CUBIC ANHARMONIC CORRECTION TO SELF-CONSISTENT PHONONS IN b.c.c. $^3$He

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Using the lowest order self-consistent phonons as basis phonons, the frequency shift and lifetime due to the cubic anharmonic term is calculated for b.c.c. $^3$He. The shift is found to be large and in many cases alters the character of the dispersion curves so that corrections to the lowest order self-consistent phonons appear to be important.

SOLID helium is characterized by weak interatomic forces and light mass so that the vibrational amplitudes are large. This means that anharmonic terms in a potential expansion about the lattice points are vital – so vital that a simple harmonic theory fails entirely and predicts an unstable solid with imaginary vibrational frequencies. Recently, this difficulty has been surmounted using self-consistent (SC) methods and in the lowest order scheme real, positive frequencies are obtained. This scheme can be made to look exactly like a harmonic theory with the usual force constants replaced by a space average

$$\Phi_{ij} = \frac{\partial^2 \nu}{\partial r_i \partial r_j} \rightarrow <\frac{\partial^2 \nu}{\partial r_i \partial r_j}>$$

and is often called the self-consistent harmonic approximation (SCH).

Usually, the SC theory is derived variationally or with linear response theory. It can also be derived by a Green function expansion with anharmonic terms treated as a perturbation in much the same as done by Choquard. The SCH theory is then recovered by summing all anharmonic terms appearing in first order and iterating the result until it is self-consistent. In this derivation we see that even anharmonic terms, principally the quartic term, are included but the cubic term, since it appears first in second order, is omitted. In weakly

anharmonic crystals where perturbation theory is rapidly convergent the quartic and cubic contributions are usually found to be of nearly equal magnitude but of opposite sign so that they tend to cancel. The application of the SCH theory to weakly anharmonic crystals would therefore give very unsatisfactory results. Since a simple comparison is not possible for very anharmonic crystals it was thought to be essential to evaluate the magnitude of the cubic term for a crystal in which the SCH theory has been very successful. We therefore report calculations of the cubic anharmonic term treated as a perturbation on the SCH frequencies in the most strongly anharmonic crystal b.c.c. $^3$He.

In solid helium, short range correlations between pairs of atoms are important. If these correlations are described using the Jastrow function introduced by Nosanow so that they can be incorporated in an effective potential, then correlations may be included naturally in the perturbation expansion method. In the two-body correlation approximation the SCH frequencies with correlations are given by

$$\Omega_{k,\Lambda}^{x} = \epsilon_{k,\Lambda} \cdot \frac{1}{M} \sum_{j} \{ \exp (i k \cdot R_{ij}) - 1 \}$$

or

$$\frac{\partial^2}{\partial r_i \partial r_j} <W_{ij}> \left( \frac{1}{<f>_{1j}^2} \right) \cdot \epsilon_{k,\Lambda}$$

(1)
Here \( f_{ij} \) is the Jastrow function
\[
f_{ij} = \exp[-\kappa v(\vec{r}_i - \vec{r}_j)/4\epsilon]
\]
and \( W_{ij} \) is the effective potential
\[
W_{ij} = f_{ij}^2 \left( v_{ij} - \frac{\hbar^2}{2M} \nabla_i^2 \log f_{ij} \right)
\]
For the bare potential, the Lennard–Jones potential
\[
v(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]
\]
with \( \epsilon = 10.22^\circ K \) and \( \sigma = 2.556 \) Å is used.

The force constants in equation (1) contain terms (involving derivatives of \( f^2 \)) in addition to those appearing in the force-constant expressions obtained variationally \(^2\) or with linear response theory. \(^3\) Numerically, we find that terms containing first derivatives of \( f^2 \) contribute \( \sim 2.4 \) per cent and those containing second derivatives \( \sim 0.5 \) per cent to the force constants so that all the expressions are largely equivalent and neglect of these terms do not substantially alter the dispersion curves. The definitions of \( \Omega_{SCH} \) also differ but we feel equation (1) is most appropriate and that these differences will not alter our basic conclusion in any case. Physically we expect \( \langle \partial^2 f/\partial r^n \rangle \) to be very small (and successive derivatives successively smaller) because \( f \) is essentially a constant, unity, for \( r \gg \sigma \). For numerical simplicity we have dropped the terms containing \( \langle \partial^2 f/\partial r^n \rangle \) and computed the Gaussian averages using a product of single particle functions*
\[
\langle f \rangle = \pi \pi \left( \frac{A}{2\pi} \right)^{1/4} \exp\left[ -\frac{1}{2} A(\vec{r}_i - \vec{R}_i)^2 \right].
\]

