$n_3(z_N) = n(z_N)$, or $\varphi(z_N) = 0$. We found

$$\epsilon_0 = 1.6°\text{K}, \tag{27}$$

again in good agreement with experiment,[4,5] thus in full support of Andreev's phenomenological model. A trivial extension of this calculation leads to m_s*. But since the m_s* measured is a Fermi liquid property, the present single-particle theory is not meaningful. (A corresponding calculation of the effective mass in bulk solutions *was* meaningful because of the low He^3 partial density. Here the two-dimensional He^3 system is at *high* density. Landau-theoretic dressing of the He^3 atoms clearly overwhelms substrate-induced renormalization effects.)

By regarding the He^3 atom as moving in a single-particle well, we can identify its probability density $\Psi_0^2(z)$ with $n_3(z)$. From the Gaussian form of $n_3(z)$, we extracted the oscillator frequency and found $\hbar\omega \approx 2.6°\text{K}$. This means an energy gap of about $2.6°\text{K}$ between the two lowest states. Thus, we conclude that the surface states of He^3 in He^3-He^4 solutions consist of just one bound state, which defines the lower edge of the two-dimensional continuum.

Finally, we wish to call attention to a recent paper by Saam,[10] whose theory is semiphenomenological in the sense that quantitative information about bulk He^3-He^4 solutions was required for the determination of an effective potential. Also, the theory depended heavily on the asymptotic behavior of the ground-state wave function of pure He^4. In particular, Saam fixed the value B in Eq. (15) by solving the one-particle Schrödinger equation at $z \to \infty$. Actually, the asymptotic region contributes insignificantly to the surface-energy expectation value and plays virtually no role in the variational calculation. In the important region around $z = 0$, B can take on any value whatsoever, so long as one assumes a correct asymptotic tail matched onto the wave function at some point far above the helium surface. Saam came to the same conclusion as ours that there exists only one bound surface state. His ϵ_0 was $3.1°\text{K}$.

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Collective Excitations in Liquid Hydrogen Observed by Coherent Neutron Scattering

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Coherent scattering of neutrons by liquid parahydrogen shows the existence of well-defined collective excitations in this liquid. Qualitative similarity with the scattering from liquid helium is found. Furthermore, in the range of observed wave vectors, $0.7 \text{ Å}^{-1} \lesssim \kappa \lesssim 3.1 \text{ Å}^{-1}$, extending from the first through the third Brillouin zones in the solid, $S(\kappa, \omega)$ is remarkably similar to the scattering law expected from a polycrystal. For $\kappa \lesssim 2.3 \text{ Å}^{-1}$ the observed spectra satisfy the one-phonon sum rule with mean square displacement $\langle u^2 \rangle = 1.0 \text{ Å}^2$.

The nature of collective excitations in simple liquids has been a subject of continuing study and debate. The dynamical correlations needed to create well-defined modes at short wavelengths, as seen by inelastic coherent neutron scattering, have been conclusively established only for liquid

TABLE I. Quantum parameters for ^{4}He, H_2, and Ne.

Liquid	de Boer parameter	Boiling point T_B (K)	Debye temperature (solid melting point) Θ (K)	Lennard–Jones ϵ/k_B (K)	Potential parameters σ (Å)
^{4}He	2.68	4.2	25	10	2.58
H_2	1.73	21.4	103	37	2.93
Ne	0.593	27.1	64	36	2.79

^{4}He, where longitudinal "phonons" are observed.[1,2] In classical liquids, constant–wave–vector measurements reported previously show that collective excitations are overdamped, with the consequence that no peak in $S(\kappa, \omega)$ exists for $\omega \neq 0$. We report here coherent inelastic neutron-scattering measurements which demonstrate the existence of well-defined collective modes in liquid parahydrogen.

