Accurate Evaluation of the Specific Heat Capacity of Solids and its Application to MgO and ZnO Crystals

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Abstract   Using binomial coefficients, new, simple, and efficient algorithms are presented for the accurate and fast calculation of the heat capacity of solids depending on the Debye temperature. As will be seen, the present formulation yields compact, closed-form expressions which enable the straightforward calculation of the heat capacity of solids for arbitrary temperature values. Finally, the algorithm is used to simulate the variation of the specific heat capacity with temperature of MgO and ZnO crystals. The results were compared with those reported in the literature and found to be in close agreement with those of other studies.

1 Introduction

Debye functions are widely used in the study of many physical problems, especially in the evaluation of the heat capacity of solids [1–21]. A knowledge of the heat capacity of a substance not only provides essential insight into its vibrational properties but is also mandatory for many applications [4, 22, 23]. In the literature, various efficient numerical methods have been proposed for improving the evaluation of the n-dimensional Debye function, Debye temperature, and other types of Debye functions [10–13].

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An accurate evaluation of the n-dimensional Debye function gives the Debye temperature of solids, which defines a boundary between the quantum-mechanical and classical behavior of phonons [24–26]. Debye functions can also be used in the computation of heat capacities of solids using Tarasov equations [6].

The aim of the study is to present an analytical expression to simplify the calculation of heat capacity in terms of an n-dimensional Debye function in any temperature range using the binomial coefficients [27]. The method is tested as an accurate and valid method for calculation of Debye functions of solids by applying it to ZnO and MgO samples [14,28–35].

2 Expression for Specific Heat Capacity and its Application to MgO and ZnO Crystals

Under the Debye approximation, the heat capacity per unit volume at constant volume is given by [4]

$$C_v = 3NkL_V\left(\frac{\theta}{T}\right) \tag{1}$$

where N is the Avogadro number, k is the Boltzmann constant, θ is the Debye temperature of solids, and T is the absolute temperature. In Eq. 1, the quantity $L_V(x)$ is defined as

$$L_V(x) = 3\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \tag{2a}$$

$$= 3\left(\frac{T}{\theta}\right)^3 I_4(2, x_D) \tag{2b}$$

where $x_D = \frac{\theta}{T}$. The quantities $I_n(s, x_D)$ occurring in Eq. 2b are generally defined as

$$I_n(s, x_D) = \int_0^{x_D} \frac{x^n e^x}{(e^x - 1)^s} dx. \tag{3}$$

We put $e^x = t$ in Eq. 3 and obtain

$$I_n(s, x_D) = \int_1^{e^{x_D}} \frac{[\ln(t)]^n}{(t - 1)^s} dt. \tag{4}$$

For the evaluation of Eq. 4, we use the following binomial expansion theorem for an arbitrary real n and $|x| > |y|$ (see [13,36]):

$$(x \pm y)^n = \sum_{m=0}^{\infty} (\pm 1)^m F_m (n) \, x^{n-m} y^m \tag{5}$$

where $F_m(n)$ is the binomial coefficient. Substituting Eq. 5 into Eq. 4, we obtain for $I_n(s, x_D)$ integrals the following series formulae:

$$I_n (s, x_D) = \lim_{N \to \infty} \sum_{m=0}^{N} (-1)^m F_m (-s) H_{nm} (s, x_D) \tag{6}$$

where

$$H_{nm} (s, x_D) = \int_1^{e^{x_D}} [\ln (t)]^n \, t^{-s-m} dt. \tag{7}$$

In order to derive the formulas for Eq. 7, we use the partial integration method. Then, finally we obtain

$$H_{nm} (s, x_D) = \frac{n! \left[1 - e^{-x_D w} \left\{1 + x_D w + \frac{1}{2!} x_D^2 w^2 \ldots \ldots \right\}\right]}{w^{n+1}}$$

$$= n! \left[1 - e^{-x_D w} \left(\sum_{k=0}^{n} \frac{(x_D w)^k}{k!}\right)\right] w^{-(n+1)} \tag{8}$$

where $w = m + s - 1$. Taking into account Eq. 6 in Eq. 1, we obtain for the specific heat capacity the following simply structured formulae:

$$C_v = 9Nk \left(\frac{T}{\theta}\right)^3 \lim_{L \to \infty} \sum_{m=0}^{L} (-1)^m F_m (-2) H_{4m} (2, x_D). \tag{9}$$

Considering Eq. 8 for $w = m + s$ and the binomial coefficients, we obtain for Debye functions the following formulae:

$$D_n (s, x_D) = \frac{n}{x_D^n} \lim_{M \to \infty} \sum_{m=0}^{M} (-1)^m F_m (-s) H_{nm} (s, x_D). \tag{10}$$

In Eqs. 6, 9, and 10, the indices N, L, and M are the upper limits of summations, respectively.

