Novel information theory techniques for phonon spectroscopy

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Abstract. The maximum entropy method (MEM) and spectral reverse Monte Carlo (SRMC) techniques are applied to the determination of the phonon density of states (PDOS) from heat-capacity data. The approach presented here takes advantage of the standard integral transform relating the PDOS with the specific heat at constant volume. MEM and SRMC are highly successful numerical approaches for inverting integral transforms. The formalism and algorithms necessary to carry out the inversion of specific heat curves are introduced, and where possible, I have concentrated on algorithms and experimental details for practical usage. Simulated data are used to demonstrate the accuracy of the approach. The main strength of the techniques presented here is that the resulting spectra are always physical: Computed PDOS is always positive and properly applied information theory techniques only show statistically significant detail. The treatment set out here provides a simple, cost-effective and reliable method to determine phonon properties of new materials. In particular, the new technique is expected to be very useful for establishing where interesting phonon modes and properties can be found, before spending time at large scale facilities.

1. Introduction
Condensed matter physicists are frequently interested in the phonon properties of materials. This is due to the important role of phonons in many phenomena such as superconductivity [1]. However, determining the attributes of phonon modes is not generally straightforward. For instance, inelastic neutron scattering is highly accurate, but experiments are lengthy and expensive. Alternatively, bulk measurements are often used to get a “quick and dirty” estimate of the PDOS by fitting sets of Debye and Einstein phonons to reduce the total number of fitting parameters [2]. The aim here is to demonstrate a technique which has a higher accuracy than the Debye/Einstein technique, is generally reliable, while remaining cost effective because measurements can be carried out in a standard condensed matter laboratory.

One can relate the specific heat at constant volume due to phonons (the main contribution to the specific heat for non-magnetic insulators) to the PDOS using the integral transform,

\[ c_v(T) = 3R \int_0^\infty d\omega \, D(\omega) \frac{\hbar^2 \omega^2 e^{\hbar \omega / kT}}{(kT)^2 (1 - e^{\hbar \omega / kT})^2} \]  

(1)

\( D(\omega) \) is the phonon DOS and \( R \) is the gas constant [3]. This equation is discretised by writing...
2. Spectral Reverse Monte Carlo

SRMC is a novel alternative scheme to MEM, which considers all possible data configurations as an ensemble [4]. Its main advantage over MEM is that no form for the data entropy is assumed. However, it is significantly slower than MEM. The spectrum is computed from the ensemble as an average weighted by the likelihood function $e^{-\chi^2 \{s_i\}/\gamma}$, with $\chi^2$ defined as

$$\chi^2 \{s_i\} = \frac{1}{N_d} \sum_{i,j=1}^{N_d} \delta c(T_i) \left[ \Sigma^{-1} \right]_{ij} \delta c(T_j)$$

N_d is the number of discrete temperatures where data were measured, $\delta c(T_i) = [c_{\text{obs}}(T_i) - c_{\text{calc}}(T_i)]$ and $\Sigma$ is the covariance matrix. $\Sigma$ takes into account the possibility that measured data points might be correlated. In the measurement of the specific heat, this is likely as a consequence of relation (1). In particular, it is normally true that (phase transitions not with standing) $c_v(T)$ monotonically increases with temperature. Measuring the co-variance matrix requires making several independent measurement runs. The matrix can then be calculated as

$$N_{\text{meas}} \Sigma_{ij} = \left( c_n(T_i) - \overline{c_n(T_i)} \right) \left( c_n(T_j) - \overline{c_n(T_j)} \right)$$
Figure 2. Results from 4 different types of simulated spectrum. In panel (a) a Debye like spectrum, in (b) a Gaussian spectrum simulating an optical phonon (c) a combined spectrum (d) a detailed spectrum, such as might be found in alkali metals. The advantage of the presented techniques is clear - multiple energy scales can be handled with the same algorithms. Panel (d) shows how the approach handles detailed spectra [Data in (a) and (c) can be found in ref. [4]]

where the subscript $n$ indicates the $n$-th set of measurements. $N_{\text{meas}} = 10$ or so independent sets of measurements should be sufficient to determine the co-variance. If data are uncorrelated, then the covariance matrix yields the standard deviation $\Sigma_{ij} = \sigma_i^2 \delta_{ij}$.

