The phonon density of states obtained from inverting specific heat data

1992 J. Phys.: Condens. Matter 4 L195

(http://iopscience.iop.org/0953-8984/4/12/001)

J. Phys.: Condens. Matter 4 (1992) L195–L198. Printed in the UK

LETTER TO THE EDITOR

The phonon density of states obtained from inverting specific heat data

S E Regan and G J Morgan
The Physics Department, The University of Leeds, Leeds LS2 9JT, UK

Received 18 November 1991

Abstract. The inversion of specific heat data to obtain the phonon density of states has been an important problem for many years. We present a new very simple and flexible iterative procedure and apply it to Einstein and Debye models. Excellent results are obtained and the method could be simply extended to more complex situations using improved numerical accuracy.

The specific heat of a harmonic solid as a function of temperature, $C(T)$, in principle determines the phonon density of states $g(\omega)$ in a relationship

$$C(T) = \int_0^\infty g(\omega) C_{\mathrm{E}}(\omega/T)\,\mathrm{d}\omega \qquad (1)$$

where

$$C_{\mathrm{E}}(\omega/T) = (\omega/T)^2 \exp(\omega/T)(\exp(\omega/T) - 1)^{-2} \qquad (2)$$

is the Einstein specific heat, using units in which $\hbar = 1$, $k_{\mathrm{B}} = 1$ and frequencies in kelvin (Loram 1986). The problem of inverting (1) to obtain $g(\omega)$ has a long history, which has been extensively reviewed recently by Loram (1986) with many references. He has presented a useful numerical method, which no doubt can be improved using refined numerical techniques. One failure of Loram's results, which we will avoid, is the density of states becoming negative. The assumption that $g(\omega)$ can be obtained from the specific heat does depend, of course, on the neglect of anharmonic effects, and in metals or semiconductors one must remove the electronic contributions either by experiment or from theoretical estimates of the electronic effects. Indeed in general one would also have to remove anharmonic effects by theroetical estimates. However, it is not necessary to know $C(T)$ over the complete range of temperature up to, say, the melting point, so that one can in principle minimize anharmonic effects by using low-temperature data.

If we differentiate (1) with respect to T then

$$\frac{\mathrm{d}C(T)}{\mathrm{d}(T)} = \int_0^\infty g(\omega') \frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{(\omega'/T)^2 \exp(\omega'/T)}{(\exp(\omega'/T) - 2)^2}\right)\mathrm{d}\omega' \qquad (3)$$

and the derivative of the function in brackets on the right-hand side gives rise to a sharpley peaked function $F(\omega)$ for $\omega \sim T$ at low temperatures. We then rewrite (3) as

$$g(\omega) = \frac{1}{I}\frac{\mathrm{d}C(\omega/\alpha)}{\mathrm{d}(\omega/\alpha)} + \left[g(\omega) + \frac{1}{I}\int_0^\infty g(x\omega/\alpha)x\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{x^2\mathrm{e}^x}{(\mathrm{e}^x-1)^2}\right)\mathrm{d}x\right] \tag{4}$$

where we have set $x = \omega'T$, $T = \omega/\alpha$, α is an adjustable parameter and

$$I = \int_0^\infty x^2\mathrm{e}^x(\mathrm{e}^x-1)^2\,\mathrm{d}x.$$

This is a trivial identity but we can start an interative solution by writing $g(\omega) \simeq I^{-}1\,\mathrm{d}C(\omega/\alpha)/\mathrm{d}(\omega/\alpha)$.

We now have to choose an upper limit for the numerical integration over x, which in general would be based on physical grounds corresponding to the highest value of the frequency ($\omega_{\max}$) to be expected in a system. In our tests on the Einstein and Debye models we have chosen the maximum frequency to be six times the Einstein temperature (θ_{E}) and three times the Debye temperature (θ_{D}).

The choice of α then determines the highest temperature needed in the specific heat data, namely $T_{\max} = \omega/\alpha$. Although a value of $\alpha \simeq 3$ locates the peak in $F(\omega)$ at low temperatures, we find a value of $\alpha = 8$ most satisfactory in practice in obtaining rapid convergence at low temperatures. There is considerable room for adjusting $\omega_{\max}$ and α in connection with the accuracy with which one performs the integral in equation (4).

We have tested the method using 300 equally spaced points in the range $\omega = 0$ to $\omega = \omega_{\max}$ and Simpson's rule to perform the integrals. The number of points used places constraints on the accuracy to be achieved, but our present intention is to demonstrate the usefulness of the method rather than push it to the limit. We have already mentioned the possibility that the density of states could 'stray' and become negative and we prevent this, and the associated possible instability, by always taking the modulus of the density of states at any given iteration. Finally, although it is not necessary to ensure that the density of states is normalized we found it useful to truncate the density of states at $\omega'_{\max}$ so that at any given iteration the density of states is normalized. The normalization is not exact at any state however, because we are using a discrete set of values for x in the integration process.

