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On the Validity of the Maier-Saupe Theory of the Nematic Transition†

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Abstract—The Maier–Saupe theory of the nematic phase transition can be viewed as arising from two basic assumptions: a kind of induced-dipole induced-dipole interaction and the neglect of the effect of orientational interactions on positional correlations. The theory makes the further assumption of the validity of the molecular field approximation for the orientational interactions. We have asked if the first-order transition predicted by Maier and Saupe is just an artificial consequence of the molecular field approximation. To answer this question, we have constructed a model based on the same two assumptions. These are augmented by the further assumptions of discretization of space and discretization of molecular orientations and by the replacement of a rotationally invariant interaction with one having a preferred axis. The latter replacement is analogous to replacing the Heisenberg model for spin systems with the Ising model. By imbedding the present model and the Maier–Saupe theory within the same sequence of variational bounds on the grand potential, it is argued that the present model is superior. It is shown that this model has no first-order phase transition, although the molecular field approximation, when applied to this model, again gives such a transition. It is therefore proposed that the failure to find a first-order transition points to a breakdown in one of the two basic assumptions.

1. Introduction

Maier and Saupe[1] (MS) have described the nematic transition with a theory involving two basic assumptions and one further approximation:

(**A**) the assumption of an induced-dipole induced-dipole interaction between molecules of the liquid as the sole source of the transition;

(**B**) the assumption that the probability of any configuration of centers of mass is not affected by the interaction between molecular orientations;

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(C) the molecular field approximation to treat the resulting problem of interacting orientations.

The MS theory has often been quoted both regarding its description of the order vs. T and the prediction of a first-order phase transition.

In this paper, we wish to argue that the first-order transition found by Maier and Saupe may be a result of the crudity of the molecular field approximation. We shall argue that a better theory (one still based on **A** and **B** but avoiding the molecular field approximation) would not show a first-order transition. Since such a transition is observed, we believe that it probably comes either from longer range forces than assumed or from detailed correlations of center of mass motions to molecular orientations. The correlations seem more likely because the important forces that have been neglected are, if anything, the shorter range hard-core forces.

In Section 2, we shall formulate a model that we believe incorporates some of the essential features of MS's first and second assumptions but which has the one drawback of breaking rotational symmetry. In Section 3, the model will be exactly solved and shown to give no phase transition for forces as short ranged as those assumed by Maier and Saupe. By contrast, when the same model is solved in the molecular field approximation, a first-order transition is predicted.

In Section 4, we attempt to compare the MS theory with the model presented here with some rigor. To this end, we formulate a systematic series of successively cruder approximations to the grand potential of a liquid crystal. The approximations that lead specifically to the MS theory and to our present model are deferred as long as possible to get the best possible direct comparison. Neither model falls into this series rigorously, but the suggestion is strong that the MS theory gives the poorer upper bound to the exact grand potential.

The possibility that the symmetry-breaking character of the soluble model is a crucial defect is not, however, excluded.

2. Formulation of Model

The Maier–Saupe theory would result if the molecular field approximation were applied to a system of distinguishable molecules

interacting with one another through an interaction of the form

$$u_{ij} = -4K(\mathbf{r}_i - \mathbf{r}_j)(\cos^2\theta_i - \tfrac{1}{3})(\cos^2\theta_j - \tfrac{1}{3}), \tag{2.1}$$

where θ_i and θ_j are the angles made by the molecular axes of the ith and jth molecules with some preferred direction. In the molecular field approximation, the details of K_{ij} are not needed because the sum over pairwise interactions (2.1) is replaced by a sum of terms, each one describing a molecule in a molecular field:

$$-4\sum_i(\cos^2\theta_i - \tfrac{1}{3})\sum_{j\neq i}K_{ij}\langle\cos^2\theta_j - \tfrac{1}{3}\rangle. \tag{2.2}$$

Only $K = \sum_i K_{ij}$ appears, because $\langle\cos^2\theta_j\rangle$ is independent of j.

Maier and Saupe, of course, do not start with an interaction of the form (2.1) but with an induced–dipole induced–dipole interaction for which there is no preferred direction in space and in which the dependence on the relative position vector $\mathbf{r}_i - \mathbf{r}_j$ and on the orientations of the two molecules can not be written as a product of independent factors. Thus, although the two interactions are "consistent" in that they yield the same result in the molecular field approximation, a consideration of (2.1) is not equivalent to considering the Maier–Saupe interaction.

We defer to Section 4 a detailed attempt at rigorously formulating the MS model so that it can be compared with a model like (2.1). In this and the next sections, we wish only to formulate a model suggested by (2.1) and to solve it exactly, showing how the molecular field approximation is able to predict a first-order transition when in fact no transition at all occurs.

We consider first N particles whose positions are characterized by $\{\mathbf{r}_i\}$ and whose orientations are given by $\{\theta_i, \phi_i\} \equiv \{\Omega_i\}$. We further assume pairwise interactions of the form (2.1).

Our task is to calculate the partition function

$$(N!)^{-1}\int(\mathrm{d}\Omega)\int(\mathrm{d}r)\exp\left[2\beta\sum_{i,j}K(\mathbf{r}_i,\mathbf{r}_j)(\cos^2\theta_i - \tfrac{1}{3})(\cos^2\theta_j - \tfrac{1}{3})\right], \tag{2.3}$$

where $\int(\mathrm{d}\Omega)$ denotes $\int\cdots\int\prod_i \sin\theta_i\,\mathrm{d}\theta_i\,\mathrm{d}\phi_i$, etc.