In order to demonstrate the accuracy and efficiency of the derived method, we have presented a comparison of numerical results using alternative methods (see Table 1). The validity and reliability of the method is then tested by applying it to ZnO and MgO crystals [14,31]. The temperature dependence of the specific heat capacity of ZnO and MgO crystals using our obtained formula, Eq. 9, are investigated. Debye temperatures θ for ZnO and MgO crystals have been taken as 920 K and 946 K, respectively [37,38].

Table 1 Comparative values of n-dimensional Debye functions

n	s	x_D	Eq. 10	N	Ref. [13]	N	Ref. [36]
2	1	5	0.1723290348576247821452831	800	0.1723290348576247821452831	800	0.172329034857624782145
5	1	4.5	0.1016411833969889096660730	800	0.1016411833969889096660730	800	0.10164118339698890968
7	1	0.8	0.6911240652686523067313944	800	0.6911240652686523067313944	800	0.69112406526865230673
9	1	3.4	0.1541377386778925414578569	800	0.1541377386778925414578569	800	0.15413773867789254146
12	1	5.4	0.03618849233828132604700982	800	0.03618849233828132604700982	800	0.036188492338281326047
15	1	2.4	0.2661409156647294951954087	300	0.2661409156647294951954087	300	0.2661409156647294951955
20	1	1.24	0.5233615850900328437661933	300	0.5233615850900328437661933	300	0.523361585088859680745
25	1	4.2	0.07296496706218587109015988	100	0.07296496706218587109015988	100	0.0729649670621858713684
30	1	3.42	0.125842610659036883497192	100	0.125842610659036883497192	100	0.1258426106590655660781
21	10	18	$2.350667712476464522923043 \times 10^{-27}$	800	$2.350667712476464522923043 \times 10^{-27}$	800	–
32	12	4.8	$8.948613400545201024874528 \times 10^{-21}$	800	–	–	–

3 Numerical Results and Discussion

Firstly, the *Mathematica* software system (Version 5.0) was used to calculate Debye functions using the formulae presented in this study. The results obtained for Debye functions are shown in Table 1. In order to demonstrate the accuracy and efficiency of the methods described above, Table 1 also includes values obtained from other studies [13,36]. For comparison with studies by other authors, the *n*-dimensional Debye functions are derived using formulas given in Refs. [13] and [36]. Table 1 demonstrates excellent agreement between our results and those of Refs. [13] and [36]. This clearly demonstrates that the formulae obtained yield significant accuracy for arbitrary values of n, s, x_D.

The variation of the specific heat capacity C_v against temperature (T) of ZnO and MgO crystals are shown in Figs. 1 and 2 for the temperature range from 0 K to 2,100 K. Figures 1 and 2 also illustrate the comparison of our results with those of Seko et al. [31] and Lu et al. [14] for MgO and ZnO samples.

