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Statistical calculation for a model ferromagnetic liquid

Laura Feijoo[*] and Chia-Wei Woo[†]
Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439
and Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60201

V. T. Rajan[‡]
Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60201

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A theoretical method is developed for treating model ferromagnetic liquids. In this method the spins are treated in the mean-field approximation while spatial correlations are retained in a manner similar to conventional theories of classical liquids. Coupled self-consistency equations for the magnetization and an effective radial distribution function are derived and solved. The method is applied to a primitive model characterized by a simple spin-dependent interparticle potential. Conditions under which such a simple liquid can exhibit ferromagnetic order are determined. Numerical examples show how the transition temperature and the temperature dependence of the magnetization can be calculated.

I. INTRODUCTION

Since 1968 there have been sporadic reports of experimental evidence that ferromagnetism can exist in the liquid state. Busch and Guentherodt[1,2] reported that such a phenomenon occurs in Au-Co alloys near the eutectic at 27 at.% Co. Their finding was disputed by Nakagawa,[3] who believed that the observed magnetization had probably originated from precipitation of the solid phase. Kraeft and Alexander[4] reported a confirmation of the results obtained by Busch and Guentherodt. However, there were certain discrepancies between the two sets of data.

Several theoretical analyses followed, by Handrich[5] and Kalaf and Wu[6] using simple Heisenberg and Ising models, and by Hemmer and Imbro[7] using a hard-sphere model with weak long range forces. The techniques employed by these authors were basically the mean-field approximation and modified mean-field theories. A different approach was used by Høye and Stell,[8] who proposed a hard-sphere model which is exactly solvable in an appropriate spherical approximation for a variety of exchange interactions.

In studying the molecular theory of liquid crystals we have developed a theoretical method[9] which is suitable for treating order-disorder transitions in liquids. In particular, we are able to calculate the change in free energy which arises from the ordering of a nonspatial degree of freedom. As a first step in developing a theory for liquid ferromagnetic alloys, we apply the method to a primitive model, and determine the conditions under which a simple liquid can exhibit ferromagnetic order. The model spin system treated here does not bear any resemblance to reality. On the other hand, we believe that our present liquid theory has an edge over lattice model calculations. Liquid ferromagnetism has at best a marginal existence. It results from critical competition between spatial ordering and spin ordering. An unrealistic description of the liquid phase would render conclusions which are totally meaningless.

We begin with N particles with a classical spin degree of freedom. The interaction potential is chosen to be of the form

$$v(1,2) \equiv v(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2) = v_0(r_{12}) + v_1(r_{12})\,\vec{s}_1 \cdot \vec{s}_2 \ , \tag{1}$$

where $\vec{r}_i$ and $\vec{s}_i$ denote the position and spin of the ith particle, respectively.

The order parameter for the spin system is defined as the magnetization along an arbitrary direction, $\hat{n}$, in space

$$m = \langle \vec{s} \cdot \hat{n} \rangle \ . \tag{2}$$

We seek to calculate T_c, the temperature at which the system undergoes a transition from a magnetic phase to a nonmagnetic phase, and the temperature dependence of the magnetization just below T_c.

In Sec. II we outline a statistical mechanical formalism which, given an interaction potential, enables us to calculate the magnetization as a function of the temperature, the number density of the system, and the strength of the coupling between two spins. We define a generalized distribution function P_N for the system and an appropriate free-energy functional $\mathfrak{F}$. An approximate form of P_N which embodies a mean-field treatment of the spins and an accurate description of pair correlations in the liquid is introduced. Minimizing $\mathfrak{F}$ with respect to such an approximate P_N yields the equilibrium distribution function

P_N^0, and with it the magnetization.

In Sec. III we apply our formalism to a model system whose pairwise potential takes the form of Eq. (1) with

$$v_0(r) = 4\epsilon_0[(\sigma/r)^{12} - (\sigma/r)^6] \ , \tag{3}$$

and

$$v_1(r) = -\epsilon_1(\sigma/r)^6 \ . \tag{4}$$

The forms of $v_0(r)$ and $v_1(r)$ are chosen arbitrarily. In particular, $v_0(r)$ is chosen since a wealth of information already exists for Lennard-Jones liquids. Coupled self-consistency equations are derived, and solved for various choices of the potential parameters ϵ_0, ϵ_1, and σ. We then summarize our results, present our tentative conclusions, and indicate the direction of future work.

