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Interpretation of Raman experiments in superfluid ^{4}He

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We consider the status of the interpretation of second-order Raman ("two-roton") scattering in superfluid ^{4}He. The experimental results are widely considered to provide evidence of the existence of and a value for the binding energy of a two-roton bound state (or resonance). We have previously shown that these conclusions are risky at best, since they are based on an analysis ignoring the fundamental fact that two molecules cannot overlap. Since the import of this argument has not been fully appreciated we reiterate and further illustrate it here. In particular, we estimate that a change in $t(k)$, the "light-helium coupling" or pair polarizability, which is on the order of the uncertainty in the correct value of this function, can shift ω_0, the frequency of the peak in the Raman scattering, by 0.24 °K. This figure is as large as the difference between the observed value of ω_0 and 2Δ, where Δ is the roton energy. So this difference, which is often cited as evidence for a two-roton bound state, may not be characteristic of quasiparticle dynamics alone.

The second-order Raman scattering intensity at frequency shift ω in fluid He may be written[1]

$$I(\omega)=\int d^3k\int d^3k'\,t(k)t(k')H(kk'\omega)\quad . \tag{1}$$

Here we have

$$H(kk'\omega)=\frac{1}{N}\int e^{i\omega t}\langle\rho_k(t)\rho_{-k}(t)\times\rho_{K'}(0)\rho_{-k'}(0)\rangle\quad , \tag{2}$$

where

$$\rho_k(t)=\sum_{i=1}^{N}e^{ikR_i(t)}\quad . \tag{3}$$

The function $t(k)$, sometimes referred to as the "light-helium coupling" is the Fourier transform of a function $t(r)$, describing the transfer of an electronic excited state from one atom to another. It may alternatively be viewed[2] as the polarizability of a *pair* of atoms in the fluid. The correlation function H depends on the dynamics of the fluid. In particular, the effects of quasiparticles (or elementary excitations) in He II on $I(\omega)$ are expressed via H. Note that it depends on two density operators at time t and two at time zero. This is because the scattering amplitude for the second-order Raman process involves two atoms, one which absorbs the incoming photon and one which emits the outgoing photon. For this reason there should be an important contribution to $I(\omega)$ from pairs of quasiparticles, in particular pairs of rotons, and there have been many attempts to gain information about their behavior by interpreting the experimental results for $I(\omega)$.

Note that in writing Eqs. (1)–(3) we have neglected the polarization dependence of the scattering, the photon momentum transfer, and an overall constant. These simplifications do not affect the present discussion. However they can lead to errors in more detailed calculations. In particular, neglecting the momentum transfer can introduce spurious terms related to the long-range behavior of the correlation function H.

Now the function $t(k)$ in Eq. (1) influences the Raman scattering strongly. Unfortunately, it is not at all well known in He II (or any other dense fluid). About all that one can say for certain is that at large r, its Fourier transform is given by the (appropriately normalized) "dipole induced dipole" (DID) form

$$t_{\mathrm{DID}}(r)=6(\alpha^2/r^3)\quad , \tag{4}$$

where α is the polarizability of an isolated helium atom. At smaller $r, t(r)$ must differ from t_{DID}, but the proper value of the correction term is not known. Oxtoby and Gelbart[3] have proposed the form

$$t_{\mathrm{OG}}(r)=t_{\mathrm{DID}}(r)-6.22\ \text{Å}^3e^{-r/0.334\ \text{Å}}\quad . \tag{5}$$

Note that this correction to t_{DID} induces changes in $t(k)$ for wave vectors in the roton region ($k\cong 2\ \text{Å}^{-1}$). Hence it affects $I(\omega)$ strongly in the region of the two-roton peak ($\omega\cong 2\Delta$, $\Delta=$ roton energy $\cong 8$ °K). We show below that a change in $t(r)$ of this type can shift the value of ω_0, the frequency at which the observed $I(\omega)$ peaks, by a significant amount. So the location of this peak cannot be regarded as characteristic of quasiparticle dynamics alone.

