Article
A Hill Equation for Solid Specific Heat Capacity Calculation
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Abstract: The Hill Equation and Hill Coefficient have been used extensively in biochemistry for the description of noncovalent binding. Previously, the Hill Coefficient was correlated with the Gibbs free energy, which suggests that the Hill Equation might be extensible to covalent binding phenomena. To evaluate this possibility, the Hill Equation was compared to the Debye Model and Einstein Solid in the calculation of heat capacity for 53 covalent solids, which included stainless steels and refractory ceramics. Hill Equation specific heat predictions showed a standard error of 0.37 J/(mole·Kelvin), whereas errors from the Debye Model and Einstein Solid were higher at 0.45 J/(mole·Kelvin) and 0.81 J/(mole·Kelvin), respectively. Furthermore, the Hill Equation is computationally efficient, a feature that can accelerate industrial chemical process simulation(s). Given its speed, simplicity, and accuracy, the Hill Equation likely offers an alternative means of specific heat calculation in chemical process models.

Keywords: heat capacity; specific heat; technical ceramics; stainless steel; semi-empirical equations

1. Introduction
Chemical engineers commonly rely on computationally efficient and readily implemented thermodynamic expressions to simulate, design, scale, and control process equipment [1–5]. Thus, although complex ab initio methods are now available for accurate thermodynamic predictions, especially for solid specific heat, classical thermodynamic models continue to pervade the process industries [4–12]. Notably, despite the current availability of both ab initio and classical thermodynamic methods for solid specific heat estimation, thermodynamic databanks still recommend empirical piecewise polynomials for heat capacity calculation [13,14]. These empirical models are likely inaccurate outside their source data and they require the implementation of ungainly lookup tables and case structures in process simulations. To find a feasible alternative for use in industrial process models we explored the accuracy of classical thermodynamic expressions for the prediction of heat capacity across 53 inorganic compounds and technical solids, which included stainless steels and refractory ceramics. Specifically, heat capacity predictions from two canonical equations, the Debye Model and Einstein Solid, were compared to results from the Hill Equation of biochemistry and an empirical Multilinear Model [15–17]. Although use of the Hill Equation in this role was novel, evidence herein shows that this facile mathematical expression can outperform alternatives. Thus, the Hill Equation presents a possible new tool for specific heat determination in industrial process simulation.

The mathematical description of solid heat capacity must capture temperature effects, which are sigmoidal. Figure 1 shows typical changes in specific heat across temperatures for a generic solid [18]. At absolute zero, solid heat capacity vanishes as molecular motion freezes. Near melting a maximal specific heat \(C_v^{\text{max}}\) is achieved as all aspects of a solid lattice are excited. If molecules within a solid are viewed as simple harmonic...
oscillators, the Dulong–Petit limit predicts \( C_v^{\text{max}} = 3R \) at incipient melting [19]. Classical expressions for heat capacity calculation respect this limit, although varied vibrational modes (phonons) and electronic effects within a solid lead to departures from Dulong and Petits’ theory [15,16,18].

\[
\frac{C_v(T)}{3R} = \frac{T^n}{K + T^n}
\]

where \( R \) is the gas constant, \( 3R \) is the maximum heat capacity for a classical three-dimensional solid lattice (Figure 1), \( T \) is absolute temperature, \( K \) is the dissociation constant, and \( n \) is the Hill Coefficient (variable definitions are available in Appendix A). Prior derivations that established an equivalence between intensive properties in molecular aggregates support the replacement of molar concentration, which is usually observed within the Hill Equation, by temperature [21,22]. For example, a similar substitution is seen across the Hill Equation and Langmuir isotherm, which share an identical functional form, but depend on molar concentration or pressure, respectively.