In figure 1 we show our results after 100 iterations for the Einstein model with $\theta_{\mathrm{E}} = 50$ K. Further iterations hardly change the results, reflecting the fact that we are integrating using a finite mesh. The resulting specific heat is shown in figure 2 and the discrepancy with the exact behaviour for high T is simply due to the density of states being not exactly normalized because of the finite mesh. This is more obvious in the case of a δ-function-like density of sates, as opposed to that of the Debye model.

In figure 3 we show results for a Debye temperature $\theta_{\mathrm{D}} = 100$ K. The full line denotes the Debye model; the lower dashed curve shows the very first approximation with the upper chain curve showing the result of iterating equation (4) one hundred times.

The main discrepancy was close to θ_{D} and further iterations do not improve matters significantly in this region. Again this difference between the exact and computed values comes about from the numerical accuracy of the calculation. In

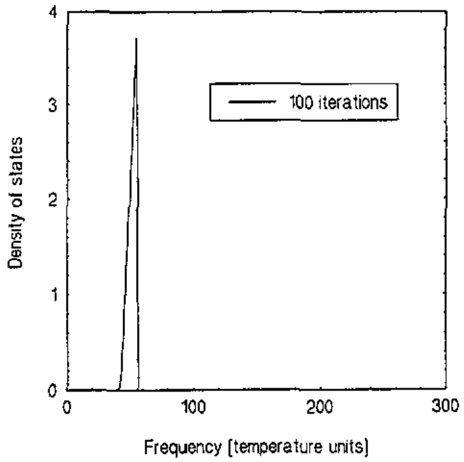

Figure 1. The approximate form of the density of states for the Einstein model with $\theta_E = 50$ K. The units correspond to $k_B = 1$ and $\hbar = 1$.

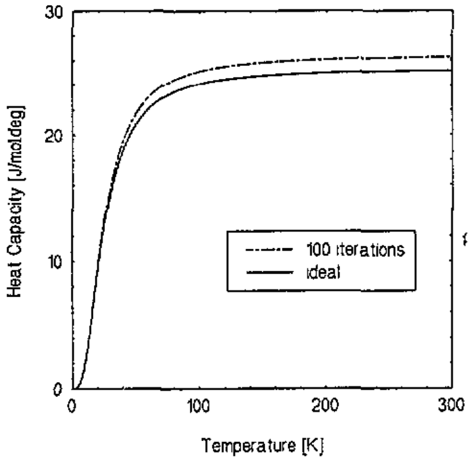

Figure 2. A comparison between the exact and computed specific heat of the Einstein model after 100 iterations. The solid line is the exact form.

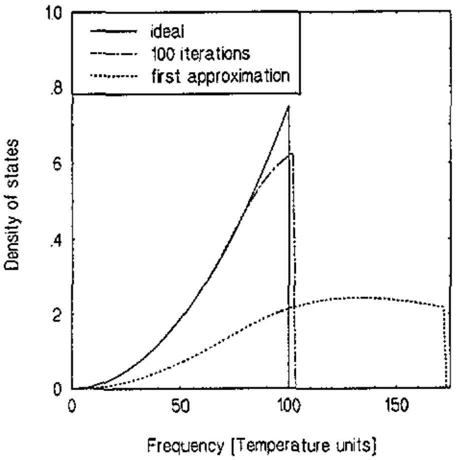

Figure 3. The approximate form of the density of states (chain curve) corresponding to a Debye temperature $\theta_D = 100$ K. The solid line is the exact form while the dashed curve is the very first approximation.

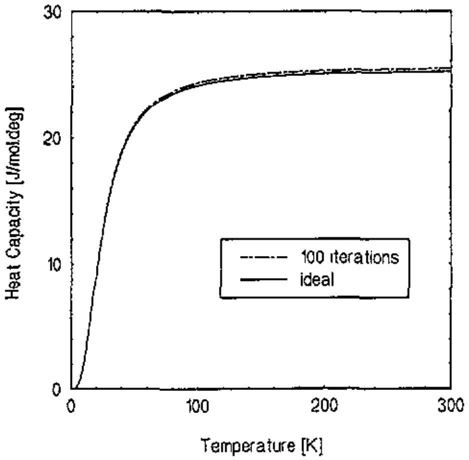

Figure 4. A comparison between the exact and computed specific heat for the Debye model after 100 iterations. The solid line is the exact form.

particular, the number of points used in the integration over x is important. Indeed, decreasing the mesh size increases the convergence of the calculated spectrum. The behaviour of the specific heat is shown in figure 4, in comparison with the exact form.

The main point of this letter is to demonstrate what can be achieved in a very simple fashion—which is very encouraging—and to illustrate the accuracy needed in an experiment to be able to obtain detailed information on the density of states. Finally it should be pointed out that the thermal conductivity could be treated in a very similar fashion. $\kappa(T)$ is given by

$$\kappa(T) = \int_0^\infty \phi(\omega)(\omega/T)^2 g(\omega) \frac{\exp(\omega/T)}{(\exp(\omega/T)-1)^2}\, \mathrm{d}\omega \tag{5}$$

where $\phi(\omega)$ determines the contribution made by the various modes to the total conductivity.

References

Loram J W 1986 *J. Phys. C: Solid State Phys.* **19** 6113