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Development of a Debye heat capacity model for vibrational modes with a gap in the density of states

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Abstract
Low-energy vibrational modes that have a gap in the density of states (DOS) have often been observed in heat capacity data in the form of ‘boson’ peaks, but the functions used to model these modes are often inadequate or are not physically meaningful. We have adapted the Debye model to represent these gapped modes and have derived the heat capacity equations for these modes in one, two, and three dimensions. Applying these equations to the low-temperature heat capacity data fitting for a large variety of materials substantially improves the fit quality relative to conventional fits. From the fitting parameters, the underlying DOS were estimated, which we show to be comparable to those reported in the literature. This model expands the methods of theoretical low-temperature heat capacity data analysis and improves the procedure of approximating a material’s DOS from its low-temperature heat capacity.

Keywords: heat capacity, density of states, gap

(Some figures may appear in colour only in the online journal)

1. Introduction

Heat capacity measurements can provide valuable information about the various energetic contributions of a material. Many theories model these contributions by simplifying the energy levels of the system to a mean energy through statistical methods and then converting the simplified energy into a heat capacity [1, 2]. Heat capacity data can then be fit with these theoretical heat capacity functions to extract valuable information about each energetic contribution of a system.

Typical contributions to the heat capacity of solids include vibrational, electronic, magnetic, superconducting, and even lattice vacancies [1–3]. The vibrational contribution dominates the heat capacity at all but low temperatures (below about 10 or 15 K) where the other contributions become observable. These contributions can be determined by fitting the low-temperature heat capacity data to different combinations of these theoretical functions and selecting the best fit, but determining the fit that most correctly models the data and underlying energy contributions is not trivial.

The best fit is determined by its physical meaningfulness, the percent root mean squared deviation (%RMS), and a deviation plot. To be physically meaningful, the fit must be a sum of functions or terms that correspond to the physical properties of the system (e.g. the fit of a nonmagnetic material should not contain a magnetic function), and the parameters should have a reasonable magnitude and be positive (with a few exceptions in the harmonic lattice expansion). The %RMS gives a gross approximation to the quality of the fit especially when comparing different fits of the same data. Generally, the best fit has the lowest %RMS, but fits of low precision data sets may have a deceptively low %RMS if a function is fitting the noise. The deviation plot overcomes this problem by showing how each data point deviates from the fit. Data points will deviate randomly from a good fit but systematically from a bad fit. Each of these aspects should be considered when determining the best fit of heat capacity data and, therefore, the underlying contributions.

We have measured the heat capacities of over thirty samples that should only have vibrational contributions but do not
fit well with conventional vibrational heat capacity models. Each of these materials either have AO₄ tetrahedra or long chains, and their heat capacities exhibit a ‘boson peak’, which is observed as a broad peak in the data plotted as $C/T^3$ versus $\ln T$ and is related to excess low-energy modes. The low-temperature data of these samples could not be reasonably fit using conventional models; therefore, we introduce a new model for the vibrational heat capacity of materials that have excess low-energy modes that also have a gap in the density of states (DOS). Fits to these data show significant improvement in both quality and meaningfulness when using this model. To provide a context for our model, we introduce several of the conventional models, but complete reviews of these theories are available elsewhere [1–4].

1.1. Vibrational heat capacity

The largest contribution to the heat capacity of a solid generally comes from atomic and molecular vibrations, which are represented by the equation [2]:

$$C_V = k \int_0^\infty \frac{(h\nu/kT)^2 e^{-h\nu/kT} g(\nu) \nu d\nu}{(1 - e^{-h\nu/kT})^2}$$  (1)

where $k$ is Boltzmann’s constant, $h$ is Planck’s constant, $\nu$ is the frequency of oscillation, $T$ is temperature, and $g(\nu)$ represents the vibrational DOS. For (1) to have a form that can be compared directly to heat capacity data, $g(\nu)$ must be known, but rather than determining the entire set of individual frequencies exactly, $g(\nu)$ can be generalized and simplified through various models that still yield heat capacity functions that agree reasonably well with experimental data.