The parameters \( A \) in (5) and \( K \) in (2) were found by minimizing the ground state energy \( E_0 \)
computed using (3), (4), and (5) yielding values of \( A = 1.49 \pm 0.01 \) Å\(^2\) and \( K = 0.174 \pm 0.002 \) at \( R = 3.59 \) Å. These agree with those quoted in reference 6. The resulting \( \Omega_{SCH} \), calculated using the usual configuration space method are shown as dashed curves in Fig. 1 for \( R = 3.59 \) Å (\( V = 21.5 \) cc/mole). These curves are similar but somewhat lower than those in reference 3 where \( A \) and \( K \) values appropriate to 2 + 3-body correlations were used.

On examining the second order terms in the Green function expansion, using the SCH theory as zero order, the leading term is the cubic term with force constant
\[
\Phi_{ij} = \frac{\partial^3}{\partial r_i \partial r_j \partial r_l} \langle W_{ij} \rangle
\]
Again terms in \( \langle \partial^2 f^2/\partial r^n \rangle \) are small and by dropping these we may use a Fourier transform method \(^7\), to compute the cubic correction. The accuracy of the method when applied to \( \langle W_{ij} \rangle \) rather than \( v_{ij} \) was checked by recalculating the \( \Omega_{SCH} \) using the transform method. The cubic correction could then be found using a program developed here previously for potassium. \(^9\) The expressions for the real and imaginary part of perturbed phonon energy, in this program are exactly those appearing in equation (3.1) and equation (3.2), reference 8 and are not reproduced here. The principle value and delta function in these expressions were approximated by \( P(x) = x/\sqrt{x^2 + \epsilon^2} \) and \( \delta(x) = 1/(x^2 + \epsilon^2) \).

A grid of 50 points \( (q \) steps of 0.1) in the f.c.c. Brillouin zone was used with \( \epsilon = 0.05 \) (THz). (For the approximate calculations in Table 1, a grid of 128 points with \( \epsilon = 0.1 \) (THz) was used.) The shifted phonon frequency was associated with the peak in the imaginary part of the retarded Green function
\[
\text{Im} G^R(\omega) = \frac{2\Omega_{SCH} \Gamma(\omega)}{|\omega - \left[ \Omega_{SCH}^2 + 2\Omega_{SCH} \Delta(\omega) \right]|^2 + |2\Omega_{SCH} \Gamma(\omega)|^2}
\]
The position of this peak, \( \Omega \), often differed substantially from the \( \Omega_L \) obtained assuming pure Lorentzian behaviour for \( \text{Im} G^R \). The
Fig. 1. The dispersion relations for the lowest order self consistent phonons and for the phonons corrected for cubic anharmonicity in b.c.c. He\(^3\) at \(T = 0^\circ\text{K}\) and \(R = 3.59\) \(\text{Å}\). The inverse lifetimes \(\Gamma^{-1}\) are also shown. In the corrected case the \([q, q, 0] T_2\) branch is unstable and is denoted by \(i\) with \(i\) denoting its 'projection' along the 'imaginary' axis.

Table 1. Sensitivity of \(\Omega_{\text{SCH}}\) and \(\Omega\) for \((0.5, 0.5, 0)\) to changes in wave function parameters.
(a) arbitrary 50 per cent change of correlation function parameter \(K\)
(b) For Gaussian parameter \(A\) obtained using a Debye model (reference 6)
(c) For \(A\) and \(K\) obtained when 3-body terms are included in the energy cluster expansion (from reference 3)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>(L)</th>
<th>(T1)</th>
<th>(T2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K = 0.134)</td>
<td>(\Omega_{\text{SCH}} = 0.8225)</td>
<td>0.4162</td>
<td>0.2151</td>
</tr>
<tr>
<td>(A = 1.49)</td>
<td>(\Omega = 0.786)</td>
<td>0.368</td>
<td>(i \times 0.142)</td>
</tr>
<tr>
<td>(K = 0.223)</td>
<td>(\Omega_{\text{SCH}} = 0.7876)</td>
<td>0.3810</td>
<td>0.2260</td>
</tr>
<tr>
<td>(\Omega = 0.762)</td>
<td>0.344</td>
<td>(i \times 0.108)</td>
<td></td>
</tr>
<tr>
<td>(A_D = 1.37) (K = 0.178) (Debye model)</td>
<td>(\Omega_{\text{SCH}} = 0.7631)</td>
<td>0.3537</td>
<td>0.2199</td>
</tr>
<tr>
<td>(\Omega = 0.740)</td>
<td>0.317</td>
<td>(i \times 0.0985)</td>
<td></td>
</tr>
<tr>
<td>(A = 1.64) (K = 0.160) (3 body terms included)</td>
<td>(\Omega_{\text{SCH}} = 0.8421)</td>
<td>0.4465</td>
<td>0.2094</td>
</tr>
<tr>
<td>(\Omega = 0.800)</td>
<td>0.392</td>
<td>(i \times 0.171)</td>
<td></td>
</tr>
</tbody>
</table>