Now the other important influence in $I(\omega)$ is the

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dynamic correlation function $H(kk'\omega)$. As mentioned, it is through H that the quasiparticle dynamics influence $I(\omega)$. Since H involves pairs of density operators $\rho_k\rho_{-k}$, it must in fact contain information about pairs of rotons. The high-resolution experiments of Murray *et al.*[4] show that $I(\omega)$ has a narrow well-defined peak at $\omega_0 = 16.97 \pm 0.03\,°\mathrm{K}$, which is below twice the roton energy[5] ($2\Delta = 17.236 \pm 0.018\,°\mathrm{K}$). These facts have been interpreted as evidence for a bound state (or resonance) of two rotons with binding energy E_B. This interpretation is based on either (i) fitting the observed $I(\omega)$ by a model calculation of H or (ii) simply subtracting 2Δ from ω_0, which gives $E_B = 0.27 \pm 0.04\,°\mathrm{K}$. [(i) gives similar values for E_B, depending on how the calculation is performed]. We consider these methods in turn. We show that the value of E_B, and even the existence of a two-roton bound state cannot be deduced with certainty from the Raman experiments at present. These points have already been made.[6] However, since the force and relevance of our arguments have either not been addressed or not been appreciated in subsequent work[5,7–15] on Raman scattering and related topics, it is appropriate to restate and further illustrate them here.

(i) Here the approach has been to calculate $H(kk'\omega)$ in a field-theoretic model for the quasiparticles. We have shown that these models[16] suffer from a fundamental problem. They neglect one of the basic properties of the fluid state, namely, that two atoms cannot overlap each other ("excluded volume condition"). This problem is important at every ω, as is proven in Ref. 6 and illustrated below, not just for the overall shape of $I(\omega)$. It may be regarded as an improper treatment of short-range correlations in the liquid, or alternatively as the result of the lack of knowledge of the wave function of a quasiparticle in real space. These points may be understood by considering a matrix element entering H,

$$m = \langle \omega | \rho_k \rho_{-k} | 0 \rangle \quad . \tag{6}$$

Here $|0\rangle$ is the ground state of the liquid and $\langle\omega|$ an excited state of energy ω. Since the Fourier transform of m with respect to k must vanish for $r \leq \sigma =$ atomic diameter $\cong 2\,\mathrm{\AA}$, it follows that any quasiparticle state contributing to the scattering must couple to a wide range ($\sim 2\pi/\sigma$) of k values. None of the calculations of H referred to exhibits this feature. It is not possible to interpret the experimental results using them. Hence in particular one cannot deduce the value of E_B or even argue for the existence of a bound two-roton state on this basis.

Note that this feature of m means that $H(kk'\omega)$ must have important "off-diagonal" parts ($k \neq k'$) for each ω. The correlation function $h(kk')$ that appears in the total (integrated over ω) Raman scattering I_R also exhibits this feature.[6] This has been illustrated in a recent calculation by Campbell and Pinski.[17] Unfortunately there is no such result for $H(kk'\omega)$.

It is also interesting to note that the behavior of m implies that each $\rho_k\rho_{-k}$ must couple to a range of ω values. This contrasts sharply with the behavior of ρ_k. For low frequencies it is known from neutron scattering experiments that ρ_k connects $|0\rangle$ to quasiparticle states of well-defined energy. This difference illustrates the extreme anharmonicity of the fluid. (In fact m may be more closely related to the multiphonon part of the neutron scattering.)

(ii) Here we consider what can be learned by comparing the frequency ω_0 of the peak in $I(\omega)$ with the roton energy Δ. As mentioned above, ω_0 is known to be significantly smaller than 2Δ, which is prima facie evidence for a two-roton bound state. The problem with this argument is related to but not quite the same as in (i). Since $H(kk'\omega)$ has important off-diagonal parts, $I(\omega)$ depends sensitively on the form of $t(k)$ at each ω. Looking at a narrow range of ω near 2Δ, as in the experiment of Murray *et al.*,[4] is not sufficient to guarantee that the line shape is independent of $t(k)$ and a feature of quasiparticle behavior only. One way to see this has been pointed out by Zawadowski.[18] If $t(k)$ were constant then $I(\omega)$ would vanish identically at all ω. [The fact that the calculations reported by Murray *et al.*[4] do not exhibit this behavior is just a reflection of their treatment of $H(kk'\omega)$]. Since, as mentioned above, $t(k)$ is not well known, it is at present impossible to untangle its effects on $I(\omega)$ from those of H. To illustrate this point explicitly, we show that adding to $t(k)$ a function of the order of the present uncertainty in its value can induce a shift in ω_0, the observed peak of $I(\omega)$, as large as $\omega_0 - 2\Delta$.

