Superfluid ³He in Restricted Geometries

G. Barton and M. A. Moore

University of Sussex, Falmer, Brighton, England

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It is shown that finite size effects stabilize a variety of phases in superfluid 3 He which do not occur in the bulk liquid. These phases are formed at temperatures at which the coherence length is comparable with the smallest linear dimension of the system. Right circular cylindrical geometries are considered explicitly.

1. INTRODUCTION

The chief purpose of this paper is to point out the variety of phases which should be induced in superfluid ³He by confining it in certain restricted geometries. Specifically we have examined the free energy and order parameter of a *p*-wave paired superfluid in a long cylindrical tube or pore. The phases produced by finite size effects are found when the temperature of the superfluid is sufficiently close to the bulk transition temperature T_c so that the coherence length $\xi(T)$ is of the same order of magnitude as the pore radius *R*, that is, when

$$R \sim \xi(T) \sim \xi_0 / (1 - T/T_c)^{1/2}$$
 (1)

The zero-temperature coherence length ξ_0 is of order 124 Å.¹ In 1- μ m-radius pores, Eq. (1) implies that the phases will be observable within a few microdegrees of the bulk transition temperature. Of course, the smaller the pores, the wider the temperature range over which the new phases will exist. More precise estimates are given in Sections 2 and 3.

On cooling from the normal Fermi liquid, we believe the sequence of phase transitions is: normal $\xrightarrow{2nd}$ polar $\xrightarrow{2nd}$ mixed axial $\xrightarrow{1st}$ transverse axial $\xrightarrow{1st}$ BW. The order of each transition is shown above the arrow. The names attached to the various phases are indicative of their properties. Thus the polar phase is a phase with an order parameter very similar to that of the bulk polar phase.² Other workers have also realized that the polar phase should be stabilized by narrow pores.³

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The axial (or ABM) phases⁴⁻⁶ exist in two forms, mixed axial and transverse axial. The mixed axial phase is stable over a small temperature region and changes at a first order transition to the transverse axial state. The chief difference between the two axial phases lies in the fact that only the transverse axial phase has a disgyration⁷ at the pore center. A disgyration is a region in which the order parameter is reduced rather like in a vortex core in superfluid ⁴He.

On further cooling, the BW⁸ or B phase will be produced from the transverse axial phase at a first order transition. The BW state in a pore differs from the bulk BW state mainly in having a disgyration at the pore center. [Note that if the pressure is much greater than the polycritical point pressure, the temperature will have to be much reduced before the BW state appears. There the coherence length $\xi(T) \ll R$ and finite size effects can be safely neglected. The transition which takes place in these circumstances is best regarded as just the usual A to B bulk liquid transition.]

The mechanism which produces the variety of phases is the competition among terms in the free energy corresponding to bulk energies, surface energies, and strain energies (which arise from spatial variations of the order parameter). A surface free energy arises through the suppression of certain of the components of the order parameters at a surface. Ambegaokar, de Gennes, and Rainer⁷ (to be referred to as AGR) have shown that the boundary conditions on the order parameter depend crucially on how ³He quasiparticles are scattered at a solid surface. It seems most likely that diffuse scattering will prevail for ordinary glass surfaces,⁹ and so we have concentrated mainly on this case. The sequence of transitions outlined above was for diffuse scattering boundary conditions. AGR suggested that at mica surfaces, specular reflection of ³He quasiparticles might be realized. The sequence of transitions for specular reflection boundary conditions is given in Section 5.

All the calculations in this paper are of mean-field character. Fluctuations about the mean-field (or Ginzburg–Landau) solution are enhanced in a pore since its geometry is essentially that of a one-dimensional system. Fluctuations will round off the sharp transitions found by minimizing the Ginzburg–Landau free-energy functional. Fortunately, this rounding-off effect has been much studied in connection with superconductivity in thin wires and so we shall just quote the result for the range of validity of meanfield theory. For a one-dimensional system, mean-field theory fails only within a temperature interval ϵ_c given by¹⁰

$$\varepsilon_c = (1 - T/T_c) \sim (k_F R)^{-4/3} \tag{2}$$

where the Fermi wave number $k_{\rm F}$ is of order 0.87 Å⁻¹ for liquid ³He. Since the intervals over which the phases exist are of order $(\xi_0/R)^2$, the fluctuation rounding effects are small in comparison. Variations in pore diameter will also be a source of rounding.

Another complication which we shall neglect throughout is the effect of the dipole–dipole interactions between the ³He nuclei. These will play a crucial role in determining the NMR properties of the phases in the pores,¹¹ but their thermodynamic effects will only be appreciable in a reduced temperature interval ε_0 of

$$v_0 = (1 - T/T_c) \sim N(0)(\gamma \hbar)^2 [\ln (1.13\hbar\omega_0/k_B T_c)]^2 \approx 2 \times 10^{-6}$$
(3)

Since the reduced temperature intervals we are concerned with are of order 10^{-3} or greater, it is clear that the dipole energy terms can be safely neglected in discussions of the stability of the phases in the pores. (A reduced temperature interval of 10^{-3} corresponds to a temperature difference from T_c of about $1 \,\mu$ K.)

An experiment such as a flow or NMR experiment on superfluid ³He in narrow pores at temperatures close to the bulk transition temperature should therefore reveal a number of "kinks" in any measured quantity as the temperature is reduced, corresponding to the various phase transitions. (Actually, we can only be sure of sharp "kinks" in thermodynamic quantities; fluctuation effects and hence rounding may be larger for transport coefficients.)¹⁰ The nature of these kinks and the temperatures at which they occur will provide much information on coherence lengths, boundary conditions, and the behavior of quasiparticle scattering off the surface of the pores. In addition we expect a similar variety of phases in any restricted geometry except that of slab geometry.¹²

The mathematical formalism is outlined in Section 2. We have concentrated mainly on the procedure to be used, for to solve the equations completely would involve a huge numerical effort. This is probably sufficient until the shape of the pores used in any particular experiment is known. For example, if the pore diameters are less than 1 μ m, the pores are unlikely to be fabricated with accurately circular cross sections. It is possible to make much progress by using simple Ansätze for the order parameter, together with a few numerical estimates. Such are given for the two axial states in Section 3 and for the BW state in Section 4. In Section 5, specular scattering boundary conditions are considered and the sequence of transitions appropriate to them is worked out. We conclude in Section 6 with discussions of the effects of magnetic fields and of metastability of the phases.

2. FORMALISM AND CALCULATIONAL TECHNIQUES

2.1. Formalism

The order parameter for the triplet-paired superfluid, $\Delta_{\mu\nu}$, is most conveniently expressed for *p*-wave pairing in the form

$$\langle a_{\mu}(\mathbf{k})a_{\nu}(-\mathbf{k})\rangle \sim \Delta_{\mu\nu} = i(\mathbf{\sigma}\cdot\mathbf{d}(\mathbf{k})\sigma_{\nu})_{\mu\nu}$$
 (4)

$$d_p(\mathbf{k}) = A_{pi}\hat{k}_i \tag{5}$$

where \hat{k}_i is a Cartesian component of the unit wave vector \hat{k} ; and A_{pi} is a complex 3×3 matrix whose elements transform under a space rotation like a vector with respect to the column index i, and under a spin rotation like a vector with respect to the row index p. For discussions of the thermodynamics of superfluid ³He in the vicinity of the phase transition, the Landau expansion of the free energy F in powers of the order parameter is most useful. Neglecting dipolar forces, the (bulk) free-energy density difference between the normal and superfluid phases to fourth order in the order parameter can be written as

$$f_{B} = -\frac{1}{2}a \operatorname{Tr} AA^{+} + \frac{1}{4} \{\beta_{1} | \operatorname{Tr} A\tilde{A} |^{2} + \beta_{2} [\operatorname{Tr} AA^{+}]^{2} + \beta_{3} \operatorname{Tr} [A^{+} A(A^{+}A)^{*}] + \beta_{4} \operatorname{Tr} (AA^{+})^{2} + \beta_{5} \operatorname{Tr} [AA^{+} (AA^{+})^{*}] \} = -\frac{1}{2}a \operatorname{Tr} AA^{+} + \frac{1}{4} \sum_{i} \beta_{i} R_{i}$$
(6)

The coefficient *a* is of the form $\lambda(1 - T/T_c)$, while the β_i are "strong coupling" coefficients whose values are not fully determined by the present experimental data.