The Hill Equation, as posed, satisfies the idealized Dulong–Petit limit [19]:

\[
\lim_{T \to 0} C_v(T) = 3R
\]

For departures from ideality due to electronic, magnetic, and cooperative modes of thermal energy, the constant \( 3R \) was allowed to vary:

\[
C_v(T) = C_v^{\text{max}} \frac{T^n}{K + T^n}
\]

Figure 1. The general characteristics of temperature-dependent specific heat in solids. At absolute zero the constant-volume heat capacity curve, \( C_v(T) \), originates and grows monotonically through the Debye Temperature (\( T_D \)). A solid is often characterized by its Debye Temperature where its highest frequency vibrations are presumably excited [18]. The constant-volume heat capacity curve terminates when a solid melts at its temperature of fusion (\( T_{\text{fusion}} \)). The solid’s maximal constant-volume specific heat is observed (\( C_v^{\text{max}} \)) at this location. Constant-pressure heat capacity, not constant-volume heat capacity, is usually engineering-relevant [20]. As shown, the constant-pressure curve \( C_p(T) \) consistently exceeds the constant-volume curve \( C_v(T) \).

The extremum and sigmoidal behavior shown in Figure 1 are hallmarks of expressions that successfully calculate constant-volume specific heat. We hypothesized that the Hill Equation from biochemistry could capture these features. To adapt this equation for specific heat, concentration within the Hill Equation was substituted with temperature:
Thus, three parameters fit the Hill Equation to specific heat data: \(C_{v_{\text{max}}}, K,\) and \(n\) (Appendix A). In solid specific heat estimation, it was expected that \(n\) would always exceed unity \((n > 1)\), which is indicative of cooperative binding in noncovalent systems [23].

The Hill Equation was compared to the Einstein Solid, which is derived from the microcanonical ensemble [16]:

\[
\frac{C_v(T)}{3R} = \left(\frac{\epsilon}{RT}\right)^2 \frac{e^{\epsilon/(RT)}}{\left(e^{\epsilon/(RT)} - 1\right)^2}
\] (4)

where \(\epsilon\) is a quantitized energy of solid vibration and all other variables are described in Appendix A. For departures from ideality due to electronic, magnetic, and cooperative modes of thermal energy, the constant \(3R\) was allowed to vary:

\[
C_v(T) = C_{v_{\text{max}}^{\text{}}\left(\frac{\epsilon}{RT}\right)^2 \frac{e^{\epsilon/(RT)}}{\left(e^{\epsilon/(RT)} - 1\right)^2}
\] (5)

Thus, two parameters fit the Einstein Solid to specific heat data: \(C_{v_{\text{max}}}\) and \(\epsilon\).

The Einstein Solid often underestimates low-temperature specific heat \((<100\, \text{K})\) [24], which prompted development of the Debye Model [15]:

\[
\frac{C_v(T)}{3R} = 3\left(\frac{T}{T_D}\right)^3 \frac{T_D/T}{0} - \frac{x^4e^x}{(e^x - 1)^2} dx
\] (6)

where \(T_D\) is the Debye temperature, indicative of the highest energy frequency supported by the solid lattice, and all other variables are as previously described. For departures from ideality due to electronic, magnetic, and cooperative modes of thermal energy the constant \(3R\) was allowed to vary:

\[
C_v(T) = C_{v_{\text{max}}}3\left(\frac{T}{T_D}\right)^3 \frac{T_D/T}{0} - \frac{x^4e^x}{(e^x - 1)^2} dx
\] (7)

Thus, two parameters fit the Debye Model to specific heat data: \(C_{v_{\text{max}}}\) and \(T_D\).

Typically, constant-pressure specific heat, not constant-volume specific heat, is engineering relevant (Figure 1). The two quantities are related as follows [20]:

\[
C_p(T) = C_v(T) + \alpha^2(T)V(T)K_T(T)T
\] (8)

where \(\alpha\) is the coefficient of isobaric thermal expansion, \(V\) is the mole volume, and \(K_T\) is the isothermal bulk modulus (Appendix A). As has been pursued previously, the last term of Equation (8) was approximated as a linear function with slope \(m\) [25]:

\[
C_p(T) = C_v(T) + mT
\] (9)

In all cases, slope \(m\) provided an additional variable for fitting specific heat data.

The Hill Equation, Einstein Solid, and Debye model were compared to an empirical model, termed the Multilinear Model, for heat capacity calculation [17]. The Multilinear Model was shown to be superior to simple polynomial fits for a wide range of solids [17]. It features four fitted parameters: \(a, b, c,\) and \(d\):

\[
C_p(T) = aT^b e^{cT} d^{dT}
\] (10)

As described in the Results, each specific heat equation was fit to the same dataset drawn from 53 covalent solids. Therein, the Hill Equation performed favorably when compared to alternatives. The Discussion attempts to explain the Hill Equation’s applicability...
to specific heat calculation, which may have a fundamental basis in theory. However, at this time the expression is, at most, potentially a semi-empirical model for specific heat calculation.

