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Liquid Crystals in Two Dimensions

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The existence of liquid crystalline order in two dimensions is discussed. It is shown that, contrary to a previous contention, a theory based on the lowest-order approximation to the virial expansion of the free energy (the Onsager limit) indicates that a nematic ordering transition does occur. The effects of the fluctuations in order are considered, and it is shown that the usual elastic theories cannot hold in two dimensions. I attempt to construct a microscopic discussion based on the Bogoliubov inequality, but find that it cannot be applied straightforwardly to this case.

I. INTRODUCTION

The existence of a two-dimensional liquid crystal can be characterized by the nonvanishing of the order parameter

$$M^2 = \lim_{N\to\infty} N^{-2} \left\langle \sum_{ij} \cos 2(\theta_i - \theta_j) \right\rangle , \qquad (1)$$

where θ_i is the inclination of a principal axis of the ith molecule to an arbitrary fixed axis. Recent Monte Carlo studies[1] of a two-dimensional gas of hard ellipses indicate the possibility of three phases: (a) a crystalline phase at high density, (b) a noncrystalline phase at intermediate density, in which M is nonvanishing, and (c) a disordered phase at low density where M vanishes. The transitions between phases appear to be first order.

It is generally assumed that long-range order corresponding to the breaking of a continuous symmetry group is not possible in a two-dimensional system of particles interacting via short-ranged forces. In particular, it can be rigorously shown that such a system cannot display normal superfluid,[2-4] superconducting,[4] or magnetic ordering,[5] nor is it likely to be crystalline.[6] In view of the Monte Carlo results it is appropriate to discuss the theory of this system.

I discuss this problem from two points of view. In Sec. II, I examine the description afforded by the virial expansion of the equation of state. The two-dimensional analog of the Onsager[7] limit can be shown to give a phase transition, contrary to previous contention.[8]

In Sec. III, I discuss the effects of disordering fluctuations. The two-dimensional analog of the usual elastic theory for liquid crystals[9-11] leads to divergent mean-square fluctuations in order. I attempt to construct an argument based on the Bogoliubov inequality,[2] modeled on its previous applications[3-6,12,13] to continuous broken symmetries, but find that in this case the construction fails in all but trivial cases. I trace the origin of this difficulty, which seems quite profound, to the special nature of the liquid-crystalline ordering.

II. VIRIAL EXPANSIONS

Onsager has given a discussion[7] of the three-dimensional gas of asymmetric molecules, based on an expansion of the free energy in powers of the density and of the orientational distribution function $f(\Omega)$ [defined by $Nf(\Omega)\, d\Omega$ = number of particles having orientations in $d\Omega$]. The expansion may be written quite generally as

$$\begin{aligned} F/Nk_BT &= \mu_0(T) + \ln\rho + \int f(\Omega) \ln[4\pi f(\Omega)]\, d\Omega \\ &- \tfrac{1}{2}\rho \int\int \beta_1(\Omega, \Omega') f(\Omega) f(\Omega')\, d\Omega\, d\Omega' \\ &- \tfrac{1}{3}\rho^2 \int\int\int \beta_2(\Omega, \Omega', \Omega'') f(\Omega) f(\Omega') f(\Omega'')\, d\Omega\, d\Omega'\, d\Omega'' \\ &+ \cdots , \end{aligned} \qquad (2)$$

where β_n is the nth irreducible cluster integral for $n+1$ molecules of fixed orientations $\Omega, \Omega', \ldots$. The coefficient $\beta_1(\Omega, \Omega')$ measures the volume from which a molecule of orientation Ω is excluded by a molecule of orientation Ω'; similarly, $\beta_2(\Omega, \Omega', \Omega'')$ is proportional to the number of configurations in which three molecules of orientations $\Omega, \Omega', \Omega''$ are simultaneously overlapping each other.

For obvious geometrical reasons, in three dimensions β_2 and higher-order coefficients are relatively small for long molecules when $\Omega, \Omega', \Omega''$ do not lie nearly in a common plane, and since most orientational configurations meet this condition, these terms may reasonably be neglected. The resulting approximation is essentially a form of mean-field theory, in that only the second virial coefficient plays a role. For given density, the stable configuration is that which minimizes the free energy. At low density this occurs for the isotropic distribution $[f = (4\pi)^{-1}]$ for which $M = 0$; at sufficiently high densities the free energy is lower for an anisotropic distribution ($M \neq 0$) sharply peaked about some direction of average orientation.