II. GENERAL FORMALISM

We define a generalized distribution function $P_N(1, \ldots, N)$ normalized such that

$$\int P_N(1, \ldots, i, \ldots, N)\, d1 \cdots dN = N! \ . \tag{5}$$

Here i denotes both the position coordinate $\vec{r}_i$ and the spin coordinate $\vec{s}_i$, and $d1 \cdots dN$ denotes $d\vec{r}_1\, d\vec{s}_1 \cdots d\vec{r}_N\, d\vec{s}_N$. In terms of this probability function, we define a free-energy functional[9]:

$$\begin{aligned}\mathfrak{F}[P_N] = F_{\text{ideal}} &+ \int \left[\sum_{i<j} v(i,j)\right] \frac{P_N(1, \ldots, N)}{N!}\, d1 \cdots dN \\ &+ kT \int \frac{P_N(1, \ldots, N)}{N!} \\ &\qquad \times \ln\left[\frac{P_N(1, \ldots, N)}{N!}\right] d1 \cdots dN \ ,\end{aligned} \tag{6}$$

where F_{ideal} denotes the Helmholtz free energy of an ideal gas.

The equilibrium distribution function P_N^0 and the free energy F for the system can be obtained by minimizing $\mathfrak{F}[P_N]$ with respect to P_N under the constraint Eq. (5), the latter introduced via a Lagrange multiplier α

$$\frac{\delta \mathfrak{F}}{\delta P_N} = \alpha = \sum_{i<j} v(i,j) + kT[\ln P_N(1, \ldots, N) + 1] \ . \tag{7}$$

Thus,

$$P_N^0 = \frac{1}{Z} \exp\left[-\sum_{i<j} \frac{v(i,j)}{kT}\right] \ , \tag{8}$$

where

$$Z = \frac{1}{N!} \int \exp\left[-\sum_{i<j} \frac{v(i,j)}{kT}\right] d1 \cdots dN \ . \tag{9}$$

This result, obtained without approximation, gives the equilibrium distribution function for a classical system as anticipated.

Equations (8) and (9) are formally exact, but are intractable from the computational point of view. We next proceed to construct a physically meaningful approximate form of P_N and use it to define $\mathfrak{F}[P_N]$ with Eq. (6). The minimization procedure will produce an approximate equilibrium distribution function and a free energy for the system consistent with the approximations introduced. In the approximation we shall neglect the correlation between spatial and spin variables. Furthermore, we shall neglect the correlation between the spin variables themselves. The form of P_N is thus given by

$$P_N(1, \ldots, N) = N! \left[\prod_{i=1}^{N} S(\vec{s}_i)\right] \Phi_N(\vec{r}_1, \ldots, \vec{r}_N) \ , \tag{10}$$

under the constraints

$$\int S(\vec{s})\, d\vec{s} = 1 \ , \tag{11}$$

and

$$\int \Phi_N(\vec{r}_1, \ldots, \vec{r}_N)\, d\vec{r}_1 \cdots d\vec{r}_N = 1 \ . \tag{12}$$

What this means is that we shall treat the spins in the fashion of a mean-field theory while retaining all short-range spatial correlations in the distribution function Φ_N. A careful treatment of Φ_N takes our theory beyond what is usually known as the mean-field approximation. To determine S and Φ_N we need the free-energy functional $\mathfrak{F}$, Eq. (7). In the present case it reduces to

$$\begin{aligned}\mathfrak{F} = F_{\text{ideal}} &+ \sum_{i<j} \int v(i,j) S(\vec{s}_i) S(\vec{s}_j) \Phi_N(\vec{r}_1, \ldots, \vec{r}_N)\, d\vec{s}_i\, d\vec{s}_j\, d\vec{r}_1 \cdots d\vec{r}_N \\ &+ kT \sum_{i=1}^{N} \int S(\vec{s}_i) \ln S(\vec{s}_i)\, d\vec{s}_i + kT \int \Phi_N(\vec{r}_1, \ldots, \vec{r}_N) \ln \Phi_N(\vec{r}_1, \ldots, \vec{r}_N)\, d\vec{r}_1 \cdots d\vec{r}_N \ .\end{aligned} \tag{13}$$