Einstein modeled the atoms in a solid as independent harmonic oscillators vibrating at the same frequency $\nu_E$ thereby modeling the DOS as a delta function (shown in figure 1). Using the delta function as $g(\nu)$ in (1) results in the Einstein heat capacity [2]:

$$C_E = 3Nk \left( \frac{\theta_E}{T} \right)^2 \frac{e^{h\nu_E/kT}}{e^{h\nu_E/kT} - 1}^2$$  (2)

where $N$ is the number of atoms, and the Einstein temperature is defined as $\theta_E = h\nu_E/k$. This simple DOS model sometimes provides adequate correlation with experimental heat capacity measurements at high temperatures but fails at low temperatures where it approximates to [1]

$$C_E(T \ll \theta_E) = 3Nk \left( \frac{\theta_E}{T} \right)^2 e^{-\theta_E/T}$$  (3)

Although this model often fails, it has been useful for modeling optical modes [1], and dispersion in acoustic modes [6], while others have used a sum of multiple Einstein functions to model heat capacity data well [7].

Debye modeled the vibrations in a solid as normal mode vibrations of a continuous elastic body, which works well for long wavelength vibrations that do not depend on the detailed atomic character of the solid. For a 3D solid, this results in a DOS that is quadratic with $\nu$ up to a cutoff frequency $\nu_D$ related to the total number of normal modes $3N$ (see figure 1). The Debye heat capacity that results when $g(\nu) \propto \nu^2$ has the form [2]

$$C_D = 9Nk \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^3} dx$$  (4)

where the Debye temperature $\theta_D = h\nu_D/k$, and $x = h\nu/kT$. At low temperatures ($T \ll \theta_D$) this approximates to [1]

$$C_D(T \ll \theta_D) = \frac{12\pi^4}{5} Nk \left( \frac{T}{\theta_D} \right)^3$$  (5)

Debye’s model was the first major step in relating a theoretical heat capacity to experimental data at low temperatures where the heat capacities of many materials were known to have a $T^3$ dependence.

Although Debye’s model fits the experimental heat capacity data of many materials well, it fails for many other materials. These materials have been found to have either a gap in the DOS (non-zero onset of the modes), many modes with frequencies higher than the Debye frequency $\nu_D$, or a DOS that does not have a $\nu^2$ dependence at low frequencies [8, 9].

The harmonic lattice dynamic theory is useful for materials that do not have a $\nu^2$ dependence at low frequencies [4, 10–16]. This theory is similar to the Debye model but includes terms that are an expansion in $\nu^2$, specifically, $g(\nu) = b_2\nu^2 + b_4\nu^4 + b_6\nu^6 + \ldots$. The extra terms produce a low temperature heat capacity expansion of the form [4]:

$$C_{HL} = A_3T^3 + A_4T^5 + A_5T^7 + \ldots$$  (6)

where

$$A_{2n+1} = \frac{\pi h}{k} \left( \frac{k}{\hbar} \right)^{2n+1} B_{2n}b_{2n}$$  (7)

in which $B_{2n}$ are the Bernoulli numbers and the $b_{2n}$ terms are related to the normal mode density and can be approximated. For the first term in (6), $b_2$ has the form [4]

$$b_2 = \frac{9N}{8\pi^3} \left( \frac{\hbar}{k\theta_D} \right)^3$$  (8)

Figure 1. Generic DOS showing Debye, Einstein, and gapped Debye (subject of this paper) models. Also shown are the various characteristic energies.
which, when inserted into (7), yields the low-temperature Debye coefficients [see (5)]. Because the Bernoulli numbers within the coefficients $A_3$ and $A_5$ in (6) are negative, the $T^3$ and $T^5$ terms should be negative, though the heat capacity fits of some metals have been reported to have positive $T^3$ terms [4].

The terms beyond $T^3$ in (6) model the deviations from a Debye crystal in the form of phonon dispersion; whereas, Debye’s model attempts to handle such deviations by imposing a variable Debye temperature [1, 2]. The extra terms also extend the temperature range over which a fit is valid. For data fit below 10 K, only the $T^3$ and $T^5$ terms should be necessary, but a $T^7$ is acceptable when $\theta_D$ is small. Although heat capacity data is often fit to (6) better than the Debye model, the extra information provided about phonon dispersion is ‘rather severely limited’ [4]. The review by Phillips [4] gives an excellent derivation of these equations and compares the various lattice heat capacity models in more detail.

