Enhanced Anharmonicity Under Pressure

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Abstract. Contradicting common sense, pressure does not monotonically harden the phonons in many systems but makes some specific modes soften at given points of the first Brillouin zone, even inducing dynamical instabilities that drive structural phase transitions. As the harmonic part of the ionic potential becomes smaller, higher order terms turn out to be more and more important. In AlH$_3$, for instance, anharmonicity suppresses the predicted high superconducting transition temperature at 110 GPa in agreement with experiments. Furthermore, anharmonicity stabilizes the high-pressure simple cubic phase of calcium even at zero temperature, explaining its mechanical stability. We will review the calculations performed in these two systems and show that anharmonicity can be tackled making use of perturbation theory or the so called self-consistent harmonic approximation.

1. Introduction

The discovery that lithium was a good superconductor reaching the outstanding 20 K value for $T_c$ at 48 GPa [1, 2] clearly addressed that Mathias’s rule [3] is obsolete when determining whether an element might be a good superconductor or not under pressure. Furthermore, it is now well established experimentally that many elements that do not superconduct at ambient pressure become superconductors when compressed regardless of their average number of valence electrons [4]. For instance, although Mathias’s rule forbids superconductors with one and six valence electrons, some alkaline metals, like the above mentioned lithium and cesium, and several group VI elements, such as oxygen, sulfur, selenium and tellurium, have been found to become superconductors [1, 2, 5, 6, 7, 8]. Moreover, calcium has recently set a new record for the superconducting transition temperature of an element, reaching 29 K at 216 GPa [9]. Remarkably, pressure not only enhances superconductivity in the elements, but several binary alloys also have been reported to dramatically increase their $T_c$ [10, 11].

The enhancement of the superconducting transition temperature is often related to the counterintuitive softening of some specific phonons in a given region of the first Brillouin zone (1BZ). This is counterintuitive because when atomic distances are reduced, interatomic forces are expected to become larger, thus leading to a phonon frequency increase. When phonons frequencies are lowered, the electron-phonon coupling is enhanced. This is rather straightforward
considering that the single mode electron-phonon coupling parameter is given by

$$\lambda_\nu(q) = \frac{1}{\pi N(\varepsilon_F)} \frac{\gamma_\nu(q)}{\omega_\nu^2(q)},$$

(1)

where $N(\varepsilon_F)$ is the density of states at the Fermi level, $\gamma_\nu(q)$ is the phonon linewidth associated to the electron-phonon interaction of mode $\nu$ at momentum $q$ and $\omega_\nu(q)$ is its frequency. Therefore, when a specific mode softens in a given region of the 1BZ, its $\lambda_\nu(q)$ is considerably enhanced. The emergence of large values of $T_c$ under pressure in lithium [12, 13, 14], sulfur [15], yttrium [16] and tellurium [17] perfectly fits into this picture since in all these cases a given phonon softens at a specific point in the 1BZ. Indeed, it seems that the lower the frequency of the softened mode, the larger $T_c$ [12, 16, 17]. The theoretical predictions recently performed in the group III hydrides also follow this trend since the predicted $T_c$ is larger the lower the hydrogen optical modes [18, 19].

The origin of the phonon softening has often been attributed to Fermi surface nesting, which is related to the electronic complexity and departure from free electron-like behavior induced by pressure [20]. This seems to be the case in the above mentioned Li [12, 21] and S [15]. However, strong Kohn anomalies can appear even in systems with spherical Fermi surfaces provided the value of the pseudopotential is large enough at $2k_F$ [22], where $k_F$ is the Fermi momentum. Interestingly, when increasing the electron density, the value of the pseudopotential at $2k_F$ is normally enhanced and, therefore, phonon anomalies are expected to appear under pressure even within the free electron-like model.

Regardless of its origin, softening leads to an important consequence: the increasing relevance of anharmonic effects. The reason is rather straightforward: if the harmonic part of the ionic potential is small, the anharmonic terms become qualitatively important and should not be neglected. This is exemplified by the one-dimensional anharmonic potentials of Fig. 1. In the figure, the eigenvalues of the Hamiltonian

$$\hat{H} = \frac{1}{2} p^2 + \frac{1}{2} \omega^2 x^2 + \alpha x^4 = \omega [\hat{a}^\dagger \hat{a} + \frac{1}{2} + \eta(\hat{a} + \hat{a}^\dagger)]^4,$$

