

Order-Parameter Collective Modes in  $^3\text{He-A}$ 

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The collective modes of the gap parameter for the axial (Anderson-Brinkman-Morel) state and their coupling to the quasiparticles are studied in the collisionless regime within a microscopic theory. In addition to the modes connected with the spontaneous breakdown of symmetries (sound, spin waves, and orbit waves), three weakly damped modes with a typical dispersion law  $\omega^2(q) = \omega^2(0) + \alpha(v_F q)^2$  are found. The feasibility of detecting these modes in the sound absorption is discussed.

The superfluid phases of  $^3\text{He}$ , now rather convincingly identified as anisotropic pairing states,<sup>1,2</sup> are probably many-body systems with the most complex spontaneous ordering so far encountered in nature. The order parameter in these phases is thought to be a three-dimensional tensor of rank two,  $d_{j\alpha}$ . As a consequence of the nine order parameter components, as contrasted to only one in an isotropic superfluid, the physical phenomena occurring in these phases are considerably richer. In particular, the dynamics show many new and fascinating features, as manifested by the appearance of various new collective modes.

The purpose of the work reported in this Letter is a *complete* and systematic investigation of the collisionless collective modes of the axial (Anderson-Brinkman-Morel) state,<sup>2</sup> currently believed to describe the *A* phase of liquid  $^3\text{He}$ .

The main results may be summarized as follows: (1) A new "superflapping" pair-vibration mode is predicted and its detection by ultrasound absorption is suggested. (2) The puzzle of how the gapless orbital mode associated with the spontaneous breakdown of rotation symmetry in orbital space may be reconciled with the previously found "flapping" mode, which also involves oscillations of the  $\hat{l}$  vector, is solved: These are different eigenmodes of the same collective variable. (3) The complete temperature dependence of the frequencies of the three pair-vibration modes is given. Previously only the limiting values as  $T \rightarrow T_c$  of two of these modes were known. (4) The unusual temperature dependence of the "normal-flapping" frequency gives rise to a significant double-peaked structure in the sound absorption as a function of temperature, providing a strong test of the axial state. (5) The especially simple temperature dependence of the "clapping" frequency,  $\omega = 1.22\Delta_0(T)$ , makes the location of the corresponding peak in the sound absorption an ideal "spectroscopic" probe for measuring the

size of the gap *at all temperatures*.

The axial state is characterized by three spontaneous axes, a spin axis  $\hat{w}$  and two orbital axes  $\hat{n}$  and  $\hat{m}$  ( $\hat{n} \perp \hat{m}$ ), such that  $d_{j\alpha} = \hat{w}_j(\hat{n}_\alpha + i\hat{m}_\alpha)$ . The gap parameter is given by (underlined quantities denote  $2 \times 2$  matrices in spin space and a summation convention is used)  $\underline{\Delta}(\hat{k}; T) = \Delta_0(T) \hat{i} \underline{\sigma}_j \underline{\sigma}_2 d_{j\alpha} \hat{k}_\alpha$ .  $\hat{w}$  and the "axis of the gap,"  $\hat{l} = \hat{n} \times \hat{m}$ , are unrelated except for the weak nuclear dipole interaction, which tends to align them. The dipole forces will not be considered explicitly in the following, apart from remarks on its principal effects.

The following collective modes have been found as eigenmodes of the coupled system of equations for the density response functions and the order parameter:

(i) There are five Goldstone modes associated with the degeneracy of the equilibrium state with respect to (a) gauge transformations (sound waves), (b) rotations of  $\hat{w}$  (two spin waves), and (c) rotations of  $\hat{l}$  (two orbit waves). Of these, sound has been studied most extensively, both experimentally<sup>3-5</sup> and theoretically.<sup>6-8</sup> Sound waves are well defined at all temperatures. Spin waves have a linear spectrum and a velocity increasing  $\propto (T_c - T)^{1/2}$  near  $T_c$  to a value of the order of the Fermi velocity at absolute zero. For a detailed discussion of the properties of collisionless spin waves we refer to Combescot's work.<sup>9</sup> Orbit waves are found to be essentially diffusive at all temperatures, with frequency  $\omega_{\text{orb}} = i\alpha q^2$ , where  $\alpha$  diverges near  $T_c$  as  $(1-i)(1 - T/T_c)^{-1/4}$  and for  $T \rightarrow 0$  as  $T^{-1}$ . Whereas the damping near  $T_c$  is caused by particle-hole excitations (energy transfer  $\omega = E_{k_+} - E_{k_-}$ , where  $\vec{k}_\pm = \vec{k} \pm \vec{q}/2$  and the quasiparticle energy is defined by  $E_k = \epsilon_k^2 + \underline{\Delta}_k \underline{\Delta}_k^+$ ), the restoring force becomes negative for  $T \rightarrow 0$ . The dipole interaction leads to gaps of the order of the longitudinal NMR frequency in the spectra of spin waves and orbit waves and gives rise to relaxation even for  $q \rightarrow 0$ , because it lifts the degeneracy with re-

