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MOLECULAR FIELD THEORY, THE ONSAGER REACTION FIELD AND THE SPHERICAL MODEL

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Abstract

We have examined the physical and formal aspects of the Onsager method [1] *of solution of the many dipole problem. Our principal conclusion is: the Onsager prescription of subtracting out the reaction field from the mean molecular field (e.g. Weiss field in ferromagnets, Lorentz field in dielectrics, van der Waals field in fluids) is the necessary modification of molecular field theory which guarantees the fluctuation theorem of statistical mechanics (equality of the mean fluctuation of a coordinate to its susceptibility in response to an external field to which it is coupled).*

We develop the theory in detail for the Ising model. In the paramagnetic phase, we show that the Onsager method reduces to the spherical model. This reduction is somewhat incidental, and does not occur in the magnetized phase. On the contrary, the Onsager method then leads to a system of simultaneous differential equations for the magnetization, which is in general intractable. We introduce a scheme of successive approximations, and recover the Weiss theory and the generalized spherical model after the first and second iterations, respectively.

Finally, we indicate how to apply these ideas in the liquid-vapor system.

1. Introduction

IN 1936, Onsager [1] introduced an important concept designed to improve the Lorentz local field approximation in a system of dipoles. The principal innovation lies in the remark that the "orienting" part of the local field on a given dipole must not include the contribution which comes from that part of the polarization of dipoles in its vicinity which arises from its

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instantaneous orientation. Again in other terms: that part of the polarization of surrounding dipoles which is due to their correlation to a given dipole does not contribute to the orienting field on that dipole. The field which arises from this correlated portion of the polarization is called the reaction field. It is proportional to the instantaneous direction μ_0 of the given dipole (we designate this latter by the index 0):

$$\mathbf{E}_0^{\text{reaction}} = \lambda \mu_0 \tag{1}$$

where λ is independent of μ_0.

The orienting part of the field is called the cavity field; it is the field at site 0 when the dipole $\mathbf{p}_0$ is removed. It is obtained from the total mean molecular field by subtracting the mean reaction field:

$$\mathbf{E}_0^{\text{cavity}} = < \mathbf{E}_0^{m} > - \lambda_0 < \mu_0 > . \tag{2}$$

In his original paper, Onsager calculated the reaction field and the cavity field by using continuum electrostatics applied to a cavity of molecular dimensions. In this case, $< \mathbf{E}_0^{m} >$ is the usual Lorentz field.

In the context of an effective molecular field theory, the mean dipole moment is then calculated according to

$$< \mu_0 > = \mathscr{L} (p\, \mathbf{E}_0^{\text{cavity}}/kT) \approx p\, \mathbf{E}_0^{\text{cavity}}/3\, kT, \tag{3}$$

where $\mathscr{L}$ is the Langevin function, and p is the dipole moment. The linear approximation is used to calculate the polarizability and thence the dielectric constant ε. Since the cavity field depends itself on the dielectric constant, this gives rise to a self-consistent equation for ε.

It is our purpose here to analyze further the physical and formal content of the Onsager procedure, and to extend it to other many particle systems, in order to make contact with many body theory as it has developed in recent years. Our formal development is carried out on the Ising model for the sake of both simplicity and definiteness. We also indicate the applicability of the idea to liquid-vapor condensation.

Our principal finding is this: The Onsager prescription of subtracting out the reaction field is the necessary modification of molecular field theory in order to guarantee the fluctuation-response function relation of statistical mechanics, i.e. susceptibility = fluctuation. It is well known that the fluctuation theorem is not satisfied in usual molecular field theory. The Onsager prescription shows how one goes about repairing the situation.

In Section 2, we present a formal development of the Onsager idea applied to the Ising model, which uses the method of response to infinitesimal fields. The advantage of this method is that of pedagogical simplicity. The formal argument emerges quite naturally from the physical statement. In the unmagnetized phase at zero magnetic field, the theory goes through simply and without difficulty. The fluctuation theorem is satisfied by construction. Furthermore, the theory is, incidentally, the same as that of the spherical model of Berlin and Kac [2]. For $T < T_c$, on the other hand, deep complications develop due to the variation of distribution functions with external field. Only upon neglect of this variation does one recover the spherical model in its generalization proposed by one of us [3]. This approximation turns out to be thermodynamically inconsistent. This fact probably accounts for the peculiar behavior found in the spherical model at finite external fields [4].