These theories form the foundation for modeling vibrational heat capacity data, but they have been adapted to better model heat capacity data through methods such as applying the Debye model to one and two dimensions [1, 17, 18], which at low temperatures ($T \ll \theta_D$) have the expressions (following the derivation of McQuarrie [2])

\[
C_V(1D) = \pi^2 N k T / \theta_D \\
C_V(2D) = 36 \zeta(3) N k (T / \theta_D)^2
\]

where $\zeta$ represents the Riemann zeta function. For the 1D system, $g(v)$ is a constant value up to the cutoff energy $v_D$, which is proportional to $\theta_D$, and for the 2D system, $g(v)$ is linear up to the cutoff energy. Also, using a sum of Einstein functions is a common alteration that has been applied to better analyze data that has low-energy modes [19–24].

1.2. Low-energy modes and gaps in the DOS

Low-energy modes are caused by phonon scattering from regions of short-range order in the crystal structure and result in the ‘boson peak’ [25]. Boson peaks have been observed most notably in glasses [26–29], but they have also been observed in other materials such as the polymer poly(methyl methacrylate) (PMMA) [30], the semiconductor $\alpha$-Se, $B_2O_3$, $As_2S_3$ [31], and the metallic glass $PdZr$ [32, 33]. Boson peaks also appear in the heat capacity data of biological compounds [34], zeolites [21, 35], and even some negative thermal expansion (NTE) materials [21]. Figure 2 shows the boson peaks of many more materials. The boson peaks in glasses, zeolites, and these NTE materials are believed to arise from coordinated vibrations of $AO_4$ tetrahedra deemed ‘rigid unit modes’ (RUMs) [21, 36–43]. Related investigations have shown that these low-energy modes have peak maxima around 5 meV (58 K) that are dependent on the size of the domain [26, 44, 45].

The energy bands of these modes typically have a gap in the vibrational DOS due to the finite size of the contributing feature [46]. Jura et al [47] noted such a low frequency cutoff or gap in the DOS of 10 nm cube particles. Burton et al [48] performed calculations that also suggest the vibrational modes of small particles have a non-zero energy onset. Savio et al [44] found a gap in the phonon DOS from 0 to 2 meV (23 K) in $TiO_2$ nanoparticles using inelastic neutron scattering (INS), which they attribute to the size of the 5 nm crystallites. Many others have also observed a gap in the DOS because of small particle size [45, 49–51].

Not surprisingly, because of the unconventional nature of these vibrations, conventional models have failed to properly analyze heat capacity data of these materials; however, a model specific to these gapped vibrational modes has never been established. Equations having an exponential dependence on temperature ($B_{gap}T^n e^{-\delta T}$—with many possible values of $n$ related to the particular system) have been derived for magnetic and superconducting systems that have a gap in the DOS [52–60], and we extend these theories to derive low-temperature heat capacity equations for one, two, and three dimensions of a gapped vibrational DOS. Our derived equations provide insight on the short-range, phonon scattering domains in crystals that create boson peaks in the DOS and heat capacity. We have applied these equations to the low temperature heat capacity data fitting of the samples shown in figure 2 and observe marked improvement in both quality and physical meaningfulness of the fits relative to fits without these terms. The fitting parameters of several samples have also been inverted into DOS, which are comparable to measured DOS data published in the literature.

2. Derivation of gapped heat capacities

The derivation of a gapped Debye function at low temperatures is similar to the derivation without the gap, but we now assume $g(v) \propto (v - v_{gap})^2$ where $v_{gap}$ is the offset from zero; therefore, $g(v)$ takes the form (similar to McQuarrie [2])

\[
g(v)dv = \begin{cases} 
0, & v_{gap} > v > v_D' \\
\frac{12\pi V}{v_0} (v - v_{gap})^2 dv, & v_{gap} < v < v_D'
\end{cases}
\]

where $V$ is the volume, $v_0$ is the average velocity of the two transverse waves and one longitudinal wave, and $v_D'$ is the high-end cutoff (where the prime indicates the cutoff of the gapped DOS as opposed to the conventional DOS cutoff $v_D$). The conventional derivation accounts for all 3N vibrational modes in the integral of $g(v)dv$, but the phonons in a band with a gapped DOS do not account for all of these modes; therefore, we will constrain the integral of the gapped $g(v)dv$ to equal $F$, and the remaining modes integrate to a value $G$ such that $F + G = 3N$. This yields the integral

