. In both figures, $p=0.01$, $U_2=U_3=0.9U_1$, and $J_2=J_3=0.9J_1$. In Fig. 1, the ratio U_1/J_1 has the value 100. In this

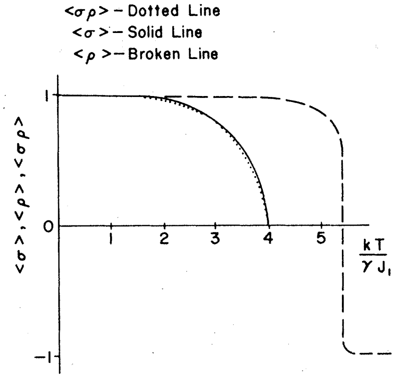

FIG. 1. $\langle\sigma\rangle$, $\langle\rho\rangle$, and $\langle\sigma\rho\rangle$ as functions of temperature with $U_2=U_3=0.9U_1$, $J_2=J_3=0.9J_1$, $p=0.01$, and $U_1/J_1=100$.

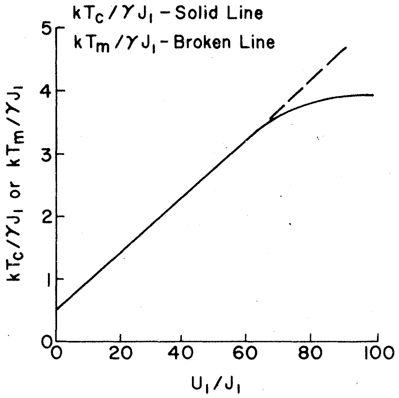

FIG. 3. Melting temperature and Curie temperature as functions of U_1/J_1 with $U_2=U_3=0.9U_1$, $J_2=J_3=0$, and $p=0.01$.

case, the magnetization vanishes at a temperature which is below the melting temperature. We interpret the temperature at which the translational order parameter $\langle\rho\rangle$ jumps discontinuously as the melting temperature T_m. The Curie temperature T_C is that temperature at which the magnetization $\langle\sigma\rangle$ becomes zero. In Fig. 2, in which the ratio U_1/J_1 is 50, the Curie temperature is greater than the melting temperature. The magnetization decreases to zero as the temperature increases, but the magnetization decreases discontinuously at the melting point, as we would expect, since the melting point is a first-order phase transition.

In Fig. 3, the melting temperature and Curie temperature are shown as functions of U_1/J_1. Here $U_2=U_3=0.9U_1$, $J_2=J_3=0$, and $p=0.01$. We see that, in this case, the melting temperature is always greater than the Curie temperature for any value of U_1/J_1. As J_2 and J_3 are increased, as shown in Fig. 4, in which $U_2=U_3=0.9U_1$, $J_2=J_3=0.9J_1$, and $p=0.01$, the melting temperature is less than the Curie temperature for the values of U_1/J_1, smaller than certain value. Thus we conclude that this model might possibly be a crude explanation of the observed ferromagnetism in liquid Au-Co alloys.

In some preliminary calculations which we performed,[8] we neglected any correlations between σ_i and ρ_i and only calculated $\langle\sigma\rangle$ and $\langle\rho\rangle$ for the above model, i.e., $\langle\sigma\rho\rangle\simeq\langle\sigma\rangle\langle\rho\rangle$. The differences between the results we obtained in this calculation which include the correlation function $\langle\sigma\rho\rangle$ and those of previous calculation are only about 1%, which is negligible compared with the inherent inaccuracy associated with the crudeness of the model. The good agreement between the results of these two calculations is not surprising because the correlation function $\langle\sigma\rho\rangle$ is almost equal to the product of $\langle\sigma\rangle$ and $\langle\rho\rangle$ shown in Figs. 1 and 2.

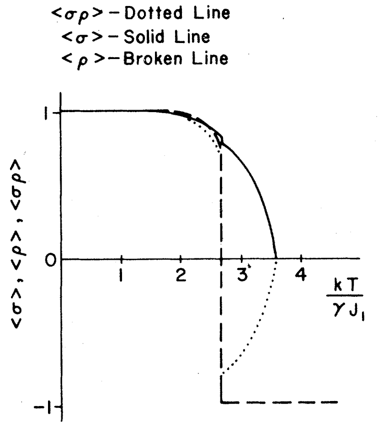

FIG. 2. $\langle\sigma\rangle$, $\langle\rho\rangle$, and $\langle\sigma\rho\rangle$ as functions of temperature with $U_2=U_3=0.9U_1$, $J_2=J_3=0.9J_1$, $p=0.01$, and $U_1/J_1=50$.

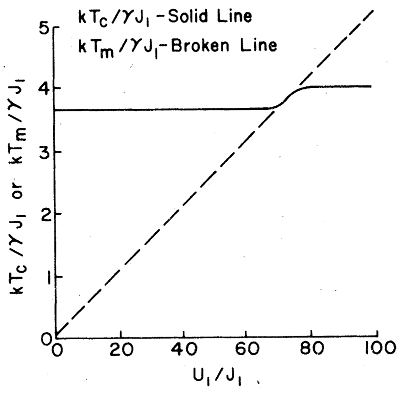

FIG. 4. Melting temperature and Curie temperature as functions of U_1/J_1 with $U_2=U_3=0.9U_1$, $J_2=J_3=0.9J_1$, and $p=0.01$.

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