These reasons then lead us to reconsider the problem directly in its integral formulation. The formal solution to this problem is presented in Section 3. The theory is now thermodynamically consistent, but analytically intractable. We introduce a scheme of successive approximations, and recover the Weiss theory and the generalized spherical model after the first and second iteration, respectively. We hope to present in future work a calculational scheme of evaluation which will show how the difficulties of the spherical model at finite field are in fact met in the present formulation.

In the last section, we discuss various aspects of the development. We indicate how to make contact with the original Onsager paper. In fact, Toupin and Lax [5] have remarked upon the equivalence between the Onsager method and the spherical model, attributing this equivalence to an "accident". This point is now clarified. Finally, we show how these ideas may be applied to the case of liquid-vapor condensation.

We repeat again. Our fundamental point is that the Onsager idea allows one to formulate molecular field theory and preserve the fluctuation theorem of statistical mechanics. The contact with the spherical model which arises in special cases is quite secondary.

2. Differential Formulation

We first develop the theory of the Ising model in the unmagnetized phase for infinitesimal external fields H^{ext}. The mean molecular field on site i is

$$H_i^{\text{Weiss}} = H_i^{\text{ext}} + \sum v_{ij} < \mu_j > , \tag{4}$$

where $-v_{ij}\mu_i\mu_j$ is the spin-spin interaction between sites i and j.

In Weiss molecular field theory, we have to linear terms

$$< \mu_i > = \beta H_i^{\text{Weiss}} = \beta\Big(H_i^{\text{ext}} + \sum_j v_{ij} < \mu_j >\Big) \tag{5}$$

($\beta = 1/kT$), or in terms of Fourier transforms,

$$< \mu_{\mathbf{q}} > = \beta(H_{\mathbf{q}}^{\text{ext}} + v(\mathbf{q}) < \mu_{\mathbf{q}} >), \tag{6}$$

where

$$\mu_{\mathbf{q}} = \frac{1}{\sqrt{N}} \sum_i \mu_i \, e^{i\mathbf{q}\cdot\mathbf{R}_i} ; \quad v(\mathbf{q}) = \sum_i v_{ij} \, e^{i\mathbf{q}\cdot\mathbf{R}_{ij}} . \tag{7}$$

We therefore obtain for the susceptibility

$$\chi(\mathbf{q})^{\text{Weiss}} = \lim_{H_{\mathbf{q}} \to 0} \frac{< \mu_{\mathbf{q}} >}{H_{\mathbf{q}}^{\text{ext}}} = \frac{\beta}{1 - \beta v(\mathbf{q})} . \tag{8}$$

The fluctuation theorem then yields

$$< | \mu_{\mathbf{q}} |^2 > = \frac{1}{\beta} \chi(\mathbf{q}) = \frac{1}{1 - \beta v(\mathbf{q})} \tag{9}$$

which is the Ornstein-Zernike theory [6].

Equation (9) implies $< \mu_i \mu_j > - < \mu_i >< \mu_j > \neq 0$. However, it is precisely the assumption of vanishing correlation which is the basic approximation of the Weiss theory. This is the crux of the inconsistency of usual molecular field theory. One way to get out of it was proposed by one of us by introducing the spherical model [3]. This was subsequently found to be a well defined graphical approximation of the Ising model [7]. However, at finite H^{ext}, this method gives rise to a spurious phase transition [4], and has therefore to be rejected. Thus, the situation at the time of writing this article is confronted with an impasse which we hope will be relieved by the present work. We also emphasize that the recipe of reference [3] is purely formal. The necessary physics is supplied by the following.

