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Alternative Approach to Teach Entropy and Einstein Temperature in Solids

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ABSTRACT

Purpose of the study: This study aims to develop an alternative theoretical approach for describing entropy and Einstein temperature in solids. The proposed framework seeks to provide a simpler and more consistent understanding of the thermal behavior of solids while offering new insights into their thermodynamic properties.

Methodology: This study employed a theoretical and analytical research method based on the Einstein model of solids and classical thermodynamics. Mathematical derivations and analytical calculations were used to develop the proposed approach. No experimental tools, survey, statistical analysis, or commercial software were used. Standard mathematical notation and symbolic analysis were applied.

Main Findings: The proposed approach produced an alternative expression for entropy and a revised definition of Einstein temperature for solids. The derived relations were mathematically consistent with thermodynamic principles, simplified the description of thermal behavior, and provided a unified framework for analyzing entropy and characteristic temperature in solid-state systems.

Novelty/Originality of this study: This study introduces a new theoretical formulation of entropy and an alternative definition of Einstein temperature for solids. The proposed framework simplifies conventional thermodynamic treatment, offers a more coherent interpretation of thermal properties, and expands the theoretical understanding of solid-state thermodynamics by providing an alternative perspective to existing models.

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1. INTRODUCTION

Entropy is one of the fundamental concepts of thermodynamics because it governs the direction of spontaneous processes and provides a quantitative measure of energy dispersal within physical systems. In solid-state physics, entropy plays a central role in understanding heat capacity, free energy, thermal stability, and phase transformations through the collective vibrations of atoms in crystalline lattices.

Entropy was originally introduced more than one and a half century ago in order to define efficiency for thermodynamic systems, specifically for Carnot engines [1]. Although the original formulation was simple, the evolution of the concept has been problematic for the majority of physicists and indeed for scientists from other disciplines [2]-[4]. Entropy has historically been the subject of various reconstructions and interpretations, making

it very confusing and difficult to understand, implement, and interpret. In 1876, the statistical formulation of entropy formulated by Boltzmann, initiated a direct link between entropy and the concept of microstates in a physical system [5]. In 1902, Gibbs defined the entropy of a macroscopic classical system as a function of a probability distribution over phase space [6]. Later, Hartley proposed that the amount of information associated with any finite set of entities could be understood as a function of the set's size and suggested an alternative definition [7]. In 1932, the concept of quantum entropy was initially defined by von Neumann in terms of the eigenvalues of the density matrix, sixteen years before Shannon entropy [8]. Later Shannon proposed the notion of entropy to measure how the information within a signal can be quantified with absolute precision as the amount of unexpected data contained in the message [9].

The thermodynamic description of entropy in crystalline solids has traditionally been developed using quantum mechanical models of lattice vibrations. Einstein's pioneering model treated atoms in a crystal as identical quantized harmonic oscillators and provided the first successful explanation of the temperature dependence of the heat capacity of solids [10]. Debye subsequently generalized this approach by introducing a continuous phonon spectrum, significantly improving the agreement between theoretical predictions and experimental observations, particularly at low temperatures [11]. Since then, numerous theoretical and computational studies have investigated entropy in solids using partition functions, Debye integrals, lattice dynamics, information-theoretical approaches, molecular simulations, and first-principles calculations. These approaches have substantially improved the quantitative prediction of thermodynamic properties for a wide variety of materials.

Although these theoretical developments have been highly successful, many existing formulations remain mathematically demanding. Classical derivations of entropy commonly require the use of partition functions, Helmholtz free energy, statistical ensembles, or numerical evaluation of Debye functions. Furthermore, the Einstein temperature is generally introduced as a characteristic fitting parameter associated with the average vibrational frequency of atoms, yet its physical interpretation is often presented only qualitatively and lacks a simple analytical relationship with the experimentally measurable Debye temperature. Consequently, many students experience difficulty understanding both the derivation of entropy and the physical significance of characteristic temperatures in solid-state thermodynamics.

These difficulties are reflected in physics education research. Previous studies have consistently reported persistent misconceptions concerning entropy, heat capacity, thermal equilibrium, and microscopic interpretations of thermodynamic quantities. Students often fail to establish meaningful connections between the quantum mechanical description of lattice vibrations and the macroscopic thermodynamic properties measured experimentally. Consequently, there is a continuing need for theoretical frameworks that preserve physical rigor while remaining sufficiently transparent for educational purposes [12]-[17].

Previously, a number of studies have tackled entropy in solids. Einstein was the first scientist to tackle entropy for solids and the entropy formulation was obtained via the partition function Z for quantized harmonic oscillators [10]. Tekuchev et al. performed the calculation of the entropy of solid and liquid metals based on acoustic data [18]. Recently, concerning liquids and solutions, an information-theoretical approach to entropy was reported by Ben-Naim [19]. Ogris and Gamsjäger calculated the heat capacities, standard entropies, and enthalpies of some compounds approximated by Debye-Einstein integrals. However, in their calculation, the characteristic temperatures of Debye and Einstein are fitted from experimental measurements[20]. In another recent work, theoretical estimation of entropy in solids using integer and non-integer n-dimensional Debye functions is reported, however the calculations are given for non-integer n numbers [21]. Lately, another work has reported the temperature dependence of the entropy and the heat capacity calculated from the Raman frequency shifts for solid substances [22]. Additionally, the vibrational entropy of crystalline solids from the covariance of atomic displacements is reported [23]. First and second law of quantum thermodynamics based on a microscopic definition of entropy was tackled in 2021 [24]. Generalized entropy was likewise studied based on microscopic interpretation [25]. Extended Regression Analysis was performed for Debye–Einstein Models Describing Low Temperature Heat Capacity Data of Solids [26].

Despite extensive research on entropy in solids, an important gap remains in the literature. Existing formulations generally derive entropy through partition-function methods or numerical Debye calculations and frequently require experimentally fitted characteristic temperatures. To the best of our knowledge, there is no simple analytical formulation that derives the entropy of crystalline solids directly from the Einstein heat-capacity equation while simultaneously providing an explicit and physically interpretable relationship between the Einstein and Debye temperatures. Moreover, relatively few studies have examined how such a simplified theoretical formulation may support conceptual understanding and teaching of solid-state thermodynamics.