Now if prime denotes differentiation with respect to ω,

$$I'(\omega_0) = 0 \tag{7}$$

defines ω_0 as a functional of $t(k)$. Differentiating Eq. (7) gives for the shift $\delta\omega_0$ in the location of the peak of $I(\omega)$,

$$\delta\omega_0 = -\int \frac{\delta I'(\omega_0)}{\delta t(k)} \delta t(k) / I''(\omega_0) \quad . \tag{8}$$

First we evaluate the denominator. $I(\omega)$ for ω near 2Δ may for our purposes be represented by a Lorentzian[4]

$$I(\omega) = I(\omega_0) \frac{\omega_L^2}{\omega^2 + \omega_L^2}, \quad \omega_L = 0.55\ °\mathrm{K} \quad . \tag{9}$$

Note that we are using the functional form of Ref. 4 as a representation of the data only, with no implication about the physical processes that determine it. If $I_R^{2\Delta}$ is the total intensity under the peak represented by Eq. (9), we have

$$I(\omega_0)=\frac{1}{\pi\omega_L}I_R^{2\Delta}\ . \tag{10}$$

On the other hand,[19,20] we have

$$I_R^{2\Delta}\cong\tfrac{1}{5}I_R\ , \tag{11}$$

where I_R is the total Raman intensity. Using Eqs. (9)–(11) we find

$$I''(\omega_0)=\frac{-2}{5\pi}\frac{1}{\omega_L^3}I_R\ . \tag{12}$$

Now consider the numerator in Eq. (8). Assuming that Eq. (11) remains valid, we have approximately

$$\tfrac{1}{5}\delta I_R=\int_{2\Delta}\delta I(\omega)\,d\omega\ , \tag{13}$$

where the 2Δ denotes integration over the two-roton peak. If the magnitude of $\delta I(\omega_0)$ is typical of $\delta I(\omega)$ in this region, we have

$$\tfrac{1}{5}\delta I_R\cong\delta I(\omega_0)2\omega_L\ . \tag{14}$$

Now we have

$$I(\omega_0)=\int_0^{\omega_0}I'(\omega')\,d\omega'\ . \tag{15}$$

Making similar assumptions for $\delta I'(\omega_0)$, we have

$$\delta I(\omega_0)\cong\delta I'(\omega_0)2\omega_L/2\ . \tag{16}$$

Combining Eqs. (14) and (16) we see

$$\delta I'(\omega_0)=\int\frac{\delta I'(\omega_0)}{\delta t(k)}\delta t(k)=\frac{1}{10}\frac{1}{\omega_L^2}\delta I_R\ . \tag{17}$$

Combining Eqs. (8), (12), and (17) gives for the shift in the peak

$$\delta\omega_0=\tfrac{1}{4}\pi\omega_L\frac{\delta I_R}{I_R}\ . \tag{18}$$

Now $\delta I_R/I_R$, the relative change in the total Raman intensity, may be estimated from the work of Campbell and Pinski.[17] If we use the difference between their value for I_R with $t(r)=t_{\mathrm{OG}}(r)$ [see Eq. (5)] and the experimental value,[19] we have $\delta I_R/I_R=0.0009/0.0016$ so that

$$\delta\omega_0=0.24\ {}^\circ\mathrm{K}\ . \tag{19}$$

Thus, this change in $t(k)$ can induce a shift in ω_0, the energy of the Raman scattering peak, as large as the observed value of $2\Delta-\omega_0$ $(0.27\pm0.04\,{}^\circ\mathrm{K})$.[4,5] Hence one is not justified in using this difference as evidence for the existence of a bound state of two rotons.

It can be objected that in deriving Eq. (19) we made some implicit assumptions about $H(kk'\omega)$ and that different assumptions would lead to different values for $\delta\omega_0$. This is correct, but the author is not aware of any way to be certain that $\delta\omega_0$ must be smaller than the value given in Eq. (19). Furthermore, our assumptions are in another sense conservative. It is possible that changing $t(k)$ has a more drastic effect on the line shape than just shifting ω_0. Hence, this objection is just another illustration of the conclusions already drawn in Ref. 6 and repeated here. The sensitivity of $I(\omega)$ to $t(k)$ and $H(kk'\omega)$ and lack of knowledge of the latter functions make it risky at best to deduce the existence and binding energy of a two-roton bound state from the results of the Raman experiments.

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