SYSTEM OF MAGNETIC PARTICLES IN AN EXTERNAL MAGNETIC FIELD: SURFACE AND BULK STRUCTURE

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ABSTRACT

A system of particles with spin interaction in an external magnetic field is studied using a general formalism applicable to the solid, liquid or glassy state. Explicit results are given in the Mean Spherical, LOGA and EXP approximations. The Laplace transform of the wall-particle correlation function near a surface is obtained. From it, analytical expressions for the orientational density profile are derived and used to calculate the magnetization and magnetic susceptibility in the bulk. Magnetostriction is also discussed.

KEY WORDS: Amorphous magnetic material, magnetic liquid, solid-fluid interface, wall-particle distribution function.

I. INTRODUCTION

In an earlier paper a general formalism was sketched that can be applied to the computation of the structure of a classical statistical-mechanical system at equilibrium in the presence of a wall and/or other external-field source. Here we apply that formalism to the computation of the one-particle distribution function and the magnetic susceptibility of a system of magnetically active particles with an interparticle spin interaction of either Ising or classical Heisenberg symmetry. (The level of approximation upon which we obtain explicit analytic results in this paper is insensitive to the difference between the Ising and Heisenberg cases, since it yields spherical-model-like results that are independent of spin dimensionality. As Høye and Stell have argued, one expects these results to be exact in the limit of infinite spin dimensionality.)

Because of the generality of our model, our results are not restricted to a particular phase -- solid, glassy, liquid or gaseous. Indeed, in principle they offer a systematic means of determining the phase in which one will find a system defined by a particular set of parameters (density, temperature, external field, interaction strength), although we do not attempt such determinations in this paper and the adequacy of the particular approximations treated herein remain to be determined in this regard.

Our general formalism is derived for systems in thermal equilibrium, and therefore is most obviously appropriate to the treatment of annealed rather than quenched systems. As discussed in some detail in ref. [3], however, the results we obtain in the Mean-Spherical Approximation (MSA) and Lowest-Order Gamma-ordered Approximation (LOGA) are

probably just as relevant to quenched as to annealed systems. (In a solid that has been quenched the translational and orientational correlations are completely decoupled, a situation exactly described by the aforementioned approximations.)^{2,3}

In ref. [2] Høye and Stell already discussed the bulk field-free properties in the MSA and LOGA of the model we consider here and established in those approximations the existence and location of a Curie point in the ferromagnetic case. In Section II of this paper we extend that work to consider the one-particle distribution function in a constant magnetic field in the vicinity of a smooth surface. In Section III we consider the spin orientation distribution function away from a wall as a function of field strength and use it to obtain the relationship between magnetization and field strength. We note the way in which our results manifest magnetostriction effects and reduce to those of Langevin in the paramagnetic limit of weak spin interaction between particles.

The model and approximations we use here complement the usual lattice-model approach to magnetic systems, which has been fine tuned over the past few decades to successfully capture the subtle and special cooperative behavior that comes into its own in the critical region. With our model, much more sophisticated approximations than those we discuss in this paper will be necessary to faithfully capture the nuances of critical behavior. Even to obtain the classical mean-field H \propto M behavior of the critical isotherm requires going a bit beyond the approximations we consider here (presumably, to the level of a Quadratic

Hypernetted Chain (QHNC) approximation).

On the other hand, certain features of magnetic systems that are either totally absent in the usual lattice-model approach (or are present only after being built in rather laboriously) can be easily studied in our particle model, which reveals its considerable richness of structure even in the rather simple approximations we use in this preliminary work. It is structure on precisely the scale of distance -- the interparticle distance -- that is typically neglected in the critical region, where it becomes too small compared to the correlation length to be important. One example of this structure is the way spin ordering in a field changes on the scale of interparticle distance as one leaves the bulk and approaches a smooth wall. Another is the phenomenon of magnetostriction, which is absent by definition in the usual rigid lattice-model treatments of magnetism. In this paper we consider briefly the simplest manifestation of magnetostriction; namely the change in overall volume of an isotropic homogeneous element of magnetic material (such as an amorphous sample in thermal equilibrium. or a magnetic fluid).