The present study addresses this gap by proposing an alternative analytical formulation for the entropy of crystalline solids based directly on Einstein's heat-capacity model. The proposed derivation leads to a closed-form expression for entropy while preserving consistency with established thermodynamic principles. In addition, an alternative definition of the Einstein temperature is developed by relating it analytically to the Debye temperature through the average vibrational properties of lattice oscillators. The resulting framework is then evaluated by comparing theoretical predictions with experimental entropy data for representative metallic crystals. Beyond its

theoretical contribution, the proposed approach is intended to provide a more accessible framework for teaching entropy, characteristic temperatures, and lattice vibrations in undergraduate and graduate physics courses. Accordingly, this study seeks to answer the following research questions:

1. Can an alternative analytical expression for the entropy of crystalline solids be derived directly from Einstein's heat-capacity equation while remaining consistent with thermodynamic principles?
2. Can a physically meaningful and analytically accessible relationship between the Einstein and Debye temperatures be established?
3. How accurately do the proposed formulations predict the experimental entropy of representative crystalline solids?
4. What educational advantages does the proposed analytical framework offer for improving conceptual understanding of entropy and lattice thermodynamics in physics education?

2. RESEARCH METHOD

2.1. Research Design

This study employs a theoretical analytical research design. The proposed entropy formulation is developed by combining Einstein's quantum model of lattice vibrations with classical thermodynamic definitions of entropy. Closed-form analytical expressions are derived using symbolic integration and algebraic transformations. The validity of the proposed equations is subsequently evaluated by comparing theoretical predictions with published experimental entropy data for representative crystalline metals. The overall research methodology follows a sequential theoretical development consisting of model formulation, analytical derivation, parameter estimation, numerical validation, and educational interpretation. Theretical flowchart is presented in figure 1.

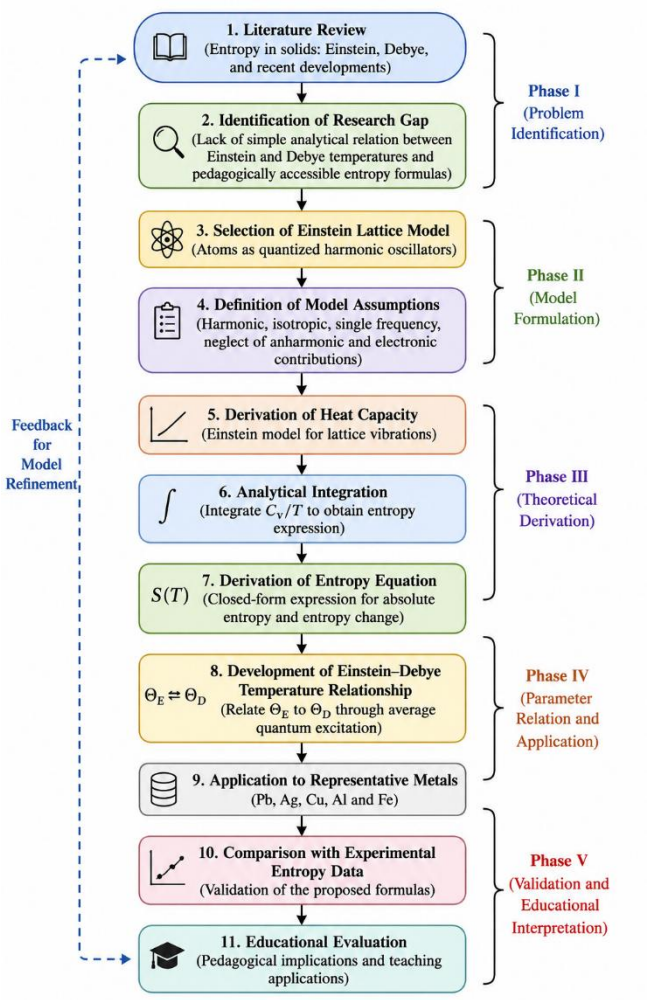

Figure 1. Flowchart illustrating the theoretical methodology employed in the present study.

2.2. Model Assumptions

The proposed analytical formulation is based on the classical Einstein model of crystalline solids together with several simplifying assumptions that enable the derivation of closed-form entropy expressions. These assumptions define the range of validity of the proposed framework.

a-Harmonic Oscillator Approximation

Each atom in the crystal lattice is assumed to behave as an independent quantum harmonic oscillator vibrating about its equilibrium position. The restoring force is proportional to the atomic displacement, and anharmonic interactions are neglected. Consequently, the vibrational energy levels remain equally spaced and are described by Einstein's quantization model.

b-Isotropic Lattice Approximation

The crystal is assumed to possess isotropic vibrational properties, implying that the average lattice dynamics are independent of crystallographic direction. Consequently, a single average vibrational behavior is considered representative of the entire crystal.

c-Single Characteristic Frequency Assumption

Following Einstein's original model, all atoms are assumed to vibrate with one effective characteristic angular frequency. This approximation replaces the continuous phonon spectrum introduced by Debye with an equivalent average frequency, allowing analytical expressions for entropy to be obtained in closed form.

d-Neglect of Anharmonic Effects

The present formulation assumes that lattice vibrations remain harmonic over the investigated temperature range. Thermal expansion, phonon-phonon interactions, and higher-order anharmonic effects are therefore neglected. This approximation is expected to be most accurate at low and moderate temperatures.

e-Neglect of Electronic Contributions

Only the vibrational contribution to entropy is considered. Electronic, magnetic, configurational, and defect-related entropy contributions are assumed to be negligible for the elemental crystalline metals investigated in this study. Accordingly, the calculated entropy represents the lattice vibrational entropy.

f-Thermodynamic Equilibrium

The crystal is assumed to remain in thermodynamic equilibrium during heating, allowing entropy to be treated as a state function and calculated by integrating the heat capacity over temperature.

2.3. Scope and Limitations

The proposed formulation is intended for crystalline solids whose thermodynamic behavior is dominated by lattice vibrations. The model is expected to provide reliable predictions primarily within temperature ranges where the harmonic approximation remains valid. Systems exhibiting strong anharmonicity, magnetic phase transitions, significant electronic heat capacities, or highly anisotropic phonon spectra fall outside the scope of the present formulation.

2.4. Alternative Formulation of Entropy

Entropy change for any systems with constant temperature is defined as, $dS = \frac{dQ}{T}$, where T is the absolute temperature and dQ is the heat exchange of the thermodynamic system with the environment. If the thermodynamic system has temperature change then overall entropy change of the system can be obtained by integrating this fundamental definition from the initial state to the final state which leads to, $\Delta S = S_f - S_i = \int_{S_i}^{S_f} dS = \int_i^f \frac{dQ}{T}$. In this definition, the amount of heat exchanged dQ can be expressed in terms of heat capacity of the solid that is $C(T) = \frac{\partial Q(T)}{\partial T}$ where obviously the heat capacity is assumed to be temperature dependent. By substituting this term within the definition of the entropy change, the entropy change can then be formulated as follows:

$$\Delta S = \int_{T_i}^{T_f} \frac{C(T)}{T}\, dT \qquad ...(1)$$

This fundamental definition is currently employed to estimate changes in entropy for all substances based on the experimental data on heat capacity. More specifically the entropy change is estimated by the area under the curve of $\frac{C(T)}{T}$ versus T graph between the temperatures of T_i and T_f.