We now suppose 3-space is replaced by a perfect lattice with mesh points $\mathbf{R}_\alpha$, $\alpha = 1, \cdots, \mathcal{N}$ and that the particle positions $\mathbf{r}_i$ are confined to be at the lattice points. For $\mathcal{N}$ sufficiently large compared with N, this could be as accurate as we wish. We shall, however, go to the other extreme and assume that $\mathcal{N} = N$, i.e., the fluid is com-

pletely dense. In this case, particles are still free to " move " in the sense that we sum over the $N!$ possible configurations, but the local density cannot vary with the degree of local orientational order.

The partition function is then

$$(N!)^{-1}\int (d\Omega)\sum_{\mathscr{P}}\exp\left[2\beta\sum_{\alpha,\gamma}K_{\alpha\gamma}(\cos^2\theta_\alpha-\tfrac{1}{3})(\cos^2\theta_\gamma-\tfrac{1}{3})\right], \quad (2.4)$$

where

$$K_{\alpha,\gamma}=K(\mathbf{R}_\alpha,\mathbf{R}_\gamma), \quad (2.5)$$

and $\mathscr{P}$ ranges over the $N!$ permutations of $(1, 2, 3, \cdots N)$. In a particular configuration characterized by $\mathscr{P}$, the $\mathscr{P}\alpha$th particle is at the position $\mathbf{R}_\alpha$, etc.

Because the variables $\Omega_1, \cdots, \Omega_N$ are just dummy variables, they can be renamed appropriately in each term of (2.4), giving for the partition function Z' and the free energy F'

$$e^{-\beta F'}=Z'$$
$$=\int (d\Omega)\exp\left[2\beta\sum_{\alpha,\gamma}K_{\alpha\gamma}(\cos^2\theta_\alpha-\tfrac{1}{3})(\cos^2\theta_\gamma-\tfrac{1}{3})\right], \quad (2.6)$$

i.e., the problem reduces exactly to that of molecules fixed on a lattice. This illustrates that once the assumption has been made that relative orientations don't affect configurational probabilities, the motion of the molecules is irrelevant.

The integration in (2.6) over all the polar angles ϕ_i can be performed immediately, leaving for the free energy the N-dimensional integral

$$\exp(-\beta F')=\int\cdots\int\prod_\alpha(\sin\theta_\alpha\,d\theta_\alpha)$$
$$\cdot\exp\left[2\beta\sum_{\alpha,\gamma}K_{\alpha\gamma}(\cos^1\theta_\alpha-\tfrac{1}{3})(\cos^2\theta_\gamma-\tfrac{1}{3})\right]. \quad (2.7)$$

The variable $\cos^2\theta_\alpha$ is a random variable ranging over (0, 1) with an *a priori* weight $\frac{1}{2}\sin\theta_\alpha d\theta_\alpha$, i.e.,

$$\text{Prob}\,(y<\cos^2\theta_\alpha<y+dy)=\tfrac{1}{2}y^{-1/2}dy \quad (2.8)$$

at infinite temperature.

At this point we " discretize " the model by making the replacement

$$\cos^2\theta_\alpha\to 1-\sigma_\alpha,\quad \sigma_\alpha=0,1 \quad (2.9)$$

attaching *a priori* weights of $\frac{2}{3}$ to $\sigma_\alpha = 1$ and $\frac{1}{3}$ to $\sigma_\alpha = 0$, so that

$$\langle 1 - \sigma_\alpha \rangle_{T\to\infty} = \langle \cos^2 \theta_\alpha \rangle_{T\to\infty} = \tfrac{1}{3}. \tag{2.10}$$

This model problem[2] defines a free energy F and partition function Z:

$$\exp(-\beta F) = Z = \sum_{\sigma_1=0}^{1} \cdots \sum_{\sigma_N=0}^{1} 2^{\Sigma\sigma_\alpha} \exp\left[2\beta \sum_{\alpha,\gamma} K_{\alpha\gamma}(\sigma_\alpha - \tfrac{2}{3})(\sigma_\gamma - \tfrac{2}{3})\right]. \tag{2.11}$$

This discretization assumption is the first we have made that is not consistent with the MS theory, i.e. (2.11) in the molecular field approximation does not agree with the results of MS theory. In some sense this assumption is like replacing an infinite-spin Ising model by a spin-$\frac{1}{2}$ model. It can be expected to affect the qualitative behavior very near a second-order transition, when there is one, and the detailed behavior elsewhere, so we shall have to see what the molecular field approximation would give for this discretized model.

3. Solution of Model

The partition sum Z is essentially that of a spin-$\frac{1}{2}$ Ising model in a special temperature-dependent magnetic field. To see this, we introduce variables τ_α,

$$\tau_\alpha = 2\sigma_\alpha - 1 \tag{3.1}$$

which take on the values -1 and 1. Then the partition function is

$$Z = \sum_{\tau_1} \cdots \sum_{\tau_N} \exp\left[-\beta(H_I + \tfrac{1}{2}NkT \ln 2 + N \sum_{\gamma} K_{\alpha\gamma}/18)\right], \tag{3.2}$$

where

$$H_I = -\tfrac{1}{2} \sum_{\alpha,\gamma} K_{\alpha\gamma}\tau_\alpha\tau_\gamma + \sum_{\alpha} h(\tau)\tau_\alpha \tag{3.3}$$

and $h(T)$ is the " field "

$$h(T) = \tfrac{1}{3} \sum_{\gamma} K_{\alpha\gamma} - \tfrac{1}{2}kT \ln 2. \tag{3.4}$$

The second term in $h(T)$ comes from the weighting factor $2^{\Sigma\sigma_\alpha}$.