II. THE WALL-PARTICLE ORIENTATIONAL CORRELATION FUNCTION IN THE PRESENCE OF A MAGNETIC FIELD

We consider magnetically active particles interacting with a pair potential 2 between particles 1 and 2 of species i and j given by

$$u_{ij}(12) = \begin{cases} u_{0,ij}(r) & r < R_{ij} \\ u_{0,ij} - J(ij)D\Delta(12) & r > R_{ij} \end{cases}$$
 (2.1)

where r is the distance between the particle centers, $u_{0,ij}$ is a nonmagnetic short-range interaction, D is spin dimensionality (3 or 1 for Heisenberg and Ising interactions respectively), $\Delta(12)$ is $\hat{s}_1 \cdot \hat{s}_2$ with \hat{s}_i a unit spin vector, and R_{ij} is a diameter inside of which only the nonmagnetic $u_{0,ij}$ is felt. (For $u_{0,ij}$ we have in mind as model potentials, e.g., a hard-sphere interaction of diameter R_{ij} or a Lennard-Jones interaction with $\sigma_{ij}^{LJ} = R_{ij}$.) In this paper J(ij) is chosen to be a Yukawa potential: $J(ij) = \frac{K_{ij}}{r} e^{-\alpha_{ij}(r-R_{ij})}, \qquad (2.2)$

although we can readily generalize our work to a sum of Yukawas with different K_{ij} and α_{ij} . When $K_{ij} > 0$, Eq. (2.2) represents a ferromagnet while for $K_{ij} < 0$ it represents an antiferromagnet. Adding nonmagnetic species interacting with each other (and with the magnetic particles) with a nonmagnetic potential $u_{0,ij}(r_{12})$ leaves the mathematics of our procedure essentially unchanged; the system then serves as a model for alloys.

The Ornstein-Zernike (OZ) equation for a mixture of particles of species $\ell=1,\ldots,\sigma$ has the form

$$h_{ij}(12) = c_{ij}(12) + \sum_{\ell}^{\sigma} \rho_{\ell} \int c_{i\ell}(13) h_{\ell j}(32) \frac{d(3)}{\Omega},$$
 (2.3)

where h_{ij} (12) and c_{ij} (12) denote the total and direct correlation functions respectively and d(i) means an integration over position \overrightarrow{r}_i and orientation $\overrightarrow{\Omega}_i$ of particle i, with normalization such that $\int d\overrightarrow{\Omega}_i = \Omega$.

In the MSA we can represent $h_{ij}(12)$ and $c_{ij}(12)$ by a truncated expansion of the form²

$$h_{ij}(12) = h_{ij}^{S}(r) + h_{ij}^{\Delta}(r)D\Delta(12)$$
,
 $c_{ij}(12) = c_{ij}^{S}(r) + c_{ij}^{\Delta}(r)D\Delta(12)$, (2.4)

where $h_{ij}^{\ S}(r)$ and $c_{ij}^{\ S}(r)$ are the spherical symmetric parts of the total and direct correlation functions respectively, and the second term represents the orientational parts of those functions. Introducing these expressions into the OZ relation, one obtains two decoupled equations for the spherical and the orientational parts of $h_{ij}(12)$ and $c_{ij}(12)$:

$$h_{ij}^{S}(r) = c_{ij}^{S}(r) + \sum_{\ell}^{\sigma} \rho_{\ell} \int c_{i\ell}^{S}(|\vec{r} - \vec{r}^{\dagger}|) h_{\ell j}^{S}(r^{\dagger}) d\vec{r}^{\dagger}, \qquad (2.5a)$$

$$h_{ij}^{\Delta}(\mathbf{r}) = c_{ij}^{\Delta}(\mathbf{r}) + \sum_{k}^{\sigma} \rho_{k} \int c_{ik}^{\Delta}(|\vec{\mathbf{r}} - \vec{\mathbf{r}}^{i}|) h_{kj}^{\Delta}(\mathbf{r}^{i}) d\vec{\mathbf{r}}^{i}. \qquad (2.5b)$$