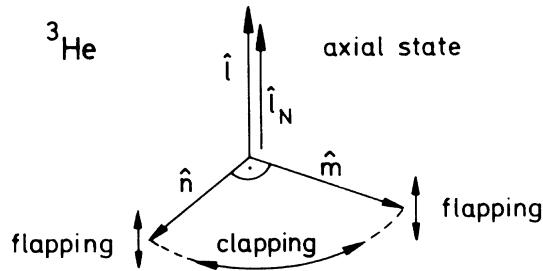


FIG. 1. Representation of collective modes in the axial state.

spect to relative rotations of spin space and orbital space. A diffusive orbit mode has also been found by Combescot.<sup>10</sup> However, a term is missing in his Eq. (7), which is responsible, e.g., for the normal-flapping mode discussed below. On the other hand, Volovik<sup>11</sup> has derived a real quadratic dispersion for orbit waves, apparently because of his neglect of certain singular terms in  $\omega/v_F q$  in the eigenvalue equation [Eq. (2) below]. The present theory does not allow comparison with the hydrodynamic theory of Cross and Anderson.<sup>12</sup>

(ii) There is a collective mode characterized by oscillations of the order-parameter axis  $\hat{l}$  (here the preferred direction of the Cooper pairs) about the axis of the energy gap of the quasiparticle excitations,  $\hat{l}_N$ , the quasiparticle readjustment being too slow to follow the rapid changes of  $\hat{l}$ . This mode may be visualized as a flapping motion of  $\hat{n}$  and  $\hat{m}$  about the fixed direction of  $\hat{l}_N$  (see Fig. 1) and will be called the normal-flapping mode. Upon lowering the temperature, the number of quasiparticles decreases and the moment of inertia associated with  $\hat{l}_N$  declines so that  $\hat{l}_N$  is gradually dragged along by the motion of  $\hat{l}$ . At absolute zero, there are no thermal quasiparticles and the restoring force is expected to vanish. Accordingly, the frequency of this mode, which near  $T_0$  rises  $\propto (T_c - T)^{1/2}$ , passes through a maximum at  $T \sim 0.75T_c$  and tends to zero for  $T \rightarrow 0$ . The dispersion law is  $\omega_{\text{nf1}}^2(q) = \omega_{\text{nf1}}^2(0) + \alpha_{\text{nf1}}(v_F q)^2$ , with  $\omega_{\text{nf1}}(q=0, T) \cong (\frac{4}{5})^{1/2}(T/T_c)\Delta_0(T)$  [the exact result for  $\omega_{\text{nf1}}(q=0)$  is plotted in Fig. 2]. At  $T=0$  a linear dispersion law is obtained,  $\omega_{\text{nf1}}(q, T=0) = (\hat{q} \cdot \hat{l})v_F q$  (neglecting dipole forces and assuming particle-hole symmetry). The damping of this mode is determined by pair-breaking processes, except near  $T_c$ , where quasiparticle collisions are of equal importance, and is small for  $\omega/\Delta_0(T) \ll 1$ . The mode couples to sound waves for intermediate orientations of  $\hat{q}$