The minimization procedure can now be carried out under the constraints Eqs. (11) and (12). Minimization of $\mathfrak{F}$

with respect to Φ_N yields

$$\frac{\delta\mathfrak{F}}{\delta\Phi_N}=\alpha_\Phi=\sum_{i<j}\bar{v}(\vec{r}_i,\vec{r}_j)+kT[\ln\Phi_N(\vec{r}_1,\ldots,\vec{r}_N)+1]\ , \tag{14}$$

where

$$\bar{v}(\vec{r}_i,\vec{r}_j)\equiv\int v(i,j)\,S(\vec{s}_i)S(\vec{s}_j)\,d\vec{s}_i\,d\vec{s}_j\ . \tag{15}$$

Hence the optimum Φ_N is given by

$$\Phi_N(\vec{r}_1,\ldots,\vec{r}_N)=\frac{1}{Z_r}\exp\left[-\sum_{i<j}\frac{\bar{v}(\vec{r}_i,\vec{r}_j)}{kT}\right]\ , \tag{16}$$

where

$$Z_r\equiv\int\exp\left[-\sum_{i<j}\frac{\bar{v}(\vec{r}_i,\vec{r}_j)}{kT}\right]d\vec{r}_1\cdots d\vec{r}_N\ . \tag{17}$$

The expression for Φ_N as defined in Eqs. (16) and (17) corresponds to a distribution function for a classical fluid whose molecular constituents interact via an effective potential Eq. (15). This result is a consequence of our choice of P_N which separates the spin and spatial variables.

Mimimization of $\mathfrak{F}$ with respect to S produces another Euler-Lagrange equation

$$\frac{\delta\mathfrak{F}}{\delta S(\vec{s}_i)}=\alpha_s=\sum_{j(\neq i)}\int v(i,j)S(\vec{s}_j)\Phi_N(\vec{r}_1,\ldots,\vec{r}_N)\times d\vec{s}_j\,d\vec{r}_1\cdots d\vec{r}_N+kT\ln[S(\vec{s}_i)+1]\ . \tag{18}$$

Thus the optimum S is given by

$$S(\vec{s}_i)=\frac{1}{Z_s}\exp[-u(\vec{s}_i)/kT]\ , \tag{19}$$

where

$$u(\vec{s}_i)\equiv\sum_{j(\neq i)}\int v(i,j)S(\vec{s}_j)\Phi_N(\vec{r}_1,\ldots,\vec{r}_N)\times d\vec{s}_j\,d\vec{r}_1\cdots d\vec{r}_N\ , \tag{20}$$

and

$$Z_s\equiv\int\exp\left[\frac{-u(\vec{s}_i)}{kT}\right]d\vec{s}_i\ . \tag{21}$$

The potential $u(\vec{s}_i)$ given by Eq. (21) represents a mean field in which each spin moves independently. But it accounts for, as indicated earlier, short-range spatial correlations through its dependence on $\Phi_N(\vec{r}_1,\ldots,\vec{r}_N)$.

Substitution of Eqs. (16) and (19) into the free-energy functional, Eq. (13), yields the free energy for the system:

$$\begin{aligned}F={}&F_{\text{ideal}}+\sum_{i<j}\int\Phi(\vec{r}_1,\ldots,\vec{r}_N)\bar{v}(\vec{r}_i,\vec{r}_j)d\vec{r}_1\cdots d\vec{r}_N+kT\sum_{i=1}^{N}\int S(\vec{s}_i)\left[-\frac{u(\vec{s}_i)}{kT}-\ln Z_s\right]d\vec{s}_i\\&+kT\int\Phi_N(\vec{r}_1,\ldots,\vec{r}_N)\left[\sum_{i<j}\left[-\frac{\bar{v}(\vec{r}_i,\vec{r}_j)}{kT}\right]-\ln Z_r\right]d\vec{r}_1\cdots d\vec{r}_N\\={}&F_{\text{ideal}}-NkT\ln Z_s-kT\ln Z_r-\sum_{i=1}^{N}\sum_{j(\neq i)}\int v(i,j)S(\vec{s}_j)S(\vec{s}_i)\Phi_N(\vec{r}_1,\ldots,\vec{r}_N)\,d\vec{s}_i\,d\vec{s}_j\,d\vec{r}_1\cdots d\vec{r}_N\ ,\end{aligned} \tag{22}$$