2. Materials and Methods

Presumably, only accurate parameter estimates for the Hill Equation, Einstein Solid, Debye Model, and Multilinear model match these equations to experimental data. To assess heat capacity prediction by each formula, parameters were fit to data for 53 inorganic solids, alloys, and technical ceramics from information in literature publications and the NIST and DIPPR databanks [13,14,26–45]. Fitted parameters were discovered through minimization of the L2 norm between model predictions and experimental heat capacity results from temperatures that spanned absolute zero to 3000 Kelvin. Specifically, MATLAB’s fmincon algorithm was used to find Einstein Solid, Debye Model, and Hill Equation parameters described in the Introduction. To initialize parameter estimates, facets of the specific heat formulas were exploited. For example, for all formulae \( m \) were approximated at high temperature prior to numerical optimization:

\[
\lim_{T \to \infty} \frac{dC_v}{dT} \approx m
\]

(11)

Similarly, high-temperature data provided an estimate of \( C_v^{\text{max}} \):

\[
\lim_{T \to \infty} C_v \approx C_v^{\text{max}}
\]

(12)

The ultimate values of parameter estimates for all models are available in the publication Supplement (Table S1). Multilinear Model parameters were fit by linear regression as previously described [17].

3. Results

Experimental data for 53 inorganic and technical solids were mined from thermochemical tables and literature reports (Table S1, https://zenodo.org/record/6779574, accessed on 11 July 2022), data which were fit to the Debye Model, Einstein Solid, Hill Equation, and Multilinear Model. Table S1 lists the results and Figure 2 plots experimental heat capacity against calculated heat capacity for all 53 solids. The correspondence between experiment and prediction appeared strong for the putative fundamental models, especially the Hill Equation, but was variable for the empirical Multilinear Model (Figure 2). Figures 3 and 4 show example fits for technical metals and refractory ceramics. Generally, the Einstein Solid underestimated heat capacity at low temperatures (<100 K), as has been previously observed, while the Hill Equation overestimated specific heat in this range [24]. To further parse model fidelity across the temperature range, absolute relative errors were evaluated:

\[
ARE(T_i) = \left| \frac{C_p(T_i) - C_{p,\text{exp}}(T_i)}{C_{p,\text{exp}}(T_i)} \right|
\]

(13)

where \( C_{p,\text{exp}} \) is the experimentally measured specific heat at temperature \( T_i \). The average absolute error was determined for each solid over \( T \leq 100 \text{ K} \) and \( T > 100 \text{ K} \). Figure 5 shows the results, wherein the Debye Model best minimized relative errors below 100 K (Figure 5A). However, the Hill Equation best minimized errors at temperatures above 100 K (Figure 5C). Furthermore, the Hill Equation also showed the lowest standard error of the estimate across the entire temperature range (Figure 5B), where the standard estimate error was:

\[
SE = \sqrt{\frac{\sum_{i=1}^{k} (C_p(T_i) - C_{p,\text{exp}}(T_i))^2}{k-l}}
\]

(14)
for \( k \) experimental observations and \( l \) fitted parameters [17]. The Hill Equation showed an average standard error of 0.37 J/(mole·Kelvin) across all the 53 examined solids. Average standard error of the Debye Model and Einstein Solid predictions were 0.45 J/(mole·Kelvin) and 0.81 J/(mole·Kelvin), respectively. Figure 6 shows that the correlation coefficient, \( R^2 \), was strong for all the putative fundamental models, but was inconsistent for the empirical Multilinear Model. Overall, the Hill Equation outperformed alternative representations of heat capacity at temperatures above 100 K and was highly accurate across all temperatures.

