

Table I. Resonances above the 2^3S threshold. Experimental energies represent peaks in absorption (Ref. 8). The theoretical positions were obtained by fitting the phase shift to the expression $\cot(\delta - \delta_0) = [E - E_j^{(n)}]^{-1/2} \Gamma$. Approximate widths obtained using the indicated background phase shifts (δ_0) appear in the third column. Resonant energies are expressed as energies above the ground state of lithium.

Theory	Experiment	Γ (eV)	δ_0	Classification
64.7	64.6-65.1	0.4	0.4	$(1s2s^3S)3p$
65.17	65.25	0.01	0.8	$(1s2p^3P)3s$
65.28	65.30	0.004	0.8	$(1s2p^3P)3d$
66.59	65.66	0.12	0.8	$(1s2p^3P)4s$
65.87	65.89	0.004	0.8	$(1s2p^3P)4d$

reported here. We also are indebted to Dr. Aaron Temkin of the Goddard Space Flight Center for arranging for the computations upon which this Letter is based to be performed at Goddard.

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¹D. L. Ederer, T. Lucatorto, and R. P. Madden, preceding Letter [Phys. Rev. Lett. 25, 1537 (1970)].

²A. W. Weiss, private communication.

³K. Smith and L. H. Morgan, Phys. Rev. **165**, 110 (1968).

⁴P. G. Burke, J. W. Cooper, and S. Ormonde, Phys. Rev. **183**, 1, 245 (1969).

⁵P. M. Morse, L. A. Young, and E. S. Haurwitz, Phys. Rev. **48**, 948 (1935).

⁶C. E. Moore, *Atomic Energy Levels*, U. S. National Bureau of Standards Circular No. 467 (U.S.G.P.O., Washington, D. C., 1948). Note that the $1s2s^1S$ level of Li^+ (490 079 cm^{-1} above the ground state) has recently found to be 491 373 cm^{-1} . [See C. H. Pekeris, Phys. Rev. **126**, 143 (1962).] The corrected value has been used in the calculations reported here.

⁷S. Ormonde, B. W. Torres, K. Thomas, M. J. Conneely, and K. Smith, Kirkland Air Force Base Report No. AFWL-TR-70-37, 1970 (unpublished).

⁸D. L. Ederer, T. Lucatorto, and R. P. Madden in "Conference sur Processes Electroniques Simples et Multiples du Domaine x et x-uv," Paris, France, 21-25 September 1970 (to be published).

⁹P. L. Altick, Phys. Rev. **169**, 21 (1968).

Can a Solid Be "Superfluid"?

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It is suggested that the property of nonclassical rotational inertia possessed by superfluid liquid helium may be shared by some solids. In particular, nonclassical rotational inertia very probably occurs if the solid is Bose-condensed as recently proposed by Chester. Anomalous macroscopic effects are then predicted. However, the associated superfluid fraction is shown to be very small (probably $\lesssim 10^{-4}$) even at $T=0$, so that these effects could well have been missed. Direct tests are proposed.

Most of the striking macroscopic properties of superfluid liquid helium can be explained if we make the following assumption, which we shall call the assumption of nonclassical rotational inertia (NCRI): Suppose that we enclose a number N of helium atoms in a cylindrical annulus of internal radius R and thickness d , and rotate the enclosing surfaces about the axis of the cylinders at constant angular velocity ω . Then the free energy $F(\omega)$ measured in the rest frame is assumed to be of the form

$$F(\omega) = F_0 + \frac{1}{2}I_0\omega^2 + \Delta F(\omega), \quad (1)$$

where F_0 is the free energy for $\omega=0$ and I_0 is the classical moment of inertia NmR^2 (here, as ev-

erywhere, we neglect terms in d/R and also the effect of density redistribution due to the centrifugal forces, which is proportional to ω^4 and negligible at low velocities). The term $\Delta F(\omega)$ by which $F(\omega)$ departs from the classical result is assumed to be even and periodic in ω with period ω_0 :

$$\omega_0 = \hbar/\alpha mR^2, \quad (2)$$

where α is a number of order 1 (not order N); for $\omega < \omega_0/2$ the function $\Delta F(\omega)$ is of the form

$$\Delta F(\omega) = -\frac{1}{2}(\rho_s/\rho)I_0\omega^2, \quad (3)$$

which defines the superfluid fraction ρ_s/ρ . For a normal system $\Delta F(\omega)$ is either identically zero

or, at most, of order \hbar^2/mR^2 so that $\rho_s/\rho = O(N^{-1})$. There is now considerable evidence that the number α is unity for liquid helium, indicating simple Bose condensation, and also that $\rho_s/\rho \rightarrow 1$ as $T \rightarrow 0$. It is generally believed that the occurrence of this phenomenon (NCRI) in superfluid helium is essentially dependent on its liquid nature.