In order obtain a theoretical formulation for the entropy change, one needs to formulate the heat capacity of solid substances. This was managed decades ago, by both Einstein and Debye employing the harmonic oscillator model of the atoms within the solid. Einstein and Debye models both successfully explain the experimental data; however, because of its simplicity, the Einstein model is employed in this work.

Einstein assumed that the atoms of the solid substance vibrate at an average frequency of ν_E and the heat capacity was formulated as,

$$C(T) = 3Nk\left(\frac{h\nu_E}{kT}\right)^2 \frac{e^{\frac{h\nu_E}{kT}}}{\left(e^{\frac{h\nu_E}{kT}}-1\right)^2} \quad ...(2)$$

where N denotes total number atoms/oscillators, T is the absolute temperature, h denotes the Planck's constant and k denotes the Boltzmann's constant. It is legitimate at this stage to define the Einstein temperature as $\frac{h\nu_E}{k} = \theta$ since the mean oscillation frequency of the atoms can equivalently expressed by temperature. If one substitutes the Einstein heat capacity within the definition of $\Delta S = \int_{T_i}^{T_f} \frac{C(T)}{T}\, dT$ it is straightforward to get the following alternative theoretical definition for the entropy of solids, *(see appendix*),

$$S = 3Nk\left[\frac{\theta}{T}\left(\frac{e^{\frac{\theta}{T}}}{e^{\frac{\theta}{T}}-1}\right) - \ln\left(e^{\frac{\theta}{T}}-1\right)\right] \quad ...(3)$$

Entropy formulation for solid substances was initially tackled by Einstein by employing the Helmholtz free energy formula $F = U - TS$ and the general definition of the entropy $S = -\frac{\partial F}{\partial T}$. In this effort, Helmholtz free energy was defined in terms of partition function Z in the form of $F = -kT \ln Z$. That effort produced the definition of,

$$S = 3\,Nk\left[\frac{\frac{\theta}{T}}{e^{\frac{\theta}{T}}-1} - \ln\left(1-e^{-\frac{\theta}{T}}\right)\right] \quad ...(4)$$

which is obviously not identical. In this definition, the Einstein temperature is not clearly and satisfactorily defined [27].

The equivalency of these two definitions may be demonstrated. The second term of the equation (3) can be evaluated as, $\ln\left(e^{\frac{\theta}{T}}-1\right) = \ln\left(e^{\frac{\theta}{T}}(1-e^{-\frac{\theta}{T}})\right) = \frac{\theta}{T} + \ln\left(1-e^{-\frac{\theta}{T}}\right)$. Substituting this equation within the formulation leads to, $S = 3Nk\left[\frac{\theta}{T}\left(\frac{e^{\frac{\theta}{T}}}{e^{\frac{\theta}{T}}-1}\right) - \frac{\theta}{T} - \ln\left(1-e^{-\frac{\theta}{T}}\right)\right] = 3Nk\left[\frac{\theta}{T}\left(\frac{e^{\frac{\theta}{T}}}{e^{\frac{\theta}{T}}-1} - 1\right) - \ln\left(1-e^{-\frac{\theta}{T}}\right)\right]$.In this formulation the following equivalency can be substituted, $\frac{e^{\frac{\theta}{T}}}{e^{\frac{\theta}{T}}-1} - 1 = \frac{1}{e^{\frac{\theta}{T}}-1}$. Performing so leads to the final definition of, $S = 3Nk\left[\frac{\frac{\theta}{T}}{e^{\frac{\theta}{T}}-1} - \ln\left(1-e^{-\frac{\theta}{T}}\right)\right]$ which is exactly Einstein's equation.

High Temperature Limit

The absolute value of entropy can be examined at high temperatures at which the specific heat and therefore the heat capacity is assumed to be constant, known as Dulong-Petit law. To do so one can employ the limit of $\frac{\theta}{T} \ll 1$ which leads to $e^{\frac{\theta}{T}} \approx \frac{\theta}{T} + 1$. Substituting this expression gives the following formulations, $S = 3Nk\left[\frac{\theta}{T}\left(\frac{e^{\frac{\theta}{T}}}{e^{\frac{\theta}{T}}-1}\right) - \ln\left(e^{\frac{\theta}{T}}-1\right)\right] = 3Nk\left[\frac{\theta}{T}\left(\frac{\frac{\theta}{T}+1}{\frac{\theta}{T}}\right) - \ln\left(\frac{\theta}{T}\right)\right] = 3Nk\left[\frac{\theta}{T} + 1 - \ln\left(\frac{\theta}{T}\right)\right] = 3Nk\left[\frac{\theta}{T} + 1 + \ln\left(\frac{T}{\theta}\right)\right]$. In this approximate expression one can easily assume $\frac{\theta}{T} \ll 1$ and $\ln\left(\frac{T}{\theta}\right) \gg \frac{\theta}{T}$, which leads to the following definition

$$S \approx 3Nk\left[\ln\left(\frac{T}{\theta}\right)\right] \quad ...(5)$$

Finally one can express approximate equations for high temperatures in terms of overall mass and specific heat concepts by employing basic definition of $N = \frac{m}{m_0}$ and the specific heat at room temperatures, $c = \frac{3\,k}{m_0}$. This leads to the following approximate high temperature expression for standard entropy:

$$S \approx m\,c\left[\ln\left(\frac{T}{\theta}\right)\right] \quad ...(6)$$

Relevant entropy change at room temperatures for solid metals can approximately be expressed as, $\Delta S = m\,c \ln\left(\frac{T_f}{T_f}\right)$ which is consistently employed for teaching purposes.