·[The truncation Eq. (2.4) and the decoupling of translational and orientational correlations appropriate to the MSA are not generally

valid for any approximation, we should note.] The MSA closure for the OZ relations (suitably generalized from its original hard-core formulation to encompass soft-core potentials) is given by

$$h_{ij}^{S}(r) = h_{0,ij}^{S}(r)$$
 $r < R_{ij}$
 $c_{ij}^{S}(r) = -\beta u_{0,ij}^{S}(r)$ $r > R_{ij}$, (2.6)

and

$$h_{ij}^{\Delta}(r) = 0 \qquad r < R_{ij}$$

$$c_{ij}^{\Delta}(r) = \beta J(12) \qquad r > R_{ij} \qquad (2.7)$$

These equations can be transformed to treat the situation in which a fluid is in the presence of a magnetic field coming out of the wall. If we label one of the species w (for "wall") and take $\lim \rho_w \to 0$, $\lim R_{\text{wi}} \to \infty$ with $\rho_w R_{\text{wi}}^3 \to 0$, Eq. (2.5) with the closure (2.6)— (2.7) describes a system of particles interacting with pair potential $u_{i,j}(r)$ in the simultaneous presence of a field and a wall. Such equations have already been solved by us and by others for the case of polar particles in the MSA and related approximations. Taking the same limit here [and suitably scaling the J(w,i) to increase appropriately as R_{wi} does] allows one to study the correlations in the presence of a magnetic field. In the above limit Eq. (2.5b) becomes:

$$h_0^{\Delta}(z) = c_0^{\Delta}(z) + 2\pi\rho_1 \int_0^{\infty} dt \ t \ c_B^{\Delta}(t) \int_{z-t}^{z+t} ds \ h_0^{\Delta}(s)$$
, (2.8)

where z is the perpendicular distance of a particle from the wall, the subscript 0 denotes a wall-particle correlation function, $c_B^{\Lambda}(t)$ is the bulk direct correlation function (which is considered known), and ρ_1 is the fluid density. Here we have restricted ourselves to the case of a one-component magnetic system of species 1 in the presence of species 2 that, in the limit, becomes the wall and field source. To transform closures (2.7), we introduce the wall and particle diameters R_W and R such that $R_{W1} = (R_W + R)/2$ and take $r \to {}^1_2R_W + z$, $K_{W1} \to \infty$, $R_W \to \infty$ such that K_{W1}/R_W is finite. We note from Eqs. (2.1) and (2.2) that the orientational part of the potential in the limit $R_W \to \infty$ becomes (with $\alpha = \alpha_{12}$):

$$\lim_{R_{w}\to\infty} u_{12}(z,\vec{\Omega}_{w},\vec{\Omega}_{1}) = -\mu \,\,\hat{s}(\vec{\Omega}_{1}) \,\,\hat{H} \,\,e^{-\alpha(z-R/2)} \tag{2.9}$$

where the magnetic field generated in this limit is given by

$$\mu \vec{H} = \frac{DK_{W1}\hat{H}}{(R_{W}/2)}.$$

Here $\hat{A} = \hat{s}(\vec{\Omega}_W)$ is a unit vector in the direction of the spin associated with the "particle" that has become a wall and μ is the magnetic moment associated to the spin $\hat{s}(\vec{\Omega})$.

Then the closures can be written as

$$h_0^{\Delta}(z) = 0$$
 $z < R/2$ $c_0^{\Delta}(z) = \frac{\mu H}{kT} e^{-\alpha(z - R/2)}$ $z > R/2$ (2.10)

where H is the magnitude of the magnetic field, which is coming out of the wall in a fixed arbitrary direction given by $\hat{s}(\vec{\Omega}_w)$. Using Baxter factorization⁶

$$1 - \rho_1 \tilde{c}_B^{\Delta}(k) = \tilde{Q}(k) \tilde{Q}^{T}(-k)$$
 (2.11)

where $\tilde{c}_B^\Delta(\textbf{k})$ is the Fourier transform (FT) of $c_B^\Delta(\textbf{r})$ and

$$\tilde{Q}^{T}(k) = 1 - 2\pi\rho_{1} \int_{0}^{\infty} dr \ e^{ikr}Q(r)$$
 (2.12)

is the FT of the factor correlation function Q(r), we can write Eq. (2.8) for z > R/2 as 7

$$h_0^{\Delta}(z) - 2\pi \rho_1 \int_0^{\infty} dr \ h_0^{\Delta}(z-r)Q(r) = -\frac{1}{2\pi} \int_{-\infty}^{\infty} dk \ \tilde{\phi}(k) \{\tilde{Q}^T(-k)\}^{-1} e^{ikz} \ . \tag{2.13}$$