The free energy per molecule is just

$$f(T) = -(kT/N) \ln Z = \tfrac{1}{2} \ln 2 + (\beta/18) \sum_{\gamma} K_{\alpha\gamma} + f_I(T, h(T)), \tag{3.5}$$

where $f_{\mathrm{I}}(T, h)$ is the free energy of the spin-$\frac{1}{2}$ Ising model at temperature T in the field h.

Let us recall two properties[3] of the spin-$\frac{1}{2}$ model in the thermodynamic limit ($N \to \infty$).

(1) In the limit of vanishing magnetic field, and below a certain temperature T_{I}, the system manifests spontaneous magnetization, i.e.

$$\lim_{h\to 0\pm}\lim_{N\to\infty}\left\langle \frac{1}{N}\sum_{1}^{N}\tau_i\right\rangle_{h,T} \equiv \pm M_s(T) = \lim_{h\to 0\pm}\left(-\frac{\partial}{\partial h}f_{\mathrm{I}}\right)_{T_{\mathrm{I}}}, \qquad T < T_{\mathrm{I}}.$$

Thus, the limiting free energy per particle f_{I} is nonanalytic along the $h = 0$ line in the interval $0 < T \leqslant T_{\mathrm{I}}$. T_{I} is the critical temperature or Curie temperature for this Ising model.

(2) In a finite magnetic field, the free energy f_{I} is analytic for all positive temperatures.

Thus, if a first-order transition is to occur for $f(T)$, it can only occur for $h = 0$ and at a temperature below T_{I}, i.e. it occurs at a temperature T_h defined by

$$h(T_h) = 0 \tag{3.6}$$

and then only if T_h is below T_{I}. The criterion for a first-order transition is therefore

$$T_h < T_{\mathrm{I}}. \tag{3.7}$$

If this condition is satisfied, the latent heat per molecule is $\frac{1}{2}kT_hM_s(T_h)$, where $M_s(T)$ is the spontaneous magnetization for the Ising model in zero field.

We also remark that if a transition occurs, the discontinuity in $\langle\tau\rangle$ must be symmetric around zero, since the spontaneous magnetization just changes sign as $h(T)$ goes through zero. In terms of the order parameter $S = \langle 1 - \frac{3}{2}\sigma\rangle = \frac{1}{4}\langle 1 - 3\tau\rangle$, this implies that the jump in the order must be symmetric around $S = \frac{1}{4}$, and that there is order at all finite temperatures. We discuss this at the end of this section.

Is the inequality (3.7) satisfied? To give a precise answer, we would have to know how $K_{\alpha\gamma}$ varies with $|\mathbf{R}_\alpha - \mathbf{R}_\gamma|$, and we would need to know T_{I} for such a non-nearest-neighbor Ising model. Lacking this information precisely, we have used the calculations of Domb and Dalton[4] to get an estimate of T_{I}. Domb and Dalton studied Ising models on various two- and three-dimensional lattices with a

constant interaction J out to a certain shell of neighbors and zero beyond.

If q is the total number of molecules interacting with a given one, and $K = qJ$, then

$$kT_h = 0.953K, \tag{3.8}$$

while for the Ising critical temperature, using series methods, Domb and Dalton made the following estimates:

$$\begin{aligned} kT_I &= 0.794K \qquad \text{b.c.c., nearest neighbors} \\ &= 0.816K \qquad \text{f.c.c., nearest neighbors} \\ &\sim \left(\frac{q}{3.5+q}\right)K, \text{ as } q \to \infty, \ K \text{ fixed.} \end{aligned} \tag{3.9}$$

We see that a first-order transition is predicted only if $q \gtrsim 71$, i.e. with a constant interaction, it must extend to third nearest neighbors in a face-centered cubic lattice. In fact, the interaction we are considering falls off far more rapidly than that, so there would be no first-order transition.

What would we have predicted had we applied the molecular field approximation to the discretized model (2.13)? To answer this question, we could, of course, carry out a calculation exactly analogous to Maier and Saupe's. But for this model, there is a simpler way. We simply use the fact that the molecular field approximation is exact for interactions of infinite range and zero strength (the limit being taken so that $qK =$ constant as $q \to \infty$). Thus if the discretized model were calculated in the molecular field approximation, we would conclude that a first-order transition always occurs at a temperature T_h defined by (3.8). This is in sharp contrast to the exact results for reasonably short-ranged interactions.

We conclude that the molecular field approximation can seriously overestimate the circumstances under which a first-order transition will occur. In the next section, we shall discuss the relation of our model to that of Maier and Saupe and the implications of this conclusion for the validity of the MS theory.

Let us discuss briefly the existence, found for our discretized model, of a non-vanishing order parameter at all temperatures. It is easy to see that the order parameter is non-vanishing for the continuous model (2.6) as well. The non-vanishing of the order para-

meter is a detailed consequence of the way the two models have broken full rotational symmetry. To see this, we compare with the classical Heisenberg and Ising models for interacting spins, where the pairwise interactions occur between spin vectors of fixed length but arbitrary direction and are, respectively, $-K_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$ and $-K_{ij}S_i^z S_j^z$. In the Heisenberg model, the reduced probability density for the ith spin is $\rho(\Omega_i) = \int \cdots \int \prod_{j \neq i} d\Omega_j \exp [\beta \sum_{j \neq i} K_{ij}\mathbf{S}_i \cdot \mathbf{S}_j]$. This is independent of the direction Ω_i of $\mathbf{S}_i$, because $\mathbf{S}_i \cdot \mathbf{S}_j$ is invariant under rotations of the coordinate axes in spin space. Thus $\langle \mathbf{S}_i \rangle \propto \int d\Omega_i \rho(\Omega_i)\mathbf{S}_i = 0$. In the Ising model, the reduced probability density is not independent of S_i^z but it is still an even function of S_i^z, because $S_i^z S_j^z$ is invariant under inversion of the coordinate axes in spin space. This is enough to insure that $\langle S_i^z \rangle = 0$.