Low Temperature Limit

Approximate low temperature value of the entropy can be derived by employing the limit of $\frac{\theta}{T} \gg 1$.In this case the first term of the definition can be approximated as, $\frac{e^{\frac{\theta}{T}}}{e^{\frac{\theta}{T}}-1} = \frac{1}{1-e^{-\frac{\theta}{T}}} = \left(1-e^{-\frac{\theta}{T}}\right)^{-1} \approx 1+e^{-\frac{\theta}{T}}$. On the other hand, at low temperatures $\ln\left(e^{\frac{\theta}{T}}-1\right) \approx \ln\left(e^{\frac{\theta}{T}}\right) = \frac{\theta}{T}$ can also be written. Substituting this within the definition leads to, low temperature value of entropy as, $S \approx 3Nk\left[\frac{\theta}{T}\left(1+e^{-\frac{\theta}{T}}\right)-\frac{\theta}{T}\right] = 3Nk\frac{\theta}{T}e^{-\frac{\theta}{T}}$. In this expression the number of particles, $N = \frac{m}{m_0}$ and room temperature specific heat, $c = \frac{3k}{m_0}$, may be used and the expression may be given by,

$$S \approx m\, c\, \frac{\theta}{T} e^{-\frac{\theta}{T}} \qquad ...(7)$$

which vanishes at absolute zero, $S \approx 3mc\frac{\theta}{T}e^{-\frac{\theta}{T}} \approx 0$ in harmony with the third law of thermodynamics. The entropy change at low temperatures can be given by, $\Delta S \approx m\, c\left(\frac{\theta}{T_f}e^{-\frac{\theta}{T_f}} - \frac{\theta}{T_i}e^{-\frac{\theta}{T_i}}\right)$. As a result, the alternative formulation underlines that, i-at low temperatures the thermal excitation is exponentially, suppressed, ii-only a tiny fraction of oscillators is excited and iii-hence, entropy vanishes exponentially rather than as a power law.

2.5. Einstein Temperature

The entropy of a solid crystal evidently depends on the Einstein temperature θ_E which is defined in terms of Einstein frequency in the form of $\theta_E = \frac{\hbar\omega_E}{k}$. In this definition, Einstein frequency ω_E is foundationally described as the *mean frequency* of atomic oscillations. In a real crystal, the oscillation frequency of atoms varies between 0 and maximum frequency of ω_m and accordingly the Einstein frequency may be theoretically calculated by employing the standard definition of mean value,

$$\omega_E = \frac{\int_0^{\omega_m} \omega\, \rho(\omega) d\omega}{\int_0^{\omega_D} \rho(\omega) d\omega} \qquad ...(8)$$

where ω_m denotes the maximum oscillation frequency of atoms, $\rho(\omega)$ denotes the 3-dimensional density of states for the lattice vibrations which may be expressed by $\rho(\omega) = \frac{V\omega^2}{2\pi^2 {v_m}^3} = C\,\omega^2$ where C is a constant. The frequency distribution issue was tackled by Debye and the upper limit of the oscillation frequency was defined as the Debye frequency so $\omega_m = \omega_D$ can be written. Substituting the density of states within the definition of Einstein frequency leads to the result of,

$$\omega_E = 0{,}750\ \omega_D \qquad ...(9)$$

In this definition, it is well-known that lattice vibrations are quantised in 1 dimensional k-space with a separation value of $\frac{2\pi}{L}$ and all the possible states may be represented by a sphere with a radius of Debye wave number k_D. This simple approach leads to the estimation that overall number of states must be equal to the number of atoms within the solid hence it is legitimate to write, $\left(\frac{L}{2\pi}\right)^3 \frac{4}{3}\pi {k_D}^3 = N$ which leads to, $k_D = (6\pi^2\frac{N}{V})^{1/3}$. The relation between the Debye frequency ω_D and Debye wave number k_D is much more complicated and primarily depends on the dispersion relation $\omega = f(k)$ and other numerous effects. However, it is possible to consider the simplest case which assumes that all lattice vibrations are within the continuum limit and the dispersion relation may be considered linear. In this case, the relation may obviously be expressed by,

$$\omega_D = v_m(6\pi^2\frac{N}{V})^{1/3} \qquad ...(10)$$

where v_m denotes the average phonon/sound velocity for acoustic phonons at Brillouin zone centre within the continuum limit, N denotes the number of oscillators/atoms and V denotes the overall volume of the solid. In this definition, the average velocity is theoretically defined in terms of longitudinal and transverse velocities in the form of, $v_m = \left[\frac{1}{3}\left(\frac{2}{v_T^3}+\frac{1}{v_L^3}\right)\right]^{-1/3}$. In real cases, the issue is much more complicated and it is not only influenced by the dispersion relation but also numerous other factors which are summarised as follows:

- Dispersion relation is not linear, quite complicated and optical modes have to be taken into account.
- The crystals are anisotropic and therefore elastic constants vary however, the Debye model assumes isotropy.
- Real crystals have direction-dependent sound velocities
- As the temperature changes anharmonic effects become important and phonon frequencies soften with temperature
- In crystals real bonding structures are more complex.
- In reality electronic effects modify phonons.

Tackling all those points is obviously very problematic hence, it is quite genuine to simplify the issue and suggest a single parameter to include all those effects. In this case, the realistic Debye frequency, taking into account of all issues, can be expressed as,

$$\omega_{DR} = \alpha\omega_D \qquad ...(11)$$

where $\omega_D = \mathrm{v}_m \left(6\,\pi^2 \frac{N}{V} \right)^{\frac{1}{3}}$ represents the theoretical continuum limit value. Accordingly, realistic Debye temperature of the solid may be extracted from $\theta_{DR} = \frac{\hbar\omega_{DR}}{k}$ which leads to the realistic Debye temperature.

In order to estimate the relation between the Einstein frequency and the Debye frequency an alternative and accessible approach may be derived by assuming the quantised energy of the oscillators. Quantum theory of oscillators expresses that overall mechanical energy of a single oscillator/atom is quantised in accordance with $E_n = \left(n + \frac{1}{2}\right)\hbar\,\omega$ and the average mechanical energy of the oscillators is given by $\langle E\rangle = \frac{1}{2}\hbar\,\omega + \langle n\rangle\,\hbar\,\omega$ where average quantum number $\langle n\rangle$ is defined as $\langle n\rangle = \frac{1}{e^{\frac{\hbar\,\omega}{kT}} - 1}$. The fundamental opinion in this approach is that the average Einstein frequency ω_E ought to be determined by the specific condition of $\frac{\hbar\,\omega}{kT} = 1$. More specifically, Einstein frequency ought to be equal to a fraction of the Debye frequency determined by the average quantum number of the oscillators, hence, the formulation can be expressed as,

$$\frac{\omega_E}{\omega_D} = \langle n\rangle \qquad ...(12)$$

This approach leads to a very useful relation between the Debye temperature and the Einstein temperature in the form of $\omega_E = 0{,}582\;\omega_D$ because the average quantum number is $\langle n\rangle = \frac{1}{e^{1-1}} = 0{,}582$ at the specific condition of $\frac{\hbar\,\omega}{kT} = 1$. Relevant Einstein temperature may obviously be obtained from $\theta_E = \frac{\hbar\omega_E}{k}$.

Alternative approach proposed can be interpreted as follows: Average quantum number for the harmonic oscillators depends on the $\frac{\hbar\,\omega}{kT}$ ratio.