When the order parameter varies spatially, there are extra terms in the free energy density, quadratic in the gradients,⁷ which we shall refer to as the "strain energy":

$$f_S = \frac{1}{2} \sum_p \left\{ K_L |\operatorname{div} \mathbf{A}_p|^2 + K_T |\operatorname{curl} \mathbf{A}_p|^2 \right\}$$
(7)

where K_L and K_T are two positive constants and A_p is the vector with components A_{ni} . There are two coherence lengths associated with the constants K_L and K_T ,

$$\xi_L^2 = K_L / |a| = \frac{9}{5} \xi_0^2 / t \qquad \text{(longitudinal)} \tag{8}$$

$$\xi_T^2 = K_T / |a| = \frac{3}{5} \xi_0^2 / t \qquad \text{(transverse)} \tag{9}$$

where $t = (1 - T/T_c)$ and ξ_0 is the zero-temperature coherence length.⁷ The total free energy F of the system is just the volume integral

$$F = \int \mathrm{d}V \left(f_B + f_S\right) \tag{10}$$

The boundary conditions on the superfluid order parameter are complicated. AGR demonstrated that whatever the temperature and the nature of the surface, the component of the order parameter normal to the surface $(A_p)_{\perp}$ vanishes:

$$(\mathbf{A}_{p})_{\perp}(\text{surface}) = 0 \tag{11}$$

The boundary conditions on the tangential components of the order parameter $(\mathbf{A}_p)_{\parallel}$ are, however, temperature and surface dependent. We shall treat separately in Section 5 surfaces that scatter ³He quasiparticles specularly. For surfaces that scatter ³He quasiparticles diffusely, AGR showed that the tangential components at a surface are reduced relative to their bulk values by a factor $\xi_0/\xi_T(T)$. Since we are interested only in the temperature region for which $\xi(T) \gg \xi_0$, i.e., near T_c , we can adopt the simpler boundary condition (for diffuse reflection)

$$(\mathbf{A}_p)_{\parallel}(\text{surface}) = 0 \tag{12}$$

In this paper we study in detail the case of ³He confined in a long cylindrical pore of circular cross section. Its axis is taken to be the z axis. We shall assume throughout that the order parameter A which makes F a minimum and satisfies the boundary conditions does not depend on z. This is because variation in z is never enjoined by the boundary conditions, and if present would produce an increase in the strain energy f_S without any reduction in the bulk energy. The A_p will therefore be taken to be functions of two variables only, r and θ , namely the usual cylindrical polar coordinates. The pore radius is denoted by R, so that the boundary conditions (11) and (12) specialize to

$$\mathbf{A}_{p}(R,\,\theta) = 0 \qquad \text{for all }\theta \tag{13}$$

2.2. The Linearized Equations

The Euler-Lagrange procedure yields partial differential equations in the A_p which, when solved subject to the boundary conditions, give a stationary expression for the free energy. Among these stationary solutions will be the true absolute minimum, which gives the equilibrium state of the superfluid. The Euler-Lagrange equations are

$$K_T \nabla^2 \mathbf{A}_p + (K_L - K_T) \operatorname{grad} \operatorname{div} \mathbf{A}_p + a \mathbf{A}_p - \frac{1}{4} \sum_i \beta_i (\partial R_i / \partial \mathbf{A}_p) = 0 \quad (14)$$

where, in our curvilinear (polar) coordinates, ∇^2 is defined as (grad div – curl curl). The last term in Eq. (14) is cubic in \mathbf{A}_p . Hence when the superfluid first condenses, the only role of the cubic terms is to fix the overall normalization of \mathbf{A}_p , and the radial and angular dependences of the order parameter

will be given by the solutions of the simpler linear equation

$$K_T \nabla^2 \mathbf{A}_p + (K_L - K_T) \operatorname{grad} \operatorname{div} \mathbf{A}_p + a \mathbf{A}_p = 0$$
(15)

This equation, together with the boundary conditions (11) and (12), can be regarded as an eigenvalue equation with a as the eigenvalue. The superfluid cannot begin to condense until the quadratic part of F [i.e. the part which gives rise to Eq. (15)] can turn negative. Since the strain terms are positive-definite, condensation in a finite geometry with diffuse boundary conditions can only take place if the temperature is less than the bulk superfluid transition temperature T_c , that is, for nonzero, positive values of a. If we denote the smallest eigenvalue of (15) by a_1 , then the exact onset temperature T_1 is given by

$$a_1 = \lambda (1 - T_1/T_c) \tag{16}$$

For the cylindrical capillary a_1 can be obtained explicitly. Notice that in Eq. (15) the different spin components—the components labeled by the index p—are decoupled from one another, which means that we can solve for each spin component separately and so ignore the subscript p in (15), i.e., set $\mathbf{A}_p \rightarrow \mathbf{A}$. For $K_L > K_T$, it turns out that the lowest eigenvalue corresponds to an eigenfunction for which div $\mathbf{A} = 0$. If one sets $\mathbf{A} = g(r, \theta)\hat{\mathbf{z}}$, where $\hat{\mathbf{z}}$ is a unit vector along the capillary axis, the divergence will vanish identically. Then Eq. (15) reduces to

$$K_T \nabla^2 g + ag = 0 \tag{17}$$

In a cylindrical geometry subject to the boundary condition $g(R, \theta) = 0$, Eq. (17) has solutions

$$J_m(\alpha_{mn}r/R) \begin{cases} \cos m\theta\\ \sin m\theta \end{cases}, \qquad m = 0, 1, 2, \dots; \quad n = 1, 2, 3, \dots$$
(18)

where α_{mn} is the *n*th zero of $J_m(x)$, not counting (for $m \ge 1$) the zero at x = 0. The eigenvalues associated with the eigenfunctions in (18) are

$$a = E_{mn} = K_T \alpha_{mn}^2 / R^2 \tag{19}$$

The smallest eigenvalue corresponds to $\alpha_{01} \approx 2.40$, and so superfluid condensation will first take place when

$$a = a_1 = E_{01}$$

or, using (9), when

$$R/\xi_T = \alpha_{01} \tag{20}$$

or

$$(T_c - T_1)/T_c = \frac{3}{5} (\xi_0/R)^2 \alpha_{01}^2$$
(20a)

Equation (20) shows that finite size effects are appreciable only when the coherence length becomes comparable to the smallest linear dimension of the system; in this case, the pore diameter. Equation (20a) indicates that the transition temperature T_1 is depressed below the bulk value of T_c by an amount which varies as the inverse square of the pore radius.

We shall attach the name "polar" to solutions of the type $\mathbf{A}_p = g(r, \theta) \hat{\mathbf{z}}$. The reason for this name is that in the bulk liquid, the polar phase has an order parameter which can be written $\mathbf{A}_p = \delta_{p1} g \hat{\mathbf{z}}$, where g is a temperaturedependent (but position-independent) constant.^{2,6} It seems likly that the strong coupling coefficients β_i have values which ensure that the polar phase is not a stable bulk phase. Its stability in a cylindrical pore is a manifestation of finite-size effects.

We shall now list the possible types of solutions of the linearized equation (15). Nontrivial details are discussed in Appendix A. Writing A in terms of cylindrical polar variables and components $(f_r(r, \theta), f_{\theta}(r, \theta), g(r, \theta))$, there exist the solutions:

(i) "Polar type":

$$\psi_{mn}^{\pm} \sim J_m(\alpha_{mn}r/R) \left\{ \begin{array}{l} \cos m\theta \\ \sin m\theta \end{array} \right\}, \qquad m = 0, 1, 2; \quad n = 1, 2, 3, \dots$$
 (21)

as in (18) with eigenvalues as in (19). The superscript \pm indicates the parity under reflection of the y axis, $(x \rightarrow x, y \rightarrow -y)$, as discussed further in Appendix A.

(ii) "Transverse type" $f_r = 0$ and

$$f_{\theta}(r) \sim J_1(\alpha_{1n}r/R), \qquad n = 1, 2, 3, \dots$$
 (22)

which satisfies the boundary condition $f_{\theta}(R) = 0$ and has eigenvalues

$$a = E_{1n} = K_T \alpha_{1n}^2 / R^2 \tag{23}$$

The lowest eigenvalue corresponds to $\alpha_{11} \approx 3.83$.

(iii) "Longitudinal type": $f_{\theta} = 0$ and

$$f_r(r) \sim J_1(\alpha_{1n}r/R), \qquad n = 1, 2, 3, \dots$$
 (24)

which satisfies the boundary condition $f_r(R) = 0$ and has eigenvalues $3E_{1n}$.