The model (2.6) can be considered as an Ising-like approximation to a Heisenberg-like interaction—$\frac{4}{3}K_{\alpha\gamma}(\cos^2 \theta_{\alpha\gamma} - \frac{1}{3})$ where $\theta_{\alpha\gamma}$ is the angle between Ω_α and Ω_γ. Because this Heisenberg-like interaction is rotationally invariant, we find that $\langle \cos^2 \theta_\alpha - \frac{1}{3} \rangle = 0$, the function $\cos^2 \theta - \frac{1}{3} \propto P_2(\cos \theta)$ being orthogonal to a constant ($P_0(\cos \theta)$). However, in passing to the Ising-like model, the fact that the reduced probability density is still invariant under inversion is of no help, because the order parameter is now the average of an even function, $\cos^2 \theta_\alpha - \frac{1}{3}$, which is not orthogonal to all even functions but only to a constant.

The order calculated above the transition temperature (if there is one) is therefore an artificial consequence of the model, although the description of short-range correlations may be good. This is just complementary to the situation with the molecular field approximation where, in order to predict correctly the absence of all long-range order at high temperatures, one must foresake the description of all short-range correlations.

Let us now turn to the relation of the present model to that of Maier and Saupe.

4. Variational Comparison of Various Models

Of the three cornerstones of the Maier–Saupe theory mentioned in Section 1, the second and third are crucial and merit restatement:

B. It is assumed that the probability of any configuration of molecular centers of mass is not affected by the interaction between molecular orientations. In the language of Maier and Saupe, time averages are performed over the orbit of a particle on the assumption that the orbits are not affected by the orientations of the particular particle or of the particles near which it passes. In the language of phase-space averages, dependence of the two-body, three-body, etc. correlation functions on position variables is not affected by the orientations of the particles involved. An effective statistical two-body interaction between orientations is thus heuristically derived from the fundamental interaction.

C. This effective interaction between orientations is treated in the approximation of a uniform " mean field " or " molecular field ".

In the original work of Maier and Saupe, these ideas are implemented in an *ad hoc* manner, rather than systematically within the framework of an otherwise rigorous statistical mechanical calculation. It is therefore not clear where **B** ends and **C** begins. We first present an attempt at putting the Maier–Saupe theory within a more rigorous context.

For a given configuration of centers of mass and a given set of orientations, the full interaction energy will be assumed to have the form

$$W(\mathbf{r}_1\Omega_1, \cdots, \mathbf{r}_N\Omega_N) = V(\mathbf{r}_1, \cdots, \mathbf{r}_N) + \sum_{(i,j)} u_{ij}, \tag{4.1}$$

where we do not assume (2.1) but only that

$$u_{ij} = u(\mathbf{r}_i\Omega_i, \mathbf{r}_j\Omega_j) \tag{4.2}$$

is symmetric in i and j. The summation goes only over distinct pairs. The only assumption we have made other than to neglect internal deformations of the molecules is that the interaction between orientations is a symmetric *two*-body interaction, i.e., we are not making assumption **B.** The decomposition (4.1) is of course not unique, since any function of the form $\sum_{(i,j)} v(\mathbf{r}_i, \mathbf{r}_j)$ could be added to $V(\mathbf{r}_1, \cdots, \mathbf{r}_N)$ and subtracted from $\sum_{(i,j)} u_{ij}$. It is made unique by the requirement that $\int d\Omega_j\, u_{ij} = 0$ for all $(\mathbf{r}_i, \mathbf{r}_j)$.

We must now calculate the configuration integral Q_N and Helmholtz free energy F_N defined by[5]

$$\exp(-\beta F_N) = Q_N$$
$$= (N!)^{-1}\int\cdots\int(dr)(d\Omega)\exp\left[-\beta(V+\sum_{(i,j)}u_{ij})\right]. \tag{4.3}$$

Assumption **B** is equivalent to the assumption that the interaction term $V(\mathbf{r}_1\cdots\mathbf{r}_N)$ alone determines the probability of any configuration $(\mathbf{r}_1\cdots\mathbf{r}_N)$. We have tried to express this idea in some rigorous mathematical development. One relatively crude way to do this is to use a multidimensional version of a well-known inequality. For single integrals with real functions $a(x)$ and $b(x)$, this inequality[6] is just

$$\int_L dx\, e^{a(x)+b(x)} \geqslant \int_L dx\, e^{a(x)}e^{\bar{b}}, \tag{4.4a}$$

where

$$\bar{b} = \int_L dx\, b(x)e^{a(x)} \Big/ \int_L dx\, e^{a(x)}, \tag{4.4b}$$

and L is any domain on the real axis for which the integrals all exist. When generalized to the integral over the $3N$-dimensional configuration space, this inequality yields

$$Q_N \geqslant Q_N{}^{c}Q_N{}^{or}, \tag{4.5}$$

where

$$Q_N{}^{c} = (N!)^{-1}\int\cdots\int(dr)\exp\left[-\beta V(\mathbf{r}_1,\cdots,\mathbf{r}_N)\right], \tag{4.6a}$$

and

$$Q_N{}^{or} = \int\cdots\int(d\Omega)\exp\left(-\beta\sum_{(i,j)}\bar{u}_{ij}\right) \tag{4.6b}$$

is the configuration integral, neglecting orientational interactions, and

$$\bar{u}_{ij} = \bar{u}(\Omega_i,\Omega_j) = \int\cdots\int(dr)\,e^{-\beta V}u_{ij} \Big/ \int\cdots\int(dr)\,e^{-\beta V} \tag{4.7}$$