A new parameter, $\gamma$ is introduced which acts to vary the average value of $\chi^2$. There is a thermodynamic analogy $\chi^2 \rightarrow E$ and $\gamma \rightarrow kT$. Thus any standard statistical mechanics algorithms can be used to compute the average. The spectrum is initialised as flat and normalised to $N_{\text{ph}}$. I recommend using Metropolis to sample the configuration space;

(i) Choose two different points $i$ and $j$ in the spectrum.
(ii) Make the transform, $s_i \rightarrow s_i + r$ and $s_j \rightarrow s_j - r$ where $r$ is a random variate.
(iii) If $s_j < 0$ reject.
(iv) If $\Delta \chi^2 < 0$ accept the change.
(v) If $\Delta \chi^2 > 0$ accept with probability $P = \exp(-\Delta \chi^2 / \gamma)$. Else keep the original spectrum.

Steps i-v are repeated, with averages of $\{s\}$ taken every few iterations until sufficient statistics have been gathered. Error bars are computed using a standard blocking procedure. The double update ensures that the spectrum remains normalised to the number of phonons, $N_{\text{ph}}$ (and by reducing the total configuration space speeds up the algorithm). The energy landscape of $\chi^2$ is complicated and has many troughs, some of which may be deep. To ensure that all troughs are sampled, $r$ is chosen from a random variate obeying the Cauchy distribution, $P(r) = \delta/(\delta^2 + r^2)$, where $\delta$ must be small enough to allow good acceptance, but not so small that the configuration space is not well sampled. The Cauchy distribution has been widely applied to fast simulated annealing, and is designed to cover the parameter space quickly. $\langle \chi^2 \rangle_{\gamma}$ is computed for several $\gamma$ to determine the value of $\gamma$ for which $\langle \chi^2 \rangle = N_d$. Then the spectrum is computed for that value of $\gamma$. Using a discrete spectrum is also possible. Then, each point in the spectrum must have $N_{\text{disc}}$ discrete values running from 0 to $N_{\text{ph}}$, so that the whole configuration space including a single $\delta$-fn can be accessed. I suggest a slight modification to step (ii) of the procedure in this
case; a completely new value is chosen for \(s_i\) and \(s_j\) is chosen to maintain normalisation of \(N_{ph}\) with step (iii) as before. Note: Sufficient \(N_s\) are needed to approximate the integrals.

3. Maximum Entropy Method

MEM has a similar thermodynamic motivation. A large number of similar configurations (i.e. a large data entropy) corresponds to a minimally contorted spectrum, where small changes in the spectrum lead to small changes in \(\chi^2\). In MEM, the regularisation is introduced via a “free energy”, which is a sum of the familiar \(\chi^2\) goodness of fit parameter and an entropy term, \(S\),

\[
\mathcal{F} = \chi^2\{s_i\} + \alpha S\{s_i\},
\]

\[
S = \sum_{i=1}^{N_s} [m_i - s_i + s_i \ln(s_i/m_i)]
\]

The hyper-parameter, \(\alpha\), has a thermodynamic analogy \(\alpha \rightarrow kT\) (similar to \(\gamma\) in SRMC). An additional regularising spectrum, \(m_i\) is introduced which is typically flat, positive and normalised to \(N_{ph}\). I used Bryan’s algorithm for the MEM analysis, which computes the spectrum as a weighted average of spectra calculated for several \(\alpha\) values [5]. See ref. [4] for a full discussion.

4. Simulated data and some considerations

Figure 2 shows results from a variety of simulated data. Panel (a) shows a Debye like spectrum, in panel (b) a Gaussian spectrum simulating an optical phonon and in (c) a combined spectrum. One of the strengths of the methods is that all energy scales are treated on an equal footing. However, ringing may occur when there is a sudden, discontinuous change in the density of states as shown in panels (a) and (c). In panel (d) a large \(N_s = 400\) is used with low (0.03%) data error to show the best possible performance of the technique. The low \(E\) features are accurately described. Accurate high \(E\) features require a large computational investment, but a partial improvement to the ringing can be seen. The error bars computed using blocking do not match the apparent error shown by the variation in spectrum. This indicates significant correlation between iterations, which might be improved with updates involving multiple points.

On the basis of the simulated data and success with experimental data [4], the outlook for deployment of these methods is good. I would like to draw attention to a caveat. A current disadvantage is that materials with phase transitions are difficult to examine, since these typically contribute divergences to the specific heat. The phase transition should be suppressed before doing the analysis, for example by doping to a regime with no phase transition. A method for treating magnetic and lattice excitations on the same footing would be useful, and I hope this article will stimulate other researchers to consider such an extension. I also note here that a similar integral transform relates resistivity to frequency dependent electron-phonon coupling [6]. The MEM analysis of that problem will be treated in a future publication.

Acknowledgments

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