(iv) Mixed solutions. These are solutions of (15) for f_r and f_{θ} which are neither purely transverse nor purely longitudinal. They are described in Appendix A. Define

$$u_{m}(r) = \frac{1}{m} \left\{ \frac{J_{m}(A)J_{m}(b)m^{2}}{Ab} - J'_{m}(B)J'_{m}(a) \right\}$$

$$v_{m}(r) = \left\{ \frac{J_{m}(A)}{A}J'_{m}(b) - J'_{m}(B)\frac{J_{m}(a)}{a} \right\}$$
(25)

where $m = 1, 2, ..., A = (a/K_T)^{1/2}R$, $B = (a/K_L)^{1/2}R = A/\sqrt{3}$, $a = (a/K_T)^{1/2}r$, $b = (a/K_L)^{1/2}r = a/\sqrt{3}$, and $J'_m(x) \equiv (d/dx)J_m(x)$. Then there are two kinds of mixed solutions labeled + and - to indicate their parities under reflection of the y axis (see Appendix A):

$$f_{mr}^{+} = v_m(r)\cos m\theta, \qquad f_{m\theta}^{+} = -u_m(r)\sin m\theta$$
 (26)

$$f_{mr}^- = v_m(r)\sin m\theta, \qquad f_{m\theta}^- = u_m(r)\cos m\theta$$
 (27)

The eigenvalue condition is

$$m^2 J_m(A) J_m(B) = A B J'_m(A) J'_m(B)$$
 (28)

Denote by γ_{mn} the *n*th solution of (28) for *A*. The lowest eigenvalue is $\gamma_{11} \approx 3.36$ and corresponds to a temperature T_M given by

$$(T_c - T_M)/T_c = \frac{3}{5}(\xi_0/R)^2 (3.36)^2$$
⁽²⁹⁾

 γ_{11} is the next smallest eigenvalue to the polar eigenvalue α_{01} .

For m = 0, the two mixed solutions reduce to the transverse and longitudinal solutions.

2.3. Sectors

Any solution of the nonlinear equation (14) can be expressed as a linear superposition of solutions of the linear equation (15). However, there exist solutions of the nonlinear equations whose expansion involves only a subset (and not all) of the solutions of the linear equation. The problem is to determine which combinations will occur in any given phase. It will help to consider first a simple example (model) for the polar phase.

Let $\psi_1(r, \theta)$ and $\psi_2(r, \theta)$ be two solutions of the linear equation, Eq. (17), with eigenvalues ε_1 and ε_2 , and suppose for the moment that it is adequate to write

$$g(r,\theta) = c_1 \psi_1 + c_2 \psi_2, \qquad c_{1,2} \text{ real constants}$$
(30)

Then, in terms of c_1 and c_2 , the free energy can be written as

$$F \sim \{ -(a - \varepsilon_1)c_1^2 - (a - \varepsilon_2)c_2^2 + \gamma_4 c_1^4 + \gamma_3 c_1^3 c_2 + \gamma_2 c_1^2 c_2^2 + \gamma_1 c_1 c_2^3 + \gamma_0 c_2^4 \}$$
(31)

where the γ_i depend on the strong coupling coefficients and on the explicit form of the functions $\psi_1(r, \theta)$ and $\psi_2(r, \theta)$. For example, the coefficient γ_3 will be related to the "interference" integral

$$\gamma_3 \sim \int dV \,\psi_1^3 \psi_2 \tag{32}$$

Assume $\varepsilon_1 < \varepsilon_2$, so that initially the superfluid will condense into the state ψ_1 . We distinguish two cases.

(i) Odd-odd interference terms (like γ_3 or γ_1) nonzero.

• We anticipate that for a just above ε_1 , when $|a - \varepsilon_1| \ll |a - \varepsilon_2|$, we should have c_2^2/c_1^2 nonzero (though small), i.e., that c_2^2 is nonzero even though $a < \varepsilon_2$. That this is indeed so is easily demonstrated. If $c_2 = 0$,

$$F \approx -(a - \varepsilon_1)c_1^2 + \gamma_4 c_1^4 \tag{33}$$

and is minimized by $c_1^2 = (a - \varepsilon_1)/2\gamma_4$. To second order in c_2 , taking $|a - \varepsilon_1| \ll |a - \varepsilon_2|$,

$$F \approx -(a - \varepsilon_1)c_1^2 + \gamma_4 c_1^4 + \gamma_3 c_1^3 c_2 + (\varepsilon_2 - a)c_2^2$$
(34)

which on calculating $\partial F/\partial c_2$ to find the minimum gives

$$\gamma_3 c_1^3 + 2c_2(\varepsilon_2 - a) = 0 \tag{35}$$

so

$$c_2 = -\gamma_3 c_1^3 / (\varepsilon_2 - a)$$

and

$$c_2/c_1 = -(\gamma_3/2\gamma_4)(a - \varepsilon_1)/(\varepsilon_2 - a)$$
(36)

which is small, as expected, and vanishes as $a \rightarrow \varepsilon_1$.

(ii) Only even-even interference terms nonzero.

In this case, the free energy F can be put in the form

$$F \sim -(a - \varepsilon_1)c_1^2 - (a - \varepsilon_2)c_2^2 + \frac{1}{2}\beta_{11}c_1^4 + \beta_{12}c_1^2c_2^2 + \frac{1}{2}\beta_{22}c_2^4$$
(37)

Depending on the relative values of β_{11} , β_{12} , β_{22} , ε_1 , and ε_2 , several possibilities exist, and are spelled out in Appendix B. For our present purposes, it is sufficient to notice that, if c_2^2 ever rises from zero, it can do so only at a further second- or first-order transition, which occurs at a temperature lower than that where condensation into the ψ_1 state begins.

Hence it is essential to recognize the differences between combinations of linear functions which have, or have not, odd-odd interference terms. We shall divide the space spanned by the solutions of the linear equation (15) subject to diffuse scattering boundary conditions into sectors, such that functions all within one sector have no odd-odd interference terms with any functions outside that sector, while there are odd-odd interference terms within each sector. (See further remarks in Appendix C.) In other words, the order parameter of any given phase in the pore is associated with just one sector. Obviously, all functions in the same sector can combine freely, and by adjusting the relative weight of each function in the sector, the shape of the order parameter adjusts itself to changing values of the temperature.

One sector for the polar phase is made up of the functions $J_0(\alpha_{0n}r/R)$. Condensation starts with the n = 1 function of this sector and it would seem reasonable to assume that the polar phase at all temperatures below T_1 is expressible as

$$g(r,\theta) = \sum_{n} c_{n} J_{0}(\alpha_{0n} r/R)$$
(38)

However, other polar sectors do exist; they all cause g to vary with the polar angle θ . An example is

$$g(r,\theta) = \sum_{m \text{ even } n} \sum_{n} c_{mn} J_m(\alpha_{mn} r/R) \sin m\theta$$
(39)

[Evidently, there are no odd-odd interference terms between (38) and (39), since all such vanish after integration over θ .] One might wonder whether the larger sector of Eq. (39) might at a certain temperature give a lower free energy than the sector of Eq. (38). Such questions cannot be answered firmly without resort to detailed numerical work, but on physical grounds we doubt whether admitting angular variation into g would lower the free energy. In other words, in this nonlinear variational problem, intuition trained on linear variational processes is unreliable; it no longer follows automatically that every extra variational parameter leads to an improvement in the trial function.

Assuming that the polar phase remains in the sector of Eq. (38), we examined numerically its development as a function of temperature. Specifically we took the first three coefficients in (38), c_1 , c_2 , c_3 , expressed the free energy in terms of them, and varied them until the free energy was a minimum. The results were as might have been expected. For values of the temperature close to T_1 , the onset temperature for polar condensation, the first term dominated g(r). As the temperature was reduced, the magnitudes of c_2 and c_3 increased, maintaining $|c_3| < |c_2|$. We were able to conclude that for temperatures in the range such that

$$2.4 < R/\xi_T < 4.5$$

a three-parameter variational calculation was adequate for the polar phase.

On cooling, the polar phase does not remain the most stable phase. This is easily understood. For temperatures well below T_c , the coherence length will be small compared to the pore size and so finite size effects will become unimportant. At such temperatures, bulk terms dominate, and the liquid will have an order parameter very similar to either that of the axial phase or the BW phase, depending upon pressure of the liquid in the pores.

The details of the passage from the polar phase to these other phases is the subject of the next two sections.