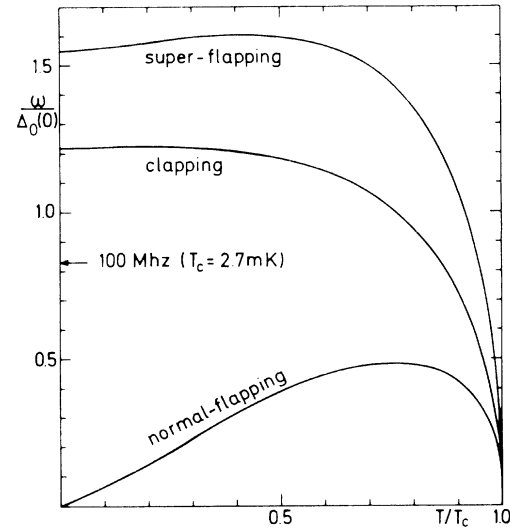


FIG. 2. Collective frequencies of the axial state at  $q = 0$  in units of  $\Delta_0(T=0)$  versus reduced temperature [based on  $\Delta_0(T) = 2.16T_c \tanh[\sqrt{2}\pi(T_c/T - 1)^{1/2}/2.16]$ ].

and  $\hat{l}$  { coupling strength  $\propto q^2(\hat{q} \cdot \hat{l})^2 [1 - (\hat{q} \cdot \hat{l})^2]$  }. The coupling to the sound vanishes as  $1/\ln(\Delta_0/T)$  for  $T \rightarrow 0$ . A mode with similar characteristics has been predicted recently by Leggett and Takagi<sup>13</sup> on the basis of phenomenological considerations in the regime  $\omega \ll \Delta_0(T)$ . Patton has also found an orbit mode with linear dispersion law at  $T=0$ .<sup>14</sup>

(iii) There are two collective modes associated with internal vibrations of the structure of the order parameter. The first one, termed "clapping" mode in Wölfle,<sup>15</sup> can be imagined as a counteroscillation of  $\hat{n}$  and  $\hat{m}$  about their equilibrium relative angle of  $\pi/2$ , as depicted in Fig. 1. The dispersion law is  $\omega_{\text{cl}}^2(q) = \omega_{\text{cl}}^2(0) + \alpha_{\text{cl}}(v_F q)^2$ , with  $\omega_{\text{cl}}^2(q=0, T) \sim 1.22\Delta_0(T)$  (see Fig. 2). The "clapping" mode couples to sound waves with a coupling strength  $\propto q^2 [1 - (\hat{q} \cdot \hat{l})^2]^2$ . The second mode, which will be called the superflapping mode, may be interpreted as a rapid flapping motion of  $\hat{n}$  and  $\hat{m}$  against the equilibrium orientation of  $\hat{l}$ . The dispersion law is  $\omega_{\text{sfl}}^2(q) = \omega_{\text{sfl}}^2(0) + \alpha_{\text{sfl}}(v_F q)^2$ , with  $\omega_{\text{sfl}}(q=0, T)/\Delta_0(T)$  decreasing rapidly [ $\propto (T_c - T)^{1/2}$ ] from the value 2 at  $T_c$  to  $(12/5)^{1/2}$  at  $T=0$  (see Fig. 2). The temperature variation of  $\omega_{\text{sfl}}$  is naturally explained by the reduced number of thermal quasiparticles at lower  $T$ , which as in the case of the normal-flapping mode tends to decrease the inertia of  $\hat{l}$ , and therefore weakens the restoring force. The given interpretation of the flapping modes is consistent with the fact that the superflapping frequency

is highest among the three modes. This mode has not been found previously since it does not couple to sound waves in the limit  $T \rightarrow T_c$ . However, the coupling is proportional to  $T_c - T$  near  $T_c$  and excitation of this mode by sound waves is possible at least for  $T \approx 0.95T_c$ . The clapping and superflapping modes are moderately damped by pair-breaking processes, which are equally effective at all temperatures, because  $\omega \sim \Delta_0(T)$  in both cases. Near  $T_c$  the additional broadening is about 2–3 times the pair-breaking width.<sup>16</sup> The limiting values as  $T \rightarrow 0$  of the clapping and flapping frequencies are in agreement with recent calculations by Tewordt and Einzel.<sup>17</sup>

The contribution of the normal-flapping mode and the clapping mode to the sound absorption in the immediate vicinity of  $T_c$  has been calculated<sup>6-8,16</sup> and seems to have been detected experimentally.<sup>5</sup>