- Firstly, if $\frac{\hbar\,\omega}{kT} \gg 1$ then average quantum number $\langle n\rangle \ll 1$ which means the oscillators all stand at their lowest energy state that is $\langle E\rangle \approx \frac{1}{2}\hbar\,\omega$ indicating zero point energy and no thermal energy kT effects.
- Secondly, if $\frac{\hbar\,\omega}{kT} \ll 1$ then average quantum number $\langle n\rangle \gg 1$ which means the oscillators all stand at their highest possible energy state that is $\langle E\rangle \approx \langle n\rangle\hbar\,\omega$ indicating strong thermal energy kT effects and highly energetic oscillators.
- Finally, if $\frac{\hbar\,\omega}{kT} \approx 1$ then average oscillation energy is given by $\langle n\rangle = 1{,}082\,\hbar\,\omega \approx \hbar\,\omega$ which indicates average thermal energy effects and therefore can be employed to determine the average Einstein temperature.

The Einstein temperature represents the characteristic temperature for solids at which all the atoms or oscillators have identical vibrational energy, indicating the point where contributions to thermal properties, such as heat capacity and entropy, become significant.

3. RESULTS AND DISCUSSION

3.1. Molar Entropy

The first research question examined whether a closed-form analytical entropy equation could be derived directly from Einstein's heat-capacity model while preserving thermodynamic consistency. The analytical derivation presented in Section 2 successfully produced an explicit expression for both entropy change and absolute entropy without employing partition functions or numerical Debye integrals. The derived equation satisfies the expected thermodynamic limits, including the vanishing of entropy as the temperature approaches absolute zero and the high-temperature behavior consistent with classical thermodynamics. Molar entropy values

for Pb, Ag, Cu, Al and Fe based on the theoretical formulation given by the equation (3) are plotted as a function of temperature, presented in the figure 2.

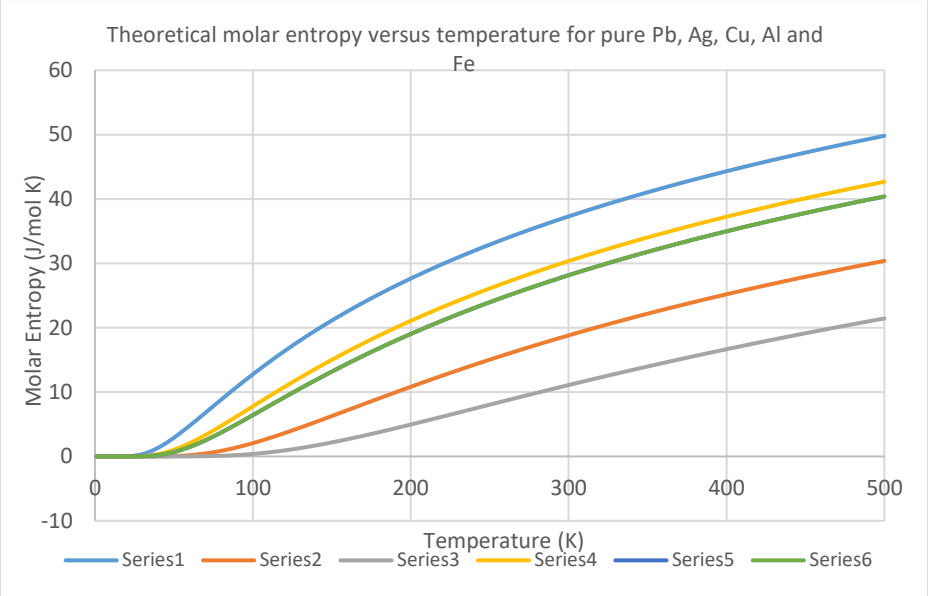

Figure 2. Theoretical molar entropies versus absolute temperature for Pb, Ag, Cu, Al and Fe are plotted according to the derived theoretical equation (3). In the figure, series 1, 2, 3, 4 and 5 correspond to Pb, Ag, Cu, Al and Fe, respectively.

Theoretical molar entropy values plotted in Figure 2 are also presented in Table 1 in order to obtain specific values for certain temperatures between absolute zero and 500K.

Table 1. Theoretical molar entropy values calculated from the simple equation of (3) for certain temperatures between the absolute zero and 500K.

T (K)	S(J/ mol K) Pb	S(J/ mol K) Ag	S(J/ mol K) Cu	S(J/ mol K) Al	S(J/ mol K) Fe
50	21,48	7,04	2,33	1,03	0,68
100	37,70	19,97	11,47	7,79	6,42
150	47,62	29,17	19,59	15,01	13,18
200	54,73	36,03	26,03	21,07	19,03
250	60,28	41,45	31,25	26,10	23,96
300	64,82	45,92	35,61	30,36	28,16
350	68,66	49,72	39,34	34,02	31,79
400	71,99	53,03	42,60	37,24	34,98
450	74,93	55,95	45,49	40,10	37,83
500	77,56	58,57	48,09	42,68	40,39

In order to test the correctness of the suggested absolute entropy equation (3), it is legitimate to compare the theoretically estimated values with the experimentally measured values. The actual theoretical entropy values calculated from the equation(3) and relevant measured entropies are presented in Table 2. In the table on the left hand side is the theoretical values and on the right in brackets are the measured entropy values. The relative errors are also calculated to highlight the accuracy and success of the mathematical model for entropy.

Table 2. Theoretically calculated and measured molar entropy values at 100K, 200K, 300K and 500K for Pb, Ag, Cu, Al and Fe solid metals and relevant relative error percentages. Experimental values in brackets are obtained from: https://www.engineeringtoolbox.com/thermodynamics-key-values-standard-enthalpy-formation-entropy-d_1986.html.

T (K)	S(J/ mol K) Pb	S(J/ mol K) Ag	S(J/ mol K) Cu	S(J/ mol K) Al	S(J/ mol K) Fe
100	37,70 (25,0)	19,97 (18,0)	11,47 (14,0)	7,79 (12,5)	6,42 (11,0)
200	54,73 (45,0)	36,03 (33,0)	26,03 (27,0)	21,07 (21,5)	19,03 (23,0)
300	64,82 (64,0)	45,92 (42,6)	35,61 (33,2)	30,36 (28,3)	28,16 (27,0)
500	77,56 (85,0)	58,57 (60,0)	48,09 (48,0)	42,68 (55,0)	40,39 (45,0)
Relative Error (%)	20,6	7,52	7,24	17,31	18,3

The relative error rates or percentages clearly show the high level of agreement between the measurements and the theoretical approach. The highest relative error is found for Pb at 20,6 %, while the lowest one is found for Cu at 7,24 %. The theoretical molar entropy values calculated using the derived formulation exhibit the expected thermodynamic behavior over the temperature range from absolute zero to 500 K. At high temperatures, the entropy increases logarithmically and the heat capacity approaches the Dulong–Petit limit of 3R, confirming the consistency of the model with classical thermodynamics. At low temperatures, the entropy approaches zero as T→0, in accordance with the third law of thermodynamics. Within the Einstein framework, this decrease follows an exponential trend, reflecting the suppression of thermal excitation of lattice oscillators. While this behaviour differs from the T^3dependence predicted by the Debye model for real crystalline solids, it nevertheless provides a reasonable approximation outside the very low-temperature regime.