It will be most convenient for the sake of subsequent generalization to formulate (4) in terms of changes of local field. The change in mean molecular field due to the imposition of a change in external field (which, for the moment, is simply the change from zero to δH_i^{ext} at site i) is

$$\delta H_i^{Weiss} = \delta H_i^{ext} + \sum v_{ij} \ \delta < \mu_j > , \tag{10}$$

where for the present case $< \mu_j >$ changes from zero to $\delta < \mu_j >$. Now, the change in $< \mu_i >$ due to δH_i^{ext} engenders with it a change in the polarization cloud around it. In other words, $\delta < \mu_j >$ has two contributions: one is from the change in H_j^{ext} as well as the surrounding milieu, and the other from the change in $< \mu_i >$ itself. Onsager's remark is that this latter must not be included in the calculation of the change in the orienting field. From the above discussion it is entirely clear that such an inclusion overcounts the effective field which orients μ_i.

We introduce the symbol H_i^{cavity} for the effective orienting field on site i. Then,

$$\delta H_i^{cavity} = \delta H_i^{ext} + \sum_j v_{ij} \ [\delta < \mu_j > - \ \delta < \mu_j >_{\mu_i}] . \tag{11}$$

$\delta < \mu_j >_{\mu_i}$ is the change in $< \mu_j >$ due to changes in $< \mu_i >$. Thus,

$$\delta < \mu_j >_{\mu_i} = \delta [p_i(+1) \ < \mu_j >_{i\uparrow} + p_i(-1) \ < \mu_j >_{i\downarrow}] , \tag{12}$$

where

$$p_i(\mu_i) = \text{probability of finding the value } \mu_i \text{ at site } i$$

$$= \frac{1}{2}(1 \pm < \mu_i >) \text{ for } \mu_i = \pm 1, \tag{13}$$

$$< \mu_j >_{i\uparrow,\downarrow} = \text{conditional average of } \mu_j \text{ at site } j \text{ if } \mu_i = \pm 1.$$

The variation of (12) then gives

$$\delta < \mu_j >_{\mu_i} = \frac{1}{2}\, \delta < \mu_i > [\, < \mu_j >_{i\uparrow} - < \mu_j >_{i\downarrow}] \tag{14}$$

which for the unmagnetized phase at zero external field reduces to

$$\delta < \mu_j >_{\mu_i} = < \mu_i \mu_j > \cdot\ \delta < \mu_i > . \tag{15}$$

Substituting into (11),

$$\begin{aligned} \delta H_i^{\text{cavity}} &= \delta H_i^{\text{ext}} + \sum_j v_{ij} [\, \delta < \mu_j > - < \mu_i \mu_j > \cdot\ \delta < \mu_i >] \\ &= \delta H_i^{\text{ext}} + \sum_j v_{ij}\ \delta < \mu_j > - \lambda\, \delta < \mu_i > \end{aligned} \tag{16}$$

or in terms of Fourier transforms

$$\delta H_{\mathbf{q}}^{\text{cavity}} = \delta H_{\mathbf{q}}^{\text{ext}} + [v(\mathbf{q}) - \lambda]\ \delta < \mu_{\mathbf{q}} > . \tag{17}$$

Here, $-\lambda/2$ is the energy per particle:

$$\lambda = -\frac{2E}{N} = \sum_j v_{ij} < \mu_i \mu_j > = \frac{1}{N} \sum_{\mathbf{q}} v(\mathbf{q}) < | \mu_{\mathbf{q}} |^2 >. \tag{18}$$

The change in the mean reaction field is then expressed as

$$\delta H_i^{\text{reaction}} = \lambda\, \delta < \mu_i > \cdot \tag{19}$$

In the unmagnetized phase, the response to the orienting field is given by

$$\delta < \mu_i > = \beta\ \delta H_i^{\text{cavity}} \tag{20}$$

or in terms of Fourier transforms

$$\delta < \mu_{\mathbf{q}} > = \beta\ \delta H_{\mathbf{q}}^{\text{cavity}} = \beta\ \delta H_{\mathbf{q}}^{\text{ext}} + \beta [v(\mathbf{q}) - \lambda]\ \delta < \mu_{\mathbf{q}} > \tag{21}$$

whence

$$\chi(\mathbf{q}) = \frac{\delta < \mu_{\mathbf{q}} >}{\delta H_{\mathbf{q}}^{\text{ext}}} = \frac{\beta}{1 - \beta [v(\mathbf{q}) - \lambda]} . \tag{22}$$