Figure 2. Accuracy of the specific heat models, where a 1:1 correspondence reflects accurate model predictions. For comparative purposes, predicted specific heat \( (C_p) \) and experimental specific heat \( (C_{p,exp}) \) were normalized by specific heat at each solid’s Debye Temperature, \( C_p(T_D) \), which yields unitless graphs. (A) Debye Model training data (x-axis) versus Debye Model predictions (y-axis) across all 53 solids. (B) Hill Equation training data (x-axis) versus Hill Equation predictions (y-axis) across all 53 solids. (C) Einstein Solid training data (x-axis) versus Einstein Solid predictions (y-axis) across all 53 solids. (D) Multilinear Model training data (x-axis) versus Multilinear Model predictions (y-axis) across all 53 solids.
Prior work has shown a correlation between the Hill coefficient and Gibbs free energy of interaction in noncovalent binding [23]. Under Richard’s Rule, the standard enthalpy of fusion underpins Gibb’s free energy in covalent solid binding [18]. A correlation between the enthalpy of fusion and the Hill Coefficient could imply a fundamental basis for use of the Hill Equation in solid specific heat estimation. To explore this possibility, the discovered Hill Coefficients were plotted against the enthalpy of fusion for alkaline metals and alkaline halides. Figure 6 shows the results. A linear trend was observed within the alkaline metals and alkaline halide groups on the periodic table, although not across alkaline metals and alkaline halides generally.
Figure 4. Model predictions for the specific heat of example technical and refractory ceramics.

Prior work has shown a correlation between the Hill coefficient and Gibbs free energy of interaction in noncovalent binding [23]. Under Richard's Rule, the standard enthalpy of fusion underpins Gibb's free energy in covalent solid binding [18]. A correlation between the enthalpy of fusion and the Hill Coefficient could imply a fundamental basis for use of the Hill Equation in solid specific heat estimation. To explore this possibility, the discovered Hill Coefficients were plotted against the enthalpy of fusion for alkaline metals and alkaline halides. Figure 6 shows the results. A linear trend was observed within the alkaline metals and alkaline halide groups on the periodic table, although not across alkaline metals and alkaline halides generally.

4. Discussion

The Hill Equation was fit to experimental heat capacity data for 53 inorganic compounds and technical solids. At common chemical process temperatures (>100 K [46]), the Hill Equation predicted specific heat capacity more accurately than the Debye Model, the Einstein Solid, and the Multilinear Model. At lower temperatures the Debye Model proved superior. However, the Debye Model requires the evaluation of a numerical integral, which can slow process simulation. Table 1 shows that use of the Debye Model...
where a linear correlation is evident between the Hill Coefficient and heat of fusion. The Debye Model proved superior. However, the Debye Model requires the evaluation of a numerical integral, which can slow process simulation. Table 1 shows that use of the Debye Model quintuples computation time relative to the Hill Equation. Such time inflation can add additional computational burden to industrial-process engineering problems, which are already resource-intensive, frequently time-sensitive, and often NP-hard [47–49]. Thus, applications for the analytic Hill Equation likely exist at elevated temperatures whenever computational efficiency is essential.

Table 1. Relative heat capacity computation time for compiled C code on an Intel i5-4690K CPU. Debye integration was by the Trapezoidal Rule with 1 Kelvin granularity.

<table>
<thead>
<tr>
<th></th>
<th>Debye</th>
<th>Einstein</th>
<th>Hill</th>
<th>Multi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>5.06</td>
<td>0.96</td>
<td>1</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Whether the Hill Equation for heat capacity harbors a fundamental basis in physics and statistical thermodynamics is unclear. Prior authors showed a correlation between the Hill Coefficient and Gibb’s free energy when molecules noncovalently interact [23]. Based on this result, the energy of covalent fusion likely also correlates with the Hill Coefficient [18]. Figure 6 shows that this proves true within groups on the periodic table, where a linear correlation is evident between the Hill Coefficient and heat of fusion. The Hill Coefficient reflects cooperativity in binding phenomena, where large $n$ indicates that multiple molecules must simultaneously coordinate to bind and relax [23]. Thus, $n$ may reflect the degrees of freedom that coordinate and/or excite a solid’s unit cell. Although nontraditional, this perspective allows a derivation that supports Hill Equation use for solid
specific heat calculation (Appendix B). Additionally, the Hill Equation is closely related to the logistic equation [30]. Thus, the Hill Equation for heat capacity might be reconciled by a statistical and/or populations view of solid lattice behavior. However, currently a rigorous derivation for the Hill Equation in specific heat calculation is lacking. Based on current evidence the Hill Equation represents, at most, an analytic and efficient expression for heat capacity calculation that is likely useful in chemical-process simulation.