The considerations which justify the simple approximation of the Onsager model are closely tied to dimensionality: In a two-dimensional system it is overwhelmingly probable that three rods will lie in a common plane. Nonetheless, Lakatos[8] has discussed the two-dimensional gas of very long hard rods in the mean-field approximation. She concluded that the only physically meaningful minimum of the free energy occurs for the isotropic distribution function. This contention is not so strong as to rigorously exclude a phase transition, but could be regarded as strong evidence that there is none.

I will briefly outline Lakatos's arguments for her contention, forewarning the reader that both the argument and the contention are incorrect. The free energy in the Onsager approximation for two dimensions is given by

$$F/Nk_BT=\mu_0(T)+\ln\rho+\int_0^\pi f(\theta)\ln[\pi f(\theta)]\,d\theta$$
$$-\tfrac{1}{2}\rho\iint_0^\pi f(\theta)\beta(\theta,\theta')f(\theta')\,d\theta\,d\theta' . \qquad (3)$$

For the case of very long rods we may justifiably approximate $\beta(\theta,\theta')$ by $B|\sin(\theta-\theta')|$. The free energy is minimized (for fixed density) if the angular distribution function satisfies

$$\ln f(\theta)=\rho\int_0^\pi f(\theta')\beta(\theta-\theta')\,d\theta'+\lambda , \qquad (4)$$

where λ is a Lagrange multiplier to be chosen so that f obeys the normalization condition

$$\int_0^\pi f(\theta)\,d\theta=1 . \qquad (5)$$

Defining

$$g(\theta)=\frac{d}{d\theta}\ln f(\theta) \qquad (6)$$

and taking several derivatives of g, Lakatos shows that g satisfies the equation

$$g(\theta)=-\int_0^\pi\frac{d\beta(\theta-\theta')}{d\theta}\,\frac{1}{g(\theta')}\,\frac{d^2g(\theta')}{d\theta'^2}\,d\theta' , \qquad (7)$$

in which the density ρ does not appear. It is then suggested that a solution of (7) is determined by the boundary conditions

$$g(0)=g(\pi)=0,\quad g'(0)=g'(\pi) . \qquad (8)$$

However, the solution of (7) with the boundary conditions (8) cannot depend on the density since ρ appears nowhere; but in the limit of low density the only minimum of the free energy (3) occurs for the isotropic distribution; hence anisotropic distributions can have no physical significance, and no phase transition can occur.

Unfortunately, the claim that the boundary conditions (8) are sufficient to determine a solution of (7), and the assumption that any solution of (7) is a solution of (4), are untenable. In fact, a continuous family of solutions of (7) are possible [parametrized by the unspecified boundary condition on $g'(0)$], only one of which is a solution of (4) for a particular value of ρ.

To demonstrate the failure of Lakatos's argument, I prove that for sufficiently high density the minimum of the free energy (3) must occur for some anisotropic distribution function. Consider the trial function

$$f_\varphi(\theta)=\begin{cases}(2\varphi)^{-1}, & 0\le\theta\le\varphi,\ \pi-\varphi\le\theta\le\pi\\ 0, & \varphi<\theta<\pi-\varphi\end{cases} \qquad (9)$$

where φ is an arbitrary parameter. This function is normalized to unity, and the family contains the isotropic function as the case $\varphi=\pi/2$. With f_φ substituted in (3), the integrals may be done to give

$$\frac{F}{Nk_BT}-\mu_0-\ln\rho=\ln\frac{\pi}{2\varphi}+\frac{\rho B}{\varphi}\left\{1-\frac{\sin 2\varphi}{2\varphi}\right\} . \qquad (10)$$

In Fig. 1, I show the dependence of this function on ρ and φ. For ρB sufficiently large the minimum value does not occur for the isotropic function. Therefore the minimum of the free energy (3) must occur for some anisotropic distribution, indicating the existence of a phase transition.

Finally, in Fig. 2 I exhibit a specific anisotropic solution to the original problem. This solution was obtained by integrating the differential equations

$$\frac{d}{d\theta}\ln f(\theta)=g(\theta) \qquad (11)$$

and

$$\frac{d^2}{d\theta^2}g(\theta)=-g(\theta)-2\rho Bf(\theta)g(\theta) \qquad (12)$$

by the point-slope method.[14] For any choice of the initial values $f(0)$ and $g'(0)$ a solution of these equations can be obtained; $f(0)$ must be determined, however, by the normalization condition (5), while $g'(0)$ is determined by the condition that $g(\theta)$ be periodic with period π [Eq. (8)]. The set of equations has an anisotropic solution for $\rho B>3\pi/2$; at low densities the numerical techniques yield only the (disordered) isotropic solution.