is the average interaction between the ith and jth orientations, the average being taken over all configurations $(\mathbf{r}_1\cdots\mathbf{r}_N)$ with weight $e^{-\beta V}$. Now if the probability that the ith and jth molecules are in unit volumes at $\mathbf{r}_i$ and $\mathbf{r}_j$ is called $f(\mathbf{r}_i,\mathbf{r}_j)$, so that

$$f(\mathbf{r}_i,\mathbf{r}_j) = \int\cdots\int\prod_{k\neq i,j}d^3r_k\,e^{-\beta V} \Big/ \int\cdots\int(dr)\,e^{-\beta V}, \tag{4.8}$$

then

$$\bar{u}_{ij} = \int\int \mathrm{d}^3 r_i \, \mathrm{d}^3 r_j \, u(\mathbf{r}_i \Omega_i, \mathbf{r}_j \Omega_j) f(\mathbf{r}_i, \mathbf{r}_j). \tag{4.9}$$

The function $f(\mathbf{r}_i, \mathbf{r}_j)$, being normalized by $\int\int \mathrm{d}^3 r_i \, \mathrm{d}^3 r_j f(\mathbf{r}_i, \mathbf{r}_j) = 1$, approaches ρ^2/N^2 as $|\mathbf{r}_i - \mathbf{r}_j| \to \infty$ and is $O(N^{-2})$ for all i and j. Since u_{ij} is of finite range, we conclude that $\bar{u}_{ij} = O(N^{-1})$.

Expression (4.5) gives an approximation to the free energy F_N which is an upper bound:

$$F_N \leqslant F_N{}^{\mathrm{c}} + F_N{}^{\mathrm{or}} = -kT(\ln Q_N{}^{\mathrm{c}} + \ln Q_N{}^{\mathrm{or}}). \tag{4.10}$$

$F_N{}^{\mathrm{c}}$ is the pure configurational contribution to the free energy (i.e., neglecting the orientational contribution). $F_N{}^{\mathrm{or}}$ is a purely orientational free energy. In evaluating $F_N{}^{\mathrm{or}}$, each molecular orientation interacts with every other one, but with a strength that is averaged over all relative positions. This effective, two-body, orientational interaction $\bar{u}_{ij}$ is therefore of essentially infinite range and infinitesimal strength.

Because of the infinite range of $\bar{u}_{ij}$, the molecular field approximation should be exact[7] to leading order in N, in evaluating $F_N{}^{\mathrm{or}}$. Thus, if approximation **B** is implemented in the crude manner of (4.5)–(4.10), then approximation **C** is not an additional approximation.

But, of course, this implementation of approximation **B** is too crude. While each particle will have interacted with every other particle after a sufficiently long period of time, most of these interactions will not have occurred before equilibrium is established. It is therefore unnecessarily crude to replace the strong but very occasional and short-lived orientational interaction between any pair of particles by an extremely weak but infinitely long-lived interaction. Yet this is what is done in (4.5)–(4.10), albeit in the language of phase space averages rather than time averages.

Let us turn to a different but equivalent formulation of the liquid crystal problem in which we can again assume that the configurational probability is independent of the molecular orientations, but in which the orientational interactions extend only to the immediate environment. Such an implementation of **B** is intuitively better than the previous one. We shall also show that it is mathematically superior in the sense of giving a better upper bound to the exact free energy (or, in this case, grand potential).

We consider 3-space to be replaced by the mesh introduced in Section 2 and further assume that the number of mesh points $\mathcal{N}$ is extremely large compared with the number of particles. We shall now describe a configuration of the molecules by assigning to each mesh point an occupation number n_R which can be zero or one, and an orientation Ω_R which gives the orientation of the molecule centered at $\mathbf{R}$ when $n_R = 1$ and is arbitrary when $n_R = 0$.

We propose to sum over all configurations for which $\sum_R n_R = N$ and for each configuration to integrate over all orientations at sites where there is a particle ($n_R = 1$). To avoid the constraint on particle number, we go to the grand canonical ensemble. Also, it is convenient to integrate over orientations at *all* sites, introducing an extra factor $(4\pi)^{\mathcal{N} - \Sigma_R n_R}$ which must then be divided out. Thus

$$Q\mu = \int \cdots \int \prod_R (\mathrm{d}\Omega_R/4\pi) \sum_{\{n_R\}} (4\pi)^{\Sigma n_R} \exp\left[-\beta \sum_{R,R'} V_2(\mathbf{R}, \mathbf{R}') n_R n_{R'} \right]$$
$$\cdot \exp\left[-\beta \sum_{R,R',R''} V_3(\mathbf{R}, \mathbf{R}', \mathbf{R}'') n_R n_{R'} n_{R''} + \cdots \right]$$
$$\cdot \exp\left[-\beta\mu \sum_R n_R \right] \exp\left[-\beta \sum_{R,R'} u(\mathbf{R}, \Omega_R; \mathbf{R}', \Omega_{R'}) n_R n_{R'} \right]. \quad (4.11)$$

Here V_2, V_3 etc. are the two-body, three-body, etc. contributions to the interaction $V(\mathbf{R}_1, \cdots, \mathbf{R}_N)$ and μ is determined so that

$$\left\langle \sum_R n_R \right\rangle = N \quad (4.12)$$

where $\langle \cdots \rangle$ denotes an average with the weighting factor

$$\exp\left[-\beta \sum_{RR'} V_2 n_R n_{R'} - \beta\mu \sum_R n_R \right].$$

For simplicity let us neglect V_3, $V_4, \cdots$.