or

$$F-F_{\text{ideal}}=-NkT\ln Z_s-kT\ln Z_r-\sum_{i\neq j}\int\bar{v}(\vec{r}_i,\vec{r}_j)\Phi_N(\vec{r}_1,\ldots,\vec{r}_N)\,d\vec{r}_1\cdots d\vec{r}_N\ , \tag{23}$$

where Φ_N and S are the equilibrium distribution functions given in Eqs. (16) and (19).

Equations (15)–(17) and (19)–(21) must now be solved self-consistently to determine Φ_N and S. For our model potential Eq. (1), we obtain

$$\bar{v}(\vec{r}_i,\vec{r}_j)=\bar{v}(r_{ij})=v_0(r_{ij})\left[\int S(\vec{s}_i)\,d\vec{s}_i\right]^2+v_1(r_{ij})\left[\int S_i(\vec{s}_i)(\vec{s}_i\cdot\hat{n})\,d\vec{s}_i\right]^2\ , \tag{24}$$

or

$$\bar{v}(r_{ij})=v_0(r_{ij})+v_1(r_{ij})m^2\ , \tag{25}$$

with m defined in Eq. (2) and the use of the relation

$$\hat{s}_i\cdot\hat{s}_j=\cos(\theta_{ij})=\cos\theta_i\cos\theta_j+\sin\theta_j\sin\theta_i\cos(\phi_i-\phi_j)\ , \tag{26}$$

where θ_i is the orientation of $\vec{s}_i$ as measured from $\hat{n}$. Since $\bar{v}(\vec{r}_i,\vec{r}_j)$ is in this case only a function of the distance r_{ij}, the equation for Φ_N becomes

$$\Phi_N(\vec{r}_1, \ldots, \vec{r}_N) = \frac{1}{Z_r} \exp\left[-\sum_{i<j} \frac{\bar{v}(r_{ij})}{kT} \right] , \quad (27)$$

which has the form of the distribution function for a fluid of classical particles interacting through a central potential $\bar{v}(r_{ij})$. As is customary in dealing with classical fluids, we now introduce the radial distribution function $g(r)$:

$$g(r_{12}) = \frac{N(N-1)}{Z_r} \frac{1}{\rho^2} \times \int \exp\left[-\sum_{i<j} \frac{\bar{v}(r_{ij})}{kT} \right] d\vec{r}_3 \cdots d\vec{r}_N , \quad (28)$$

where ρ denotes the number density. On account of the pairwise nature of the interactions only the radial distribution function $g(r)$ is needed in the following. The spatial part of our calculation thus reduces to the determination of $g(r_{12})$ from Eq. (28) for a given temperature, density, and $\bar{v}(r_{12})$. For this we can use known techniques of classical liquids theory. Details of this calculation will be given in Sec. III.

The spin mean-field potential $u(\vec{s}_i)$ defined in Eq. (20) can now be written as

$$u(\vec{s}_1) = \frac{1}{N} \rho^2 \int v(1,2) S(\vec{s}_2)\, g(r_{12})\, d\vec{r}_1\, d\vec{r}_2\, d\vec{s}_2 , \quad (29)$$

and using Eqs. (1) and (11), it becomes

$$u(\vec{s}_1) = \rho\left[\gamma_0 + \gamma_1 \int S(\vec{s}_2)(\vec{s}_1 \cdot \vec{s}_2)\, d\vec{s}_2 \right] , \quad (30)$$

where

$$\gamma_0 \equiv \int v_0(r) g(r)\, d\vec{r} , \quad (31)$$

and

$$\gamma_1 \equiv \int v_1(r) g(r)\, d\vec{r} . \quad (32)$$

Using Eqs. (2) and (26), we finally get

$$u(\vec{s}) = \rho(\gamma_0 + \gamma_1 m s_n) , \quad (33)$$

where

$$s_n \equiv \vec{s} \cdot \hat{n} . \quad (34)$$

Then, from Eq. (19), the spin distribution function is

$$S(\vec{s}) = \frac{1}{Z_s} \exp\left[-\frac{\rho}{kT}(\gamma_0 + \gamma_1 m s_n) \right] , \quad (35)$$

where

$$Z_s = \exp\left[\frac{-\rho\gamma_0}{kT} \right] \int \exp\left[\frac{-\rho\gamma_1 m s_n}{kT} \right] d\vec{s} . \quad (36)$$