To complete the calculation, we now impose the fluctuation theorem

$$\chi(\mathbf{q}) = \beta < | \mu_{\mathbf{q}} |^2 > . \tag{23}$$

By multiplying this relation by $v(\mathbf{q})$, summing over $\mathbf{q}$, and using (18) and (22), we obtain the sum rule

$$\lambda\beta = \frac{1}{N}\sum_{\mathbf{q}} v(\mathbf{q})\,\chi(\mathbf{q}) = \frac{1}{N}\sum_{\mathbf{q}} \frac{\beta v(\mathbf{q})}{1 - \beta[v(\mathbf{q}) - \lambda]} , \tag{24}$$

which because of $\frac{1}{N}\sum_{\mathbf{q}} 1 = 1$ can also be written in the form

$$1 = \frac{1}{N}\sum_{\mathbf{q}} \frac{1}{1 - \beta[v(\mathbf{q}) - \lambda]} = \frac{1}{\beta N}\sum_{\mathbf{q}} \chi(\mathbf{q}) . \tag{25}$$

Equations (22) and (25) are the spherical model equations in the unmagnetized phase. The fluctuation theorem has been imposed on the theory and hence is satisfied by the theory. This explains why the spherical model is the correct way to go about improving molecular field theory. The sum rule (25) is an irrelevant by-product.

In the presence of a uniform magnetization R, the problem is considerably more difficult. It turns out to be necessary to take into account the field dependence of the correlation functions. We return to this point in Section 3, and for the rest of this section work in the approximation that this variation is neglected.

The differential method may then be followed through in a straightforward manner. The reasoning up to equation (14) is unchanged, but the passage from equation (14) to (15) must be modified. In the next section (equations (44)), we prove that in the presence of uniform magnetization $< \mu_i > = < \mu_j > = R$,

$$< \mu_j >_{i\uparrow} - < \mu_j >_{i\downarrow} = 2\frac{< \mu_i \mu_j > - R^2}{1 - R^2} . \tag{26}$$

Hence, (17) is to be replaced by

$$\delta H_{\mathbf{q}}^{\text{cavity}} = \delta H_{\mathbf{q}}^{\text{ext}} + [v(\mathbf{q}) - \delta]\, \delta < \mu_{\mathbf{q}} > , \tag{27}$$

where

$$\delta = \frac{-\frac{2E}{N} - v(0)\, R^2}{1 - R^2} . \tag{28}$$

Another important modification is that the response to the orienting field is no longer given by (20) but by

$$\delta < \mu_i > = \frac{\partial < \mu_i >}{\partial H_i^{\text{cavity}}}\, \delta H_i^{\text{cavity}} , \tag{29}$$

where the derivative is taken about the equilibrium value of the magnetization at fixed T and uniform H^{ext}. Assuming that $< \mu_i > = \tanh \beta H_i^{\text{cavity}}$, we have

$$\frac{\partial < \mu_i >}{\partial H_i^{\text{cavity}}} = \beta(1 - R^2) \tag{30}$$

so that by substituting (27) and (30) into (29) and taking the Fourier transform, we obtain

$$\delta < \mu_{\mathbf{q}} > = \beta(1 - R^2) \; \{\delta H_{\mathbf{q}}^{\text{ext}} + [v(\mathbf{q}) - \delta] \, \delta < \mu_{\mathbf{q}} >\} \, . \tag{31}$$

Thus, the susceptibility becomes

$$\chi(\mathbf{q}) = \frac{\delta < \mu_{\mathbf{q}} >}{\delta H_{\mathbf{q}}^{\text{ext}}} = \frac{\beta(1 - R^2)}{1 - \beta(1 - R^2)[v(\mathbf{q}) - \delta]} \, . \tag{32}$$