If we neglect all interactions, then

$$\left\langle \sum_R n_R \right\rangle = \mathcal{N}(1 + e^{-\beta\mu})^{-1} = N \quad (4.13)$$

so that as $\mathcal{N} \to \infty$, we require that

$$e^{\beta\mu} \to \mathcal{N}/N \quad \text{or} \quad \mu \to -\infty. \quad (4.14)$$

Even when the interactions are turned on, this behavior of μ is substantially unchanged.

Now we can make an analogous approximation to that of (4.5),

$$Q_\mu \geqslant (4\pi)^N Q_\mu{}^c \int \cdots \int \prod_R (\mathrm{d}\Omega_R/4\pi) \cdot \exp\left[-\tfrac{1}{2}\beta \sum_{R,R'} u(\mathbf{R}, \Omega_R; \mathbf{R}', \Omega_{R'}) \langle n_R n_{R'} \rangle \right] \tag{4.15}$$

where $Q_\mu{}^c$ is now the grand partition function neglecting orientational effects. If we let the mesh size shrink to zero, Eq. (4.15) can be replaced by one involving a functional integral over the functions $\Omega(\mathbf{R})$:

$$Q_\mu \geqslant Q_\mu{}^c Q_\mu{}^{(\theta,\phi)} \tag{4.16}$$

where

$$Q_\mu{}^{(\theta,\phi)} = (4\pi)^N \int \mathscr{D}[\Omega] \cdot \exp\left[-\tfrac{1}{2} n^2 \beta \int\int \mathrm{d}^3R\, \mathrm{d}^3R' u(\mathbf{R}, \Omega(\mathbf{R}) ; \mathbf{R}'\Omega(\mathbf{R}')) f(\mathbf{R} - \mathbf{R}') \right] \tag{4.17}$$

and $n = N/\mathscr{V}$ is the average particle density.

To simplify the further approximations, we shall assume that the basic two-body interaction is what we have called a " Heisenberg-like " interaction:

$$u(\mathbf{R}, \Omega(\mathbf{R}); \mathbf{R}', \Omega(\mathbf{R}')) = -(8/3)K(\mathbf{R} - \mathbf{R}')(\cos^2 \Theta_{RR'} - \tfrac{1}{3}) \tag{4.18}$$

where $\Theta_{RR'}$ is the angle between $\Omega(\mathbf{R})$ and $\Omega(\mathbf{R}')$. This interaction is, of course, not the induced-dipole induced-dipole interaction, but it is invariant under rotations of orientation space and, with a proper choice of $K(\mathbf{R} - \mathbf{R}')$, it has all the properties of the induced-dipole induced-dipole interaction used by Maier and Saupe, and will give identical results in the molecular field approximation. There is no *a priori* reason for thinking that if the molecular field approximation is valid for the induced-dipole induced-dipole interaction, it won't work equally well on this interaction. Conversely, if the molecular field fails for the interaction (4.17), it should fail for the induced-dipole induced-dipole interaction.

Now we get a further bound on $Q_\mu{}^{(\theta,\phi)}$ if we avoid the difficulties associated with the functional integration over the functions $\phi(\mathbf{R})$ by making an approximation analogous to (4.5). Using a uniform weight for all functions $\phi(\mathbf{R})$, we get a lower bound to $Q_\mu{}^{(\theta,\phi)}$:

$$Q_\mu^{(\theta,\phi)} \geqslant Q_\mu^{(\theta)} \equiv \int \mathscr{D}[\theta] \cdot \exp\left[-\tfrac{1}{2}\beta n^2 \int\int \mathrm{d}^3R\, \mathrm{d}^3R' \bar{u}(\mathbf{R}, \theta(\mathbf{R}); \mathbf{R}', \theta(\mathbf{R}')) f(\mathbf{R} - \mathbf{R}') \right], \tag{4.19}$$

where

$$\mathscr{D}[\theta] = \lim_{\mathscr{N}\to\infty} \int \cdots \int \prod_R (\tfrac{1}{2} \sin\theta_R \, \mathrm{d}\theta_R)$$

and

$$\bar{u}(\mathbf{R}, \theta(\mathbf{R}); \mathbf{R}', \theta(\mathbf{R}')) = \int \mathscr{D}[\phi] u(\mathbf{R}, \Omega(\mathbf{R}); \mathbf{R}', \Omega(\mathbf{R}')). \tag{4.20}$$

Using the expansion

$$P_2(\cos\Theta) = P_2(\cos\theta)P_2(\cos\theta') + \sum_{m=1}^{2} A_m P_2^m(\cos\theta) P_2^m(\cos\theta') \cos m(\phi - \phi'), \tag{4.21}$$

we find that

$$\bar{u}(\mathbf{R}, \theta(\mathbf{R}); \mathbf{R}', \theta(\mathbf{R}')) = -4K(\mathbf{R} - \mathbf{R}')(\cos^2\theta(\mathbf{R}) - \tfrac{1}{3})(\cos^2\theta(\mathbf{R}') - \tfrac{1}{3}). \tag{4.22}$$

From the point of view of bounds on the grand partition function, the bounds $Q_\mu^c Q_\mu^{(\theta,\phi)}$ and $Q_\mu^c Q_\mu^{(\theta)}$ are progressively poorer estimates of the exact grand partition function Q_μ. The orientational function $Q_\mu^{(\theta)}$ can be further approximated in two ways: On way leads to the approximate grand potential that Maier and Saupe would have found had they considered the interaction (4.18); the other way leads to the exactly soluble model investigated in Sections 2 and 3.