The comparison between theoretical and experimental standard molar entropies for Pb, Ag, Cu, Al, and Fe shows satisfactory agreement, particularly near room temperature. Relative deviations are generally within acceptable limits for a simplified single-frequency model. Larger discrepancies observed for certain materials, such as Pb and Fe, can be attributed to several factors:

- Anharmonic lattice effects, which become significant at elevated temperatures.
- Electronic contributions to the heat capacity, especially in transition metals like Fe.
- Magnetic ordering effects in ferromagnetic materials.
- Limitations of the single-frequency approximation inherent in the Einstein model.

Despite these limitations, the proposed formulation successfully captures the essential thermodynamic behaviour of solids and provides a practical tool for estimating entropy when detailed phonon information is unavailable.

In order to underline certain important points of the present effort, table 3 is presented to compare the existing approaches in terms of method, advantages and limitations.

Table 3. The cpomparison of various studies in terms of method, advantages and limitations.

Study	Method	Advantages	Limitations
Einstein (1907)	Heat capacity	Analytical	Single frequency
Debye (1912)	Phonon spectrum	Accurate	Numerical integration
Ogris (2021)	Debye–Einstein	Good accuracy	Parameter fitting
Çopuroğlu (2022)	n-dimensional Debye	Flexible	Numerical
Present study	Closed-form entropy	Simple + analytical	Harmonic approximation

3.2. Einstein Temperature

The proposed relationship provides an analytically transparent interpretation of the Einstein temperature as an average quantum excitation parameter. Unlike conventional empirical estimations, the present formulation establishes a direct mathematical connection between the Einstein and Debye temperatures while preserving the physical interpretation of both characteristic temperatures.

Direct measurement or calculation of Einstein temperature is not possible instead the Debye temperature is employed to determine the Einstein temperature. Debye temperature, on the other hand, is measured via heat capacity, sound velocity or diffraction experiments. The outcomes of the measurements unfortunately vary depending on the method however, the range of various measurements for Pb, Ag, Cu, Al and Fe crystals are tabulated in the table 4. The table also provides genuinely accepted Debye temperatures of those crystals based on these measurements.

Table 4. The Debye temperatures for Pb, Ag, Cu, Al and Fe crystals obtained from different experimental measurements and relevant genuinely accepted values. The accepted values are obtained from the most widely engaged textbook of Kittel.

Solid	$\theta_D(K)$ (Heat capacity)	$\theta_D(K)$ (Sound velocity)	$\theta_D(K)$ (Diffraction)	$\theta_D(K)$ (Accepted *)
Pb	85 – 105	95 – 115	90 – 110	105,0
Ag	200 – 230	210 – 240	205 – 235	225,0
Cu	310 – 340	330 – 360	320 – 350	343,5
Al	390 – 430	410 – 440	400 – 430	428,0
Fe	420 – 470	440 – 490	430 – 480	470,0

Based on those measurement outcomes and accepted values, the relation between the simple theoretical definition of Debye frequency and measurement results can be estimated through previously described parameter α. In order to manage this task, theoretical continuum limit value of the theoretical Debye temperatures, accepted values and the ratios of experimental to theoretical are presented in table 5 for five bulk crystals, namely Pb, Ag, Cu, Al, and Fe.

Table 5. Theoretically calculated and experimentally measured Debye temperatures for Pb, Ag, Cu, Al and Fe. Phonon velocities are effective bulk and taken from https://ims.evidentscientific.com/en/learn/ndt-tutorials/thickness-gauge/appendices-velocities .

Solid	$v_m(ms^{-1})$	$m_0(kg)$	$n(m^{-3})$	${\theta_D}^{theo}(K)$	${\theta_D}^{exp}(K)$	${\theta_D}^{exp}/{\theta_D}^{theo}$
Pb	1960	$3{,}44x10^{-25}$	$3{,}30x10^{28}$	186,4	105,0	0,563
Ag	3600	$1{,}79x10^{-25}$	$5{,}86x10^{28}$	414,6	225,0	0,543
Cu	4700	$1{,}06x10^{-25}$	$8{,}49x10^{28}$	612,4	343,5	0,561
Al	6300	$4{,}48x10^{-26}$	$6{,}02x10^{28}$	732,1	428,0	0,584
Fe	5900	$9{,}27x10^{-26}$	$8{,}49x10^{28}$	768,7	470,0	0,611

The ratio of the experimental to the theoretical Debye temperatures is quite close and the mean value of the ratio is approximately $\left(\frac{{\theta_D}^{exp}}{{\theta_D}^{theo}}\right)_{mean} = \alpha = 0{,}57$. This ratio can now be employed to estimate the realistic Debye temperatures from the simplified theoretical calculations of Debye temperatures by employing $\theta_D = 0{,}57\ {\theta_D}^{theo}$. In order to estimate the Einstein temperatures, it is legitimate to employ the previously derived equation of $\theta_E = 0{,}582\ \theta_D$ which are given in the table 6.

Table 6. The estimated Einstein temperatures extracted from the measured Debye temperatures by employing the alternative definition of $\theta_E = 0{,}582\ \theta_D$.

Crystal	$\theta_D(K)$	$\theta_E(K)$
Pb	105,0	61,1
Ag	225,0	130,9
Cu	343,5	199,9
Al	428,0	249,1
Fe	470,0	273,5

The estimation of the Einstein temperature is central to the proposed formulation of entropy. In the present study, the Einstein temperature is derived from experimentally measured Debye temperatures through a simplified theoretical relationship. This approach provides a practical means of determining a characteristic vibrational temperature without resorting to complex phonon spectrum calculations. The analysis of Pb, Ag, Cu, Al, and Fe demonstrates that the ratio between experimentally accepted Debye temperatures and their theoretical continuum-limit values remains relatively consistent across different materials. This observation justifies the introduction of a scaling parameter that effectively incorporates the influence of anisotropy, non-linear dispersion relations, optical phonon modes, and anharmonic effects. Although simplified, this treatment offers a realistic approximation suitable for many crystalline solids. The resulting Einstein temperatures fall within physically reasonable ranges and enable accurate predictions of thermodynamic properties. Nevertheless, it is important to recognize that the Einstein model assumes a single characteristic vibrational frequency, whereas real solids exhibit a distribution of phonon modes. Consequently, the proposed relationship should be interpreted as a *phenomenological approximation* rather than a universal physical law.