In the MSA $\tilde{\phi}(k)$ is the FT of the wall-particle potential $+\beta u_{1w}(z)$, i.e., $\tilde{\phi}(k)=\beta \tilde{u}_{1w}(k)$ and the r.h.s. of Eq. (2.13) becomes

i Res[
$$\beta \tilde{u}_{1W}(k) \{ \tilde{Q}^{T}(-k) \}^{-1} e^{ikz}]_{k=z_{m}}$$
 (2.14)

where \boldsymbol{z}_m are the poles of $\beta \boldsymbol{\tilde{u}}_{1w}(k)$ in the lower half complex plane. Since

$$\tilde{\phi}(k) = \int_{R/2}^{\infty} dz \ e^{ikz} \phi(z) = \frac{\beta \mu H}{k + i\alpha} e^{ikR/2} , \qquad (2.15)$$

the expression (2.14) has a pole at $k=-i\alpha$. Høye and Blum⁸ have obtained Q(r) in the MSA for a system interacting with a Yukawa potential or a sum of Yukawas. In the former case the result is 8 (with $q=\alpha_{11}$):

$$Q(r) = Q_0(r) + de^{-qr}, \qquad r > 0$$
 (2.16a)

$$Q_{o}(r) = 0$$
, $r > R$
= $c(e^{-qr} - e^{-qR})$, $r < R$ (2.16b)

with c and d related by the equations

$$d = \frac{\beta K_{11} e^{qR}}{q\tilde{Q}^{T}(iq)},$$

$$q(c+d) = \frac{2\pi \rho_{1} dcq e^{-2qR}}{2q\tilde{Q}^{T}(iq)},$$
(2.17)

where $\tilde{Q}^T(iq)$ can be calculated from Eq. (2.12). Thus $\tilde{Q}(k)$ and $\tilde{Q}^T(-k)$ are known functions and one can evaluate the residue Eq. (2.14). Then Eq. (2.13) becomes

$$h_0^{\Delta}(z) - 2\pi\rho_1 \int_0^{\infty} dr \ h_0^{\Delta}(z-r)Q(r) = \frac{\mu H}{kT} \frac{e^{-\alpha(z-R/2)}}{\tilde{Q}^T(i\alpha)},$$
 (2.18)

with

$$\widetilde{Q}^{T}(i\alpha) = 1 - 2\pi\rho_{1}c \left[\frac{-1}{\alpha + q} \left[e^{-(\alpha + q)R} - 1 \right] + \frac{e^{-qR}}{\alpha} \left[e^{-\alpha R} - 1 \right] \right] - \frac{2\pi\rho_{1}d}{q + \alpha} . \tag{2.19}$$

The Laplace transform of Eq. (2.19) yields

$$\hat{h}_0^{\Delta}(s) = \frac{\mu H}{kT} \frac{e^{-sR/2}}{s + \alpha} \frac{1}{\tilde{Q}^T(i\alpha)\tilde{Q}^T(is)}, \qquad (2.20)$$

where $\boldsymbol{\tilde{Q}}^T(\text{is})$ has the same functional form as $\boldsymbol{\tilde{Q}}^T(\text{i}\alpha)$.

When $\alpha \neq 0$, the magnetic field decays exponentially with the distance from the wall. When $\alpha = 0$, H is constant and we can study the correlation function in the bulk infinitely far away from the wall. Thus, when $\alpha = 0$,

$$\hat{h}_0^{\Delta}(s) = \frac{\mu H}{kT} \frac{e^{-sR/2}}{s} \frac{1}{\tilde{Q}^T(0)\tilde{Q}^T(is)}. \qquad (2.21)$$

The inverse transform of this formula provides a means of studying the orientational correlation function and the magnetic properties of a magnetic system in the presence of a constant magnetic field at any distance from a smooth wall.

One useful representation of $h_0^\Delta(z)$ is a zonal representation obtained from the inversion of $L(s)=e^{-sR/2}/s\widetilde{Q}^T(is)$. We have

$$\hat{\mathbf{h}}_0^{\Delta}(\mathbf{s}) = \frac{\mu H L(\mathbf{s})}{k T \tilde{\mathbf{Q}}^T(0)} . \tag{2.22}$$

From (2.19) we can write

$$\tilde{Q}^{T}(is) = 1 - e^{-Rs} \left[\frac{A}{s(q+s)} + B(s)e^{sR} \right]$$
 (2.23a)

where

$$A = 2\pi \rho_1 c e^{-qR} q \qquad (2.23b)$$

$$B(s) = -\frac{2\pi\rho_1 s(c-d) + 2\pi\rho_1 ce^{-qR}(q+s)}{s(q+s)}.$$
 (2.23c)