Let us first show that a certain lower bound on $Q_\mu^{(\theta)}$ (or upper bound on the corresponding grand potential $\Xi_\mu^{(\theta)}$) is equivalent to the molecular field approximation of Maier and Saupe. We start by formulating the most general molecular field approximation as a further application of the multidimensional version of (4.4). Specifically, we approximate the weight function

$$\exp\left[-2\beta n^2 \int\int \mathrm{d}^3R\, \mathrm{d}^3R' K(\mathbf{R} - \mathbf{R}') f(\mathbf{R} - \mathbf{R}') \cdot (\cos^2\theta(\mathbf{R}) - \tfrac{1}{3})(\cos^2\theta(\mathbf{R}') - \tfrac{1}{3}) \right] \tag{4.23}$$

in the functional integral over $\theta(\mathbf{R})$ by a factorized density

$$\rho[w(\theta)] = \exp\left[-\beta n \int \mathrm{d}^3 R w(\theta(\mathbf{R}))\right], \tag{4.24}$$

i.e. the orientations $\theta(\mathbf{R})$ and $\theta(\mathbf{R}')$ are assumed independent for all pairs of points $\mathbf{R}$ and $\mathbf{R}'$ and we have used the translational symmetry in assuming that $w(\theta(\mathbf{R}))$ does not depend explicitly on $\mathbf{R}$. Then, using the generalization of (4.4) once again, we have an upper bound on the grand potential $\Xi_\mu^{(\theta)}$:

$$\begin{aligned}\Xi_\mu^{(\theta)} &\equiv -kT \ln Q\mu^{(\theta)} \\ &\leqslant \Xi_\mu[w] + 2n^2 \iint \mathrm{d}^3 R\, \mathrm{d}^3 R' K(\mathbf{R}-\mathbf{R}') f(\mathbf{R}-\mathbf{R}') \langle \cos^2\theta(\mathbf{R}) - \tfrac{1}{3}\rangle_w \\ &\quad \cdot \langle \cos^2\theta(\mathbf{R}') - \tfrac{1}{3}\rangle_w \end{aligned} \tag{4.25}$$

where

$$\Xi_\mu[w] = -kT \ln \int \mathscr{D}[\theta] \rho[w(\theta)] \tag{4.26}$$

and

$$\begin{aligned}\langle \cos^2\theta(\mathbf{R}) - \tfrac{1}{3}\rangle_w &= \frac{\int \mathscr{D}[\theta](\cos^2\theta(\mathbf{R}) - \tfrac{1}{3})\rho[w(\theta)]}{\int \mathscr{D}[\theta]\rho[w(\theta)]} \\ &= \frac{\int \mathrm{d}\theta \sin\theta (\cos^2\theta - \tfrac{1}{3}) e^{-\beta w(\theta)}}{\int \mathrm{d}\theta \sin\theta e^{-\beta w(\theta)}}. \end{aligned} \tag{4.27}$$

If we take the functional derivative of this bound with respect to the " effective potential " $w(\theta)$, we obtain a self-consistent equation for the best function, $w_{\mathrm{sc}}(\theta)$:

$$\begin{aligned} w_{\mathrm{sc}}(\theta(\mathbf{R})) &= \frac{4\int \mathscr{D}_R[\theta](\cos^2\theta(\mathbf{R}) - \tfrac{1}{3}) \int \mathrm{d}^3 R K(\mathbf{R}-\mathbf{R}') f(\mathbf{R}-\mathbf{R}')(\cos^2\theta(\mathbf{R}') - \tfrac{1}{3})}{\int \mathscr{D}_R[\theta] \exp\left[-\beta \int \mathrm{d}^3 R'' w_{\mathrm{sc}}(\theta(\mathbf{R}''))\right]} \\ &\quad \cdot \exp\left[-\beta \int \mathrm{d}^3 R'' w_{\mathrm{sc}}(\theta(\mathbf{R}''))\right], \end{aligned} \tag{4.28}$$

where $\int \mathscr{D}_R[\theta]$ denotes integration over all functions θ having a fixed value $\theta(\mathbf{R})$ at $\mathbf{R}$. Interchanging $\int \mathrm{d}^3 R'$ and $\int \mathscr{D}_R[\theta]$ in the numerator of (4.28), we have the simpler self-consistent equation for the molecular field:

$$w_{\mathrm{sc}}(\theta(\mathbf{R})) = 4(\cos^2\theta(\mathbf{R}) - \tfrac{1}{3}) \int \mathrm{d}^3 R' K(\mathbf{R}-\mathbf{R}') f(\mathbf{R}-\mathbf{R}') \langle \cos^2\theta - \tfrac{1}{3}\rangle_{w_{\mathrm{sc}}}, \tag{4.29}$$

the theory of Maier and Saupe. When this best $w_{sc}(\theta)$: is substituted in (4.25), we have what we shall call Ξ_μ^{mf}, an upper bound on $\Xi_\mu^{(\theta)}$, ("mf" for "molecular field" or "mean field").

Before leaving the development of the Maier–Saupe theory for the interaction (4.18), we should comment on the role of rotational invariance. The approximation leading from $\Xi_\mu^{(\theta,\phi)}$ to $\Xi_\mu^{(\theta)}$ destroys the invariance of the problem under rotations in orientation space, but the subsequent molecular field approximation leading to Ξ_μ^{mf} effectively restores this invariance above the transition (the molecular field being zero). Thus while the molecular field approximation gives a still higher (hence worse) upper bound to the grand potential, it could be argued that Ξ_μ^{mf} is nevertheless better than $\Xi_\mu^{(\theta)}$ because it occurs in a rotationally invariant theory, i.e., although Ξ_μ^{mf} is worse than $\Xi_\mu^{(\theta)}$ in the sense of leading to a poorer variational estimate of $\Xi_\mu = -kT \ln Q_\mu$ for all T, its analytic properties as a function of T (existence and nature of a phase transition) could conceivably be better. This is a universal drawback of any variational approach, but it seems to us that the burden of proof lies with the method giving the poorer variational bound to the grand potential.