\[
\int_0^\infty g(v)dv = \int_{v_{gap}}^{v_D'} \frac{12\pi V}{v_0} (v - v_{gap})^2 dv \\
= \frac{4\pi V}{v_0^3} (v_D'^3 - 3v_D'^2 v_{gap} + 3v_D' v_{gap}^2 - v_{gap}^3) = F
\]
We can now eliminate the volume and velocity terms to get $g(v)dv$ in terms of the frequencies and $F$ by solving for $v$ and substituting this into (11) producing the equation

$$g(v)dv = \begin{cases} 0, & \nu_{gap} > \nu > \nu_D \\ \frac{3F(\nu - \nu_{gap})^2dv}{(\nu_D^2 - 3\nu_D^2 \nu_{gap} + 3\nu_D \nu_{gap} - \nu_{gap}^2)}, & \nu_{gap} < \nu < \nu_D \end{cases}$$

(12)

This can now be inserted into (1), which yields, with the substitution $x = h\nu/kT$,

$$C_v = \frac{3Fk}{(x_D^3 - 3x_D^2 \nu_{gap} + 3x_D \nu_{gap} - \nu_{gap}^3)} \int_{x_{gap}}^{x_D} \frac{x^2e^x}{(e^x - 1)^2} (x - x_{gap})^2dx$$

(13)

This integral can be evaluated in closed form for low temperatures, where $x_D$ can be assumed to approach infinity ($x_D = hv/kT \approx \infty$), and if we assume $x_{gap}$ is approximately zero. With these assumptions, the integral in (13) evaluates to

$$\frac{4\pi^4}{15} - 2x_{gap} 6\zeta(3) + x_{gap}^2 \frac{\pi^2}{3}$$

By factoring out $4\pi^4/15$ this becomes

$$\frac{4\pi^4}{15} \left[ 1 - \frac{90\zeta(3)}{\pi^4} \left( \frac{x_{gap}}{2} \right) + \frac{5}{\pi^2} \left( \frac{x_{gap}}{2} \right)^2 \right]$$

Because $90\zeta(3)/\pi^4 \approx 1$ and $5/\pi^2 \approx 1/2$, we can use the expansion

$$e^{-x} = 1 - x + \frac{x^2}{2} - \ldots$$

and the integral of the heat capacity expression becomes
Plugging this back into (13) while making the substitutions $x_{gap} = \delta/T$ and $x_0 = \theta_D/T$ produces the heat capacity equation

$$C_V = \frac{4\pi^4 Fk}{5} \left[ 1 - 3 \left( \frac{\delta}{\theta_D} \right) + 3 \left( \frac{\delta}{\theta_D} \right)^2 - \left( \frac{\delta}{\theta_D} \right)^3 \right] \frac{T^3}{\theta_D^3} e^{-\frac{\delta}{\theta_D}}$$

(14)

In line with the previous assumption that $\nu_{gap}$ or $\delta$ is small ($\delta \ll \theta_D$) this becomes

$$C_V = \frac{4\pi^4 Fk}{5} \left( \frac{T}{\theta_D} \right)^3 e^{-\frac{\delta}{\theta_D}}$$

(15)

By setting $\delta = 0$ and $F = 3N$, the original Debye equation for low temperatures [see (5)] is produced.

This derivation is of a 3D Debye equation with a gap in the DOS, but the one and 2D derivations are similar, resulting in the equations:

$$C_V = \frac{\pi^2 Fk}{3} \left( \frac{T}{\theta_D} \right)^2 e^{-\frac{\delta}{\theta_D}}$$

(16)

$$C_V = 12 Fk\zeta(3) \left( \frac{T}{\theta_D} \right)^2 e^{-\frac{\delta}{\theta_D}}$$

(17)

These also produce the conventional Debye heat capacity equations at low temperatures when $\delta = 0$ and $F = 3N$ [see (9) and (10)]. These three equations (15)–(17) can be generalized to the $n$ dimensional expression:

$$C_V = 2 \times 6^{n-1} \zeta(n+1) Fk \left( \frac{T}{\theta_D} \right)^n e^{-\frac{\delta}{\theta_D}}$$

(18)

We note that we have also applied a gapped DOS to the harmonic lattice dynamic theory. The derivation is essentially the same as the gapped Debye derivation but results in the expansion $A_3 T^3 e^{-\delta/T} + A_5 T^5 e^{-\delta/T} + \ldots$. Fits with these extra gapped terms, however, were found to be cumbersome and did not show any significant improvement in quality versus fits with just a gapped $T^3$ (15).