Using the fluctuation theorem in the form valid for non-zero magnetization,

$$\chi(\mathbf{q}) = \beta[< |\mu_{\mathbf{q}}|^2 > - | < \mu_{\mathbf{q}} > |^2] \tag{33}$$

we have, because of $< \mu_{\mathbf{q}} > = N^{1/2} R \cdot \delta_{\mathbf{q},0}$,

$$\beta\delta \cdot (1 - R^2) \equiv \beta \left[- \frac{2E}{N} - \right] v(0) R^2 = \frac{1}{N} \sum_{\mathbf{q}} v(\mathbf{q}) \; \chi \; (\mathbf{q}) . \tag{34}$$

We therefore obtain the sum rule

$$1 = \frac{1}{N} \sum_{\mathbf{q}} \frac{1}{1 - \beta(1 - R^2)[v(\mathbf{q}) - \delta]} = \frac{1}{\beta(1 - R^2)} \cdot \frac{1}{N} \sum_{\mathbf{q}} \chi(\mathbf{q}) . \tag{35}$$

Under our assumption of negligible variation of the correlation function, the variation of δ with H^{ext} is neglected. Then, equation (32) for $\mathbf{q} = 0$ may be integrated to

$$R = \tanh \; \{ \beta \, [v(0) - \delta] \, R + H^{\text{ext}} \} . \tag{36}$$

Equations (32), (35) and (36) are the generalized spherical model proposed in reference [3]. As discussed in reference [4], this theory yields close to T_c a spurious phase transition at finite H^{ext}, and must therefore be discarded.

It is clear that the neglect of the variation of correlation functions with field is unwarranted. It is probably this fact which is responsible for the catastrophe in question. This important point was overlooked in the original formulation of reference [3].

To proceed further, we now present an alternative approach which yields a direct generalization of (36) taking into account the field variation of the correlations.

3. Integral Formulation

In Onsager's original formulation, the total molecular field acting on a given dipole is decomposed into two parts: The first part, the reaction field, is always parallel to the instantaneous direction of the dipole: it is the field due to interaction with the polarization cloud around the dipole. The second part, the cavity field, is independent of the direction of the dipole, and is the sum of the external field and the field due to interaction with the uncorrelated fraction of all the other dipoles. As we have emphasized repeatedly, only the cavity field has an orienting effect on the given dipole.

Applying the concept in this form to the Ising model, we observe that the total molecular field H_i^{m} at site i can be decomposed into the sum of the cavity field H_i^{cavity} which is independent of μ_i, and the reaction field $H_i^{\mathrm{reaction}} = \lambda_i \mu_i$ which changes sign on spin reversal:

$$H_i^{\mathrm{m}}(\mu_i) = H_i^{\mathrm{cavity}} + \lambda_i \mu_i \; . \tag{37}$$

It is only the cavity field which gives rise to an orientation dependence of the effective single particle energy

$$\varepsilon_i(\mu_i) = -\,\mu_i H_i^{\mathrm{m}}(\mu_i) = -\,\mu_i H_i^{\mathrm{cavity}} - \lambda_i \; , \tag{38}$$

and which, therefore, enters into the expression for $<\mu_i>$:

$$<\mu_i> = \frac{tr_i \mu_i \; e^{-\beta\varepsilon_i(\mu_i)}}{tr_i \; e^{-\beta\varepsilon_i(\mu_i)}} = \tanh \beta H_i^{\mathrm{cavity}} \; . \tag{39}$$

It is important to realize that so far no approximation has been made. Equation (39) would give the correct magnetization, if one would use the true molecular field defined by

$$e^{\beta\mu_i H_i^{\mathrm{m}}(\mu_i)} = tr' \; e^{-\beta\mathscr{H}} , \tag{40}$$

where tr' means the trace over all spins except μ_i. The calculation of this true molecular field is, of course, an impossibly difficult problem. It is the essence of the Onsager method in the present context to construct an approximate expression for H_i^{m} by physical reasoning. Consider the situation in which the spin at site i is up, i.e. $\mu_i = +1$. The mean interaction energy of this spin with all other spins is then $-\sum_j v_{ij} <\mu_j>_{i\uparrow}$, where $<\mu_j>_{i\uparrow}$ is the conditional average of the spin at site j introduced in the previous section. We take as effective single particle energy of spin μ_i the sum of this interaction energy and the energy $-\mu_i H_i^{\mathrm{ext}}$ in the external field:

$$\varepsilon_i(\mu_i = +1) = -\sum_j v_{ij} <\mu_j>_{i\uparrow} - H_i^{\mathrm{ext}} \; .$$

