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# Numerical solution of the inverse problem of reconstructing phonon density of states from experimental heat capacity

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ABSTRACT

A method is proposed to numerically solve the inverse problem of reconstructing phonon density of states $g(\omega)$ based on the experimental heat capacity $C(T)$. A feature of this method is that, at the initial step, we calculate the $g(\omega)$ behavior at low and cutoff frequencies. The method is considered for several model objects of varying complexity. The phonon density of states of copper has been calculated and compared with published data. Analysis demonstrates that up to three peaks can be distinguished in $g(\omega)$ with correct description of their shapes. The new method can be used for a widest class of solids provided that very precise data on $C(T)$ in a wide range of low temperatures are available.



## 1. Introduction

The phonon density of states $g(\omega)$ is one of the most important characteristics of a solid. Determination of information on $g(\omega)$ plays a key role in the study of various phenomena in solids. The phonon density of states can be determined using various methods [1–13], with the most important approach based on neutron scattering [1–3]. Information on $g(\omega)$ can also be obtained from theoretical investigations [4–10]. Here the most common is the method of lattice dynamics [4–8]. Various approaches for obtaining information on $g(\omega)$ also exist that include both theoretical and experimental techniques [11–13].

The work [14] for the first time considered an approach related to determination of the phonon density of states for a Bose system from its heat capacity, based on the possible existence of stable solutions to inverse problems [15]. Since then, various methods to solve this problem have been suggested [16–25]. All these solutions share the use of Tikhonov regularizing operators [16–21] or rapidly decaying functions [22–24]. In Ref. [25] the maximum entropy and reverse Monte Carlo methods are applied to the computation of the phonon density of states from heat capacity data. The diversity of approaches to reconstruct density of states $g(\omega)$ from heat capacity demonstrates that a search for simple methods to solve this problem still continues. This is due to the current lack of a method that would allow reconstructing $g(\omega)$ in practice for a wide range of substances.

This work suggests a new approach to determine the phonon density of states from heat capacity data. An important feature of this approach is consideration, at the initial step of the calculation, of $g(\omega)$ in the regions of low and cutoff frequencies.

## 2. The phonon density of states from the heat capacity

The solution of the above problem first of all requires highly accurate experimental data on heat capacity obtained in a wide low-temperature range. The phonon density of states $g(\omega)$ of solids, which characterizes the ground state of a crystal lattice ($T=0$), is related to heat capacity at constant volume $C_V(T)$. Therefore, before attempting to solve the mentioned problem, it is first necessary to correctly and accurately extract the component that is obtained in experiment from heat capacity at constant pressure $C_P(T)$. We shall use the denotation $C(T)\equiv C_V(T)$ further in the text.

The calculation of the phonon density of states using the suggested approach can be divided into three steps. At the first step asymptotic characteristics of $g(\omega)$ are found, i.e., a zero approximation $g_0(\omega)$ is chosen that correctly describes the behavior of $g(\omega)$ at $\omega\to 0$ and $\omega\to\omega_c$ (where $\omega_c$ is cutoff frequency). The choice of $g_0(\omega)$ is made so that it describes well the asymptotic behavior of heat capacity (at $T\to 0$ and $T\to\infty$). At the second step the approximate description of $g(\omega)$ related to the use of the zero approximation $g_0(\omega)$ is improved by a certain redistribution of the number of vibrational modes over frequency. This redistribution of modes is performed iteratively using a method, which, by stepwise

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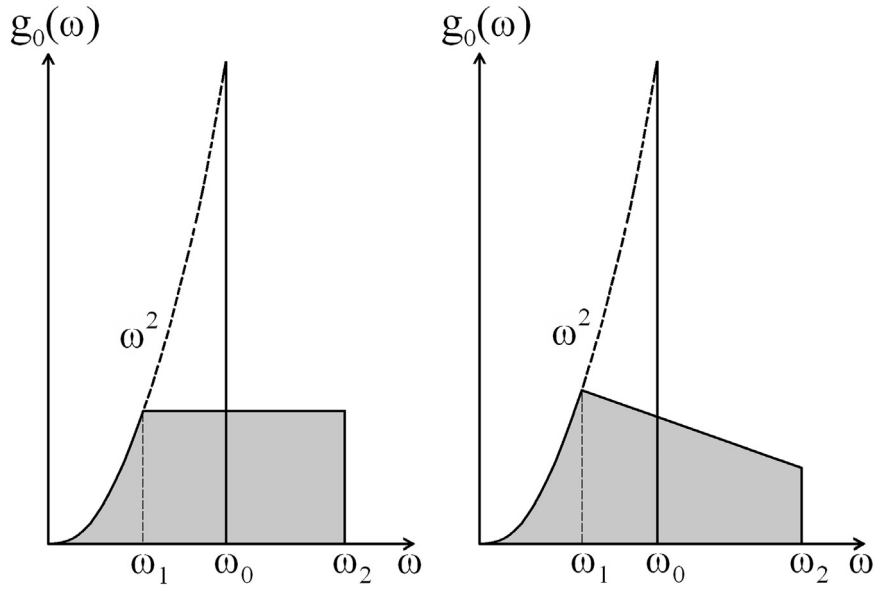