In this Letter we shall suggest that, on the contrary, it is impossible to exclude the occurrence of NCRI also in insulating¹ solids (where "solid" is defined phenomenologically—see below), and that if it does occur it should produce a number of interesting phenomena analogous to those of superfluidity. However, we shall show that the associated "superfluid fraction" must be very small even at $T=0$ (probably always $\lesssim 10^{-4}$). As a result, these phenomena could well have escaped notice even if "superfluid solids" do exist at temperatures already reached, since they have not (to the best of the author's knowledge) been specifically looked for. While the ideas discussed here are somewhat speculative, an experiment to test them should be relatively simple and seems well worthwhile.

We consider,²⁻⁵ as above, a set of N identical atoms of mass m confined in a cylindrical annulus of internal radius R , height h , and width d and will be implicitly interested in the limit $N, R, d, h \rightarrow \infty, d/R \rightarrow 0, h/R, N/dRh \rightarrow \text{const.}$ The atoms will be treated as structureless point particles obeying either Bose or Fermi statistics. We confine ourselves to the case $T=0$. The enclosing surfaces are assumed to behave quite classically; when the system is at rest they provide a time-independent potential $V(\vec{r})$ which is appreciable only within a fraction of order d^{-1} of the total volume. When we say that the system of atoms forms a solid, we mean that $\rho(\vec{r})$, the expectation value in the ground state of the local density of particles, does not tend to a constant value even deep inside the sample [in general, $\rho(\vec{r})$ shows strong variations over distances of the order of an atomic spacing]. It is unimportant whether or not $\rho(\vec{r})$ is periodic, that is, whether our solid is crystalline or amorphous; however, for definiteness we shall consider the crystalline case.⁶ The "solid" nature of our system can then in principle be directly verified by, say, x-ray scattering. Note that we have carefully avoided the ambiguous characterization "the atoms are localized."

When the enclosing walls are at rest the ground-state wave function⁷ $\Psi_0(\vec{r}_1\vec{r}_2\cdots\vec{r}_N)$ and energy E_0 are to be found by minimizing the expectation val-

ue of the Hamiltonian \hat{H} subject to the appropriate constraints. \hat{H} is given by the expression (U is the interparticle potential)

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \frac{1}{2} \sum_{i,j=1}^N U(\vec{r}_i - \vec{r}_j) + \sum_{i=1}^N V(\vec{r}_i). \quad (4)$$

The constraints which the wave function must obey are the requirement of symmetry or antisymmetry with respect to interchange of any pair of indices, and also the condition of single-valuedness with respect to each argument \vec{r}_i . If we introduce cylindrical polar coordinates $(r_i Z_i \theta_i)$ in the obvious way, then this condition may be written

$$\begin{aligned} \Psi_0(r_1 Z_1 \theta_1; r_2 Z_2 \theta_2; \cdots r_i Z_i \theta_i + 2\pi \cdots r_N Z_N \theta_N) \\ = \Psi_0(r_1 Z_1 \theta_1; r_2 Z_2 \theta_2; \cdots r_i Z_i \theta_i \cdots r_N Z_N \theta_N) \end{aligned} \quad (5)$$

for all i and all values of the indices. Hereafter, we suppress the r and Z coordinates when they are not needed. Note that the ground-state wave function Ψ_0 is always real.

Now we consider what happens when the enclosing surfaces are rotated with constant angular velocity ω . The potential V is now time dependent in the rest frame, but the problem can be solved, in principle, with the aid of the transformations

$$\begin{aligned} \theta_i = \theta_i' + \omega t, \\ \Psi(\theta_i, t) = \Psi'(\theta_i', t) \exp\{im\omega R^2 \sum_i \theta_i'(t)/\hbar\} \end{aligned} \quad (6)$$

(where, as usual, we neglect for simplicity the finite value of d/R). We then easily find

$$\Delta F(\omega) = -[E_{\min}(\omega) - E_0], \quad (7)$$

where $E_{\min}(\omega)$ means the minimum of the expectation value of the operator \hat{H} , Eq. (4), but subject now not to condition (5) but to the altered boundary condition

$$\begin{aligned} \Psi(\theta_1, \theta_2, \cdots, \theta_i + 2\pi \cdots \theta_N) \\ = \exp(-2\pi im R^2 \omega / \hbar) \Psi(\theta_1, \theta_2, \cdots, \theta_i, \cdots, \theta_N). \end{aligned} \quad (8)$$

From (7) and (3) we have

$$\rho_s/\rho = \lim_{\omega \rightarrow 0} I_0^{-1} \partial^2 E_{\min}(\omega) / \partial \omega^2. \quad (9)$$

We see at once that (1) if $E_{\min}(\omega)$ is independent of ω , the system cannot be superfluid, and (2) by inspection of Eq. (8), that $E_{\min}(\omega) \equiv E_{\min}(\omega + \hbar/mR^2)$. Hence, the quantity α in Eq. (2) must be an integer.