A corresponding expression is obtained for the $\mu_i = -1$ situation. Since by definition $\varepsilon_i = -\mu_i H_i^{\mathrm{m}}$, the molecular field at site i is thus given by

$$H_i^{\mathrm{m}}(\mu_i = \pm 1) = \sum_j v_{ij} <\mu_j>_{i\uparrow,\downarrow} + H_i^{\mathrm{ext}} \; ,$$

which can be written in the form (37):

$$
\begin{aligned}
H_i^{m}(\mu_i) &= \frac{1}{2} \sum_j v_{ij} [< \mu_j >_{i\uparrow} + < \mu_j >_{i\downarrow}] + H_i^{ext} \\
&+ \frac{\mu_i}{2} \sum_j v_{ij} \, [< \mu_j >_{i\uparrow} - < \mu_j >_{i\downarrow}] \, .
\end{aligned}
\tag{41}
$$

This is the required expression. The nature of the approximation made becomes transparent by observing that instead of calculating the effective single particle energy at site i, $\varepsilon_i(\mu_i) = - \mu_i H_i^{m}(\mu_i)$, as a free energy according to (40), we have obtained it as a mean energy.

By comparison with (37),

$$
\begin{aligned}
H_i^{cavity} &= \frac{1}{2} \sum_j v_{ij} \, [< \mu_j >_{i\uparrow} + < \mu_j >_{i\downarrow}] + H_i^{ext} \\
\lambda_i &= \frac{1}{2} \sum_j v_{ij} \, [< \mu_j >_{i\uparrow} - < \mu_j >_{i\downarrow}] \, .
\end{aligned}
\tag{42}
$$

The conditional averages $< \mu_j >_{i\uparrow,\downarrow}$ can be expressed by the correlation function $< \mu_i \mu_j >$ and the unconditional averages $< \mu_i >$ and $< \mu_j >$: We have

$$
\begin{aligned}
& p_i(+1) \; < \mu_j >_{i\uparrow} + p_i(-1) \; < \mu_j >_{i\downarrow} = < \mu_j > \\
& p_i(+1) \; < \mu_j >_{i\uparrow} - p_i(-1) \; < \mu_j >_{i\downarrow} \qquad < \mu_i \mu_j > ,
\end{aligned}
\tag{43}
$$

where $p_i(\pm 1) = \frac{1}{2} \, (1 \pm < \mu_i >)$ is the probability (13) of finding $\mu_i = \pm 1$. Thus,

$$
< \mu_j >_{i\uparrow} = \frac{< \mu_j > + < \mu_i \mu_j >}{1 + < \mu_i >} ; \quad < \mu_j >_{i\downarrow} = \frac{< \mu_j > - < \mu_i \mu_j >}{1 - < \mu_i >} .
\tag{44}
$$

Using the spatial equivalent of the fluctuation theorem (33),

$$
< \mu_i \mu_j > - < \mu_i >< \mu_j > = \frac{\chi_{ij}}{\beta} \, .
\tag{45}
$$

we obtain the rigorous result

$$
< \mu_j >_{i\uparrow} = < \mu_j > + \frac{\chi_{ij}}{\beta(1 + < \mu_i >)} ; \quad < \mu_j >_{i\downarrow} = < \mu_j > - \frac{\chi_{ij}}{\beta(1 - < \mu_i >} \, .
\tag{46}
$$

With (46), the mean molecular field becomes equal to the Weiss field,

$$
< H_i^{m} > = H_i^{cavity} + < \mu_i > r_i = \sum_j v_{ij} \, < \mu_j > + H_i \equiv H_i^{Weiss} \, .
\tag{47}
$$