Thus the mean-field theory predicts the existence of a liquid-crystalline phase in two dimensions.[15] This result is in accord with our experience with other types of systems, and is thus not really surprising.

Timling[16] has given a scaled-particle treatment of the two-dimensional gas of hard asymmetric particles. The angular distribution function is again determined by an integral equation of the form (4), but the factor ρ is replaced by a function

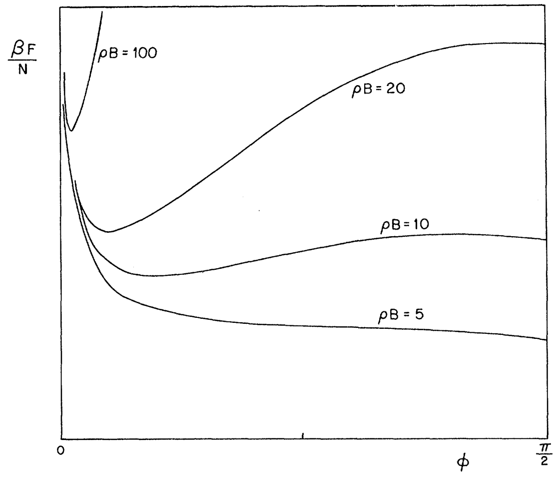

FIG. 1. Behavior of the right-hand side of Eq. (10) as a function of the parameter φ, for various densities. The case $\varphi = \pi/2$ is the isotropic limit; we see that for sufficiently high density the minimum free energy occurs for some nonisotropic distribution function.

of the density. He finds a second-order phase transition at a density in reasonable agreement with the Monte Carlo studies.

I commented above that the deletion of the higher-order terms in the virial expansion (2) cannot be justified in two dimensions by the argument Onsager used in three dimensions. The effect of these higher-order terms can be estimated by study of a model first proposed by Zwanzig.[17] He considers a gas of very long rods which are allowed to have only two orthogonal orientations. If only the graph integrals of leading order in the length-to-breadth ratio are kept, a great simplification in the computation of the virial coefficients results; in this way the coefficients of terms through ρ^7 in the expansion (2) have been calculated.[18,19] In the Onsager or mean-field approximation, this model predicts a second-order phase transition; however, with the successive inclusion of the higher-order terms the position of the transition is strongly affected, and in some truncations the transition does not occur at all.[17]

The higher-order terms in the expansion (2) will be comparable to the corresponding terms of the Zwanzig model; since the latter are important, no definite conclusions may be drawn concerning the existence of liquid-crystalline order in two dimensions.

III. ORDER-DESTROYING FLUCTUATIONS

Our previous experience with two-dimensional[20] systems having a broken continuous symmetry (such as the continuous range of possible axes of average orientation of a gas of ellipses) is that long-range order is destroyed by the long-wavelength fluctuations in order. Several parallel, but not wholly equivalent, arguments of this sort can be given.

A. Anisotropic Elastic Medium

The simplest but least rigorous of these approaches is based on the concept of an elastic restoring force.[21] We assume that we may assign locally a unit vector $\hat{n}(\vec{r})$ (the "director") indicating the mean orientation at r, which will fluctuate about an average orientation $\hat{n}_0$. Symmetry requires that the free energy does not depend on the orientation of $\hat{n}_0$, and hence suggests that it should depend only on the gradients of $\hat{n}(\vec{r})$. A low-order expansion then gives[22]

$$F = F_0 + \tfrac{1}{2}\int \left[\kappa_\perp(\vec{\nabla}\cdot\hat{n})^2 + \kappa_\parallel(\vec{\nabla}\times\hat{n})^2\right] d^2r \ . \qquad (13)$$

This is the two-dimensional analog of the Oseen[9]-Zocher[10]-Frank[11] elastic theory. This expansion could equally well be made in terms of the derivatives of a position-dependent orientation angle $\theta(\vec{r})$, related to $\hat{n}(\vec{r})$ by $\hat{n}(\vec{r}) = \hat{x}\cos\theta(\vec{r}) + \hat{y}\sin\theta(\vec{r})$:

$$F = F_0 + \tfrac{1}{2}\int \left[\kappa_\perp(\hat{n}\times\vec{\nabla}\theta)^2 + \kappa_\parallel(\hat{n}\cdot\vec{\nabla}\theta)^2\right] d^2r \ . \qquad (14)$$