3. THE AXIAL PHASES

In the bulk liquid the A matrix of the axial phase, in a Cartesian basis labeled by (x, y, z), is

$$A \sim \begin{pmatrix} 0 & i & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$
(40)

This is a standard form, which may be pre- or post-multiplied by independent real orthogonal matrices representing rotations in spin space and in configuration space. When the liquid is confined to a pore, we look for an Ansatz which is a minimal modification of (40), capable of satisfying the boundary conditions yet remaining, locally, as similar as possible to the bulk form. (Recall that to date even the bulk problem is too complicated for complete solution from first principles; a fortiori we do not tackle the restrictedgeometry problem head on.) In constructing such an Ansatz for the cylinder. we bear in mind that the cylinder axis (z direction) is physically distinguished from the x and y directions, and that the strain energy introduces an explicit and basic distinction between row and column (i.e., spin and space) indices of A. Accordingly, we chose an Ansatz which maintains zero vectors in the second and third rows of A (since there is no physical reason why restricted geometry should induce spin rotations); and in the remaining vector of the first row we maintain its x and y components (those in the cross-sectional plane) as pure imaginary relative to the z component, i.e., the polar component. But we allow for the possibility that confinement will (i) rotate the x and y components in their own plane (about the z axis) through an angle depending on r and θ , and (ii) alter the relative normalization of the in-plane and of the z components, also by a position-dependent amount. Thus, our Ansatz is 1.0....

$$A \sim \begin{pmatrix} if_x & if_y & g \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \mathbf{f}, g \text{ real}$$
(41)

i.e.,

$$\mathbf{A}_{p} = \delta_{p1}(if_{x}, if_{y}, g) = \delta_{p1}(if, g)$$
(42)

(We expect, though we shall not pursue the argument quantitatively, that for very large radius, $|\mathbf{f}|$ and g assume their bulk values, except in a surface layer whose local structure is independent of the curvature, and except also very near the axis, where there is a disgyration. There are obvious analogies in this limit between the behavior of **f** and the fixed-magnitude director in nematic liquid crystals.)

The polar phase is a special case of the Ansatz with $\mathbf{f} = 0$. The free energy in terms of \mathbf{f} and g becomes

$$F = \int dV \left\{ \frac{1}{2} K_T [(\operatorname{curl} \mathbf{f})_z^2 + (\operatorname{grad} g)^2] + \frac{1}{2} K_L (\operatorname{div} \mathbf{f})^2 - \frac{1}{2} a (\mathbf{f}^2 + g^2) + \frac{1}{4} \beta (\mathbf{f}^4 + g^4) + \frac{1}{2} \beta C \mathbf{f}^2 g^2 \right\}$$

with

 $\beta \equiv \beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5$, $\beta C \equiv \beta_2 + \beta_4 + \beta_5 - \beta_1 - \beta_3$ (43) In the original spin-fluctuation model,* $\beta \sim (3 - \delta)$, $C = (1 - \delta)/(3 - \delta)$, which, on taking $\delta = \frac{1}{4}$, gives $\beta \sim 2.75$ and C = 0.27.

The Euler-Lagrange equations are

$$K_T \nabla^2 g + ag - \beta g^3 - \beta C \mathbf{f}^2 g = 0, \qquad (44)$$

$$K_T \nabla^2 \mathbf{f} + (K_L - K_T) \operatorname{grad} \operatorname{div} \mathbf{f} + a\mathbf{f} - \beta \mathbf{f}^2 \mathbf{f} - \beta C g^2 \mathbf{f} = 0$$
(45)

Because C is nonzero, the solutions for **f** and g are coupled. The polar component g forms first (while **f** is still zero) and develops as the solution to the equation

$$K_T \nabla^2 g + ag - \beta g^3 = 0 \tag{46}$$

The solution to (46), alone, for $\xi_T \ll R$, will be

$$g^2 = a/\beta$$
, with free energy $F = -Va^2/4\beta$ (47)

for, in such a region, finite size effects will be negligible, $\nabla^2 g \approx 0$, and g^2 will take its bulk liquid value. By the same argument the solution of (44) and (45) for $\xi_T \ll R$ will be

$$g^2 = f^2 = (a/\beta)(1+C)^{-1}$$
, with free energy $F = -Va^2/2\beta(1+C)$ (48)

just as in the bulk axial phase. In view of the fact that in the bulk liquid it is the axial phase which is stable and not the polar phase, which implies C < 1, one concludes that the polar phase in the pore must disappear on lowering the temperature sufficiently. There will be a temperature at which it is possible to obtain a lower free energy than the polar free energy obtained from (46), by making **f** nonzero.

An upper bound on the temperature at which f first appears can be found by dropping the cubic terms in (45), when the resulting linear differential equation is similar to Eq. (15), viz.

$$K_T \nabla^2 \mathbf{f} + (K_L - K_T) \operatorname{grad} \operatorname{div} \mathbf{f} + a\mathbf{f} = 0$$
(49)

*See Ref. 5. Somewhat different expressions were obtained in a later paper.¹⁵

The lowest eigenfunction of (49) corresponds to the m = 1 mixed state solution (26) and forms when

$$(T_c - T)/T_c = \frac{3}{5}(\xi_0/R)^2(3.36)^2$$
(50)

The exact temperature at which **f** condenses could be obtained by finding the lowest eigenvalue of

$$K_T \nabla^2 \mathbf{f} + (K_L - K_T) \operatorname{grad} \operatorname{div} \mathbf{f} + a\mathbf{f} - \beta C g^2 \mathbf{f} = 0$$
(51)

In principle, one must first solve (46) for g, and substitute the solution into (51). The resulting differential equation, though linear, would be quite intractable, so we shall make the approximation of replacing g^2 by a constant, its bulk polar value, a^2/β , which should give a lower "bound" on the temperature at which **f** condenses, since g^2 in the pore is unlikely to much exceed its bulk value over large regions of the pore. The resulting expression for the onset temperature is

$$(T_c - T)/T_c = \frac{3}{5}(\xi_0/R)^2 (3.36)^2 (1 - C)^{-1}$$
(52)

Notice that because C > 0, the effect of cross-coupling between Eqs. (44) and (45) for **f** and g is to delay the condensation of **f**, or increase the stability of the polar phase. We shall call the phase which develops from the polar phase the mixed axial state (or phase), because it is initially dominated by the m = 1 mixed solution. Its development as the temperature is lowered can only be obtained from a study of (44) and (45). The angular variation of the mixed solution for **f** will induce, via the cross-coupling term, only even multipoles in g (that is, terms in $\cos m\theta$ and $\sin m\theta$ with m even). **f** itself probably remains in the sector consisting of just the \mathbf{f}_{odd}^+ solutions [see Eq. (26)], since initially it condenses into just this sector. (The cubic term $\beta \mathbf{f}^2 \mathbf{f}$ in (45) mixes different m values, but odd values of m remain in a separate sector to the even values. A summary on the sectors is given in Appendix C.)

However, we believe that the mixed axial phase will probably be overtaken at a first-order transition by the "transverse" state which has

$$\mathbf{f}(r,\theta) = (0, f_{\theta}(r)), \qquad g(r,\theta) = \sum_{n} c_{n} J_{0}(\alpha_{0n} r/R)$$
(53)

where

$$f_{\theta}(r) = \sum_{n} b_{n} J_{1}(\alpha_{1n} r/R)$$
(54)

The transverse state has no chance of forming until

$$(T_c - T)/T_c = \frac{3}{5}(\xi_0/R)^2 \alpha_{11}^2, \qquad \alpha_{11} \approx 3.83$$
 (55a)

as can be seen by the same type of argument which led to (50). The transverse state is the one which AGR suggested would be the most stable state in a

cylindrical pore. Because $|\mathbf{f}| \to 0$ at the center of the pore $[J_1(x) \sim x/2$ as $x \to 0]$ it has a disgyration there, in contrast to the mixed state, whose disgyrations, if any, are at the surface.