During the last few years, molecular hydrogen has been investigated in detail in the solid phase, so that the phonon energies, density of states, Debye-Waller factor, etc. are now well known.[3-6] The experience from these investigations indicates that despite the large incoherent cross section, coherent measurements in the liquid phase are accessible and should contribute to the knowledge of not only this particular liquid but to the understanding of the liquid state as a whole. There are two characteristics of hydrogen relevant to the present study:

(i) Liquid hydrogen is a quantum liquid. In Table I we compare the quantum characteristics of the three liquids ^{4}He, H_2, and Ne. One measure of the quantum character of a substance is the de Boer parameter $\Lambda^* = (h^2/m\sigma^2\epsilon)^{1/2}$, which characterizes the importance of zero-point motion relative to potential energy. Also closely related to the quantum nature of the liquid is the degree of thermal excitation, qualitatively characterized by the ratio T/Θ, where Θ is the Debye temperature. From the data in Table I we see that short-wavelength modes in both H_2 and He are essentially unpopulated at liquid temperatures, whereas for Ne and other more classical fluids this is not true. Both Λ^* and T/Θ indicate that liquid H_2 is intermediate in character between He and classical fluids.

(ii) Molecular hydrogen has very special neutron-scattering properties.[7] Because of the small moment of inertia of the H_2 molecule, the rotational quantum number J is well defined at liquid temperatures and the rotational states are well separated. Since at the boiling point the equilibrium content of $(J = 1)$ orthohydrogen is about 0.2%, the scattering from orthohydrogen gives only a small known correction to that of pure $(J = 0)$ parahydrogen. This implies that the neutron can only undergo one of the two scattering processes $J = 0 \rightarrow J = 0$, or $J = 0 \rightarrow J = 1$.

Since the state $J = 0$ has only a single spin eigenstate, scattering within $J = 0$ is purely coherent. The differential cross sections for the two processes are as follows. (1) $J = 0 \rightarrow J = 0$; coherent scattering:

$$\frac{d^2\sigma}{d\Omega\,d\omega} = N\frac{k}{k_0}\frac{\hbar}{\pi}\sigma_{\text{coh}}j_0^2(\tfrac{1}{2}\vec{\kappa}d)S(\vec{\kappa}, \omega), \tag{1a}$$

where

$$S(\vec{\kappa}, \omega) = (2\pi\hbar)^{-1}\int_{-\infty}^{\infty}dt\int d^3r\,\{\exp[i(\vec{\kappa}\cdot\vec{r} - \omega t)]G(\vec{r}, t)\}, \quad \sigma_{\text{coh}} = 1.77 \text{ b.} \tag{1b}$$

(2) $J = 0 \rightarrow J = 1$; incoherent scattering:

$$\frac{d^2\sigma}{d\Omega\,d\omega} = N\frac{k}{k_0}\frac{\hbar}{\pi}3\sigma_{\text{inc}}j_1^2(\tfrac{1}{2}\kappa d)S_i(\vec{\kappa}, \omega - \hbar^{-1}\Delta E), \tag{2a}$$

where

$$S_i(\vec{\kappa}, \omega) = (2\pi\hbar)^{-1}\int_{-\infty}^{\infty}dt\int d^3r\,\{\exp[i(\vec{\kappa}\cdot\vec{r} - \omega t)]G_s(\vec{r}, t)\}, \quad \sigma_{\text{inc}} = 78.8 \text{ b.} \tag{2b}$$