3.3. Pedagogical Implications

Beyond its theoretical contribution, the proposed formulation offers several pedagogical advantages. First, the closed-form equations allow undergraduate students to derive entropy directly from heat capacity without requiring advanced statistical mechanics. Second, the explicit relationship between Einstein and Debye temperatures provides a physically intuitive interpretation of characteristic lattice temperatures. Third, the analytical formulation facilitates classroom demonstrations, problem-solving activities, and computational exercises that strengthen conceptual understanding of lattice thermodynamics.

Bridging Macroscopic and Microscopic Descriptions

Entropy is often perceived by students as an abstract and mathematically challenging concept. The derivation presented in this study establishes a clear connection between the *macroscopic thermodynamic definition*, $S = \int_0^T \frac{C(T)}{T}\, dT$ and the *microscopic quantum mechanical description* of lattice vibrations. By starting from the Einstein heat capacity, students can directly observe how quantized harmonic oscillators give rise to measurable thermodynamic properties, thereby reinforcing the link between statistical mechanics and classical thermodynamics.

Conceptual Understanding of Characteristic Temperatures

The introduction of a transparent relationship between the *Debye* and *Einstein temperatures* provides an intuitive framework for understanding characteristic vibrational temperatures in solids. Students often struggle with the physical meaning of these parameters; the present approach clarifies their roles by interpreting the Einstein temperature as an effective average vibrational energy scale derived from the broader phonon spectrum described by the Debye model.

Analytical Accessibility

The Einstein model leads to closed-form expressions for entropy and its temperature dependence, in contrast to the Debye model, which requires numerical integration. This analytical simplicity makes the approach particularly suitable for the following:

- Undergraduate and graduate instruction, where mathematical tractability is essential.
- Problem-based learning, enabling students to perform calculations without advanced computational tools.
- Visualization of thermodynamic behavior, such as plotting entropy as a function of temperature.

Understanding Model Limitations

An important educational benefit of the proposed framework is its ability to illustrate the *strengths and limitations of theoretical models*. By comparing the Einstein and Debye predictions, students can appreciate:

- Why the Einstein model predicts an exponential decrease in entropy at low temperatures.
- How the Debye model improves upon this by introducing a T^3 dependence.
- The role of *phonon dispersion* and *density of states* in determining thermal properties.

Such comparisons foster critical thinking and help students understand the process of scientific model development.

Interdisciplinary Relevance

The simplified entropy formulation can also be integrated into courses beyond solid-state physics, including:

- *Materials science,* for estimating thermodynamic properties of metals.
- *Chemical thermodynamics,* where standard molar entropies are frequently used.
- *Engineering thermodynamics,* providing practical tools for material property estimation.

Suggested Educational Applications

The framework proposed in this study can be effectively incorporated into teaching through numerous activities:

1. Classroom Demonstrations
   Plotting entropy versus temperature for different materials.
   Comparing Einstein and Debye predictions.
2. Student Projects
   Estimating Einstein temperatures from reported Debye temperatures.
   Investigating the influence of lattice vibrations on thermodynamic properties.
3. Problem-Solving Exercises
   Deriving entropy from the Einstein heat capacity.
   Evaluating thermodynamic limits at low and high temperatures.
4. Computational Activities
   Implementing the entropy equations using software such as MATLAB, Python, or Mathematica.
   Performing sensitivity analyses on the Einstein temperature.

3.4. Educational Significance

The simplified formulation of entropy derived in this work provides a valuable pedagogical tool for illustrating the connection between quantum mechanics and thermodynamics [27], [28]. By offering analytically tractable expressions and physically intuitive interpretations of characteristic temperatures, the approach enhances conceptual understanding and supports active learning in undergraduate and graduate physics education [29], [30]. The framework also encourages critical evaluation of theoretical models and promotes interdisciplinary applications in materials science and engineering.

The present study contributes to the literature in several respects beyond a straightforward reformulation of Einstein's model. First, unlike conventional derivations of lattice entropy that rely on statistical partition functions, Helmholtz free energy, or numerical evaluation of Debye integrals, the proposed approach derives a closed-form analytical expression for entropy directly from Einstein's heat-capacity equation. This provides a mathematically transparent route that preserves thermodynamic consistency while substantially reducing the mathematical complexity of the derivation.

Second, the study introduces an alternative interpretation of the Einstein temperature by establishing an explicit analytical relationship with the Debye temperature. Rather than treating the Einstein temperature solely as an empirical fitting parameter, the proposed formulation provides a physically interpretable connection between these two characteristic temperatures based on average lattice vibrations. To our knowledge, such a direct analytical relationship has not previously been presented in a simple closed form suitable for both theoretical analysis and physics instruction.

Third, comparison with experimental entropy data for representative crystalline metals demonstrates that the simplified formulation reproduces the overall temperature dependence of lattice entropy with satisfactory accuracy despite relying on the single-frequency approximation of the Einstein model. This indicates that relatively simple analytical models can still provide useful quantitative predictions when detailed phonon spectra are unavailable.

Finally, the study makes an educational contribution by integrating solid-state physics, quantum mechanics, and thermodynamics into a unified analytical framework. The derived equations can be followed using only elementary calculus and basic thermodynamics, thereby lowering the mathematical barrier for undergraduate and graduate students while maintaining physical rigor. Consequently, the proposed framework serves not only as a theoretical alternative but also as a pedagogically valuable model for improving conceptual understanding of entropy, lattice vibrations, and characteristic temperatures.

Several limitations should be considered when interpreting the present findings. The proposed formulation is derived within the framework of the classical Einstein model and therefore inherits the assumptions associated with that model. In particular, the harmonic approximation neglects anharmonic lattice vibrations, thermal expansion, and phonon-phonon interactions, which become increasingly important at elevated temperatures. The model also assumes that all atoms vibrate with a single characteristic frequency. Although this assumption enables a simple analytical solution, it cannot fully represent the continuous phonon spectrum found in real crystalline solids. Consequently, the proposed formulation is expected to be less accurate for materials whose thermodynamic behavior is strongly influenced by phonon dispersion, anisotropy, or multiple vibrational branches.

Furthermore, only the vibrational contribution to entropy is considered. Electronic, magnetic, configurational, defect-related, and surface contributions are neglected. This simplification may partly explain the larger deviations observed for materials such as iron, where magnetic ordering and electronic effects contribute significantly to the measured entropy. The validation performed in this study is restricted to five elemental crystalline metals (Pb, Ag, Cu, Al, and Fe) over a moderate temperature range. Although these comparisons demonstrate encouraging agreement with experimental data, broader validation involving semiconductors, ceramics, ionic crystals, alloys, molecular solids, and low-dimensional materials is required before the proposed formulation can be considered generally applicable.