Thus, as in Onsager's dipole case, the Weiss field overestimates the orienting field by the average reaction field. The orienting field takes the form

$$H_i^{\text{cavity}} = \sum_j v_{ij} \langle \mu_j \rangle - \frac{1}{\beta} \Big(\sum_j v_{ij} \chi_{ij} \Big) \frac{\langle \mu_i \rangle}{1 - \langle \mu_j \rangle^2} + H_i^{\text{ext}} . \tag{48}$$

By substituting into (39), we obtain the self-consistency equations for the determination of the $\langle \mu_i \rangle$,

$$\langle \mu_i \rangle = \tanh \beta \left\{ \sum_j v_{ij} \langle \mu_j \rangle - \frac{1}{\beta} \Big(\sum_j v_{ij} \chi_{ij} \Big) \frac{\langle \mu_i \rangle}{1 - \langle \mu_i \rangle^2} + H_i^{\text{ext}} \right\} . \tag{49}$$

Since

$$\chi_{ij} = \frac{\partial \langle \mu_i \rangle}{\partial H_j^{\text{ext}}} , \tag{50}$$

this is a set of N simultaneous first order differential equations for the functions $\langle \mu_i \rangle = f(H_1^{\text{ext}}, \ldots H_N^{\text{ext}})$. They can be somewhat simplified if they are converted into equations for the orienting field $H_i^{\text{cavity}} \equiv \xi_i$ by substituting

$$\langle \mu_i \rangle = \tanh \beta \xi_i . \tag{51}$$

One then obtains

$$\xi_i = \sum_j v_{ij} \tanh \beta \xi_j - \Big(\sum_j v_{ij} \xi_{i,j} \Big) \tanh \beta \xi_i + H_i^{\text{ext}} \tag{52}$$

where we have used the notation

$$\xi_{i,j} = \frac{\partial \xi_i}{\partial H_j^{\text{ext}}} = \frac{\chi_{ij}}{\beta (1 - \langle \mu_i \rangle^2)} . \tag{53}$$

This is the end point of the general analysis. If we specialize to the paramagnetic phase and small external fields, we immediately recover the results of the previous section, equations (22) and (25). However, for non-zero magnetization, the system is, in general, intractable. For this reason it is of interest to introduce a scheme of successive approximations which may yield physically sensible results after a few iterations. We set

$$H_i^{\text{ext}} = H + h_i \tag{54}$$

and expand around the uniformly magnetized state:

$$\xi_i = \frac{1}{\beta} \operatorname{artanh} R + \sum_j \xi_{i,j}^0 h_j + \frac{1}{2} \sum_{jk} \xi_{i,jk}^0 h_j h_k + \ldots \tag{55}$$

Equating terms of equal order in the h_i, we obtain a hierarchy of equations for the derivatives of the ξ_i, where the n'th derivative is expressed in terms of all derivatives up to order $n+1$. We can close this system by neglecting the derivatives of some order n_0, and thus obtain a hierarchy of approximations.

The leading approximation, in which already the first derivatives $\xi_{i,j}$ are neglected, is the Weiss theory:

$$R = \tanh \beta \left[v(0)\, R + H \right] .$$

In the next approximation, neglecting the second derivatives $\xi_{i,jk}$, one recovers the modified spherical model of the previous section, equations (32), (35) and (36). We note here that it actually makes more sense to neglect the field dependence of $\xi_{i,j} = \dfrac{\chi_{ij}}{\beta(1 - <\mu_i>^2)}$ than that of χ_{ij} alone.

As mentioned at the end of the previous section, this approximation is inadequate. We suggest here that a fruitful line of attack is to proceed with one more step of the iteration including the $\xi_{i,jk}$ as well. We hope to return to this problem at a future date.