These equations for gapped vibrational DOS (15)–(17) resemble the equations derived for the gapped DOS associated with superconducting and magnetic materials in terms of temperature dependence, but here we have explicitly derived the equations with all parameters defined in terms of constants and physically meaningful variables that can be directly related to the vibrational DOS. Thus, we have made it possible to invert heat capacity data into a meaningful vibrational DOS, but we note that inverting heat capacity data into a DOS is much less quantitative than directly measuring the DOS; nevertheless, heat capacity data can be inverted into a DOS with some degree of accuracy [61, 62].

### 3. Comparison to measured heat capacity data

The low-temperature heat capacity data ($T < 10$ K) of all samples listed in table 1 were fit to two basic functions: one having only conventional contributions and the other having conventional contributions and any necessary gapped terms (15)–(17). These functions have the general expression

$$C_{fit} = \gamma T + A_1 T^3 + A_3 T^5 + A_5 T^7 + A_7 T^9 + B_{gap} T^n e^{-\frac{\delta}{\theta_D}}$$

(19)

where the $\gamma$ term represents lattice vacancies [5], the $A_3$ through $A_7$ terms represent the harmonic lattice expansion [4], and the $B_{gap}$ term represent the bands of excess low-energy modes that have a gap. The dimensionality, given by $n$, was determined by fitting data to (19) using all three dimensions and selecting the fit that had the lowest %RMS and the most random deviation. $B_{gap}$ is zero for the conventional fits but nonzero for the fits with the gapped term. As mentioned in section 1, the $T^9$ harmonic lattice term is not valid for fits below 10 K, but we include it in the conventional fits in order to have the same number of terms as the fits with the gapped term. Even with the excessive terms, the conventional fits are worse than the fits that have a reasonable number of expansion terms but include the gapped term. Table 1 compares the %RMS of the fits both with and without the gapped term, but we will discuss the fitting details of a few representative samples.

#### 3.1. 1D gapped phonons

Several of the samples with boson peaks are polymers that behave as 1D chains. In our recent work on cellulose, we found that a gapped $T^{3/2}$ term substantially improved the low temperature heat capacity fitting [63]. We have revisited this data and have found a 1D gapped term [see (16)] to be more meaningful and produce a better fit. Table 1 gives the %RMS for amorphpous cellulose, but the other cellulose samples had similar improvement in fit quality with the 1D gapped term. Other polymers that we have investigated have also shown a substantial improvement in fit quality and plausibility by adding the 1D gapped term: poly(3-hydroxybutyrate) (P3HB) [23], poly(N-isopropylacrylamide) (PNIPA) [24], PNIPA with poly(sodium acrylate) (PNIPA-SA), and polyurethane (PU) (see table 1).

Stephens et al [30] also observed boson peaks in the heat capacity data of several polymers and suggested three possible causes, the most probable being attributed to 1D motion along the polymer backbone between entanglement points. Vibrations along the polymer backbone would likely have low-energies because the backbone chain is quite large relative to typical molecules allowing for longer wavelength modes; furthermore, a nonzero onset of these modes is understandable since the length of the vibrating backbone is small relative to typical bulk crystals that obey the Debye model.

As part of another investigation, we have measured the heat capacities of several sodalite samples containing ReO$_4^-$, $\Gamma^-$, $\text{Cl}^-$, and SO$_4^{2-}$ ions that exhibit pronounced boson peaks.
The data fitting of these materials greatly benefited by the addition of a 1D gapped term. Table 2 gives the fit parameters and %RMS of the ReO₄ sodalite fits. The %RMS of the fit with the gapped term is an order of magnitude smaller than the fit without the gapped term. The signs of several parameters of the fit without the gapped term are inverted from what they should be (see table 2), and the deviation plot of the conventional fit shows strong systematic error [see figure 3(a)]. Even when adding more terms to the harmonic lattice expansion, the quality of the conventional fit did not improve significantly; therefore, the fit with the gapped term is best with regards to the meaningfulness of the terms, %RMS, and the lack of a systematic deviation of the fit.