corrected frequencies, \(\Omega\), and the inverse lifetimes \(\tau^{-1} = \Gamma(\Omega)\) are shown for the 3 principal symmetry directions in Fig. 1 as solid lines.

From Fig. 1 we see that the cubic correction is large and in some cases alters the character of the dispersion curve. In particular \(T_2\) for
[\mathbf{q}, \mathbf{q}, 0] \text{ is } '\text{imaginary}' \text{ (in the sense that there is no solution for the real part along the real axis) for all } \mathbf{q} \text{ values and is shown as } i; \text{ the height of } i \text{ giving the 'projection' of } T_2 \text{ along the imaginary axis. Also a significant change in the shape of the dispersion relations occurs for modes propagating along } [\mathbf{q}, 0, 0] \text{ and } [\mathbf{q}, \mathbf{q}, 0]. \text{ The change in shape along } [\mathbf{q}, 0, 0] \text{ is interesting because a similar crossing of the } L \text{ and } T \text{ modes has been observed in lithium}^{10} \text{ and our results indicate that this is due to anharmonicity as suggested by Brockhouse.}^{11} \text{ Although the changes in the frequencies of these modes are quite large the lifetimes are always greater than 10 periods.}

To test the sensitivity of } \Omega \text{ to } f_{ij}, \text{ the parameter } K \text{ was arbitrarily changed to 25 per cent above and below the determined value of } K = 0.174. \text{ Since } K \text{ as determined by minimizing } E_0 \text{ varies } \lesssim 10 \text{ per cent over the b.c.c. volume range this represents a significant variation. The } \Omega \text{ for wave vector } (0.5, 0.5, 0)2\pi/a \text{ for these } K \text{ values are shown in Table 1 and indicate that } \Omega \text{ is not critically sensitive to this kind of change in } f_{ij}. \text{ } \Omega \text{ might, however, change substantially if a new function were used. Also } \Omega \text{ at } (0.5, 0.5, 0)2\pi/a \text{ was calculated using the } A_D \text{ value found for a Debye model at } T = 0^\circ\text{K and for the parameters obtained when 3-body terms}^{11,3} \text{ are included in the energy cluster expansion of } E_0. \text{ For all cases } T_2 [\mathbf{q}, 0, 0] \text{ remains 'imaginary'.}

\text{From the results in Fig. 1 we conclude that the cubic correction is large although not so large as might be expected from comparisons with conventional anharmonic perturbation theory. The numerical results here could be improved by using correlated rather than single particle functions but we do not expect the basic conclusion to be changed. (Comparing the results in Fig. 1 with those in Table 1, Section (b) gives an estimate of the sensitivity of the } \Omega_{\text{SCH}} \text{ and } \Omega \text{ to the Gaussian function parameters.) We think that it is unlikely that an improved treatment of correlations will markedly alter our results and therefore conclude that the cubic and possibly higher order anharmonic terms are important in the self consistent hierarchy for b.c.c. He$^3$.}

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\textbf{REFERENCES}

11. BROCKHOUSE B.N., in Ref. 11, p. 163.
Nous avons calculé le temps de vie et le décalage de fréquence,
dus à la composante anharmonique cubique, pour le $^3$He (b.c.c.),
en utilisant comme base de phonons les phonons self-consistents
d'ordre minimal. Le décalage est grand et dans plusieurs cas
change l'apparence des courbes de dispersion, ce qui indique que
les corrections aux phonons self-consistents d'ordre minimal
semblent importantes.