The alternative way to proceed from $\Xi_\mu^{(\theta)}$ leads to the model we have presented in Sections 2 and 3. What we have done there is to try to avoid the molecular field approximation in (4.18) by discretizing $\cos\theta$ and replacing the continuous 3-space by a lattice. The statistical mechanical problem remains non-trivial after these approximations, in contrast to what results from the molecular field approximation.

We have already discussed the effects of the discretization of $\cos\theta$. Similar comments apply to the discretization of 3-space: Since we know of no estimates of T_I for Ising models on a continuum, rather than a lattice, we can only repeat the observation that the molecular field approximation on the lattice predicts the first-order transition that an exact theory shows to be absent.

5. Conclusion

We have attempted to avoid the molecular field approximation that is fundamental to the Maier–Saupe theory, in order to see if the first-order phase transition is a consequence of the molecular field or is

a real consequence of assumptions **A** and **B** stated in the Introduction.

We have constructed a model which we believe to be closely related but superior to the Maier–Saupe model. In this model, no first-order transition occurs. Since such a transition occurs in nature, the failure to predict it could arise from several sources:

(1) The discretizations of space and $\cos\theta$ could make our model inferior to the MS theory, but this seems unlikely in view of the fact that the molecular field approximation incorrectly predicts a first-order transition for our model.

(2) The averaging over ϕ could conceivably make the grand potential $\Xi_\mu^{(\theta)}$ have less accurate analytic properties than Ξ_μ^{mf} even though, in magnitude, $\Xi_\mu^{(\theta)}$ is the better bound on the exact grand potential.

These two possibilities suggest the need for a more detailed study of the interaction $J_{ij}(\cos^2\theta_{ij} - \frac{1}{3})$ on a lattice:—can it ever show no phase transition, as the present paper suggests?

Two other possible sources of the failure to predict a phase transition are these:

(3) The assumption of an interaction of the form (4.18). Consideration of interactions that depend on the direction of $\mathbf{R}_i - \mathbf{R}_j$ relative to Ω_i and Ω_j and which involve higher harmonics in Ω_i and Ω_j could conceivably restore the first-order transition, although we think it unlikely.

(4) The neglect of correlations of spatial positions with orientational interactions. This approximation, which underlies both the Maier–Saupe theory and the present model, seems to us the most serious approximation. It suggests that further work be specifically oriented toward studying the interplay of orientational and positional correlations.

Note Added in Proof

The model solved in Section 3 has also been solved by R. G. Priest in a paper that has just appeared, *Phys. Rev. Letters.* **26**, 423 (1971). Priest takes the point of view, in contrast to ours, that the persistence of the long-range order at high temperatures and the lack of a first-order transition invalidate this model as a qualitative guide to models with rotationally invariant interactions.

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2. We have also applied this model to the problem of solid orthohydrogen (unpublished) only to find that a similar analysis of solid orthohydrogen had been done independently by G. M. Bell and W. M. Fairbairn, *Mol. Phys.* **4**, 481 (1961) and A. Brooks Harris, *Sol. State Comm.* **6**, 149 (1968). In solid orthohydrogen, the two "discretization approximations" are very good, the system consisting essentially of three-level subsystems on a lattice.
3. The limiting procedures in the first of these properties are discussed by T. Schultz, D. Mattis and E. Lieb, *Revs. Mod. Phys.* **36**, 856 (1964). The second of these properties was proved by T. D. Lee and C. N. Yang, *Phys. Rev.* **87**, 410 (1952).
4. Domb, C. and Dalton, N. W., *Proc. Phys. Soc.* **89**, 859 (1966), Table 4 and Eq. 5.
5. We have neglected the contributions to the Helmholtz free energy of the kinetic energy and internal molecular degrees of freedom.
6. This inequality is readily proved. If we let

$$\rho(y)\,\mathrm{d}y = \int_{y<b(x)<y+\mathrm{d}y} \mathrm{d}x\, e^{a(x)} \Big/ \int \mathrm{d}x\, e^{a(x)}$$

$$\int \mathrm{d}x\, e^{a(x)+b(x)} = \int \mathrm{d}x\, e^{a(x)} \times \int \mathrm{d}b\, e^{b} \rho(b).$$

   Expanding e^b around $\bar{b} \equiv \int \mathrm{d}b\, b\rho(b)$ to first order, and using the upward concavity of the exponential function,

$$e^b > e^{\bar{b}} + (b - \bar{b})e^{\bar{b}},$$

   we obtain (4.4) when this lower bound to e^b is substituted in $\int \mathrm{d}b\, e^b\, \rho(b)$.
7. In some problems where the molecular field approximation is made, such as for short-range antiferromagnetic interactions, the molecular field that minimizes the free energy is a symmetry-breaking field. In the present case, where every particle interacts with every other particle with the same interaction, this cannot be so. To see this, consider the molecular fields seen by two different particles, say, the i^{th} and j^{th}. Each of the two particles sees a field resulting from the average orientations of *all* the other particles. Even if we assume that the average orientations of these two particles are more than infinitesimally different, the fields that the two particles see are identical except for the negligible difference between $\bar{u}(\Omega_i, \langle\Omega_j\rangle)$ and $\bar{u}(\Omega_j, \langle\Omega_i\rangle)$. Thus the molecular field is the same for all particles, and hence so are the average orientations.