Hence we can obtain an expression for the magnetization

$$m \equiv \langle s_n \rangle = \left[\frac{1}{Z_s'} \right] \int \exp\left[\frac{-\rho\gamma_1 m s_n}{kT} \right] s_n\, d\vec{s} , \quad (37)$$

where

$$Z_s' = \exp\left[\frac{\rho\gamma_0}{kT} \right] Z_s = \int \exp\left[\frac{-\rho\gamma_1 m s_n}{kT} \right] d\vec{s} . \quad (38)$$

By choosing the z axis parallel to $\hat{n}$, Eq. (37) can be written as

$$m = f(m) , \quad (39)$$

where

$$f(m) \equiv \frac{1}{(\rho\gamma_1 m/kT)} - \frac{1}{\tanh(\rho\gamma_1 m/kT)} . \quad (40)$$

These equations can be solved for given ρ, T, and γ_1. γ_1 depends on $g(r)$, which in turn depends on m through Eqs. (28) and (25). Thus Eqs. (17), (25), (28), (32), (39), and (40) must be solved self-consistently. When this is done, using Eq. (23) we can obtain the free energy for the system:

$$F = F_{\text{ideal}} - NkT \ln Z_s - kT \ln Z_r - N\rho \int \bar{v}(r) g(r)\, d\vec{r} . \quad (41)$$

The term proportional to $\ln Z_s$ can be easily calculated since, from Eq. (36),

$$Z_s = 4\pi \exp\left[\frac{-\rho\gamma_0}{kT} \right] \left[\frac{\sinh(\rho\gamma_1 m/kT)}{(\rho\gamma_1 m/kT)} \right] . \quad (42)$$

To calculate the term that contains Z_r we need to evaluate

$$Z_r = \int \exp\left[-\sum_{i<j} \frac{\bar{v}(r_{ij})}{kT} \right] d\vec{r}_1 \cdots d\vec{r}_N . \quad (43)$$

Note that for fixed values of T and ρ,

$$\begin{aligned} \frac{\partial \ln Z_r}{\partial m^2} &= -\frac{1}{Z_r} \int \left[\sum_{i<j} \frac{v_1(r_{ij})}{kT} \right] \times \exp\left[\sum_{i<j} \frac{\bar{v}(r_{ij})}{kT} \right] d\vec{r}_1 \cdots d\vec{r}_N \\ &= -\tfrac{1}{2} N\rho \int \frac{v_1(r_{12})}{kT} g(r_{12})\, d\vec{r}_{12} \\ &= -\tfrac{1}{2} N\rho \frac{\gamma_1}{kT} . \end{aligned} \quad (44)$$

Therefore,

$$\ln Z_r = -\tfrac{1}{2} N\rho \int^{m^2} \frac{\gamma_1(x)}{kT}\, dx , \quad (45)$$

to within a constant of integration that does not depend on m and can be included in F_{ideal}. Consequently, the free energy per particle is given by

$$\frac{F-F_{\text{ideal}}}{N}=-kT\ln\left[4\pi\frac{\sinh(\rho\gamma_1 m/kT)}{(\rho\gamma_1 m/kT)}\right]+\tfrac{1}{2}\rho\int^{m^2}\gamma_1(x)\,dx-\rho\gamma_1 m^2\ , \qquad (46)$$

where F_{ideal} now contains additional m-independent contributions. Equation (46) represents a definite and consistent way of evaluating the free energy in our context. Cluster expansion procedures, which are not valid in the range of densities of interest to us are not called upon to obtain the free energy.