These samples are very similar to zeolites in that they are composed of SiO₄ and AlO₄ tetrahedra that form cages [64]; therefore, it is not unreasonable to expect these compounds to have excess low-energy modes caused by the concerted motion of rigid tetrahedra (RUMs) as observed in zeolites [41]. Because sodalites form small cages, having diameters on the order of a few nanometers, vibrations of these domains will have a relatively small minimum wavelength causing a gap in the DOS. The origin of the 1D vibrational character is unknown, but we postulate that the ring and wireframe-like structure of the connected tetrahedra creates pseudo-linear vibrations.

### 3.2. 2D gapped phonons

We have recently investigated eight samples of Al doped TiO₂ to determine the location of the Al³⁺ dopant ions from the low-temperature heat capacities, electron energy-loss spectroscopy (EELS), and x-ray diffraction (XRD) [65, 66]. We have shown that these dopant ions enter the TiO₂ lattice and form small domains of short-range order that resemble a TiAlOₓ glass-like structure.

The five samples with the lowest concentrations of Al³⁺ dopant (5–22 mol% Al) required 2D gapped terms [see (17)] to fit the low-temperature heat capacity data; whereas, the pure TiO₂ and TiO₂ doped with 50 mol% Al did not need the gapped terms. The %RMS and fitting parameters of fits with and without the gapped term are given in table 2 for the sample with 5 mol% Al prepared with the dry-rinse-calcine (DRC) method. Justification for fitting the data of these samples with the gapped term versus conventional fits is similar to the other samples discussed thus far. The %RMS is significantly lower with the gapped term, the deviation is random [see figure 3(b)], and the terms are physically meaningful.

The small regions of the TiAlOₓ structure form in the TiO₂ lattice during crystal growth. We speculate that the synthesis begins with the formation of small TiO₂ clusters having on the order of a hundred atoms. Clusters that form near regions having a high concentration of Al³⁺ (related to the solvent deficient synthesis that creates a slightly inhomogeneous environment on the nanoscale [67, 68]) react with the Al³⁺, which forms thin island-like structures. The TiO₂ structure continues to grow and eventually grows over the Al islands, similar to how a tree grows over a sign nailed to its trunk, creating highly disordered 2D regions of TiAlOₓ within the TiO₂ lattice. These particles retain the TiO₂-like structure as observed with EELS and XRD but have these small glass-like domains that are responsible for the excess low-energy modes similar to RUMs observed in glasses. The gap in the DOS exists in the particles with low concentrations of dopant because the TiAlOₓ domains are small; whereas, at higher dopant concentrations these domains become sufficiently large that their

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<th>%RMS w/o gapped term</th>
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<td>5.48&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.72&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>PNIPA</td>
<td>0.638</td>
<td>2.36&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Zr₆O₈</td>
<td>10.9</td>
<td>9.51&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>PNIPA-SA</td>
<td>1.04</td>
<td>1.87&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PU</td>
<td>1.24</td>
<td>1.45&lt;sup&gt;c,b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Harmonic lattice parameters have incorrect sign.
<sup>b</sup> Number of harmonic lattice parameters is unreasonable.
<sup>c</sup> Two gapped terms used.
Table 2. Fit parameters and %RMS of Na$_8$Al$_6$Si$_6$O$_{24}$(ReO$_4$)$_2$ (Re sodalite), Ti$_{0.95}$Al$_{0.05}$O$_{1.975}$ (TiO$_2$ 5mol% Al), and MFI zeolite based on fits to (19) showing the benefit of fitting the data with a gapped parameter as discussed in the text. Fits on the left include the gapped term where the $n$ in (19) is equal to the dimensionality given with the sample name.