The competition between the mixed and transverse states can be illustrated in a mathematically very crude way by ignoring the polar components, and retaining only the leading term for the mixed state (the f_1^+ eigenfunction) and the transverse state (the ψ_{11}^+ eigenfunction). This leads to the model problem of Appendix B, where the relative stability of two states labeled (x) and (y) is worked out [see also Eq. (37)]. Identifying (x) with the mixed state and (y) with the transverse state, the parameters are $\varepsilon_1 = 3.36$, $\varepsilon_2 = 3.83$, $\beta_{11} \sim 1.44$, $\beta_{12} \sim 1.69$, and $\beta_{22} \sim 0.98$. In this case β_{11}, β_{12} , and β_{22} just involve overlap integrals, e.g.,

$$\beta_{22} \sim \int dV (\psi_{11}^+)^4 \left/ \left[\int dV (\psi_{11}^+)^2 \right]^2 \right.$$

It is shown in Appendix B that if the parameters satisfy the inequality $\beta_{12} > \beta_{11} > \beta_{22}$, then the transition from (x) to (y) (or mixed to transverse) will take place at a first-order transition, at a temperature given by

$$a = a^* = (\varepsilon_2 \beta_{11}^{1/2} - \varepsilon_1 \beta_{22}^{1/2}) / (\beta_{11}^{1/2} - \beta_{22}^{1/2})$$
(55b)

that is,

$$(T_c - T)/T_c = \frac{3}{5}(\xi_0/R)^2(6.04)^2$$

A more refined calculation, taking more functions in each sector and allowing for cross-coupling to the polar components, would be needed to obtain an accurate expression for the transition temperature.

The mechanism by which at lower temperatures the mixed axial phase becomes less stable than the transverse axial phase is hard to describe in physical terms but would seem to be connected with the small value of the parameter β_{22} in the model. It is shown in Appendix B that if the β_{ij} had satisfied, for example, the inequalities $\beta_{11} > \beta_{12} > \beta_{22}$ and $(\beta_{11}\beta_{22} - \beta_{12}^2) > 0$, then there would have been an intermediate phase lying between the mixed and transverse phases, which would have formed and disappeared at second-order transitions. Presumably in other restricted geometries, this possibility, or other similar ones, might be realized. It is not obvious either that a more refined calculation for a pore might not show the existence of, say, the intermediate phase, but we would doubt it, mainly because of the generous margin by which the β_{ij} of the model satisfy the inequality governing the existence of a first-order transition.

4. THE BW PHASE

In the bulk liquid the standard form of the A matrix of the BW phase is

$$A = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
(56)

To construct a corresponding Ansatz for the pore, we follow the same line of reasoning as at the beginning of Section 3; in particular, we now maintain the three rows of A as mutually orthogonal real vectors. Thus one is led at once to the Ansatz

$$A = \begin{pmatrix} f_x & f_y & 0\\ h_x & h_y & 0\\ 0 & 0 & g \end{pmatrix}, \quad \mathbf{f}, \mathbf{h}, g \text{ real}$$
(57)

$$\mathbf{f} \cdot \mathbf{h} = f_x h_x + f_y h_y = 0 \tag{58}$$

We shall see presently that (58) is an extremely strong constraint which practically determines our choice of **f** and **h**.

The free energy in terms of f, h, and g becomes

$$F = \int dV \left\{ \frac{1}{2} K_T [(\operatorname{curl} \mathbf{f})_z^2 + (\operatorname{curl} \mathbf{h})_z^2 + (\operatorname{grad} g)^2] \right. \\ \left. + \frac{1}{2} K_L [(\operatorname{div} \mathbf{f})^2 + (\operatorname{div} \mathbf{h})^2] \right. \\ \left. - \frac{1}{2} a (\mathbf{f}^2 + \mathbf{h}^2 + g^2) + \frac{1}{4} \beta (\mathbf{f}^4 + \mathbf{h}^4 + g^4) + \frac{1}{2} \beta C' (\mathbf{f}^2 g^2 + \mathbf{h}^2 g^2 + \mathbf{f}^2 \mathbf{h}^2) \right\}$$
(59)

where

$$\beta \equiv \beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5, \qquad \beta C' \equiv (\beta_1 + \beta_2) \tag{60}$$

 β has the same form as for the axial Ansatz but C', in terms of spin-fluctuation model parameters, is $(1 + \delta)/(3 - 8) \approx 0.45$ at $\delta = \frac{1}{4}$, which is greater than C for the axial Ansatz.

We shall be driven by the complexity of (59) to assume that the BW state lies in the sectors

$$g(r,\theta) = \sum_{n} a_{n} J_{0}(\alpha_{0n} r/R)$$

$$\mathbf{f}(r,\theta) = (0, f_{\theta}(r)), \quad \text{i.e., } \mathbf{f} \text{ is purely transverse}$$
(61)

$$\mathbf{h}(r,\theta) = (h_{r}(r), 0), \quad \text{i.e., } \mathbf{h} \text{ is purely longitudinal}$$

where

$$f_{\theta}(r) = \sum_{n} b_{n} J_{1}(\alpha_{1n} r/R), \qquad h_{r}(r) = \sum_{n} c_{n} J_{1}(\alpha_{1n} r/R)$$
(62)

Notice that (61) and (62) imply that there is a disgyration at the center of the pore for the BW state, since, as $r \to 0$, $|\mathbf{f}| \to 0$ and $|\mathbf{h}| \to 0$. At this disgyration, the BW phase locally resembles the polar phase.

When outlining the sequence of transitions in Section 1, we indicated that the axial phases would always be formed before the first-order transition to the BW phase takes place. This will certainly be true if the pressure on the superfluid is greater than the pressure at the polycritical point (PCP), for then the transition will resemble the bulk A to B transition. Finite size effects will modify the AB transition more strongly near the PCP, and Privorotskii¹² has worked out their effects on the shape of the AB phase boundary in its vicinity. Well below the PCP the situation is uncertain, and one might envisage transitions from, say, the mixed axial phase direct to the BW phase, omitting the transverse axial phase. However, detailed analysis is impossible without values for β and C', and at low pressures nothing is known about them.

5. SPECULAR BOUNDARY CONDITIONS

So far, all the discussion has been for boundary conditions on the order parameter appropriate to diffuse scattering of ³He quasiparticles at a solid surface. For the case of specular reflection, the boundary condition on the component of the order parameter normal to the surface remains as before⁷:

$$(A_p)_{\perp} = 0 \tag{63}$$

but that on the tangential components is radically altered. The strain terms F_s in the free energy are

$$F_{S} = \frac{1}{2} \int dV \left\{ K_{L} \operatorname{div} \mathbf{A}_{p}^{*} \operatorname{div} \mathbf{A}_{p} + K_{T} \operatorname{curl} \mathbf{A}_{p}^{*} \cdot \operatorname{curl} \mathbf{A}_{p} \right\}$$
(64)

which, using Gauss' theorem, can be rewritten as

$$F_{\mathbf{S}} = -\frac{1}{2} \int dV \left\{ K_{L}(\mathbf{A}_{p}^{*} \cdot \nabla) \operatorname{div} \mathbf{A}_{p} + K_{T}\mathbf{A}_{p}^{*} \cdot \operatorname{curl} \operatorname{curl} \mathbf{A}_{p} \right\}$$
$$+ \frac{1}{2}K_{L} \int d\mathbf{S} \cdot \mathbf{A}_{p}^{*} \operatorname{div} \mathbf{A}_{p} + \frac{1}{2}K_{T} \int d\mathbf{S} \cdot \mathbf{A}_{p}^{*} \times \operatorname{curl} \mathbf{A}_{p}$$
(65)

The longitudinal surface term in (65) is automatically zero because of the boundary condition (63) on the components of the order parameter normal to the surface.

In the Euler-Lagrange minimization procedure, both bulk and surface terms must be minimized. On varying A_p^* in the transverse surface term in

(65), one has

$$\int d\mathbf{S} \cdot \delta \mathbf{A}_p^* \times \operatorname{curl} \mathbf{A}_p = 0 \tag{66}$$

But \mathbf{A}_p^* and $\delta \mathbf{A}_p^*$ are constrained on the surface by $(\mathbf{A}_p)_{\perp} = (\mathbf{A}_p^*)_{\perp} = 0$, so both $\delta \mathbf{A}_p^*$ and \mathbf{A}_p^* lie in the tangent plane. Thus for a plane surface lying parallel to the xy plane, (66) becomes

$$\int dS_z \left\{ (\delta A_p^*)_x (\operatorname{curl} \mathbf{A}_p)_y - (\delta A_p^*)_y (\operatorname{curl} \mathbf{A}_p)_x \right\} = 0$$
(67)

which implies

$$(\operatorname{curl} \mathbf{A}_p)_x = (\operatorname{curl} \mathbf{A}_p)_y = 0$$

or

$$\frac{\partial A_{pz}}{\partial y} - \frac{\partial A_{py}}{\partial z} = \frac{\partial A_{px}}{\partial z} - \frac{\partial A_{pz}}{\partial x} = 0$$
(68)

But, on the surface, A_{pz} is zero, hence $\partial A_{pz}/\partial y = 0 = \partial A_{pz}/\partial x$ on the surface. Hence, from (68) we have

$$\partial A_{py}/\partial z = 0 = \partial A_{px}/\partial z$$
 at the surface (69)

Equations (69) are the appropriate boundary conditions on the tangential Cartesian components of the order parameter for the case of specular reflection from a plane surface.