In the following the derivation of the above re-

sults is briefly sketched. In general, collective modes are obtained as poles of the generalized density response function  $\delta f_{k\mu\nu}(q, t) = \delta \langle c_{k+\mu}^+(t) \times c_{k-\nu}(t) \rangle$ , where  $c_{k\sigma}^+(t) [c_{k\sigma}(t)]$  creates (annihilates) a fermion of momentum  $\vec{k}$  and spin  $\sigma$  at time  $t$ .  $\delta f$  denotes the linear deviation from equilibrium caused by an external field of wave vector  $\vec{q}$  and frequency  $\omega$ . In the pair-correlated state one has to take into account the coupling of  $\delta f$  to the quasiconserved order-parameter response function  $\delta g_{k\mu\nu}(q, t) = \delta \langle c_{-k-\mu}(t) c_{k+\nu}(t) \rangle$ . For the purpose of studying the nonhydrodynamic collective modes, it is more convenient to consider the potentials instead of the distribution functions, i.e., the change in the quasiparticle energy  $\delta \epsilon_k(q, \omega) = \delta \epsilon_k^{\text{ext}}(q, \omega) + \text{Tr}_{\sigma'} \sum_{k'} f_{kk'} \delta f_{k'}(q, \omega)$  and the pair-potential (gap parameter)  $\delta \Delta_k(q, \omega) = \sum_{k'} g_{kk'} \delta g_{k'}(q, \omega)$ , where  $f_{kk'}$  is the Fermi liquid interaction and  $g_{kk'}$  is the pair interaction.

The basic equation for the gap-parameter response function, as given in Ref. 6, has the form

$$\delta \Delta_k + \sum_{k'} g_{kk'} \theta_{k'} \delta \Delta_{k'} = \frac{1}{2} \int \frac{d\Omega'}{4\pi} N_F g_{kk'} \bar{\lambda}_{k'} [\Delta_{k'}(\omega + \eta') \delta \epsilon_{k'} - (\omega^2 - \eta'^2) \delta \Delta_{k'} + \Delta_{k'} \Delta_{k'}^+ \delta \Delta_{k'} + \Delta_{k'} \delta \Delta_{k'}^+ \Delta_{k'}], \quad (1)$$

where

$$\bar{\lambda}_k = \int d\epsilon_k \frac{-4(\omega^2 \theta_k + \eta^2 \epsilon_k d\theta_k/d\epsilon_k)}{\omega^2(\omega^2 - 4E_k^2) - \eta^2(\omega^2 - 4\epsilon_k^2)},$$

with  $\theta_k = (1/2E_k) \tanh(E_k/2T)$  and  $\eta = (\vec{k} \cdot \vec{q})/m^*$ . For later use we define  $\lambda_k = |\Delta_k|^2 \bar{\lambda}_k$  and  $\lambda_m = \int d\Omega_k |Y_{1m}(\hat{k})|^2 \times \lambda_k$ .

One now looks for eigensolutions of Eq. (1), regarding the terms involving  $\delta \epsilon$  as sources (which they are in the limit of vanishing Fermi liquid interaction). The effect of the coupling of  $\delta \Delta$  to the equation for  $\delta \epsilon$  [Eq. (3a) of Ref. 6a] is described in the relevant cases below. Employing the representation in terms of spherical harmonics  $\Delta_k = i\Delta_1(T) Y_{11}(\hat{k}) \hat{v} \cdot \vec{\sigma} \sigma_2$  and  $\delta \Delta_k(q, \omega) = i\Delta_1(T) Y_{1m}(\hat{k}) d_{mj}(q, \omega) \sigma_j \sigma_2$ , the equations for the 18 order-parameter components  $d_{mj}^{\pm}(q, \omega) = d_{mj}(\vec{q}, \omega) \pm d_{mj}(-\vec{q}, -\omega)$  decouple in the limit  $q \rightarrow 0$  and one finds the following:

(A)  $m = +1$ .— $d_{1z}^-(d_{1x,y}^+)$  is the variable associated with the broken gauge symmetry (rotation symmetry in spin space). The collective frequency  $\omega_{1z}^- = \alpha_- v_F q$  ( $\omega_{1x,y}^+ = \alpha_+ v_F q$ ) is strongly renormalized by the coupling to the density fluctuations (spin fluctuations). For instance, at  $T=0$  the ratio  $s_- = \omega_{1z}^-/v_F q = (\frac{1}{3})^{1/2}$  is renormalized to  $s = \omega_{\text{sound}}/v_F q = [\frac{1}{3}(1 + F_0^s)(1 + F_1^s/3)]^{1/2} \gg s_-$ , where the  $F_i^s$ 's are the usual Landau parameters.  $d_{1z}^+$  and  $d_{1x,y}^-$  ( $\omega^2 = 4\lambda_1/\bar{\lambda}_1$ ) do not couple to  $\delta \epsilon_k$ . It is unclear how these modes could be excited.