In (1) and (2) $G(\vec{r}, t)$ and $G_s(\vec{r}, t)$ are the total and the self-correlation functions, respectively, $\vec{k}_0$ and $\vec{k}$ are the incoming and outgoing wave vectors of the neutrons, $\hbar\vec{\kappa} = \hbar(\vec{k} - \vec{k}_0)$ and $\hbar\omega = \hbar^2(k^2 - k_0^2)/2m_n$ are the momentum and energy transferred to the liquid by the neutron, and N is the number of mole-
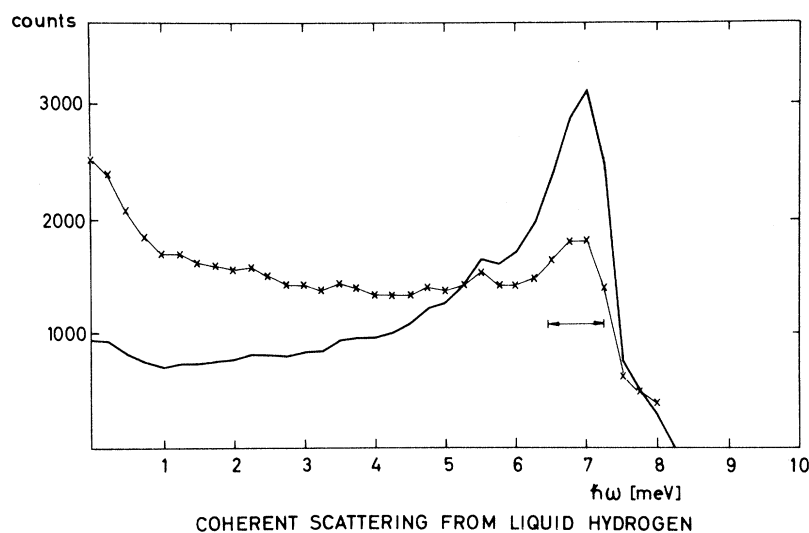
COHERENT SCATTERING FROM LIQUID HYDROGEN

FIG. 1. Neutron intensities at $\kappa = 1.4$ Å^{-1}, $T = 14.7\kappa$, saturated vapor pressure. Crosses, uncorrected data measured in counts, with instrumental resolution (full width at half-maximum) indicated. Solid line, data corrected as stated in text.

cules. The internuclear bond length $d = 0.746$ Å introduces the form factor $j_i(\kappa d/2)$, j_i being the ith spherical Bessel function. In (2) ΔE is the energy of the first rotational state: $\Delta E = E_{(J=1)} - E_{(J=0)} = 14.6$ meV.

Since the total width of the coherent spectrum is observed to be 8 meV, (1) and (2) show that it is effectively separated from the incoherent by the translation in energy ΔE. In the coherent-scattering experiment we therefore make the neutron energy smaller than 14.6 meV, so that only scattering according to (1) is possible. When the incoming energy is between ΔE and $2\Delta E$, the scattering is dominated by the incoherent process (2). This is true even if $S(\kappa, \omega)$ differs from zero in this range, because of the large ratio $\sigma_{inc}/\sigma_{coh}$.

The two functions $G(\vec{r}, t)$ and $G_s(\vec{r}, t)$ play an important role for the theoretical description of liquids, and the fact that one can, on a single sample, obtain independent information about $G(\vec{r}, t)$ and $G_s(\vec{r}, t)$ is a unique property of H_2 (a recent study[8] on liquid Ar extracts this information by measurements on samples of varying isotopic content). We have measured both the coherent and the incoherent scattering functions, but in this Letter we concentrate on the coherent scattering.

In preparing the sample we carefully catalyzed the hydrogen gas before letting it condense in a 30-mm–i.d. aluminum container with an ortho/ para catalyst at the top and bottom. The experiments were preformed on the Risø triple-axis

spectrometers. Second-order contamination was reduced by use of either a graphite filter or a germanium monochromator.

Scans were performed in the region 0.7 Å$^{-1} \leq \kappa \leq 3.1$ Å^{-1} at three different temperatures in the liquid phase; but since there is no drastic change in the coherent scattering with temperature, we show only the results obtained at 14.7 K and at saturated vapor pressure. One of the measured neutron groups at $\kappa = 1.4$ Å^{-1} is shown in Fig. 1, both in raw form and after correction. The following corrections have been considered and taken into account where significant: scattering from the empty can (uniformly 300 counts), instrumental sensitivity (essentially a k^3 correction[9]), the molecular form factor, multiple scattering ($< 2\%$ in this region[10]), and incoherent scattering from the small amount of $J = 1$ hydrogen ($< 2\%$).