Now, a system which is to avoid superfluidity must keep $|E_{\min}(\omega) - E|$ of order \hbar^2/mR^2 or less. This can be achieved in either of two principal

ways: As ω varies, the system can either make a succession of jumps between states which (for fixed boundary conditions) are mutually orthogonal, or it can essentially stay in the ground-state wave function Ψ_0 but modify it in a trivial way so as to obey the changing boundary condition (8). In the analogous problem of electrical conduction these are the mechanisms appropriate to a normal metal and a Mott insulator, respectively. Only if both fail is the system superfluid.

If conventional ideas about the localization of atoms in a crystal are accepted it is certainly the second ("Mott-insulator") mechanism which operates, and it is the possible breakdown of this, therefore, that we shall now investigate. Of course, once we abandon (as we shall do) these conventional ideas, we cannot rule out the possibility of a "normal-metal" mechanism operating to compensate for the breakdown.⁸ However, by ignoring this we at any rate obtain an upper limit for the superfluid fraction.

We can try to keep the expectation value of \hat{H} , Eq. (4), equal to E_0 while obeying the new boundary condition (8) by keeping Ψ equal to Ψ_0 except in regions where it essentially vanishes,⁹ and there modifying the phase so as to satisfy (8). This, however, is possible only if the wave function Ψ_0 is "disconnected,"⁴ that is, if all paths in the $3N$ -dimensional phase space which lead from $(\theta_1, \theta_2, \dots, \theta_N)$ to $(\theta_1 + 2m_1\pi, \theta_2 + 2m_2\pi, \dots, \theta_N + 2m_N\pi)$ ($m_1, m_2, \dots = 0$ or 1) cross at least one region in which the wave function essentially vanishes. In particular, it is not possible, if for given $\theta_2, \theta_3, \dots, \theta_N$ the wave function $\Psi(\theta_1, \theta_2, \dots, \theta_N)$ is everywhere a nonvanishing function of θ_1 . A sufficient, though not necessary, condition for this is

$$|G(\vec{r}, \vec{r}')| > \epsilon \text{ for all } \vec{r}, \vec{r}', \quad (10)$$

where $G(\vec{r}, \vec{r}')$ is the one-particle Green function and ϵ is a finite number independent of N (or R).

If one assumes the conventional picture of a solid, where Ψ_0 is a sum of terms in which each atom is localized on or near a given lattice site, the wave function is clearly disconnected [cf. Ref. (4)] and superfluidity cannot occur. However, once one allows for the possibility of two or more atoms changing places, the question is open. More specifically, a recent article by Chester¹⁰ suggests that in a Bose solid a nonzero fraction of atoms may occupy the zero-momentum state. If this is correct, then (barring a pathological case) Eq. (10) must hold and hence the "Mott-insulator" mechanism cannot be invoked. It seems very plausible, by analogy with the liquid case,

that in this case the "normal-metal" mechanism must also at least partly fail. If this is so, then such a crystal should show NCRI, with $\alpha = 1$.

We shall now show that if NCRI does exist in a crystal we can put a very low upper limit on the superfluid fraction ρ_s/ρ . To do this we construct a trial wave function satisfying Eq. (8) in the form

$$\begin{aligned} \Psi(r_1 r_2 \dots r_N; \omega) \\ = \exp\left\{i \sum_{i=1}^N \varphi(\vec{r}_i; \omega)\right\} \Psi(\vec{r}_1 \vec{r}_2 \dots \vec{r}_N), \end{aligned} \quad (11)$$

where $\varphi(\vec{r})$ is real and satisfies

$$\varphi(\theta + 2\pi) = \varphi(\theta) - 2\pi m R^2 \omega / \hbar. \quad (12)$$

Using the reality of Ψ_0 , we find for the corresponding value of $\langle H \rangle$

$$\langle H \rangle_{\text{trial}} = E_0 + (\hbar^2/2m) \int (\nabla \varphi)^2 \rho(\vec{r}) d\vec{r}. \quad (13)$$

Since we are neglecting terms in d/R , the problem is unchanged if we "unroll" the annulus⁶ to form a rectangular parallelepiped of length $2\pi R$ and change the boundary condition (12) to

$$\varphi(2\pi R; yz) = \varphi(0; yz) - 2\pi m R^2 \omega / \hbar, \quad (14)$$

where x , y , and z are Cartesian coordinates and x runs from 0 to $2\pi R$. Then, taking for simplicity a trial form of φ that is a function of x only, and using the assumed periodic symmetry of the crystal, we apply the standard calculus of variations to choose φ so as to minimize (13). For simplicity we give the result for the case of a crystal with orthorhombic unit cell with axes of length a , b , and c parallel to the x , y , and z directions, respectively. Introducing the notation $x' \equiv x/a$, $y' \equiv y/b$, $z' \equiv z/c$, and $\rho'(\vec{r}) \equiv \rho(\vec{r})V/N$, we find

$$\langle H \rangle_{\text{trial}} = E_0 + \frac{1}{2} N m R^2 \omega^2 Q_0, \quad (15)$$

where

$$Q_0 \equiv \left\{ \int_0^1 \frac{dx'}{\int_0^1 \int_0^1 \rho'(y'z') dy' dz'} \right\}^{-1} \leq 1. \quad (16)$$