The theory as described lends itself to systematic improvements. For example, it is possible to introduce into P_N *some* form of coupling between the spin and spatial variables. In the case of liquid crystals, the spin variable is replaced by the molecular orientation $\hat{\Omega}_i$, and dependences of P_N on $\hat{\Omega}_i\cdot\vec{r}_{ij}$, $\hat{\Omega}_j\cdot\vec{r}_{ij}$, and $\hat{\Omega}_i\times\hat{\Omega}_j\cdot\vec{r}_{ij}$ can be brought into the theory. The mathematics becomes much more complicated and the numerical work horrendous. But with the help of high-capacity computers, the task is not insurmountable. The work is in fact in progress in our group, and will be used to guide us in future calculations for liquid ferromagnets.

III. NUMERICAL EXAMPLES

The formalism described in Sec. II will now be applied to a model system characterized by the pairwise potential of Eqs. (1), (3), and (4). We take ϵ_0 and $\epsilon_1>0$.

Reduced units will be used throughout: energies will be expressed in units of ϵ_0, and lengths in units of σ. The only free parameter in the potential will thus be ϵ_1/ϵ_0: the strength of the spin-aligning part of the potential relative to the strength of the spatial part. There will be two thermodynamic variables, ρ and T. When we refer to the density ρ in the following, we shall mean $\rho\sigma^3$; and when we refer to the temperature T, we shall mean kT/ϵ_0.

We present in this section numerical results obtained for the rather high density $\rho=1.0$. The transition temperature T_c will be determined and $m(T)$ below T_c calculated, for four values of ϵ_1/ϵ_0: 0.40, 0.50, 0.60, and 0.70. A typical calculation will begin with some initial value of the magnetization $m^{(1)}$, placed in Eq. (25) for the effective potential $\overline{v}^{(1)}(r_{ij})$, for which one calculates the effective radial distribution function $g^{(1)}(r_{ij})$. The calculation of g can proceed along one of many alternative paths. We choose to use the hypernetted-chain approximation described in the Appendix. With $g^{(1)}$ one finds $\gamma_0^{(1)}$ and $\gamma_1^{(1)}$ through Eqs. (31) and (32), and solves the transcendental equations (39) and (40). The solution, $m^{(2)}$, is then used to start a new round of calculations. This iterative procedure is carried on until it converges to within a predetermined accuracy. The same procedure is repeated for every set of (ϵ_1,ρ,T).

In practice it is more convenient to first determine for each set of ϵ_1 and ρ the transition temperature T_c. This is possible if the ferromagnetic transition here is of second order in nature. In that case, as soon as a nontrivial solution of m appears, the transition to a magnetically ordered phase would take place. One could set m to zero at T_c, resulting in an effective potential $v(r)=v_0(r)$, an m-independent $g(r)$, and an m-independent γ_1. Let us rewrite the transcendental equations (39) and (40) in the form

$$\alpha\gamma=\frac{1}{y}-\frac{1}{\tanh y}\equiv h(y)\ , \qquad (47)$$

with

$$\alpha=\frac{kT}{\rho\gamma_1}\ , \qquad (48)$$

and

$$\alpha y=m\ . \qquad (49)$$

The slope of $h(y)$ goes to $-\frac{1}{3}$ as y, or m, approaches 0. Since Eq. (47) indicates that the slope is given by α, we find for every set of ϵ_1 and ρ

$$\frac{kT_c}{\rho\gamma_1(T_c,\epsilon_1)}=-\tfrac{1}{3}\ , \qquad (50)$$

which can be graphed to yield T_c. We then apply the iterative procedure described earlier to obtain $m(T)$ for a range of $T<T_c$.

That the transition is of second order can be seen from the following derivation. In Eq. (46), expand $\gamma_1(x)$ at small x

$$\gamma_1(x)=\gamma_{10}+\gamma_{11}x+\cdots\ . \qquad (51)$$

Thus,

$$\int_0^{m^2}\gamma_1(x)\,dx=\gamma_{10}m^2+\tfrac{1}{2}\gamma_{11}m^4+\cdots \qquad (52)$$

also,

$$\ln\left[\frac{\sinh(\rho\gamma_1 m/kT)}{(\rho\gamma_1 m/kT)}\right]=\tfrac{1}{6}\left[\frac{\rho\gamma_{10}}{kT}\right]m^2+O(m^4)\ . \qquad (53)$$