A simple equipartition argument[23] shows that the thermal average of the $\vec{k}$th Fourier component of the fluctuating part of $\theta(\vec{r})$ is given by[24]

$$\langle|\theta_{\vec{k}}|^2\rangle = \Omega k_B T\left[\kappa_\parallel k_\parallel^2 + \kappa_\perp k_\perp^2\right]^{-1} \ , \qquad (15)$$

where $k_\parallel$ and $k_\perp$ are the appropriate components of $\vec{k}$ with respect to the equilibrium director $\hat{n}_0$. As in Landau's discussion of crystalline order,[21] this expression may be used to show that the mean-squared displacement $\langle|\theta(\vec{r}) - \theta_0|^2\rangle$ diverges logarithmically with the size of the system; it can also be used to show that the correlation function $\langle|\theta(\vec{r}) - \theta(\vec{r}\,')|^2\rangle$ increases indefinitely at large

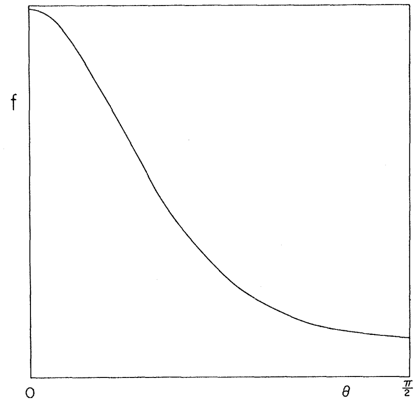

FIG. 2. Function $f(\theta)$ for the case $\rho B = 5.23$, as determined by a numerical solution to Eqs. (11) and (12) with boundary values (5) and (8). Since this density is not much greater than the critical density $\rho B = 3\pi/2$, the function is not too strongly peaked.

separation (compare Ref. 6). The conclusion we would like to draw is that the equilibrium director $\hat{n}_0$ does not exist, i.e., there can be no "spontaneous order"; but to do so we must defend the other assumptions leading to (15), in particular, the validity of the phenomenological expansion (14).

B. Bogoliubov Inequality

A more rigorous discussion of order in two dimensions generally can be afforded by use of the Bogoliubov inequality.[2] The conclusion of this subsection will be, however, that this technique seems to have no direct application to the present problem. I will attempt to construct an argument patterned on its previous applications to classical systems,[6, 12, 13] motivating as completely as possible the steps involved, and indicating how this problem differs from those previously considered.

Let N particles be confined within a square (two-dimensional) box of side L, and assume that their configuration can be specified by a set of position coordinates $\vec{r}_i$ and orientations θ_i. We define the configurational partition function Q by

$$Q=\frac{1}{N!}\int\cdots\int e^{-\beta U}d^N\vec{r}\,d^N\theta , \tag{16}$$

and the configurational average of a function f by

$$\langle f\rangle=\int\cdots\int f(\vec{r}_i,\theta_i)\,e^{-\beta U}d^N\vec{r}\,d^N\theta/Q , \tag{17}$$

where

$$U=\tfrac{1}{2}\sum_{i\neq j}\Phi(\vec{r}_i-\vec{r}_j,\theta_i,\theta_j)-\zeta\sum_i\cos 2(\theta_i-\theta_0)$$

is the potential energy, ζ is an orienting field, and where the integrals all run over the interior of the square box. The field ζ will eventually be put equal to zero; however, it serves to break the symmetry and allow the order parameter

$$M=\langle\cos 2(\theta_i-\theta_0)\rangle \tag{18}$$

to be defined.[25]

Since all weighting factors in the average (17) are positive, we can establish a Schwartz inequality

$$\langle|A|^2\rangle\geq|\langle AB\rangle|^2/\langle|B|^2\rangle . \tag{19}$$

I hope to make use of this inequality by showing that it is inconsistent with the existence of an order parameter. The choice of A and B can be motivated by the following considerations: The average $\langle AB\rangle$ is to be proportional to the order parameter, and $\langle|B|^2\rangle$ should describe the small energy ($\sim k^2$) required for a long-wavelength fluctuation in order. Then the inequality (19) will have the form $\langle|A_{\vec{k}}|^2\rangle\geq M^2/ck^2$; when this inequality is integrated over $\vec{k}$, the resulting divergence in two dimensions forces us to conclude that M is zero.