Finally, comparing the trial result (15) with Eq. (9), we get

$$\rho_s/\rho \leq Q_0. \quad (17)$$

Note that for a liquid, where $\rho'(\vec{r}) \equiv 1$, the parallel argument would give only the trivial result $\rho_s \leq \rho$. It is essential to realize that it is the lack of translational invariance of the ground-state wave function, not that of the Hamiltonian, which reduces the superfluid fraction to a value less than one.

The quantity Q_0 obviously becomes very small when there exists any yz plane in the unit cell near which there is very small probability of finding an atom. In other words, it is extremely small unless there is an appreciable probability of "exchange" of particles between sites. The most favorable case would therefore seem to be solid helium. Unfortunately, although the inequality (17) is rigorous, it is not very useful in practice in setting a numerical upper limit on ρ_s/ρ , since Q_0 is very sensitive to the unknown details of the wave function. Purely in order to get an idea whether the proposed effect, if it occurs, is ever likely to be observable at all, we might speculate about the maximum value of ρ_s/ρ as follows: The effect is likely to be (at most) of the same order of magnitude as another effect in solid helium, namely the antiferromagnetic exchange interaction of He^3 nuclear spins,¹¹ which would vanish in the limit $Q_0 \rightarrow 0$. If J is the usual exchange constant and a the lattice constant, this would give the order-of-magnitude limit $\rho_s/\rho \lesssim J(\hbar^2/ma^2)^{-1} \sim 3 \times 10^{-4}$. However, it should be emphasized that this estimate is extremely tentative.

If NCRI should indeed occur in a solid, how would it manifest itself? The most direct experiment to look for it would be to rotate the solid in the form of an annulus¹² below its transition temperature; then the apparent moment of inertia should be slightly less than the classical value I_0 (and, more relevantly, presumably temperature dependent). A second test would be to rotate the solid above its presumed critical angular velocity ω_c and then bring the container to rest; if we assume that NCRI is associated with the metastability of flow states as in other superfluid systems, we should expect a persistent residual angular momentum $(\rho_s/\rho)I_0\omega_c$. In view of the small value of ρ_s/ρ , it seems highly unlikely that these effects would have been discovered by accident even if "superfluid solids" do exist at attained temperatures.

I am grateful to Professor J. G. Valatin for a conversation which sowed the seeds of some of the ideas discussed here.

¹We do not want to consider here the case of metals, which adds complications due, *inter alia*, to the possibility of superconductivity in the electron system.

²The discussion that follows clearly owes much to the work of C. N. Yang, *Rev. Mod. Phys.* **34**, 644 (1962); W. Kohn, *Phys. Rev.* **133**, A171 (1964); and F. Bloch, *Phys. Rev.* **137**, A787 (1965), among others. However, I believe some points may be new, in particular the treatment of the superfluid density. This has implications beyond the present context and I hope to discuss it further elsewhere.

³Yang, Ref. 2.

⁴Kohn, Ref. 2.

⁵Bloch, Ref. 2.

⁶A solid packed into an annular volume obviously cannot form a perfect crystal in the usual sense. However, the complications associated with this are trivial and will be ignored in what follows.

⁷To keep the notation simple we write the formulas explicitly for atoms of spin zero.

⁸This question is quite troublesome. In effect, the idea we develop below amounts to assuming a kind of long-range coherence between atomic diffusion processes. It is obvious that a complete description of the solid must also incorporate any incoherent diffusion processes which may occur, and these might well give rise to a certain amount of "normal-metal" type behavior. It is tempting to speculate, however, that (as in the liquid case) at $T=0$ there will be either complete coherence or none at all (in the latter case, one would expect no new results). At finite temperatures the existence of a (very small) mobile "normal component" might complicate the thermal properties.

⁹"Essentially vanishes" is shorthand for "becomes of order $e^{-R/a}$ or smaller, where a is a microscopic length independent of R or N " (cf. Kohn, Ref. 2).

¹⁰G. V. Chester, *Phys. Rev. A* **2**, 256 (1970).

¹¹See, e.g., R. A. Guyer and L. I. Zane, *Phys. Rev.* **188**, 445 (1969).

¹²In the case of a simply connected sample there are complications connected with penetration of vortices, as in the liquid.