4. Concluding Remarks

The methods discussed in the previous sections can be generalized to other types of interaction without major difficulties. In order to make contact with the original Onsager theory, we consider specifically the case of a system of interacting dipoles. The interaction energy between sites i and j is $-\mu_i \mathbf{v}_{ij} \mu_j$ where μ_i and μ_j are three-dimensional unit vectors, and $\mathbf{v}_{ij}$ is the dipolar interaction tensor

$$\mathbf{v}_{ij} = \frac{p^2}{r_{ij}^{5}} \left[3\, \mathbf{r}_{ij} \mathbf{r}_{ij} - r_{ij}^{2} \cdot 1 \right] . \tag{56}$$

p is the dipole moment. The coefficient λ of the reaction field (1), $\mathbf{E}_i^{\text{reaction}} = \lambda\, \mu_i$, is again related to the energy per particle:

$$p\lambda = -\frac{2E}{N} = \frac{1}{N} \sum_{\mathbf{q},\alpha} v_\alpha(\mathbf{q}) \, <|\mu_{\mathbf{q}}^{\alpha}|^2> . \tag{57}$$

Here, $v_\alpha(\mathbf{q})$ are the eigenvalues of the Fourier transform of $\mathbf{v}_{ij}$, and $\mu_{\mathbf{q}}^{\alpha}$ are the corresponding eigenvectors ($\alpha = 1, 2, 3$).

The orienting field is the mean molecular field less the reaction field, and the polarization induced by the orienting field is given by (3) instead of (20). One thus obtains for the eigenvalues of the susceptibility tensor (susceptibility per unit volume)

$$\chi_\alpha(\mathbf{q}) = \frac{\beta\, n\, p^2}{3 - \beta \left[v_\alpha(\mathbf{q}) - \lambda \right]} , \tag{58}$$

where n is the number of dipoles per unit volume. Imposing the fluctuation theorem leads to the sum rule

$$1 = \frac{1}{N} \sum_{\mathbf{q},\alpha} \frac{1}{3 - \beta\left[v_\alpha(\mathbf{q}) - \lambda \right]} . \tag{59}$$

Special attention is required for the $\mathbf{q} = 0$ component, since the Fourier sums of the $v_\alpha(0)$ are only conditionally convergent and depend, therefore, on the shape of the sample. For this reason $\chi_\alpha(0)$ is defined as the response to the field in the sample, which differs from the external field by the depolarizing field. One obtains

$$\chi_\alpha(0) = \frac{\beta n p^2}{3 - \beta(w_\alpha - \lambda)} . \tag{60}$$

The w_α are the eigenvalues of the shape-independent tensor $\mathbf{w} = \mathbf{v}(0) + 4\pi n p^2 \mathbf{L}$, where $\mathbf{L}$ is the depolarization tensor.

Contact with the original Onsager theory proceeds most easily through the spherical model method of Toupin and Lax (TL) [6]. Our equations (59) and (60) are the equations (44) and (47) of TL, and the symbol t' of TL is related to our λ by $3 + \beta\lambda = \beta n p^2 \cdot t'$.

For the isotropic continuum model of Onsager, the $v_\alpha(\mathbf{q})$ are simply

$$\begin{aligned} v_1(\mathbf{q}) &= v_2(\mathbf{q}) = +\frac{4\pi}{3} n p^2 \quad (\text{eigenvector} \perp \mathbf{q}) \\ v_3(\mathbf{q}) &= -\frac{8\pi}{3} n p^2 \quad (\text{eigenvector} \parallel \mathbf{q}), \end{aligned} \tag{61}$$

and w has the value

$$w = \frac{4\pi}{3} n p^2 .$$

Substitution into (59) and (60) and elimination of λ leads immediately to the Onsager formula for the dielectric constant $\varepsilon = 1 + 4\pi\chi$.

Finally, we mention briefly the application of the underlying concept of this paper to the liquid-vapor system. In response to an imposed force, the density increases at a point in space. The surroundings of this point also increase in density; that part of the density change of the surroundings due to the density change of the point in question must be subtracted out. This means that one must introduce both correlations to particles and holes in the ultimate formulation.* This example also illustrates the irrelevance of the sum rule. In fact, there is no sum rule whatever on the density fluctuations $\rho_{\mathbf{q}} = \sum \exp(\mathbf{q} \cdot \mathbf{r}_i)$.

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* This problem is now being investigated in collaboration with S. Vadek.

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