It follows that

$$[\tilde{Q}^{T}(is)]^{-1} = \sum_{n=0}^{\infty} (e^{-sR})^{n} \left[\frac{A}{s(q+s)} + B(s)e^{sR} \right]^{n} (-1)^{n}$$
 (2.24)

Then,

$$L(s) = \frac{e^{-sR/2}}{s} \sum_{n=1}^{\infty} (-1)^n (e^{-sR})^n \left[\frac{A}{s(q+s)} + B(s)e^{sR} \right]^n =$$

$$= e^{-sR/2} \sum_{n=1}^{\infty} \frac{A^{n-1}(q+s)e^{-(n-1)s}}{\left[s(q+s)(1+B(s)) \right]^n}.$$
(2.25)

The equation E(s) = 0, where

$$E(s) = s^{2} + s [q + 2\pi\rho_{1}ce^{-qR} - 2\pi\rho_{1}(c-d)] + 2\pi\rho_{1}ce^{-qR}q,$$
(2.26)

gives the poles of each term of (2.25). As in Smith and Henderson, 9 we can write

$$L(z) = Inv[L(s)] = \sum_{n=1}^{\infty} g_n^*(z-n+1)\theta(z-n+1)$$
, (2.27)

where $\theta(x) = 1$ for x > 0 and 0 for x < 0 and

$$g_{n}^{*}(x) = \frac{1}{(n-1)!} \sum_{i=0}^{1} \lim_{t \to i} \frac{d^{n-1}}{dt^{n-1}} \left[\frac{(t-t_{i})^{n} A^{n-1}(q+t)}{E(t)} \right] e^{t(x-R/2)}$$
(2.28)

where t are the roots of E(t). One can proceed following Henderson and Smith 10 and convert $\mathbf{g}_n^*(\mathbf{x})$ to the form

$$g_n^*(x) = \sum_{i=0}^{1} \exp t_i(x - R/2) \sum_{r=0}^{n-1} (x - R/2)^{n-r-1} \beta_{nr}^i$$
 (2.29)

with

$$\beta_{nr}^{i} = \begin{pmatrix} n-1 \\ r \end{pmatrix} \sum_{s=0}^{r} \begin{pmatrix} r \\ s \end{pmatrix} A_{n,r-s}(t_i) \beta_{n,s}(t_i)$$
 (2.30a)

where

$$A_{n,k}(t) = [A(q+t)]^{(k)}$$
 (2.30b)

$$B_{n,k}(t) = \left\{ \left[\frac{(t-t_i)}{E(t)} \right]^n \right\}^{(k)} . \tag{2.30c}$$

and the superscript (k) denotes the $\boldsymbol{k}^{\mbox{th}}$ derivative.

III. BULK MAGNETIC PROPERTIES

In this section we study Eq. (2.21) in the limit $z \to \infty$ when wall effects are not present. More precisely, we consider Eq. (2.5b) in the limits $R_W \to \infty$, then $z \to \infty$ (in that order). In this case the inverse transformation of Eq. (2.21) can be made very easily. We obtain then

$$\mathbf{h}_{0}^{\Delta}(\mathbf{H})\,\hat{\mathbf{s}}(\vec{\Omega}) \, \cdot \, \hat{\mathbf{H}}_{0} = \mu \, \frac{\hat{\mathbf{s}}(\vec{\Omega}) \, \cdot \, \vec{\mathbf{H}}}{kT} \, \frac{1}{\left[\tilde{\mathbf{Q}}^{T}(0)\right]^{2}} \, . \tag{3.1}$$

This function is independent of position and enables us to calculate the one-particle orientational density function $\rho^{OR}(\vec{\Omega}, \vec{H})$, which in the MSA is given by

$$\rho^{\text{OR}}(\vec{\Omega}, \vec{H}) = \frac{\rho_1}{\Omega} \left[1 + h_0^{\Delta}(H) (\hat{s} \cdot \hat{H}) \right]$$

$$= \frac{\rho_1}{\Omega} \left[1 + \mu \frac{\hat{s} \cdot \vec{H}}{kTF} \right]$$
(3.2)

where

$$F = [\tilde{Q}^{T}(0)]^{2} = [1 - \rho_{1}\tilde{c}_{B}^{\Delta}(0)] = [1 + \rho_{1}\tilde{h}_{B}^{\Delta}(0)]^{-1}.$$
 (3.3)