**Fig. 1.** Function $g_0(\omega)$ (painted region) with parameter $\alpha=1$ (left) and $\alpha=½$ (right).

changing the shape of the zero approximation density of states, ultimately results in a decreased difference between the calculated and experimentally obtained heat capacity (using the method of least squares). It should be noted that taking into account the asymptotic behavior of $C(T)$ at high temperatures at the initial step of calculating $g(\omega)$ is an important factor, since it significantly reduces the degree of ill-posedness of the problem being solved, and allows arranging a converging iterative process. At the third step, we calculate the density of states by averaging a number of spectra obtained using various calculation parameters. This reduces considerably the random error in specific solutions. Moreover, these results together with possible implementations can be used to determine the degree of uncertainty of the solution.

### 2.1. Choice of zero approximation

A general relation between the heat capacity at constant volume $C(T)$ of a solid and its phonon density of states $g(\omega)$ is as follows:

$$C(T) = 3Nk_B \int_0^\infty g(\omega)\Psi(\omega, T)d\omega, \tag{1}$$

where

$$\Psi(x) = \frac{x^2e^{-x}}{(1-e^{-x})^2},\ x = \frac{\hbar\omega}{k_BT};$$

and where $\Psi(x)$ – the Einstein function, $N$ – the number of atoms, $k_B$ – the Boltzmann constant, $\hbar$ – the Planck's constant. Function $g(\omega)$ in expression (1) is normalized to unity:

$$\int_0^\infty g(\omega)d\omega = 1. \tag{2}$$

Since vibrational characteristics of a crystal are related only to the lattice component of heat capacity, which amounts to 95% or more of the total heat capacity of solids in the overwhelming majority of situations, accurate information on the temperature dependence of this component is required. Thus, when reconstructing the phonon density of states from heat capacity data, all other heat capacity components, i.e., electronic, anharmonic, magnetic, if present, etc., have to be correctly accounted for and subtracted.

The functional dependence of heat capacity $C(T)$ of solids in the vicinity of zero and at high temperatures is substantially determined by asymptotic characteristics of the phonon density of states $g(\omega)$, which can be determined from heat capacity data at low and high temperatures, respectively.

It is well known that heat capacity of any solid, starting from some sufficiently low temperature $T_0$, obeys the Debye law:

$$\frac{C(T)}{3Nk_B} = \frac{4\pi^4}{5}\left(\frac{T}{\Theta_D(0)}\right)^3, \tag{3}$$

where $\Theta_D(0)=\hbar\omega_0/k_B$, and $\omega_0$ is the cutoff frequency of the Debye model, with the phonon density of states in the low frequency range being proportional to frequency squared $g(\omega)$–$\omega^2$. Therefore, heat capacity experiments below $T_0$ can yield the parameter $\omega_0$, which is related to Debye temperature at zero $\Theta_D(0)$, and thus the dependence $g(\omega)$ at low frequencies.

At high temperatures, where a high temperature expansion of function (1) over even moments of $g(\omega)$ is valid (see, e.g., Ref. [26]), the heat capacity is substantially determined by the cutoff frequency of the phonon spectrum $g(\omega)$. This cutoff frequency is close to the limiting moment of $g(\omega)$ and can be determined using the technique described in Ref. [26,27]. The cutoff frequency can also be estimated from the dependence of the Debye temperature $\Theta_D(T)$ at $T\to\infty$. If the general features (the shape) of $g(\omega)$ are known, the cutoff frequency can be readily and accurately found by varying the scale of the frequency axis for $g(\omega)$. The criterion for choosing the cutoff frequency in this case is the coincidence of the original heat capacity with heat capacity calculated from expression (1) at high temperatures. Thus, the functional behavior of $C(T)$ at high temperatures can be used to find (or estimate) the cutoff frequency of the phonon spectrum.

In view of the above, an approximation of the experimental $C(T)$ curve with its correct asymptotic description (at $T\to0$ and $T\to\infty$) can be achieved using function $g_0(\omega)$ shown in Fig. 1. This function $g_0(\omega)$ is obtained by transforming the Debye spectrum (see Fig. 1, dashed line) with characteristic frequency $\omega_0$ determined from the requirement of correct description of $C(T)$ in the vicinity of zero. Parameter $\omega_2$, having the meaning of the new phonon cutoff frequency, is determined from the requirement of correct asymptotic description of $C(T)$ at high temperatures. Parameter $\omega_1$ provides an upper limit to the frequency range in which function $g_0(\omega)$ is described by the Debye model, and is