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On the Determination of Molar Heat Capacity of Transition Elements: From the Absolute Zero to the Melting Point

Ivaldo Leão Ferreira, José Adilson de Castro and Amauri Garcia

Abstract

Molar specific heat is one of the most important thermophysical properties to determine the sensible heat, heat of transformation, enthalpy, entropy, thermal conductivity, and many other physical properties present in several fields of physics, chemistry, materials science, metallurgy, and engineering. Recently, a model was proposed to calculate the Density of State by limiting the total number of modes by solid–liquid and solid–solid phase nucleation and by the entropy associated with phase transition. In this model, the new formulation of Debye’s equation encompasses the phonic, electronic, and rotational energies contributions to the molar heat capacity of the solids. Anomalies observed in the molar specific heat capacity, such as thermal, magnetic, configurational transitions, and electronic, can be treated by their transitional entropies. Model predictions are compared with experimental scatter for transitional elements.

Keywords: molar heat capacity, density of state, phase transition entropies, transitional elements

1. Introduction

Einstein [1] developed the first model approach regarding the atoms in a crystalline solid as independent harmonic oscillators vibrating at the same frequency by assuming the density of state as a delta function. Debye [2–4] modeled the vibrations in a solid as normal modes of a continuous elastic body, which corroborates well for long-wavelength vibrations that do not depend on the detailed atomic character of the solid and do conform better with experimental scatters at lower temperatures. The density of state modeled by Debye failed for many materials, which present a gap in the density of state [5, 6]. The Debye model does not consider rotational, electronic, and magnetic contributions [7–11]. Ferreira et al. [12, 13] considering Gibbs–Thomson coefficients for equilibrium and non-equilibrium nucleation conditions, and the assumption that when cleaved, certain crystals exhibit surface stress that gives rise to small but detectable strains in the interior of the crystal, i.e., microscopic considerations that predict the presence of surface stress whenever a new surface is created [14], derived a model for pure

elements and compounds, regarding the critical radius expressed in terms of the temperature drop employing the correlation between the solid–liquid surface tension and the bulk melting entropy by unit volume, given in terms of the Gibbs–Thomson coefficient [15, 16]. Consequently, based on the nucleation of solid–liquid or solid–solid phases, the total number of atoms in the volume and a correspondent density of n atoms limited by nucleation conditions were proposed to calculate the density of state. Ferreira et al.’s model consists of the phonic, electronic, rotations contributions and predicts magnetic anomalies, such as phase transition temperatures.

In this paper, model predictions of the molar heat capacity of transitional elements from absolute zero to the melting point are compared with the Thermo-Calc Software simulations and experimental data.

2. Modeling

The Gibbs–Thomson coefficient describes for pure elements the melting temperature depression $\Delta T_m [K]$, based on the solid–liquid interface energy $\gamma_{sl} [N.m^{-2}]$ and on the bulk melting entropy by unit volume $\Delta S_v [J.K^{-1}.m^{-3}]$. Let us consider an isolated solid particle of radius r in the liquid phase; the Gibbs–Thomson equation for the structural melting point depression can be expressed by [12, 13]:

$$\Gamma = \frac{\gamma_{sl}}{\Delta S_v} \quad (1)$$

According to Gurtin et al. [14], surface stress gives rise to detectable strains in the interior of the crystal whenever a solid surface is created. A relation of surface tension in terms of η and ζ parameters is given by:

$$\Gamma = \eta \frac{\sigma_{sl}}{\Delta S_v} \zeta \quad (2)$$

and,

$$\eta \cong \frac{\sigma_{sl}}{\gamma_{sl}} \quad (3)$$

By substituting (3) into (2) and making $\zeta = 1 [m]$ provides

$$\Gamma \cong \frac{\sigma_{sl}}{\Delta S_v} \cong \frac{\sigma_{sl} T_m^{bulk}}{\Delta H_v} = \frac{2 \Gamma}{r} \quad (4)$$

where σ_{sl} is the solid–liquid interface tension $[N.m^{-1}]$, T_m^{bulk} is the bulk melting temperature $[K]$, ΔH_v is the latent heat of melting per unit volume $[J.m^{-3}]$ and r is the spherical grain radius $[m]$, respectively.