The resulting $S(\kappa, \omega)$ is presented in Fig. 2 for the wave-vector values $\kappa = 0.7$, 1.1, 1.5, 1.9, 2.3, 2.7, and 3.1 Å^{-1}. For small κ, momentum conservation limits the accessible range of ω in $S(\kappa, \omega)$ for a given energy of the incoming neutrons, which has been kept below 14.6 meV. In liquid hydrogen this means that we did not measure the longitudinal phonon branch for $\kappa \leq 1.0$ Å^{-1} because of the high sound velocity.

Figure 2 demonstrates that a well-defined peak exists in $S(\kappa, \omega)$ for $\omega \neq 0$, signifying the existence of a collective excitation in the density autocorrelation function. In other liquids such as argon[8] and neon[11] such peaks are not seen in $S(\kappa, \omega)$ but

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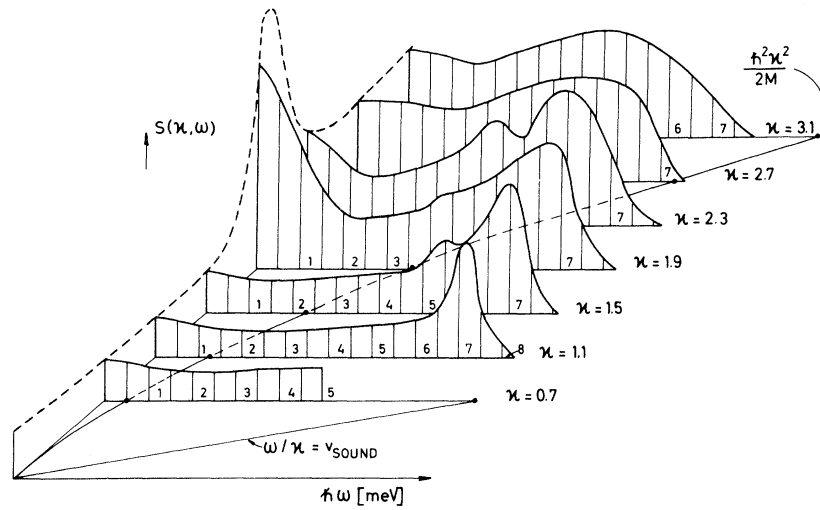
SCATTERING LAW FOR LIQUID HYDROGEN

FIG. 2. Scattering function $S(\kappa, \omega)$ for liquid parahydrogen, $T = 14.7$ K. Complete spectra could not be observed below $\kappa = 1.1$ Å^{-1} because of the high velocity of sound. In the base plane the recoil energy curve is shown.

only in the velocity autocorrelation function $\omega^2 S(\kappa, \omega)$, which of course has a peak at finite energy, even if the density autocorrelation function is overdamped. Since recent results reported on liquids at higher temperatures are presented in terms of a "symmetrized scattering law," we would like to comment that this is a mathematical convenience when thermal population of excitations occurs. Since in our case there is no thermal population, this transformation is neither convenient nor relevant.

The total spectra have been tested for the ACB (Ambegaokar, Conway, and Baym) one-phonon sum rule.[12] For $\kappa \lesssim 2.3$ Å^{-1} our results are consistent with one-phonon scattering, with a mean square displacement $\langle u^2 \rangle = 1.0$ Å.^{2} At larger κ's, however, $S(\kappa, \omega)$ shows a significant multiphonon contribution. The magnitude of the Debye-Waller factor indicates that multiphonon scattering should predominate for $\kappa > 1.5$ Å^{-1}, but this scattering seems to be concentrated mainly at energies above 8 meV, a region not accessible in this experiment.