<table>
<thead>
<tr>
<th></th>
<th>Na$_8$Al$_6$Si$<em>6$O$</em>{24}$(ReO$_4$)$_2$—1D</th>
<th>Ti$<em>{0.95}$Al$</em>{0.05}$O$_{1.975}$—2D</th>
<th>MFI zeolite—3D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma J \text{ mol}^{-1} \text{ K}^{-2}$</td>
<td>5.5819 $\times 10^{-4}$</td>
<td>2.2403 $\times 10^{-4}$</td>
<td>5.8107 $\times 10^{-4}$</td>
</tr>
<tr>
<td>$A_1 J \text{ mol}^{-1} \text{ K}^{-4}$</td>
<td>2.6741 $\times 10^{-3}$</td>
<td>1.3499 $\times 10^{-3}$</td>
<td>1.9402 $\times 10^{-4}$</td>
</tr>
<tr>
<td>$A_2 J \text{ mol}^{-1} \text{ K}^{-6}$</td>
<td>$-2.3023 \times 10^{-5}$</td>
<td>2.5513 $\times 10^{-4}$</td>
<td>$-1.6269 \times 10^{-6}$</td>
</tr>
<tr>
<td>$A_3 J \text{ mol}^{-1} \text{ K}^{-8}$</td>
<td>$-9.8407 \times 10^{-7}$</td>
<td>$-6.8482 \times 10^{-9}$</td>
<td>5.3012 $\times 10^{-9}$</td>
</tr>
<tr>
<td>$A_4 J \text{ mol}^{-1} \text{ K}^{-10}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_0 J \text{ mol}^{-1} \text{ K}^{-(n+1)}$</td>
<td>9.6643</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta J \text{ K}^{-1}$</td>
<td>42.993</td>
<td></td>
<td></td>
</tr>
<tr>
<td>%RMS</td>
<td>0.419</td>
<td>4.59</td>
<td>0.329</td>
</tr>
</tbody>
</table>
vibrations can be treated as traditional Debye modes. (See [66] for more details.)

### 3.3. 3D gapped phonons

The other samples with boson peaks shown in figure 2 required a 3D gapped term to fit the data well. Although our original publication of the fresnoites $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and $\text{Sr}_2\text{TiSi}_2\text{O}_8$ used a gapped $T^{3/2}$ term (ferromagnetic) [69], we have found that a gapped $T^3$ term [see (15)] models the data better and is more meaningful since these materials are known to have TiO$_4$ tetrahedra [70]. The heat capacity fitting of Rb hollandite benefits from a gapped $T^3$ term as well; however, the Sr and Cs hollandites appear to have slightly better fits with the 1D gapped $T$ term, though the difference between the 3D gapped $T^3$ and 1D gapped $T$ fits is very small for these samples.

We have also revisited the heat capacity data published by Boero-Goates et al [21] of the negative thermal expansion (NTE) materials ZrW$_2$O$_8$ and ZrMo$_2$O$_8$ and the zeolites BEA, MFI, and FAU using gapped terms rather than the five Debye and Einstein functions originally used to fit each data set. The quality of our fits is comparable to those published in terms of modeling the heat capacity data; however, we will show that our fits are more meaningful with regards to the derived DOS. We note that the FAU zeolite and ZrMo$_2$O$_8$ fits required two gapped $T^3$ parameters which are related to separate contributions. To illustrate the quality of our fits we present the MFI fitting results. The %RMS of the fit with the gapped term is about half that of the fit without the gapped term even when using lattice terms up to $T^9$ (see table 2). The deviation plot [figure 3(c)] shows that the fit with the gapped term is random at all temperatures above 2K; whereas, the conventional fit is systematic at all temperatures.

The fits of the other zeolites and NTE samples improve similarly by adding the gapped term, but we note that the %RMS of FAU and ZrW$_2$O$_8$ are slightly better for the conventional fits (see table 1). We believe this is because the conventional fit is fitting the noise below 1K as a result of the unrealistically large number of lattice expansion terms. The deviation plots of these samples show that the gapped fits are less systematic than the conventional fits, and the $T^3$ term of the ZrW$_2$O$_8$ conventional fit is positive and therefore not physical; therefore, the fits of these samples using the gapped term are still better than conventional fits.

Low frequency modes in these NTE materials and zeolites have been related to tetrahedra and RUMs [21, 35, 71–75].