Consider first a deformation of a given configuration described by the transformation

$$\theta_i\rightarrow\theta_i+\varphi(\vec{r}_i) , \tag{20}$$

where φ is some slowly varying function which vanishes near the edges of the box. The change in potential energy caused by this deformation is

$$\delta U=\sum_j\varphi(\vec{r}_j)\frac{\partial}{\partial\theta_j}U+\tfrac{1}{2}\sum_{j,k}\varphi(\vec{r}_k)\varphi(\vec{r}_j)\frac{\partial^2}{\partial\theta_j\partial\theta_k}U+\cdots . \tag{21}$$

We will take the energy associated with a fluctuation described by $\varphi(\vec{r})$ to be the average of (21):

$$\langle\delta U\rangle=\left\langle\sum_j\varphi(\vec{r}_j)\frac{\partial}{\partial\theta_j}U\right\rangle+\left\langle\frac{1}{2}\sum_{j,k}\varphi(\vec{r}_j)\varphi(\vec{r}_k)\frac{\partial^2}{\partial\theta_j\partial\theta_k}U\right\rangle . \tag{22}$$

The first term may be shown to vanish by consideration of the integral over θ_j. After an integration by parts the second term becomes

$$\langle\delta U\rangle=\tfrac{1}{2}\beta\left\langle\sum_i\varphi(\vec{r}_i)\frac{\partial}{\partial\theta_i}U\sum_j\varphi(\vec{r}_j)\frac{\partial}{\partial\theta_j}U\right\rangle , \tag{23}$$

which is of the form $\frac{1}{2}\beta\langle|B|^2\rangle$, with[26]

$$B=\sum_i\varphi(\vec{r}_i)\frac{\partial}{\partial\theta_i}U . \tag{24}$$

In the special case that the interparticle potential has the form[27]

$$\Phi(\vec{r}_i-\vec{r}_j,\theta_i,\theta_j)=u(\vec{r}_i-\vec{r}_j)\,v(\theta_i-\theta_j) , \tag{25}$$

Eq. (22) can be written as

$$\beta\langle|B|^2\rangle=\left\langle\frac{1}{2}\sum_{i,j}[\varphi(\vec{r}_i)-\varphi(\vec{r}_j)]^2u(\vec{r}_i-\vec{r}_j)\times\frac{\partial^2}{\partial\theta_i^2}v(\theta_i-\theta_j)+4\zeta\sum_i\varphi^2(\vec{r}_i)\cos 2(\theta_i-\theta_0)\right\rangle . \tag{26}$$

Since u is short ranged, the only terms that enter the double sum are pairs of particles that are close to each other; since φ is slowly varying, $\varphi(\vec{r}_i)-\varphi(\vec{r}_j)$ equals $(\vec{r}_i-\vec{r}_j)\cdot\nabla\varphi(\vec{r}_i)$ to good accuracy. Then this expression is reminiscent of the elastic theory considered above in that the first term is a function of only the gradients of φ.[28]

Putting $\varphi=\cos\vec{k}\cdot\vec{r}$, we then have

$$\beta\langle|B|^2\rangle=\left\langle\frac{1}{2}\sum_{i,j}[\vec{k}\cdot(\vec{r}_i-\vec{r}_j)]^2\sin^2\left(\frac{\vec{r}_i+\vec{r}_j}{2}\cdot\vec{k}\right)u(\vec{r}_i-\vec{r}_j)\frac{\partial^2}{\partial\theta_j}v(\theta_i-\theta_j)+4\zeta\sum_i\cos^2\vec{k}\cdot\vec{r}_i\cos 2(\theta_i-\theta_j)\right\rangle . \tag{27}$$

Since u is short ranged, the double sum is only of order N; in the small-$\vec{k}$ limit this term is dependent on the direction of $\vec{k}$ and proportional to k^2. The oscillatory part of the $\cos^2\vec{k}\cdot\vec{r}$ may be neglected in taking the indicated average; thus, we have

$$\beta\langle|B|^2\rangle = NC_{\parallel}k_{\parallel}^2 + NC_{\perp}k_{\perp}^2 + 2N\zeta M \tag{28}$$

for some $C_{\parallel}$ and $C_{\perp}$.