The boundary conditions (63) and (69) give results in agreement with those produced by a full microscopic calculation by AGR.⁷ It is important to realize that as far as pure phenomenology goes, other surface terms could be added to (65).¹² Such terms, if present, could completely alter the boundary condition (69) and produce results at variance with the microscopic calculation. We feel that the agreement with the microscopic calculation justifies the neglect of such further surface terms. (It must be remembered also that surface terms are defined uniquely only once a particular form has been adopted for the bulk free-energy density. In other words, the introduction of a total divergence in fact modifies the surface energy.)

For a cylindrical surface, (66) gives the condition

$$(\operatorname{curl} \mathbf{A}_p)_{\theta} = (\operatorname{curl} \mathbf{A}_p)_z = 0 \tag{70}$$

But

$$(\operatorname{curl} \mathbf{A}_p)_{\theta} = \partial A_{pr}/\partial z - \partial A_{pz}/\partial r$$

and since $\partial A_{pr}/\partial z = 0$ at the surface since $A_{pr} = 0$ at r = R from (63), we must have

$$\partial A_{nz}/\partial r = 0$$
 at $r = R$ (71)

Also,

$$(\operatorname{curl} \mathbf{A}_p)_z = \frac{1}{r} \frac{\partial}{\partial r} (r A_{p\theta}) - \frac{1}{r} \frac{\partial A_{pr}}{\partial \theta}$$

and since $\partial A_{pr}/\partial \theta = 0$ at r = R from (63), we have

$$(\partial/\partial r)(rA_{p\theta}) = 0$$
 at $r = R$ (72)

Equations (63), (71), and (72) are the appropriate boundary conditions if ³He quasiparticles are reflected specularly at a solid cylindrical surface. We expect them to be valid only for the treatment of phenomena which vary on a length scale greater than ξ_0 . For effects on the scale of ξ_0 , the microscopic approach will be necessary.

Specular boundary conditions result in some striking differences in behavior. The formalism and the general approach of Section 2 still apply, and the solutions of the linearized equations (15) with specular boundary conditions are given in Appendix A. The first phase to condense from the normal phase will be the polar phase, as before, but because of the changed boundary conditions, $\partial g(R, \theta)/\partial r = 0$, (46) now admits the solution $g^2 = a/\beta$. Notice that this phase will start to condense exactly at the bulk critical temperature T_c , and appears as if it knew nothing of the presence of the walls.

As the temperature is lowered, the polar phase will become unstable relative to an axial phase. The temperature at which **f** begins to be nonzero can be determined exactly, for in (51) one can set $g^2 = a/\beta$ without approximation. The lowest eigenfunction of (51) with specular boundary conditions is the transverse solution (see Appendix A)

$$f_r = 0, \qquad f_\theta \sim J'_0(\alpha_{01}r/R)$$
 (73)

and appears at a temperature

$$(T_c - T)/T_c = \frac{3}{5} (\xi_0/R)^2 (2.4)^2 (1 - C)^{-1}$$
(74)

Because of the form of the solutions to the linearized problem (Appendix A), there is now no plausible reason to expect an analog to the transition between the mixed axial and transverse axial phases as found in the case of diffuse scattering boundary conditions, although such behavior cannot be ruled out rigorously without extensive numerical calculation. We believe that the most likely development of the axial phase as the temperature is

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lowered is in the sectors

$$f(r,\theta) = (0, f_{\theta}(r))$$

$$g(r,\theta) = \sum_{n=0}^{\infty} a_n J_0(\alpha_{1n} r/R), \qquad \alpha_{10} = 0$$
(75)

where

$$f_{\theta}(r) = \sum_{n=1}^{\infty} b_n J'_0(\alpha_{0n} r/R)$$
(76)

Note that (75) satisfies the boundary condition

$$\partial g(r,\theta)/\partial r = 0$$
 at $r = R$ (77)

because

$$J'_{0}(\alpha_{1n}) = -J_{1}(\alpha_{1n}) = 0$$
(78)

and that (76) satisfies the boundary condition that

$$(\partial/\partial r)(rf_{\theta}(r)) = 0$$
 at $r = R$ (79)

because $AJ_0''(A) + J_0'(A) = -AJ_0(A)$ for any A, so A must be $(\alpha_{0n}r/R)$ to satisfy (79).

On cooling further, the BW phase will form. Arguing by analogy with the case of diffuse scattering boundary conditions, we believe the appropriate Ansatz is as in (57), but with g given by (75), f given by (76), and h by

$$h_r(r,\,\theta) = \sum_n c_n J'_0(\alpha_{0n} r/R), \qquad h_\theta = 0 \tag{80}$$

which is a superposition of longitudinal solutions.

To summarize, the sequence of transitions for specular reflection boundary conditions will be normal $\xrightarrow{2nd}$ polar $\xrightarrow{2nd}$ axial $\xrightarrow{1st}$ BW, where the order of each transition between the phases has been indicated.

6. DISCUSSION

The only experiment to date (of which we are aware) in which there might have been a chance of observing phases similar to those predicted for restricted geometries is the experiment of Dundon *et al.*¹⁶ on superfluid ³He in sintered copper. Their sintered copper was made up of copper "spheres" of diameter 1 μ m. Because of experimental difficulties, their results were lacking in precision. However, they did find one interesting feature, namely, metastability involving the A to B transition of a peculiar kind, suggesting that finite size effects may enhance metastability. One would

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not expect metastability to be associated with any of the second-order transitions at which components of the order parameter begin to grow gradually. However, at a first-order transition such as that between the mixed and transverse axial states, metastability effects may preserve the mixed state over a larger temperature range than equilibrium considerations would allow, and thereby make its detection easier.

In a sufficiently large magnetic field, the predicted sequence of phase transitions will be changed. The first phase formed in the bulk liquid in a field is the A_1 or y phase (in the notation of Ref. 6). It is a phase in which only one spin component of the order parameter (Δ_1) is nonzero, while Δ_1 = $\Delta_0 = 0$. However, in a pore, the β phase, which also has only Δ_{\uparrow} nonzero, will form preferentially, for the same reasons that cause, in the zero-field situation, the condensation of the polar phase before the axial phase. The order parameter of the bulk β phase can be written as $\mathbf{A} \sim \boldsymbol{\alpha}(0, 0, 1)$, where α , a spin-space vector, is such that $|\alpha| = 1$, $\alpha^2 = 0$. On lowering the temperature, a transition will have to take place to a γ phase, for this is favored by the bulk free energy over the β phase. The order parameter of the bulk γ phase can be expressed as $\mathbf{A} \sim \boldsymbol{\alpha}(0, i, 1)$, which suggests an Ansatz for the γ phase in a pore of $\mathbf{A} = \alpha(if_x, if_y, g)$ [cf. Eq. (42) for the axial phase]. By analogy with the behavior of the axial phase, we expect there to be two γ phases, mixed and transverse, with a second-order transition taking place from β to mixed γ , and a first-order transition from mixed γ to transverse γ.

What happens on further cooling is complicated, depending on the strength of the field and the radius of the pores. One would guess that an axial phase and a BW phase would eventually be produced. We have not studied the resulting crossover problems, but expect the behavior of superfluid ³He in pores and in a magnetic field to be of great interest and complexity.