Figure 6. Enthalpy of fusion and Hill Coefficient correlations for the alkali metals and alkali halides. Fusion energies were taken from the CRC Handbook [51].

5. Conclusions

Four different specific heat equations were fit to the same dataset drawn from 53 covalent solids. Therein, the Hill Equation performed favorably when compared to established alternatives, especially above 100 Kelvin. Below 100 Kelvin, the Debye Model remains the best descriptor of solid heat capacity, but requires the evaluation of a numerical integral. Conversely, the simpler Hill Equation calculates substantially faster than Debye computations (Table 1), but remains highly accurate. In heat capacity prediction, Hill Equation standard error of the estimate (0.37 J-kelvin⁻¹-mole⁻¹) was similar to the Debye Equation (0.45 J-kelvin⁻¹-mole⁻¹). Thus, the Hill Equation is likely useful as a fast and reliable expression for heat capacity calculation in applied industrial-process simulations. However, without a rigorous theoretical basis, currently the Hill Equation is, at most, potentially a semi-empirical model of specific heat.

Supplementary Materials: The following supporting information can be downloaded at https://zenodo.org/record/6779574 (accessed on 11 July 2022).

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Appendix A

Variable definitions used in equations herein:
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Kelvin⁻¹</td>
<td>coefficient of isobaric thermal expansion</td>
</tr>
<tr>
<td>a</td>
<td></td>
<td>fitted parameter of the empirical multilinear model</td>
</tr>
<tr>
<td>ARE</td>
<td>unitless</td>
<td>absolute relative error</td>
</tr>
<tr>
<td>b</td>
<td></td>
<td>fitted parameter of the empirical multilinear model</td>
</tr>
<tr>
<td>c</td>
<td></td>
<td>fitted parameter of the empirical multilinear model</td>
</tr>
<tr>
<td>Cₚ(T)</td>
<td>J/(mole·Kelvin)</td>
<td>constant pressure temperature dependent solid heat capacity</td>
</tr>
<tr>
<td>Cₚ,exp(Tᵢ)</td>
<td>J/(mole·Kelvin)</td>
<td>specific heat observed in experiment at temperature Tᵢ</td>
</tr>
<tr>
<td>Cᵥₓₐₜ</td>
<td>J/(mole·Kelvin)</td>
<td>constant-volume solid heat capacity as near melting</td>
</tr>
<tr>
<td>Cᵥ(T)</td>
<td>J/(mole·Kelvin)</td>
<td>temperature-dependent solid heat capacity</td>
</tr>
<tr>
<td>d</td>
<td></td>
<td>fitted parameter of the empirical multilinear model</td>
</tr>
<tr>
<td>D</td>
<td>[Joules]ⁿ</td>
<td>deabsorption constant</td>
</tr>
<tr>
<td>ε</td>
<td>Joules/mole</td>
<td>quantitized energy level within the Einstein Solid</td>
</tr>
<tr>
<td>k</td>
<td>integer</td>
<td>number of datapoints</td>
</tr>
<tr>
<td>kᵦ</td>
<td>Joules/Kelvin</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
<td>dissociation constant</td>
</tr>
<tr>
<td>Kᵦ</td>
<td>Pascals</td>
<td>isothermal bulk modulus</td>
</tr>
<tr>
<td>l</td>
<td>integer</td>
<td>number of fitted parameters in a given heat capacity model</td>
</tr>
<tr>
<td>m</td>
<td>J/(mole·Kelvin²)</td>
<td>fitted slope</td>
</tr>
<tr>
<td>n</td>
<td>unitless</td>
<td>Hill Coefficient</td>
</tr>
<tr>
<td>Q</td>
<td>unitless</td>
<td>partition function</td>
</tr>
<tr>
<td>R</td>
<td>J/(mole·Kelvin)</td>
<td>gas constant</td>
</tr>
<tr>
<td>T</td>
<td>Kelvin</td>
<td>absolute temperature</td>
</tr>
<tr>
<td>Tᵦ</td>
<td>Kelvin</td>
<td>Debye temperature</td>
</tr>
<tr>
<td>Tₛᵦ</td>
<td>Kelvin</td>
<td>Temperature of solid fusion (phase change)</td>
</tr>
<tr>
<td>Tᵢ</td>
<td>Kelvin</td>
<td>The ith temperature in an experimental dataset</td>
</tr>
<tr>
<td>U</td>
<td>Joules/mole</td>
<td>internal energy</td>
</tr>
<tr>
<td>V(T)</td>
<td>m³/mole</td>
<td>temperature-dependent mole volume</td>
</tr>
<tr>
<td>SE</td>
<td>J/(mole·Kelvin)</td>
<td>standard error of the estimate</td>
</tr>
</tbody>
</table>