Now we choose

$$A = \frac{1}{N}\sum_i \sin^2(\theta_i - \theta_0)\sin\vec{k}\cdot\vec{r}_i\ , \tag{29}$$

and the average $\langle AB\rangle$ becomes

$$\langle AB\rangle = \frac{2}{\beta}\left\langle \frac{1}{N}\sum_j \cos^2\vec{k}\cdot\vec{r}_i\cos 2(\theta_i - \theta_0)\right\rangle = k_B TM\ , \tag{30}$$

where again the oscillatory part is negligible. Then the inequality (19) becomes

$$N\left\langle\left(\frac{1}{N}\sum_i \sin 2(\theta_i - \theta_0)\sin^2\vec{k}\cdot\vec{r}_i\right)^2\right\rangle \geq k_B T\,\frac{M^2}{C_{\parallel}k_{\parallel}^2 + C_{\perp}k_{\perp}^2 + 2\zeta M}\ , \tag{31}$$

which is standard form for arguments of this sort. The thermodynamic limit is now taken, and the inequality is integrated over a restricted region of $\vec{k}$ space ($\epsilon < |k| < K$). The left-hand side is bounded by unity; the right-hand side can be made arbitrarily large by choice of ϵ and ζ small enough, if the order parameter is finite. In order to retain the inequality we are forced to conclude that M vanishes.

Unfortunately, the interparticle potential is not generally of the form (25), and hence the rewriting of U in terms of the gradients of φ [Eq. (26)] cannot be done. The physical meaning of this is simply that the deformation $\theta_i \to \theta_i + \varphi(\vec{r}_i)$, in which the particles rotate but do not move, is not a good description of a fluctuation in a liquid-crystalline phase. The geometrical basis for this fact is illustrated in Fig. 3.

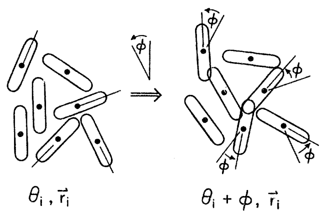

FIG. 3. Typical configuration before and after the transformation $\theta_i \to \theta_i + \varphi$. The potential energy is greatly increased, because of the overlapping particles, even though φ is constant in space. Thus, the change in energy is not a function of the gradient of φ alone.

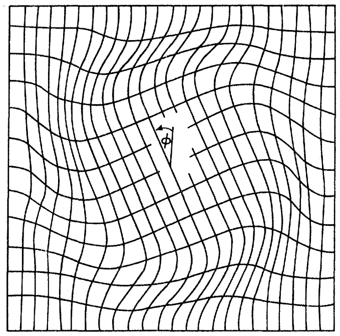

FIG. 4. Transformation (32) retains local order, and thus does not suffer from the disadvantages of transformation (20). Small angular displacements over a large region give rise to large positional displacements, however, and thus inevitably to large strains.

There is a second obvious choice of deformation: the transformation

$$\theta_i \to \theta_i + \varphi(\vec{r}_i),\quad \vec{r}_i \to \vec{r}_i + \vec{A}_i(\vec{r}_i)\ , \tag{32}$$

where $\varphi(\vec{r}_i) = \vec{\nabla}\times\vec{A}_i(\vec{r}_i)$. This class of deformations includes the uniform rotation of a configuration about a fixed point, and the potential energy does not change in regions in which φ is constant, because the transformation retains relative orientations locally. Nevertheless, the change in potential energy caused by a deformation of this form is, in general, of order φ rather than of order $\nabla\varphi$, due to terms in the expansion of U of order $\nabla|A|$. The point is that a small angular displacement over a large area gives rise to a large positional displacement. In Fig. 4, I show how the transformation (32) attempts to retain relative orientations locally, treating the initial configuration as if painted on an elastic sheet. Thus, our conclusion is closely related to Mermin's observation[6] that the two-dimensional harmonic lattice retains directional long-range order.

Analogy with previous applications of the Bogóliubov inequality suggests the choice $B = dJ_q/dt$, with

$$J_q = \textstyle\sum_i \sin\vec{q}\cdot\vec{r}_i(I\dot{\theta}_i + \vec{r}_i\times\vec{p}_i)\ , \tag{33}$$

where I is the moment of inertia of a particle about its center of mass. This choice fails even for a noninteracting system, for which case it can be shown that

$$\langle|B_k|^2\rangle = \tfrac{1}{2}k_B T\langle\textstyle\sum_i \cos^2\vec{q}\cdot\vec{r}_i \times[\tfrac{1}{2}Ik_B Tq^2 + 3r_i^2q^2 - 2(\vec{q}\cdot\vec{r}_i)^2]\rangle\ , \tag{34}$$

where the averages over momentum space have already been taken. Although this expression vanishes as q^2 in the long-wavelength limit, the coefficient of q^2 is of order NL^2: The denominator of Eq. (19) cannot be regarded as small.