From Fig. 1, it is shown that our results for MgO crystals are in excellent agreement with the results of Seko et al. [31]. Our results are also in agreement with those of Lu et al. [14], particularly in the temperature ranges, (50 K to 300 K) and (700 K to 2,100 K).
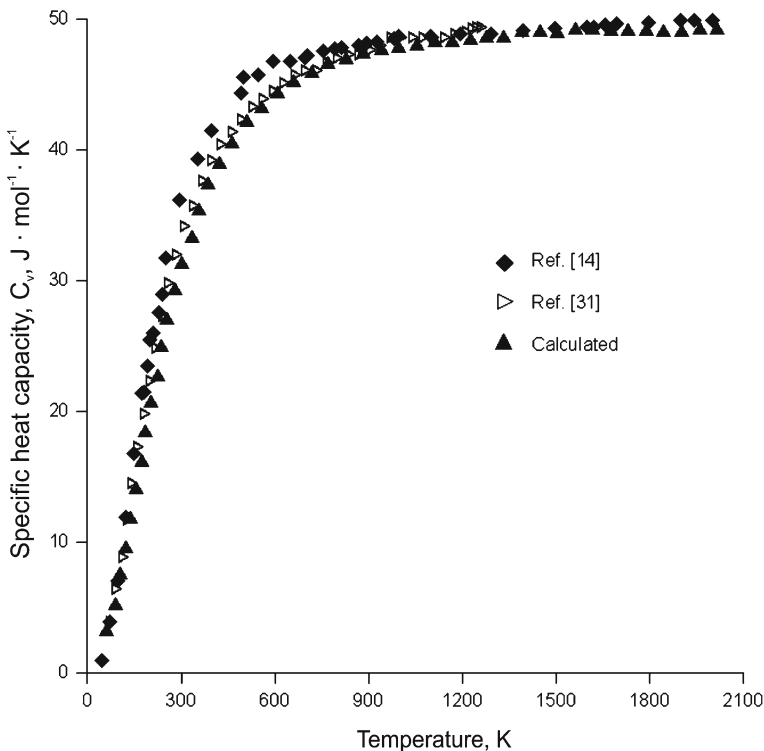

Fig. 1 Temperature dependence of heat capacity C_v for MgO crystals: Lu et al. [14]; Seko et al. [31]; "Calculated"
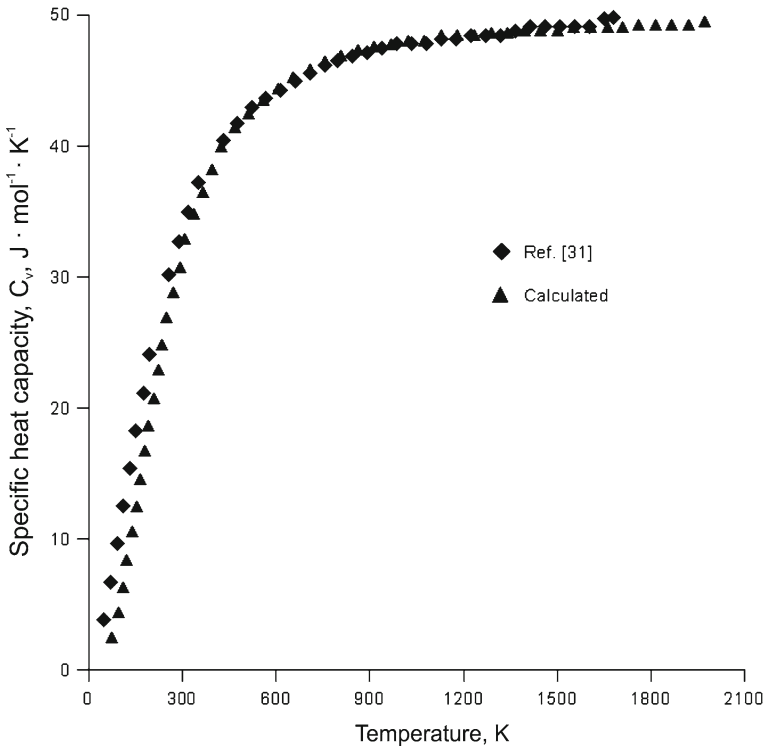
Fig. 2 Temperature dependence of heat capacity C_V for ZnO crystals: Seko et al. [31]; "Calculated"

In Fig. 2, we compare the results for ZnO crystals, which demonstrate excellent agreement between our results and those of Seko et al. [31] in the temperature range from 250 K to 1,800 K.

In this study, an efficient and accurate method is presented for calculation of the heat capacity of a solid depending on the Debye temperature for all values of m, s, n, and x_D. We are not aware of any previously published research undertaking calculation of Debye functions with n, s, x_D, except for Ref. [13]. The use of the simple analytical expression for modeling and simulation can be useful in the development of high-quality devices and has wide fields of application.

In conclusion, we have presented a simple analytical expression for calculation of specific heat capacities of solids depending on Debye functions using binomial coefficients with all integer values of parameters n, s, and x_D. The analytical expression obtained in this work can be used in the study of many physical problems, especially in the calculation of the heat capacity of solids. The use of the computer programs presented for calculation of n-dimensional Debye functions can be also used in the investigation of the quantum-mechanical behavior of phonons. We note that the derived expressions for the n-dimensional Debye functions can be evaluated efficiently, quickly, and accurately.

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