**Appendix B**

A basic derivation for specific heat from the Hill Equation borrows liberally from kinetic theory, statistical thermodynamics, and continuum mechanics. Within the context of kinetic theory, the Hill Coefficient $n$ can be viewed as degrees of freedom for the equipartition of energy that excites a solid’s unit cell:

$$n \frac{kᵦT}{2}$$

(A1)

where $kᵦ$ is the Boltzmann Constant and $T$ is absolute temperature. For simplicity, we consider the energy needed to excite two unit cells, the minimal realization of a solid:

$$nkᵦT$$

(A2)
This energy can be absorbed or released by the solid C:

\[ n(k_B T) + C \leftrightarrow (k_B T)_n C \]  

(A3)

Within a continuum solid this energetic equilibrium can be summarized by a deabsorption coefficient:

\[ D = \frac{[C][k_B T]^n}{[(k_B T)_n C]} \]  

(A4)

The sum of states within the continuum solid is partitioned between excited and relaxed sites:

\[ [C]Q = [C] + [(k_B T)_n C] = [C]\left(1 + \frac{[k_B T]^n}{D}\right) \]  

(A5)

where Q is a partition function. This interpretation of the partition function Q, sometimes called the “binding polynomial,” aligns with established published analysis [52]:

\[ Q = 1 + \frac{(k_B T)_n^D}{D} \]  

(A6)

It can be used within the definition of internal energy at constant volume from statistical thermodynamics:

\[ U = k_B T^2 \frac{\partial \ln \{Q\}}{\partial T} \]  

(A7)

where the temperature derivative of \( U \) gives specific heat:

\[ C_v = \frac{\partial U}{\partial T} = 2k_B T \frac{\partial \ln \{Q\}}{\partial T} + k_B T^2 \frac{\partial}{\partial T} \left( \frac{\partial \ln \{Q\}}{\partial T} \right) \]  

(A8)

If the rightmost higher derivative is considered negligible, Equation (A8) simplifies:

\[ C_v \approx 2k_B T \frac{\partial \ln \{Q\}}{\partial T} \]  

(A9)

The Hill Equation results when partition function Q (Equation (A6)) is subjected to the approximate derivative for \( C_v \) (Equation (A9)):

\[ C_v = 2k_B T \frac{\partial \ln \{1 + (k_B T)_n^D\}}{\partial T} = \frac{2nk_B(k_B T)_n^D}{D + (k_B T)_n^D} \]  

(A10)

Equation (A10) is from an extensive analysis based on a minimal solid composed of two-unit cells. The intensive heat capacity of a single-unit cell is presumably half:

\[ C_v = \frac{nk_B(k_B T)_n^D}{D + (k_B T)_n^D} \]  

(A11)

Multiplication by Avogadro’s number gives:

\[ C_v = \frac{nR(k_B T)_n^D}{D + (k_B T)_n^D} \]  

(A12)

Finally, rearrangement gives:

\[ C_v = \frac{nRT_n^D}{D/k_B^D + T_n^D} \]  

(A13)
where \( D/k^n = K \) and this division lends the dissociation constant units of Kelvin\(^n\). The postulated Hill Equation for heat capacity calculation (Equation (1)) arises for \( n = 3 \) degrees of freedom:

\[
C_v = \frac{3RT^n}{K + T^n}
\]  

(A14)

This derivation for the Hill Equation in specific heat is speculative. However, conceptually it provides some justification for the Hill Equation in this role. A more rigorous derivation is likely needed to truly rationalize the Hill Equation's use for solid heat capacity.

References