APPENDIX A. SOLUTION OF THE LINEARIZED EQUATIONS

We aim to obtain the complete set of solutions of the linearized Euler-Lagrange equations (15), replacing the quantity *a* there by eigenvalues *E* to be determined. For this purpose the spin index *p* can be ignored; **A** is a two-dimensional vector independent of *z* and lying in the cross-sectional plane. We use plane polar coordinates and components, so that $\mathbf{A} \equiv (A_r(r, \theta), A_{\theta}(r, \theta))$. We shall deal separately with diffuse and with mirror reflection, since they lead to different boundary conditions at the walls (r = R), as explained in the text. Readers who suspect that the resulting formalism is unnecessarily complicated can convince themselves of the contrary by consulting Chapter 13 of Morse and Feshbach.¹⁷

A1. Diffuse Scattering

The boundary conditions are

$$\mathbf{A}(R,\theta) = 0 \tag{A1}$$

It turns out to be convenient to express A in terms of its "potentials":

$$\mathbf{A} = \operatorname{grad} \phi + \operatorname{curl} \mathbf{V} \tag{A2}$$

Though the equations for ϕ and V decouple, the boundary conditions do not. Since only the z component of V is relevant, we write

$$\mathbf{V} = \mathbf{\hat{z}} V(r, \theta) \tag{A3}$$

and note

$$A_{r} = \frac{\partial \phi}{\partial r} + \frac{1}{r} \frac{\partial V}{\partial \theta}, \qquad A_{\theta} = \frac{1}{r} \frac{\partial \phi}{\partial \theta} - \frac{\partial V}{\partial r}$$
(A4)

The equations to be solved, subject to (A1), become

$$\nabla^2 \phi + \kappa_L^2 \phi = 0, \qquad \nabla^2 V + \kappa_T^2 V = 0 \tag{A5}$$

where we have set, in terms of the eigenvalue E,

$$\kappa_L^2 = E/K_L, \qquad \kappa_T^2 = E/K_T \tag{A6}$$

For later use we define also

 $a = \kappa_T r$, $A = \kappa_T R$, $b = \kappa_L r = a/\sqrt{3}$, $B = \kappa_L R = A/\sqrt{3}$ (A7) The (real) solutions of (A5) are

$$\phi = J_m(b) [c_m e^{im\theta} + c_m^* e^{-im\theta}]$$

$$V = J_m(a) [d_m e^{im\theta} + d_m^* e^{-im\theta}]$$
(A8)

where m = 0, 1, 2, ...

Using (A8) and (A4), the boundary condition (A1) eventually leads to

$$\begin{pmatrix} imJ_m(B) & -AJ'_m(A) \\ BJ'_m(B) & imJ_m(A) \end{pmatrix} \begin{pmatrix} c_m \\ d_m \end{pmatrix} = 0$$
 (A9)

which yields the eigenvalue condition

$$m^2 J_m(A) J_m(B) = AB J'_m(A) J'_m(B)$$
 (A10)

Here, $J'_m(x) \equiv dJ_m(x)/dx$.

For m = 0, the solutions for ϕ and V decouple, giving

$$\phi_0 = NJ_0(b), \qquad V_0 = MJ_0(a) \tag{A11}$$

where N and M are mutually independent and arbitrary normalization constants. But for $m \ge 1$, ϕ and V do not decouple [essentially because J_m and J'_m do not vanish simultaneously, so that (A9) has no solutions with $c_m = 0$ or $d_m = 0$ for $m \ge 1$], and from (A9) we obtain, after setting $d_m = D_m \times \exp(i\delta_m)$,

$$\phi_m = D_m [AJ'_m(A)/mJ_m(B)] J_m(b) \sin (m\theta + \delta_m)$$

$$V_m = D_m J_m(a) \cos (m\theta + \delta_m)$$
(A12)

where D_m and δ_m are arbitrary but common to both expressions. The two choices $\delta_m = 0$ and $\delta_m = \frac{1}{2}\pi$ give two mutually orthogonal though degenerate solutions, both being needed to make a complete set. Choosing the normalization for later convenience, we construct the solutions

$$\phi_m^+ = [AJ'_m(A)/m]J_m(b) \cos m\theta$$

$$V_m^+ = -J_m(B)J_m(a) \sin m\theta$$

$$\phi_m^- = [AJ'_m(A)/m]J_m(b) \sin m\theta$$

$$V_m^- = J_m(B)J_m(a) \cos m\theta$$
(A13)

The relative normalization of ϕ and V in each set is fixed by the boundary condition; but the two sets (A13) and (A14) are of course independent of each other and the overall normalization of each is arbitrary.

The superscript indicates the parity of ϕ_m under reflection of the y axis, i.e., under the transformation $(x \to x, y \to -y, z \to z)$, or $(r \to r, \theta \to -\theta, z \to z)$. (Recall that V is the z component of a vector V and has no intrinsic sign change under this reflection.) From (A11), (A13), and (A14) we construct the corresponding solutions for A itself by appeal to (A4):

$$A_{0r}^{+} = J_{0}'(b) = -J_{1}(b), \qquad A_{0\theta}^{+} = 0$$
 (A15)

$$A_{0r}^- = 0,$$
 $A_{0\theta}^- = J_0'(a) = -J_1(a)$ (A16)

$$A_{mr}^+ = v_m(r)\cos m\theta, \qquad A_{m\theta}^+ = -u_m(r)\sin m\theta \qquad (A17)$$

$$A_{mr} = V_m(r) \sin m\theta, \qquad A_{m\theta} = u_m(r) \cos m\theta \qquad (A18)$$

where $u_m(r)$ and $v_m(r)$ are given by Eq. (25) in Section 2. Note that \mathbf{A}_0^+ is purely longitudinal, \mathbf{A}_0^- is purely transverse, while for $m \ge 1$ the \mathbf{A}_m^\pm are neither. Note also the special feature of the solutions with m = 1, that they give nonsingular yet finite fields at the origin.

As $r \rightarrow 0$, one finds, reconstructing the Cartesian components of A,

$$A_{1x}^{+} = (\cos \theta) A_{1r}^{+} - (\sin \theta) A_{1\theta}^{+} \sim \frac{1}{2} [J_{1}(A) / A - J_{1}'(B)], \qquad A_{1y}^{+} \to 0$$

while similarly

$$A_{1x}^{-} \to 0, \qquad A_{1y}^{-} \sim \frac{1}{2} [J_1(A)/A - J_1'(B)]$$

Finally, in Appendix C we shall need the parities of the solutions (A15)–(A18) under separate reflections of the x and of the y axes.

It is evident that under y reflection $(r \rightarrow r, \theta \rightarrow -\theta)$, A_{θ} has intrinsic parity -1, while A_r has intrinsic parity +1; thus we see that under this transformation the \mathbf{A}_m^{\pm} transform precisely with the parities given by their superscripts: $\mathbf{A}_m^{\pm} \rightarrow \pm \mathbf{A}_m^{\pm}$. By contrast, under x reflection, i.e., $(x \rightarrow -x, y \rightarrow y)$, so $(r \rightarrow r, \theta \rightarrow \pi - \theta)$, the positive parity functions are \mathbf{A}_{even}^+ and \mathbf{A}_{odd}^- , and the negative parity functions are \mathbf{A}_{odd}^+ and \mathbf{A}_{even}^- , where the subscripts "even" and "odd" specify whether the index *m* is even or odd.

For completeness, note that our functions are of course orthogonal. Thus, with $N_{\pi m}$ a normalization constant, one has

$$\iint r \, dr \, d\theta \, \mathbf{A}_{m}^{\pi} \cdot \mathbf{A}_{m'}^{\pi'} = N_{\pi m} \, \delta_{\pi \pi'} \, \delta_{mm'}$$

A2. Specular Reflection

As discussed in Section 5, the boundary conditions now replacing (A1) are

$$A_r(R,\theta) = 0, \qquad (\partial/\partial r)(rA_\theta)|_{r=R} = 0 \tag{A19}$$

while the field equations are unchanged. Consequently (A9) is now replaced by

$$\begin{pmatrix} imBJ'_m(B) & -A[J'_m(A) + AJ''_m(A)] \\ BJ'_m(B) & imJ_m(A) \end{pmatrix} \begin{pmatrix} c_m \\ d_m \end{pmatrix} = 0$$
 (A20)

Note from Bessel's equation that $-A[J'_m(A) + AJ''_m(A)] = (A^2 - m^2)J_m(A)$.

In sharp contrast to diffuse reflection, (A20) admits pure longitudinal $(d_m = 0)$ and pure transverse $(c_m = 0)$ solutions for all *m*. The pure longitudinal solutions are

$$\phi_m^{\pm} = J_m(b) \begin{cases} \cos m\theta \\ \sin m\theta \end{cases}, \qquad \mathbf{A}_m^{L\pm} = \nabla \phi_m^{\pm} \tag{A21}$$

corresponding to eigenvalues determined by

$$J'_{m}(B) = 0 \tag{A22}$$

The pure transverse solutions are

$$V_{m}^{\pm} = J_{m}(a) \begin{cases} \sin m\theta \\ \cos m\theta \end{cases}, \qquad A_{m}^{T\pm} = \operatorname{curl} V_{m}^{\pm} \hat{z}$$
(A23)

corresponding to eigenvalues determined by

$$J'_m(A) + AJ''_m(A) = 0$$

which by appeal to Bessel's equation becomes simply

$$J_m(A) = 0 \tag{A24}$$

Finally, it is easy to convince oneself that with these boundary conditions there exist no additional nontrivially mixed solutions (with interdependent c_m and d_m). To see this, note from (A20), (A22), and (A24) that for such additional solutions to exist one would need to satisfy the conditions $J'_m(B) \neq 0$, $J_m(A) \neq 0$, and yet have the determinant of the coefficients on the left of (A20) vanish. But this determinant may be expressed in the form

$$-BJ'_m(B)A^2J_m(A)$$

For completeness note that the set of functions (A21) and (A22) are, once again, orthogonal as well as complete.