Hence, at small m,

$$\frac{F-F_{\text{ideal}}}{N}=-kT\ln 4\pi-\tfrac{1}{2}kT\left[\frac{\rho\gamma_{10}}{kT}\right]\times\left[\tfrac{1}{3}\left[\frac{\rho\gamma_{10}}{kT}\right]+1\right]m^2+O(m^4)\ . \qquad (54)$$

From Eq. (50), we find

$$\frac{\rho\gamma_{10}}{kT}=-3-\delta \qquad (55)$$

for $T \lesssim T_c$, where δ is a small non-negative number. Therefore

$$\frac{F - F_{\text{ideal}}}{N} = -kT\ln 4\pi - \delta\frac{1}{2}kTm^2 + O(m^4) \quad .(56)$$

The difference in free energy between the ordered state ($m \neq 0$) and the disordered state ($m = 0$), $-\delta\frac{1}{2}kTm^2$, is always nonpositive, which renders the ordered state more stable as soon as it emerges as a possible solution to the self-consistency equation. The transition is thus second order.

Table I displays T_c and $m(T)$ for the four values of ϵ_1. All these results appear in Fig. 1 plotted against the reduced temperature $|T - T_c|/T_c$.

In conclusion we would like to offer the following observations:

(i) The method discussed in this paper can be used to analyze ferromagnetic transitions in liquids. The method is not limited to any particular form of the interaction potential. Potential functions other than those described by Eqs. (1), (3), and (4) are also amenable to our analysis. We intend to use more realistic forms in future work.

(ii) As indicated by Eq. (50) the ferromagnetic transition temperature is determined mainly by the magnetic interaction strength. In the range of temperature under consideration $g(r)$ does not vary appreciably with temperature and thus γ_1 depends only weakly on the temperature. As a consequence, $m(T)$ when plotted against $|T - T_c|/T_c$, as shown in Fig. 1, is almost universal.

(iii) We have not attempted here to determine the melting temperature of the system. Work in this direction is in progress. The advantage of our present method is that the liquid-solid transition and the ferromagnetic transition can be treated on the same footing; so that once the melting problem is solved it will be possible to determine accurately the minimum magnetic interaction strength required for the existence of a ferromagnetic liquid phase.

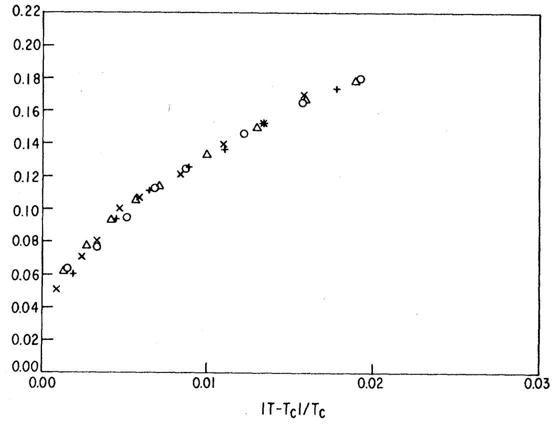

FIG. 1. Magnetization as a function of reduced temperature. +: $\epsilon_1 = 0.40$; o: 0.50; Δ: 0.60; ×: 0.70, all in units of ϵ_0.

(iv) The method given in this paper can be extended to the treatment of binary alloys consisting of both magnetic and nonmagnetic materials. The results of such a study can then be compared with experimental data on Au-Co alloys for which the ferromagnetic liquid phase is purported to exist.

TABLE I. Transition temperature and temperature dependence of magnetization calculated at $\rho = 1.0$ for (a) $\epsilon_1 = 0.40$, (b) 0.50, (c) 0.60, and (d) 0.70, all in units of ϵ_0.