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**Figure 3.** (a) Deviation plots of Na$_8$Al$_6$Si$_6$O$_{24}$ (ReO$_4$)$_2$ (Re-sodalite) comparing fit quality between fits with (red circles) and without (blue triangles) a gapped term in the low-temperature heat capacity fitting. (b) Deviation plots of TiO$_2$ doped with 5 mol% Al using DRC method comparing fit quality between fits with (red circles) and without (blue triangles) a gapped term in the low-temperature heat capacity fitting. (c) Deviation plots of zeolite MFI comparing fit quality between fits with (red circles) and without (blue triangles) a gapped term in the low-temperature heat capacity fitting.
and because these span the volume of the crystal, it is reasonable that the gapped term is 3D. The FAU zeolite is composed of tetrahedra that make secondary building units (primarily α-cages and β-cages), and the different characteristics of these units give rise to different vibrational bands [35]. We believe these distinct bands create the need for two gapped terms.

We note that fitting the heat capacity data of complex materials such as these is much easier when more is known about the materials. By knowing that many of these samples have tetrahedra, we could deduce the presence of low-energy modes; likewise, we knew that FAU and ZrMo2O8 have more than one excess, low-energy contribution to the DOS from the work of Greaves et al [35] and Mittal et al [73].

4. Derived DOS compared to measured DOS

Because the fitting parameters have been measured in terms of values related to the DOS, we can further verify the validity of these fits by converting the parameters into a DOS that can be compared to the measured DOS. Recall that δ in (15)–(17) is proportional to the low-energy gap in the DOS $\nu_{\text{gap}}$, while $\theta_D$ is related to the energy cutoff $\nu_D$ [see (12)]. Because the fitting coefficient that contains $\theta_D$ also contains $F$, and $F$ is not necessarily known, we approximated $F$ either from the number of tetrahedra or simply from the value that results in a realistic DOS. Table 3 gives the values of $F$ used as well as the derived DOS parameters $\nu_{\text{gap}}$ and $\nu_D$ of all samples in table 1. We also note that several of the values of $\delta$ given in table 3 are somewhat larger than permissible by our assumption that $\delta$ is small, but we consider these values to be qualitatively acceptable, nonetheless.

The DOS data of several of the materials discussed herein have been measured with INS. Muller et al [76] showed that cellulose has low-energy modes that are nearly a constant with energy such as would be expected for 1D phonons. The energies of the excess modes derived from our gapped fit of the amorphous cellulose data (table 3) correspond to the energies in the measured DOS.

The DOS of ZrMo2O8 and ZrW2O8 have been measured by Mittal et al [73–75]. Figures (a) and (b) show their data as well the DOS derived from our heat capacity data fitting. As can be seen, the derived DOS grossly simplifies the actual DOS, but many of the most prominent features are identifiable. For example, the magnitude of the derived low energy peak in the ZrW2O8 data [figure 4(b)] is rather large compared to the actual data, but the peak maximum corresponds to the peak from the INS data. Also included in figure 4(b) is the DOS derived from the fitting method of Boerio-Goates et al [21] which models the heat capacity data well, but the derived DOS does not appear to match any of the features of the actual DOS.

Greaves et al [35] measured the DOS of zeolite Y, Na56Al56Si136O384, which has the same structure as FAU but with Al3+ and Na+ ions replacing some of the Si4+ ions. For the DOS of FAU to be comparable to the DOS of zeolite Y, it was scaled from SiO2 to Na56Al56Si136O384 using a factor of 192 (number of equivalent SiO2 in Na56Al56Si136O384). Figure 4(c)
shows the measured data with our derived DOS showing that our DOS is qualitatively similar to the measured DOS despite having a slightly different composition.

5. Conclusions

We have derived gapped heat capacity functions in one, two, and three dimensions from DOS with a non-zero onset of vibrational modes and have shown that adding these functions to the low-temperature heat capacity data fitting greatly improves fit quality for samples that have excess low-energy modes. From the fitting parameters, we have derived meaningful DOS that are comparable to the measured DOS of several materials. This study provides a physically meaningful method for analyzing low-temperature heat capacity data of materials that have an excess of low-energy modes with a gap in the DOS that also yields a crude approximation of the DOS.

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