(2)

are plotted for different values of $\omega$ keeping $\alpha$ fixed. In Eq. (2), $\eta = \alpha/4\omega^3$, $\hat{x}$ and $\hat{p}$ are position and momentum operators, and $\hat{a}^\dagger$ and $\hat{a}$ creation and annihilation operators. In the

Figure 1. The $\frac{1}{2} \omega^2 x^2 + \alpha x^4$ potential of Eq. (2) (black curve), its harmonic part (red curve) and the ground state eigenfunction of $\hat{H}$ (green curve) for different values of $\omega$ keeping the same $\alpha$. The harmonic ground state energy, $\varepsilon_h = \omega/2$ (red dashed line), its first order correction given by perturbation theory, $\varepsilon_p = \omega/2 + 3\eta$ (blue dashed line), and the ground state numerical energy, $\varepsilon_n$ (black dashed line), are depicted as well.
figure, the harmonic ground state eigenvalue, \( \varepsilon_h = \omega/2 \), its first order correction given by perturbation theory, \( \varepsilon_p = \omega/2 + 3\eta \), and the ground state eigenvalue obtained solving numerically the associated Schrödinger equation, \( \varepsilon_n \), are compared for three different values of the harmonic frequency, \( \omega \). As shown in Fig. 1(a), when the harmonic frequency is large and \( \eta \) small, the harmonic part of the potential approximates very closely the total potential, and \( \varepsilon_h, \varepsilon_p \) and \( \varepsilon_n \) are very similar. Thus, the harmonic approximation is extremely accurate. However, when \( \omega \) is reduced as in Fig. 1(b), the harmonic energy starts to differ from the exact value, but first-order perturbation theory still yields a good approximation to the energy. Finally, as depicted in Fig. 1(c), if the harmonic frequency is slightly imaginary, then, the harmonic approximation completely breaks down and it is impossible to apply perturbation theory directly as the energy of the unperturbed system has no lower bound. On the other hand, the exact solution still yields a positive energy and, despite being wider, the wave function is similar to those obtained previously and peaks at \( x = 0 \).

The main message to be drawn from this is that the harmonic approximation can often lead to a wrong interpretation of a system’s behavior. For instance, we might think that a system is completely unstable while it is observed experimentally and that eigenvalues are too low with respect to the real excitations of the system. Undoubtedly, taking into account anharmonicity can correct all these issues. Considering that under pressure phonon softening becomes very important, anharmonicity becomes crucial as well. In order to stress this idea, here we will briefly review the strong effect that anharmonicity has in the superconducting properties of AlH\(_3\) at 110 GPa [23] and of simple cubic (sc) calcium at 50 GPa [24].

2. Suppression of \( T_c \) in AlH\(_3\)

It has been suggested that metal hydrides could be good superconductors at experimentally attainable pressures as the metal ions act to precompress hydrogen [25], which is itself expected to be a large \( T_c \) superconductor at very high pressures. In this context, alane (AlH\(_3\)) has received considerable attention: a metallic phase of cubic symmetry has been found to be stable above 70 GPa [19, 26]. Computations based on the harmonic approximations suggested that this phase could have a \( T_c \) as large as 24 K at 110 GPa, but measurements could not detect any superconducting transition down to 4 K.

As it turns out, most of the electron-phonon coupling in this system comes from a small region of the first Brillouin zone. In order to identify the origin of the discrepancy between computed and measured \( T_c \), selected representative phonon modes at the X point were studied further [23]. Frozen phonon calculations suggested that, although the system is stable, anharmonic terms significantly renormalize the shape of the effective ionic potential, akin to the situation presented in Fig. 1(b). Although indicative, the potential obtained from frozen ionic displacements commensurate with the unit cell is insufficient to describe quantitatively the anharmonic renormalization of the phonon frequencies; a method was devised to extract all the necessary anharmonic coefficients from \textit{ab initio} calculations in order to compute the frequency renormalization to lowest order in perturbation theory [23].

It was found that the harmonic phonon frequencies of the modes in question were renormalized by anharmonicity from 19 to 32 meV for one mode and from 87 to 109 meV for the other. Given the relationship between electron-phonon coupling and frequency, as given by Eq. (1), it is clear that an increase in frequency suppresses the coupling; in the case of AlH\(_3\), it was argued that this suppression could be sufficient to reduce the predicted \( T_c \) to below 5 K, consistent with the observation that no transition appears to occur down to 4 K.