(a) $\epsilon_1 = 0.40$			(b) $\epsilon_1 = 0.50$			(c) $\epsilon_1 = 0.60$			(d) $\epsilon_1 = 0.70$		
T	$\frac{\lvert T - T_c\rvert}{T_c}$	m	T	$\frac{\lvert T - T_c\rvert}{T_c}$	m	T	$\frac{\lvert T - T_c\rvert}{T_c}$	m	T	$\frac{\lvert T - T_c\rvert}{T_c}$	m
1.1047	0.000 00	0.000	1.4021	0.000 00	0.000	1.7046	0.000 00	0.000	2.0119	0.000 00	0.000
1.1025	0.001 99	0.060	1.4000	0.001 50	0.064	1.7025	0.001 26	0.061	2.0100	0.000 94	0.050
1.1000	0.004 25	0.093	1.3975	0.003 28	0.077	1.7000	0.002 72	0.079	2.0075	0.002 19	0.070
1.0975	0.006 52	0.111	1.3950	0.005 06	0.095	1.6975	0.004 19	0.093	2.0050	0.003 45	0.080
1.0950	0.008 78	0.126	1.3925	0.006 85	0.113	1.6950	0.005 66	0.105	2.0025	0.004 67	0.098
1.0925	0.011 04	0.137	1.3900	0.008 63	0.125	1.6925	0.007 12	0.114	2.0000	0.005 91	0.106
1.0900	0.013 31	0.153	1.3850	0.012 20	0.146	1.6875	0.010 05	0.133	1.9950	0.008 40	0.120
1.0850	0.017 83	0.174	1.3800	0.015 76	0.165	1.6825	0.012 99	0.152	1.9900	0.010 89	0.138
1.0800	0.011 36	0.194	1.3750	0.019 33	0.180	1.6775	0.015 92	0.167	1.9850	0.013 37	0.152
1.0750	0.026 89	0.212	1.3700	0.022 89	0.196	1.6725	0.018 85	0.179	1.9800	0.015 86	0.166

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APPENDIX

We choose to use the hypernetted chain (HNC) approximation to determine the pair-correlation function $g(r)$ because for a Lennard-Jones fluid at high densities it appears to be superior to other approximation schemes.[10]

The HNC approximation for $g(r)$ is[11]:

$$g(r)=\exp[-\bar{v}(r)/kT+h(r)-c(r)] \ , \qquad \text{(A1)}$$

where

$$h(r)\equiv g(r)-1 \ , \qquad \text{(A2)}$$

and $c(r)$ is defined by the relation[12]

$$c(r)=h(r)-\rho\int d\vec{r}\,'c(r')h(|\vec{r}-\vec{r}\,'|) \ . \qquad \text{(A3)}$$

We solved the set of equations (A1)–(A3) iteratively by means of well-known numerical techniques.[13]

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[*] On leave from School of Physics and Astronomy, University of Minnesota, Minneapolis, Minn. 55455.

[†] Present address: Department of Physics, University of California, San Diego, LaJolla, Calif. 92093.

[‡] Present address: Department of Physics, New York University, New York, N.Y. 10003.

[1] G. Busch and H. J. Guentherodt, Phys. Lett. 27A, 110 (1968).

[2] G. Busch and H. J. Guentherodt, *Phase Transitions* (Interscience, New York, 1971), p. 179.

[3] Y. Nakagawa, Phys. Lett. 28A, 494 (1969); see also E. Wachtel and N. Kopp, *ibid.* 29A, 164 (1969).

[4] B. Kraeft and H. Alexander, Phys. Kondens. Mater. 16, 281 (1973).

[5] K. Handrich, Phys. Status Solidi 32, K55 (1969).

[6] T. R. Kalaf and T. M. Wu, J. Magn. Magn. Mater. 1, 286 (1976); and (unpublished).

[7] P. C. Hemmer and D. Imbro, Phys. Rev. A 16, 380 (1977).

[8] J. S. Høye and G. Stell, Phys. Rev. Lett. 36, 1569 (1976).

[9] L. Feijoo, V. T. Rajan, and C-W. Woo, Phys. Rev. A 19, 1263 (1979).

[10] W. G. Madden and D. D. Fitts, J. Chem. Phys. 61, 5475 (1974).

[11] R. J. Baxter, in *Physical Chemistry—An Advanced Treatise: Liquid State*, edited by H. Eyring, D. Henderson, and W. Jost (Academic, New York, 1971), Vol. 8, Chap. 4, and references therein.

[12] L. S. Ornstein and F. Zernike, Proc. Acad. Sci. (Amsterdam) 17, 793 (1914).

[13] D. Levesque, Physica (Utrecht) 28, 1124 (1962).