From a preliminary analysis, several qualitative features are evident. One of these is the similarity with the dynamics of a solid. Adherence to the ACB sum rule was mentioned above. Furthermore, the characteristic excitation energies are in some respects solidlike. For instance, the longitudinal phonon energy at the first zone boundary in the solid at a density equal to that of liquid H_2 would be 7.5 meV, as estimated by the Grüneisen relation and the data of Ref. 6. This

is to be compared with the peak in our $S(\kappa, \omega)$ at $\kappa = 1.0$ Å^{-1} which is at 7.2 meV.

At higher κ's, corresponding to the second and third Brillouin zones in the solid, intensity appears in the liquid at lower energy, reminiscent of the neutron scattering law calculated for a polycrystalline powder.[13] In the latter case this feature is related to modes which possess appreciable transverse character, suggesting that transverse modes may contribute to the scattering in the liquid, although it is not clear how the neutron can couple to transverse modes in the absence of a reciprocal lattice. In addition to the maximum at finite frequency there is also a portion of the spectrum centered at zero frequency, most pronounced at $\kappa = 2$ Å^{-1}; i.e., near the major peak in the structure factor. In this respect liquid H_2 is similar to classical liquids.

It seems instructive to compare $S(\kappa, \omega)$ in H_2 with that of ^{4}He and Ne. It is well known that superfluid ^{4}He shows a sharp phonon-roton curve at low temperatures. The measurements of Dietrich et al.[2] show that thermal broadening becomes significant below the λ point and that, although heavily damped, the excitations persist in the normal phase. The characteristic energies are, however, much greater in H_2, and here thermal broadening is not as severe even at the boiling point. Neon offers an interesting comparison to hydrogen since it has approximately the same Lennard-Jones parameters as H_2 (cf. Table I) but a mass 10 times greater, decreasing the quantum character as measured by Λ^*. Neu-

tron scattering in liquid neon[11] shows that the dynamics here consist entirely of overdamped modes, so that a maximum in $S(\kappa, \omega)$ deviates from $\omega \sim 0$ only for $\kappa > 4$ Å^{-1}, where recoil effects become important.

The quantum character of liquid hydrogen can be smoothly decreased by external pressure, increasing the potential energy relative to the zero-point energy, and this offers a means of studying the transition to a classical liquid. Such measurements are now is progress.

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Temperature Dependence of the Accommodation Coefficient of Liquid-Helium Film*

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We have determined the accommodation coefficient γ of a helium film from 1.15 to 4°K by measuring the time constant of a rotating superconducting Nb sphere levitated in vapor and covered with a saturated helium film. The conventianal assumption of the phenomenological theory of superfluidity, that the order parameter ψ vanishes at the free surface of helium II, implies that γ is unity and independent of temperature. We find that γ is nearly unity above the λ point, suffers an abrupt drop close to T_λ, and gradually levels off to the value of $\simeq 0.8$ at lower temperatures.

In phenomenological theories of superfluidity,[1,2] two possible boundary values have been proposed for the order parameter $\psi(r)$, at the free surface, $\psi = 0$ and $\partial\psi/\partial r = 0$. Recently, third-sound experiments[3,4] by the University of California, Los Angeles group seem to favor the boundary condition $\psi = 0$. Calculation[5] and experimental measurement[6] of the surface tension of He II also support the conclusion that $\psi = 0$ at the free surface.

This boundary condition implies that all the atoms in the first layer or two on the liquid surface, through which interaction with the vapor takes place, are in the normal state. Consequently, the accommodation coefficient γ, defined as the fraction of incident gas molecules that stick

on the surface, should have no temperature dependence and be equal to unity, as is expected in He I.

In fact, experiments of Atkins, Rosenbaum, and Seki[7] indicate that in He II γ is close to unity at 1.2°K, while those of Hunter and Osborne[8] indicate γ to be no less than 0.9 and probably unity. Recently, however, Blair and Matheson[9] reported that γ is orders of magnitude lower than previously reported.

One purpose of this experiment is to provide a direct and accurate measurement of γ and its temperature dependence and thus shed light on the behavior of ψ at a free boundary. These two quantities are most simply related by assuming