Finally, while the proposed framework is intended to facilitate the teaching of entropy and solid-state thermodynamics, its educational effectiveness has not yet been investigated empirically. Future physics education research should evaluate whether the simplified analytical formulation improves students' conceptual understanding, problem-solving ability, and long-term retention when compared with conventional instructional approaches.

4. CONCLUSION

This study developed an alternative analytical framework for describing the entropy of crystalline solids directly from Einstein's heat-capacity model and introduced a simplified analytical relationship between the Einstein and Debye temperatures. The derived closed-form entropy equation satisfies the fundamental laws of thermodynamics, reproduces the overall temperature dependence of entropy with satisfactory agreement with experimental data for representative crystalline metals, and provides a physically transparent interpretation of characteristic lattice temperatures. By avoiding partition-function methods and numerical Debye integrals, the proposed framework offers a mathematically accessible approach that is particularly valuable for both theoretical analysis and physics education. Future research should extend the model by incorporating anharmonic lattice vibrations, multiple phonon frequencies, electronic and magnetic entropy contributions, and validation across a wider range of crystalline materials. In addition, empirical studies in physics education are recommended to evaluate the effectiveness of the proposed framework in improving students' conceptual understanding of entropy, lattice vibrations, and solid-state thermodynamics.

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APPENDIX

Derivation of Entropy

If one substitutes the Einstein heat capacity within the equation $\Delta S = \int_{T_i}^{T_f} \frac{C(T)}{T}\, dT$ it is straightforward to get the following, $\Delta S = 3Nk\theta^2 \int_{T_i}^{T_f} \frac{e^{\frac{\theta}{T}}}{\left(e^{\frac{\theta}{T}}-1\right)^2} \frac{dT}{T^3} = 3Nk\theta^2 I_1$ where the integral is defined as $I_1 = \int_{T_i}^{T_f} \frac{e^{\frac{\theta}{T}}}{\left(e^{\frac{\theta}{T}}-1\right)^2} \frac{dT}{T^3}$. In order to integrate this expression one can define new variable $\frac{\theta}{T} = x$ and transform the integration accordingly, such that $-\frac{\theta}{T^2} dT = dx$ and $dT = -dx \frac{T^2}{\theta} = -dx \frac{\left(\frac{\theta}{x}\right)^2}{\theta} = -dx \left(\frac{\theta}{x^2}\right)$, hence $I_1 = \int \frac{e^x}{(e^x-1)^2} \frac{-dx\left(\frac{\theta}{x^2}\right)}{\left(\frac{\theta}{x}\right)^3} = -\int \frac{e^x}{(e^x-1)^2} \frac{x}{\theta^2}\, dx = -\frac{I_2}{\theta^2}$.

In this equation the integral is defined as, $I_2 = \int \frac{e^x\, x}{(e^x-1)^2}\, dx$. In order to integrate this expression, one again needs to define a new variable, $e^x - 1 = y$ and accordingly the following can easily be managed $e^x dx = dy$ and $e^x = y + 1$, and $x = \ln(y+1)$. The integral I_2 can now be expressed as, $I_2 = \int \frac{\ln(y+1)}{y^2} dy$. In order to execute this integral one can employ the partial integration definition, $\int u\, dv = uv - \int v du$. Accordingly, one can perform the following, $\ln(y+1) = u$, and $\frac{dy}{y^2} = dv$ and $v = -\frac{1}{y}$, and $du = \frac{dy}{y+1}$. So, the integral is transformed in to $I_2 = -\frac{\ln(y+1)}{y} + \int \frac{dy}{y(y+1)}$.

In this expression the integral term can be named and defined as $I_3 = \int \frac{dy}{y(y+1)}$. In order to integrate this expression one can easily employ the equation of $\frac{1}{y(y+1)} = \frac{1}{y} - \frac{1}{y+1}$ which leads to $I_3 = \int \frac{dy}{y(y+1)} = \int \frac{1}{y}\, dy - \int \frac{1}{y+1}\, dy = \ln(y) - \ln(y+1)$. It is now straightforward to substitute the integral I_3 within the integral $I_2 = -\frac{\ln(y+1)}{y} + \ln(y) - \ln(y+1)$. The integral I_2 can be substituted within the integral I_1 and this substitution leads to $I_1 = -\frac{I_2}{\theta^2} = -\frac{1}{\theta^2}\left[-\frac{\ln(y+1)}{y} + \ln(y) - \ln(y+1)\right]$. The overall entropy change can now be expressed as $\Delta S = 3N\, k\, \theta^2 I_1 = 3Nk\theta^2 \left\{-\frac{1}{\theta^2}\left[-\frac{\ln(y+1)}{y} + \ln(y) - \ln(y+1)\right]\right\} = 3Nk\left[\frac{\ln(y+1)}{y} - \ln(y) + \ln(y+1)\right]$. In order to express this final expression in terms of the original variables one needs to substitute the variables which was defined as $y = e^x - 1 = e^{\frac{\theta}{T}} - 1$. Performing this leads to the final entropy change of, $\Delta S = 3Nk\left[\frac{\ln\left(e^{\frac{\theta}{T}}\right)}{e^{\frac{\theta}{T}}-1} - \ln\left(e^{\frac{\theta}{T}}-1\right) + \ln\left(e^{\frac{\theta}{T}}\right)\right] = 3Nk\left[\frac{\frac{\theta}{T}}{e^{\frac{\theta}{T}}-1} - \ln\left(e^{\frac{\theta}{T}}-1\right) + \frac{\theta}{T}\right] = 3Nk\left[\frac{\theta}{T}\left(\frac{e^{\frac{\theta}{T}}}{e^{\frac{\theta}{T}}-1}\right) - \ln\left(e^{\frac{\theta}{T}}-1\right)\right]$. This indefinite integration can now be employed in order to get the entropy change between the initial and final temperature values, which is given by,

$$\Delta S = 3Nk\left[\frac{\theta}{T}\left(\frac{e^{\frac{\theta}{T}}}{e^{\frac{\theta}{T}}-1}\right) - \ln\left(e^{\frac{\theta}{T}}-1\right)\right]_{T_i}^{T_f}$$

It is now easy to employ the definition of entropy change, $\Delta S = S_f - S_i$, to obtain the absolute value of entropy as a state function of the solid substance at a temperature of T,

$$S = 3Nk\left[\frac{\theta}{T}\left(\frac{e^{\frac{\theta}{T}}}{e^{\frac{\theta}{T}}-1}\right) - \ln\left(e^{\frac{\theta}{T}}-1\right)\right]$$