3. Stabilization and superconductivity of simple cubic calcium

The situation in sc Ca is even worse considering that, as it has been noted already [27, 28, 29, 30], it presents imaginary phonon frequencies throughout the whole 1BZ. In this sense many
Figure 2. (Left panel) Harmonic phonon spectra and renormalized anharmonic phonon spectra at 0 K of sc Ca at 50 GPa. For the 0 K anharmonic branches the value of $\lambda_\nu(q)$ is proportional to the area of each filled circle. (Right panel) At zero temperature, the anharmonic results for the integrated electron-phonon coupling parameter, $\lambda(\omega)$, and the Eliashberg function, $\alpha^2 F(\omega)$.

authors have doubted whether the sc is the real ground state structure of Ca in the 32-119 GPa pressure range where it is experimentally found [31, 32, 33] and alternative phases have been proposed [34]. Therefore, we are in the situation sketched in Fig. 1(c) and the method based on perturbation theory used in Section 2 cannot be employed. However, as we have recently demonstrated [24], the self-consistent harmonic approximation (SCHA) [35, 36] can be employed to build a variational nonperturbative approach that allows to tackle the problem of imaginary phonons efficiently. According to our results the sc phase is dynamically stable when anharmonicity is taken into account [24].

The basic idea behind the SCHA is that the most adequate phonon frequencies of the system are not those given by the harmonic approximation, but those that minimize the free energy. The ionic Hamiltonian $\hat{H} = \hat{T} + \hat{U}$, with $\hat{T}$ the ionic kinetic energy and $\hat{U}$ the potential, is redefined as $\hat{H}_0 + \hat{H}_1$, with $\hat{H}_0 = \hat{T} + \hat{U}_0^0$ and $\hat{H}_1 = \hat{U} - \hat{U}_0^0$. $\hat{U}_0^0$ is an arbitrary harmonic term that yields real frequencies. In this case, the Gibbs-Bogoliubov inequality states that the exact free energy of the system is always lower than the free energy calculated with $\hat{H}_0$ plus the statistical quantum average of $\hat{H}_1$,

$$ F \leq F_0 + \langle \hat{H}_1 \rangle_0. \tag{3} $$

Hence, if we find the $\hat{U}_2^0$ that minimizes Eq. (3), the frequencies that diagonalize $\hat{U}_2^0$ will be the renormalized anharmonic frequencies of the system. In the calculation, the $\hat{U}$ potential was expanded up to fourth order and anharmonic coefficients were obtained in the whole 1BZ. As in the case of AlH$_3$, these coefficients were estimated taking numerical second derivatives of dynamical matrices calculated in supercells [24].

As shown in Fig. 2, the imaginary branches of sc Ca at 50 GPa become positive when anharmonicity is treated according to the SCHA. Thus, quantum anharmonic effects fully stabilize the high pressure sc phase of Ca in agreement with experiments. Moreover, the renormalized anharmonic phonon spectra allowed us to estimate the renormalized Eliashberg function. This is simply done substituting in Eq. (1) the harmonic frequencies by the anharmonic frequencies. The Eliashberg function is shown in Fig. 2 and shows a clear peak related to the low energy mode. Integrating it we obtain the value of $\lambda = 0.74$ for the electron-phonon coupling.
parameter and $\omega_{\text{log}} = 53 \text{ K}$ for the logarithmic frequency average. With these values and using the standard $\mu^* = 0.1$ in the Allen-Dynes modified McMillan equation [37] we obtain $T_c = 2.1 \text{ K}$. We should stress that this value is in close agreement with experimental results [38, 39] and that could not have been estimated earlier as a consequence of the imaginary frequencies that the harmonic approximation yields.

4. Conclusions

In this work we have argued that due to the rather common softening of phonon modes under pressure, anharmonicity becomes crucial in many cases and cannot be neglected in the calculations. We have briefly reviewed the effect that anharmonicity has in AlH$_3$ at 110 GPa and sc Ca. In the former, the frequencies renormalized by anharmonicity reduce the value of the electron-phonon coupling parameter and, as a consequence, suppress $T_c$ as hinted by experiments. In the latter, we have seen that anharmonicity stabilizes the structure and that superconductivity can only be understood including anharmonic corrections in the calculations. We also have presented two different methods to treat anharmonicity: perturbation theory and the SCHA. As a final remark, we should stress that whenever soft phonons appear under pressure anharmonicity might have a crucial effect in the predicted value of $T_c$.

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