C. Broken Symmetry

In Sec. III B, I have attempted to provide a rationale for the choice of functions A and B to use in the Bogoliubov inequality. I will now restate those considerations in a different language in order to make clear that no simple resolution of the difficulties found there has eluded me. Consider now the quantum-mechanical version of the Bogoliubov inequality[2, 3]: For any operators A and C,

$$\tfrac{1}{2}\beta\langle AA^{+}+A^{+}A\rangle \geq \left|\langle[A,C]\rangle\right|^{2}/\langle[[C^{+},H],C]\rangle\ , \qquad (35)$$

where H is the Hamiltonian operator, and the angular brackets now represent canonical-ensemble averages. The first desideratum of any proof we should construct is a series of operators $C_{\vec{k}}$ such that the denominator in (35) vanishes as k^2 in the small-$\vec{k}$ limit. This requires that the limit $C_{\vec{k}=0}$ be a constant of the motion. The simplest constants of motion are the conserved quantities conjugate to a symmetry of the Hamiltonian; the relevant symmetry is in general the one broken by the ordering. In our case, it is the rotational symmetry that is broken by the existence of M; the only explicitly known constant of motion related to this symmetry is the total angular momentum

$$L=\sum_i \dot{\theta}_i I+\sum_i \vec{\mathrm{r}}_i\times\vec{\mathrm{p}}_i\,. \qquad (36)$$

The angular momentum operator generates the rotation

$$\theta_i\rightarrow\theta_i+\delta,\quad \vec{\mathrm{r}}_i\rightarrow\vec{\mathrm{r}}_i+\vec{\mathrm{r}}_i\times\delta\hat{z}\ , \qquad (37)$$

which is the special case of the transformation (32) for which φ is a constant. Thus, in the absence of a specialized assumption such as Eq. (25), which decouples the position coordinates $\vec{\mathrm{r}}_i$ and the orientation coordinates θ_i, one is naturally led to the transformation (32). I conclude that one cannot improve on the simple considerations presented above.

IV. CONCLUSION

I have shown that neither the low-order approximate equations of state based on the Onsager virial expansion nor the usual Bogoliubov techniques can be justifiably interpreted as ruling out long-range order of the liquid-crystalline type. I have succeeded only in showing that two-dimensional liquid crystals, if they exist, cannot obey the Oseen-Zocher-Frank elastic equations.

In the Onsager theory for the ordering of long hard rods it is essentially the differences in entropy (i.e., the relative regions of available configuration space) between ordered and isotropic phases which cause the phase transition. The unsuccessful use of the Bogoliubov inequality was motivated by consideration of the change in potential energy involved in a fluctuation in order. All previous successful[29] applications of this technique to classical systems have been dominated by the potential energy in the sense that the ordered state could be characterized by a potential energy minimum. In view of the fundamentally different nature of the Onsager ordering, it is perhaps not surprising that the Bogoliubov technique fails, and until a method of estimating the changes in entropy associated with a fluctuation is found, the question of two-dimensional liquid-crystalline order will lack a rigorous discussion.

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[1] J. Vieillard-Baron, J. Chem. Phys. (to be published).

[2] N. N. Bogoliubov, Phys. Abhandl. S. U. 6, 229 (1962).

[3] H. Wagner, Z. Physik 195, 273 (1966).

[4] P. Hohenberg, Phys. Rev. 158, 383 (1967).

[5] N. D. Mermin and H. Wagner, Phys. Rev. Letters 17, 1133 (1966).

[6] N. D. Mermin, Phys. Rev. 176, 250 (1968).

[7] L. Onsager, Ann. N. Y. Acad. Sci. 51, 627 (1949).

[8] K. Lakatos, J. Chem. Phys. 50, 3844 (1969).

[9] C. W. Oseen, Trans. Faraday Soc. 29, 883 (1933).

[10] H. Zocher, Trans. Faraday Soc. 29, 945 (1933).

[11] F. C. Frank, Discussions Faraday Soc. 25, 19 (1958).

[12] N. D. Mermin, J. Math. Phys. 8, 1061 (1967).

[13] N. D. Mermin, in *Proceedings of the International Conference on Statistical Mechanics, Kyoto*, 1968 [J. Phys. Soc. Japan Suppl. 26 (1968)], p. 203.

[14] W. E. Milne, *Numerical Solution of Differential Equations* (Wiley, New York, 1953), p. 19.

[15] For a discussion of a similar problem see *John Gamble Kirkwood, Collected Works*, edited by F. H. Stillinger, Jr. (Gordon and Breach, New York, 1965), Vol. 1, p. 152.