From its definition 2 the LOGA result for ρ^{OR} is the same as that given by Eqs. (3.2) and (3.3) but with F associated with the exact spherically symmetric short-range correlation function rather than the approximation to it. In the classical Heisenberg case, in which spin orientation is continuous in 3-space, magnetization M is given by

$$M = \mu \int \rho^{OR}(\vec{\Omega}, \vec{H}) \cos \gamma \, d\gamma , \qquad (3.4)$$

, where $\cos\gamma$ is the angle between the magnetic field and the spin of a

given particle in the fluid. Substituting Eq. (3.2) in Eq. (3.4), we obtain

$$\vec{M} = \frac{\mu^2 \rho_1 \vec{H}}{3kTF} \tag{3.5}$$

both for the MSA and the LOGA. This result is appropriate for liquid, solid and glassy systems on the level of approximation upon which we work. In particular, the LOGA should give a good representation of quenched alloys. From Eq. (3.5)

$$M/H = \beta \mu^2 \rho_1/3F$$

or equivalently in the Heisenberg case

$$[1 - \rho_1 \tilde{c}_B^{\Delta}(0)]^{-1} = 3M/\beta \mu^2 \rho_1 H . \qquad (3.6)$$

The left-hand-side of this equation can be identified with the differential isothermal susceptibility χ = $\partial M/\partial H$ in the limit H \rightarrow 0 according to the relation

$$[1 - \rho_1 \tilde{c}_B^{\Delta}(0)]^{-1} = 1 + \rho_1 \tilde{h}_B^{\Delta}(0) = D\chi/\beta \mu^2 \rho_1$$
 (3.7)

which is the magnetic analog of the well-known compressibility equation relating $\tilde{c}^S(0)$ and isothermal compressibility $\partial p/\partial \rho$. Above the Curie temperature, isotherms in the H-M plane can be expected to approach the origin linearly, so that

$$\lim_{H\to 0} \chi = M/H.. \tag{3.8}$$

Comparing (3.6) and (3.7), using (3.8), we find consistency in the low-field limit, $H \rightarrow 0$. In the MSA and LOGA, which rest on Eq. (2.1)

and thus are fundamentally linear theories in the field, the linear regime is all we can hope to treat faithfully. Høye and Stell² found that these approximations do predict a Curie point¹¹ at which $1-\rho_1 \tilde{c}^\Delta(0)=0 \text{ for the ferromagnetic case } (K_{11}>0). \text{ Below the Curie temperature these approximations are not useful. When } K_{11}<0 \text{ (the antiferromagnetic case)} \text{ no orientational transition is found. We note that if the magnetic interaction is described by a magnetic dipoledipole potential, no orientational transition is found in these theories either. }^{12}$

To go beyond the linearity of the MSA and LOGA, we can consider the relevant extension of the EXP approximation 13 to the problem at hand. This approximation is accurate for arbitrary field strength to lowest order in density. Its one-particle density function in the limit under consideration is

$$\rho^{\text{EXP}}(\vec{\Omega}, \vec{H}) = \frac{\rho_1}{\Omega} \exp\left[\frac{\mu \hat{s} \cdot \vec{H}}{kTF}\right]$$
 (3.9)

which gives for the magnetization

$$M = \mu \rho L(\eta) \tag{3.10}$$

with $\eta = \mu H/kTF$ and $L(\eta)$ is the Langevin function $\coth \eta - 1/\eta$. In (3.10) ρ is the density established <u>after</u> the field H is turned on. When $\eta \to \infty$ (from either $H \to \infty$ or $F \to 0$), $L(\eta) \to 1$ and $M = \mu \rho$, i.e., complete saturation is obtained. When no correlations between spin particles are present, F = 1 and the classical Langevin result is recovered. At $T = T_c$,

F=0 so that for any H=0, $\eta \to \infty$ and $M=\mu\rho$. This indicates that the critical isotherm in the H-M plane defined by F=0 is of zero curvature; a more sophisticated approximation is needed to get a realistically shaped isotherm.