APPENDIX B. TWO-PARAMETER MODEL

With reference to the discussion in Section 2, we study a model free energy defined by

$$F = -(a - \varepsilon_1)x - (a - \varepsilon_2)y + \frac{1}{2}\beta_{11}x^2 + \beta_{12}xy + \frac{1}{2}\beta_{22}y^2$$
(B1)

Comparing with Eq. (37), $x = c_1^2$ and $y = c_2^2$ are the squared order parameters measuring the condensation amplitudes in two different sectors (see Appendix C); ε_1 and ε_2 are the eigenvalues of the linearized equations and we take $\varepsilon_2 > \varepsilon_1$; $a = \lambda(1 - T/T_c)$, where T_c is the bulk critical temperature. The β_{ij} depend on the strong coupling coefficients and on overlap integrals of products of four basis functions.

The problem is to find the true minimum of F as a function of a, as a increases (i.e., as T decreases), bearing in mind that x and y are nonnegative. This is a straightforward exercise, though the algebra is tedious because one has to allow for many different possibilities depending on the relative magnitudes of the β_{ij} . [The only general stability condition is that the quadratic part of (B1) be strictly positive.] We shall set up just enough formalism to show the provenance of the expressions entering the end results, and then confine ourselves to quoting these.

First, if one maintains y = 0, then x begins to condense (increase from zero) at $a = a_1 = \varepsilon_1$, and for $a > \varepsilon_1$, F is given by

$$F_1 = -(a - \varepsilon_1)^2 / 2\beta_{11}$$
 (B2)

Similarly, if one were to keep x = 0, then y would begin to condense at $a = \varepsilon_2$, and F would be given by

$$F_2 = -(a - \varepsilon_2)^2 / 2\beta_{22}$$
(B3)

If all other possibilities were excluded, then, provided that $\beta_{22} < \beta_{11}$, one would certainly have a first-order transition from F_1 to F_2 ($x \neq 0, y = 0$ to $x = 0, y \neq 0$), at a temperature a^* determined by $F_1 = F_2$, i.e.,

$$a^* = \frac{(\beta_{11}^{1/2} \epsilon_2 - \beta_{22}^{1/2} \epsilon_1)}{(\beta_{11}^{1/2} - \beta_{22}^{1/2})}$$
(B4)

Second, if we ignore for the moment the nonnegative nature of x and y, and formally minimize F with respect to x and y, then we obtain the equations

$$\begin{pmatrix} \beta_{11} & \beta_{12} \\ \beta_{12} & \beta_{22} \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} a - \varepsilon_1 \\ a - \varepsilon_2 \end{pmatrix}$$
(B5)

solved by

$$x = \frac{(\beta_{22} - \beta_{12})}{D}(a - a_3), \qquad y = \frac{(\beta_{11} - \beta_{12})}{D}(a - a_2)$$
(B6)

where we have defined

$$D = \det \beta = \beta_{11}\beta_{22} - \beta_{12}^2$$
(B7)

$$a_{2} = \frac{(\varepsilon_{2}\beta_{11} - \varepsilon_{1}\beta_{12})}{(\beta_{11} - \beta_{12})}, \qquad a_{3} = \frac{(\varepsilon_{1}\beta_{22} - \varepsilon_{2}\beta_{12})}{(\beta_{22} - \beta_{12})}$$
(B8)

The true minima of F are quoted below, in terms of the quantities D, a^* , a_2 , and a_3 defined so far, and using the following symbolism. (x), (x + y), and (y) denote phases where the indicated order parameters are nonzero; arrows denote phase transitions, those occurring at a^* being first order and those occurring at a_2 or a_3 being second order.

$$\begin{array}{l} \beta_{11} < \beta_{22}:\\ (y) \text{ never stable.} \end{array}$$

$$\beta_{11} < \beta_{12}$$
: (x) stable everywhere (B9)

$$\beta_{12} < \beta_{11}: (x) \to (x+y) \text{ at } a = a_2$$
 (B10)

$$\beta_{11} > \beta_{22}$$
:

$$\beta_{12} > \beta_{11} > \beta_{22}$$
: $(x) \to (y)$ at a^* (B11)

$$\beta_{11} > \beta_{12} > \beta_{22}$$
 and $D < 0$: $(x) \to (y)$ at a^* (B12)

$$\begin{array}{l} \beta_{11} > \beta_{12} > \beta_{22} \text{ and } D > 0: \\ (x) \to (x+y) \text{ at } a_2; \quad (x+y) \to (y) \text{ at } a_3 \end{array}$$
(B13)

$$\beta_{11} > \beta_{22} > \beta_{12}$$
: $(x) \to (x + y)$ at a_2 (B14)

The particular numerical values of the β_{ij} considered in Section 3 lead to (B11).

APPENDIX C. SECTORS

When the order parameters are expressed as linear combinations of solutions of the linearized Euler-Lagrange equations, there is a physically significant division of the basis functions into sectors, as explained in Section 2. The sectors are defined with a view to the quartic terms in the free energy. The test for a sector is as follows. Taking any three basis functions from the sector, and a fourth basis function not in the sector, the integral over any quartic scalar containing all four functions must vanish. The physical significance is that the order parameter in any one phase is a linear combination of (in general) all the functions in one sector; functions from another sector can enter the order parameter only at a phase transition point.

In this appendix we confine ourselves to diffuse scattering boundary conditions; specular scattering can be treated straightforwardly along the same lines. Though we believe that most of the sectors are irrelevant to the actual physics in the cylinder, nevertheless we quote the full results as an illustration (and a warning) of how complicated the situation could become in principle, and, for other geometries, perhaps even in practice.

It is convenient to start with the axial phase, and the vector functions \mathbf{A}_{m}^{\pm} defined in Appendix A1. A privileged role is played by the two types of functions independent of θ , i.e., by \mathbf{A}_{0}^{+} and \mathbf{A}_{0}^{-} ; evidently each constitutes a sector by itself, as does their combination. Thus we obtain the three sectors

$$\{\mathbf{A}_{0}^{+}\}, \{\mathbf{A}_{0}^{-}\}, \{\mathbf{A}_{0}^{+}, \mathbf{A}_{0}^{-}\}$$
 (C1)

Further arguments are based on the x and y parities discussed in Section 2 and Appendix A. The minimal consistent extensions of $\{A_0^{\pm}\}$ are $\{A_{even}^{\pm}\}$; they, and the sets $\{A_{odd}^{\pm}\}$, constitute four fundamental sectors, "even" and "odd" specifying that *m* is even or odd. Thus we find

$$\{\mathbf{A}_{\text{even}}^+\}, \{\mathbf{A}_{\text{odd}}^+\}, \{\mathbf{A}_{\text{even}}^-\}, \{\mathbf{A}_{\text{odd}}^-\}$$
 (C2)

established by noting that their y and x parities, respectively, are (+1, +1), (+1, -1), (-1, -1), (-1, +1).

Finally, one can readily convince oneself that any pair of sets from (C2) can be combined to yield further sectors; four such pairs are distinguished by embracing all functions sharing either a common y parity or a common x parity, and two further pairs by embracing all the functions with m even or with m odd. These six pairs together with (C1) and (C2) yield a total of 13 sectors. Those in which we have been especially interested in this paper are $\{A_0^-\}$, the pure transverse function, and its minimal extension $\{A_{even}^-\}$; and $\{A_{even}^+\}$, the mixed axial function.

The sectors for the polar phase can be obtained from the axial ones simply by substituting ψ_m^{\pm} for A_m^{\pm} [the functions ψ_m^{\pm} are defined in Eq. (21)], and remembering that ψ_0^- vanishes identically, so that (C1) yields only one polar sector. Thus there are 11 polar sectors all together.

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