[16] K. Timling, Philips Res. Rept. 25, 223 (1970).

[17] R. Zwanzig, J. Chem. Phys. 39, 1714 (1963).

[18] W. G. Hoover and A. G. DeRocco, J. Chem. Phys. 36, 3141 (1962).

[19] L. K. Runnels and C. Colvin, J. Chem. Phys. 53, 4219 (1970).

[20] Arguments of this section are readily generalized to three-dimensional systems with one dimension finite: G. V. Chester, M. E. Fisher, and N. D. Mermin, Phys. Rev. 185, 760 (1969).

[21] The model for this approach is Landau's discussion of two-dimensional crystallinity. See L. D. Landau, Physik. Z. Sowjetunion 11, 26 (1937) [English transl.: *Collected Papers of L. D. Landau*, edited by D. ter Haar (Gordon and Breach, London, 1965), p. 193].

[22] The pseudoscalar product is defined by $A \times B = A_x B_y - A_y B_x$.

[23] P. G. de Gennes, Mol. Cryst. Liquid Cryst. 7, 325 (1969).

[24] The derivation of Ref. 20 is for $\langle |n_k|^2 \rangle$; however, it is valid only for small fluctuations since $\langle |\hat{n}(\vec{r}) - \hat{n}_0|^2 \rangle$ is necessarily bounded. The variable $\theta(\vec{r})$ is more appropriate to the present problem.

[25] This definition of M is consistent with Eq. (1).

[26] We will consider φ in this expression for B as arbitrary even though the expansion (21) which motivated it is valid only for small φ. The Bogoliubov argument is independent of any physical picture for B.

[27] The argument which follows is a slight generalization of example 3 of Ref. 12.

[28] This can be shown to be true for a system interacting by a potential of the form (25) without the need of the expansion (21).

[29] The two-dimensional lattice of hard spheres (Ref. 6) is an interesting failure.

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Short-Range Correlations in Quantum Liquids*

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A relationship between the Brueckner and Jastrow many-body theories, which was previously derived for three- and four-particle wave functions, is shown to be valid for any number of particles.

I. INTRODUCTION

Two widely used approaches to the ground-state problem of quantum fluids are the reaction-matrix perturbation theory of Brueckner and Goldstone[1-4] and the Jastrow method of correlated basis functions[5,6] (called for brevity the Jastrow-CBF method). Both methods can be applied to either fermions or bosons,[7] and are applicable to liquid ^{3}He, liquid ^{4}He, and nuclear matter. The two theories are based on similar physical ideas, but the precise relationship between them remains to be clarified. Bäckman, Chakkalakal, and Clark[8] have made a numerical comparison of the two theories for nuclear matter. Wong[9] has shown how the leading approximation in one theory is related to that in the other. Sim, Woo, and Buchler[10] have found, for weak potentials, that there is complete agreement between these two approaches through the first four orders of perturbation theory. In the development of practical methods for calculating three- and four-body terms in the Brueckner theory, a simple approximation has been found that leads to the Jastrow form for the three- and four-body wave functions.[11,12] The purpose of this paper is to demonstrate that this connection between the two theories is valid for any number of particles. A certain subclass of diagrams in the Brueckner theory, evaluated in a well-defined approximation, gives a total wave function of the Jastrow form, i.e., a product of two-body correlation functions, one for each pair of particles.

II. DERIVATION

The result will be derived for spinless bosons. The fermion wave function can then be approximated by multiplying the boson result by the unperturbed fermion ground-state Slater determinant, as suggested by Wu and Feenberg.[13]

A complete reaction-matrix perturbation expansion for a system of many spinless bosons has been derived by Brandow.[7] His result can be understood in terms of the corresponding Brueckner-Goldstone expansion for fermions, interacting through the two-body boson-boson potential. If the spin degeneracy of the fermions is taken to be greater than or equal to the number of particles N, then the unperturbed fermion ground state is the product of two factors. The first factor is a completely symmetric spatial function consisting of a product of N zero-momentum plane waves. The second factor is the completely antisymmetric Slater determinant of spin functions. The two-body boson potential does not affect the spins of the fermions. Thus, in all higher approximations this spin function remains as a constant factor, multiplying a completely symmetric spatial function. When the calculation is finished, the fermion spin function is discarded, leaving a completely symmetric spatial wave function, which will be the correct many-boson wave function.[7]

We therefore consider the Brueckner-Goldstone expansion for the many-body wave function Ψ. The two-body potential is assumed to have a hard core