(B)  $m = -1$ .— $d_{1z}^-$  and  $d_{1x,y}^+$  are found to oscillate at a frequency given by  $\omega_{c1}^2 = 2\lambda_1/\bar{\lambda}_1 + O(q^2)$ . The admixture of an oscillating  $Y_{1,-1}(\hat{k})$  component to  $\Delta(\hat{k})$  can be imagined as a clapping motion of  $\hat{n}$  and  $\hat{m}$  (Fig. 1). Whereas  $d_{1z}^-$  couples to sound waves [subsection (iii)],  $d_{1x,y}^+$  (which in principle couples to spin fluctuations) is not easily excited by spin waves, because the spin wave velocity is so low that the two dispersion curves do not intersect. Again  $d_{1z}^-$  and  $d_{1x,y}^-$  do not couple to available fields.

(C)  $m = 0$ .—This is the most interesting case, because here the left-hand side of Eq. (1) does not vanish (the so-called Goldstone condition is not satisfied) and one has an eigenvalue equation

$$\int d\Omega_k [Y_{10}(\hat{k})]^2 \{ (\omega^2 - \eta^2 - 2|\vec{d}_k|^2 + 2\vec{d}_k^2) \bar{\lambda}_k + 4\bar{\theta}_k \} = 0, \quad (2)$$

with  $\bar{\theta}_k = -|\vec{d}_k|^2 \int (d\epsilon/2E)(d/dE)[\tanh(E/2T)/2E]$ , and  $\Delta_k = i\vec{d}_k \cdot \vec{\sigma} \sigma_2$ . Equation (2) has three solutions:

(a) The Goldstone mode corresponding to the breakdown of rotation symmetry in orbital space [by in-

spection,  $\omega=0$ ,  $q \rightarrow 0$  is a solution of Eq. (2)]; (b) the normal-flapping mode; and (c) the superflapping mode. Again, in principle  $d_{0z}^-$  couples to density fluctuations,  $d_{0x,y}^+$  to spin fluctuations, but only  $d_{0z}^-$  is easily excited by sound waves.

The coupling of the various modes of  $\delta\Delta$  among themselves at finite  $q$  can be neglected for not-too-large  $q$  values.

In conclusion, I suggest sound propagation experiments in the  $A$  phase at lower temperatures (possibly in a magnetic field to suppress the  $B$  phase) and higher frequencies as in Refs. 3–5, to verify the considerable structure predicted for the sound absorption by this theory. In particular, it would be interesting to observe the re-entrance of the normal-flapping mode at lower temperatures (around  $0.5T_c$ ) in the absorption of, for example, 50-MHz sound. The observation of these phenomena would furnish strong proof for the realization of the axial state in  $^3\text{He-A}$ .

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## Multiple Oxidation States of Al Observed by Photoelectron Spectroscopy of Substrate Core Level Shifts\*

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Substrate core chemical shifts upon chemisorption of oxygen on aluminum are observed using variable-excitation-energy photoelectron spectroscopy. At low exposures a unique intermediate oxidation state evolves where the Al  $2p$  level is shifted by only 1.3 eV toward higher binding energy as compared to the 2.6-eV shift observed for heavily oxidized aluminum ( $\text{Al}_2\text{O}_3$ ). Simultaneous observation of the O  $2p$  resonance shows evidence for a sharp phase change at exposures close to monolayer formation.

In a photoelectron spectroscopy study of the initial oxidation of aluminum, we have discovered a core-level shift of the Al  $2p$  atomic energy level which is considerably smaller than the shift for fully oxidized aluminum ( $\text{Al}_2\text{O}_3$ ).<sup>1</sup> This previously unobserved but widely sought phenomenon is observed for oxygen exposures in the range 50–400 langmuir (L) (1 L =  $10^{-6}$  Torr sec). The

onset of a shifted substrate core peak is followed by an abrupt change in the shape of the O  $2p$  resonance between 100 and 200 L oxygen exposure. These observations show the existence of an intermediate oxide phase or a chemisorbed state. The observation is important not only in understanding the present system but also in the general use of core-level shifts to study the interaction of