The fact that the density which appears in Eq. (3.10) differs from the density ρ_1 (the density in the absence of the magnetic field) is due to magnetostriction. The MSA or LOGA do not predict this effect. The EXP does, giving

$$\rho = \int \rho^{\text{EXP}}(\vec{\Omega}, \vec{H}) \, d\vec{\Omega} = \rho_1 \, \frac{\sinh \eta}{\eta} \, . \tag{3.11}$$

Expanding ρ to order H^2 we find, as a measure of magnetostriction

$$\frac{\Delta \rho}{\rho_1} = \frac{1}{6} \left(\frac{\mu H}{kTF} \right)^2 \tag{3.12}$$

where $\Delta \rho = \rho - \rho_1$. We can compare this formula to a thermodynamic formula exact through $O(H^2)$:¹⁴

$$\frac{\Delta \rho}{\rho_1} = \frac{1}{2kT} \left(\frac{\partial \chi^L}{\partial \rho} \right)_{T,g} \frac{H^2}{Q}$$
 (3.13)

where g is chemical potential, Q = $\beta/\rho_1\kappa_T$, κ_T is the zero-field isothermal compressibility and χ^L is the "linear" susceptibility M/H in the limit H \rightarrow 0, which can be identified with the differential susceptibility χ in this limit.

Equation (3.12) is exactly compatible with (3.13) only for an ideal-gas κ_T = β/ρ_1 (Q = 1) and an ideal-gas susceptibility given by χ^L = $\beta\mu^2\rho_1/3$. The comparison between (3.12) and (3.13) shows that

the EXP result is likely to be useful only for magnetic fluids of rather low density, i.e., magnetic gases, in strong fields. Very recently, electrostriction has been studied using the Quadratic Hypernetted Chain approximation (QHNC). The techniques used in that computation are exactly analogous to those necessary in the computation of magnetostriction, and we refer the reader to that work for computational details. The magnetostriction result is

$$\frac{\Delta \rho^{\text{QHNC}}}{\rho_1} = \frac{1}{6} \left(\frac{\mu H}{kTF} \right)^2 \frac{1}{Q} . \tag{3.14}$$

This is a considerable improvement over the EXP result, although it too is exactly consistent with (3.13) only for F = 1, which is compatible with the ideal susceptibility $\chi^L = \beta \mu^2 \rho_1/3$. The most useful of these expressions is (3.13), into which χ^L and Q obtained from the field-free properties of any one of the approximations considered here can be inserted. The χ^L and Q from the MSA are particularly convenient for this purpose, since they have a relatively simple analytic structure as discussed in ref. [2].

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REFERENCES

- 1. L. Blum and G. Stell, J. Stat. Phys. 15, 439 (1976).
- 2. J. S. Høye and G. Stell, Phys. Rev. Lett. 36, 1569 (1976).
- 3. P. T. Cummings and G. Stell, Mol. Phys. (in press).
- 4. L. Blum and J. S. Høye, J. Stat. Phys. 19, 317 (1978).
- D. Isbister and B. Freasier, J. Stat. Phys. <u>20</u>, 331 (1979).
 J. Eggebrecht, D. Isbister, and J. C. Rasaiah, J. Chem. Phys. <u>73</u>, 3980 (1980). E. Martina and G. Stell, to be published.
- 6. R. Baxter, Aust. J. Phys. <u>21</u>, 563 (1968).
- 7. L. Blum and G. Stell, J. Stat. Phys. 15, 439 (1976).
- 8. J. S. Høye and L. Blum, J. Stat. Phys. 16, 399 (1977).
- 9. W. R. Smith and D. Henderson, Mol. Phys. 19, 411 (1970).
- 10. D. Henderson and W. R. Smith, J. Stat. Phys. 19, 191 (1978).
- 11. This has been predicted by other researchers using different approximation techniques. See, e.g., P. C. Hemmer and D. Imbro, Phys. Rev. A 16, 380 (1977), L. Feijoo, C. W. Woo, and V. T. Rajan, Phys. Rev. B 22, 2404 (1980).
- 12. G. S. Rushbrooke, J. S. Høye and G. Stell, Mol. Phys. 26, 1199 (1973).
- 13. H. C. Andersen and D. Chandler, J. Chem. Phys. <u>57</u>, 1918 (1972).
- 14. J. Kirkwood and I. Oppenheim, "Chemical Thermodynamics" (McGraw-Hill, New York, 1961), Chapter 14.
- Polar Fluids; a Molecular Theory of Electrostriction", to be published.