For a stable nucleus, the critical radius can be expressed in terms of the temperature drop $\Delta T(r)$ through the correlation between the solid–liquid surface tension σ_{sl} and the bulk melting entropy by unit volume ΔS_v , which can be written in terms of the Gibbs–Thomson coefficient Γ .

$$\Delta T(r \geq r_C) = \frac{2 \Gamma}{r} \quad (5)$$

The density of state $D(\omega)$ for a given grain of volume \forall regarding the critical nucleation radius, is defined as

$$D(\omega) = \frac{\forall \omega^2}{2 \pi^2 \nu^3} \quad (6)$$

where ω is the frequency, ν is the speed of sound in the solid. For a total number of atoms N in the volume \forall and a correspondent density of atoms n , these variables can be expressed as,

$$N = n\forall \quad (7)$$

The first Brillouin zone is exchanged by an integral over a sphere of radius k_D , containing precisely N wave vectors allowed. As a volume of space k by wave vector requires,

$$\frac{(2\pi)^3}{\forall} N = \frac{4\pi k_D^3}{3} \quad (8)$$

Then, the density of atoms n can be obtained as,

$$n = \frac{k_D^3}{6\pi^2} = \frac{1}{6\pi^2} \left(\frac{k_B \Theta_D}{\hbar \nu} \right)^3 \quad (9)$$

As observed in Eq. (9), the element fundamental frequency is expressed as

$$\omega_D = \frac{k_B \cdot \Theta_D}{\hbar} \quad (10)$$

where, Θ_D is the Debye's temperature of the element, k_B and \hbar are the constants of Boltzmann and Planck, respectively.

The electronic contribution to c_{ve} is written in terms of the phonon energy c_v^{Vib} as,

$$\frac{c_{ve}}{c_v^{Vib}} = \frac{5}{24 \pi^3} Z \frac{\Theta_D^3}{T^2 T_m^{bulk}} \quad (11)$$

where, Z is the valence of the element, T_m^{bulk} is the melting temperature of the element [K] and T is the absolute temperature [K].

In 2019, Ferreira et al. [15, 16] considered the following approach for the rotational energy,

$$E_{Rot} = \frac{5}{4} \hbar^2 \frac{J(J+1)}{\bar{M} \cdot r^2} [J] \quad (12)$$

where, J is the rotational level corresponding to integer $J = 0, 1, 2, 3, \dots, r$ and \bar{M} are the atomic radius and the molar mass, respectively. The rotational contribution c_v^{Rot} to the molar heat capacity can be derived as,

$$c_v^{Rot} = \frac{5}{4} \frac{R \cdot \hbar^3}{k_B^2 \omega_D (T + \Theta_D)^2} \frac{J(J+1)}{\bar{M} \cdot r^2} [J.mol^{-1}.K^{-1}] \quad (13)$$

where, ω_D is the maximum admissible frequency known as Debye's frequency and, R is the universal gas constant $[J.mol^{-1}.K^{-1}]$.

Debye's temperature for transition elements is found in the literature [4]. The additions of Eq. (17) of the electronic and of Eq. (19) of the rotational contributions to c_v , provide,

$$c_v = (1.0 + D(\omega)) 9 N_a k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\frac{T}{\Theta_D}} \frac{x^4 e^x}{(e^x - 1)^2} dx (1 + c_{ve}) + \left(n + \frac{1}{2} \right) \left[9.0 c_v^{Rot} + \left(1 - \sqrt{\frac{E \cdot \rho_{Dia}}{E_{Dia} \cdot \rho}} \right) \frac{RT^3}{\Theta_D T_m^2} \right] \quad (14)$$

3. Results and discussion

Figure 1 presents the model predictions of molar heat capacities for pure Chromium and experimental data from absolute zero to the melting point. Debye's model predictions are presented as a reference for Ferreira's model calculations [15, 16]. Thermo-Calc equilibrium calculations were performed in the range 176 K

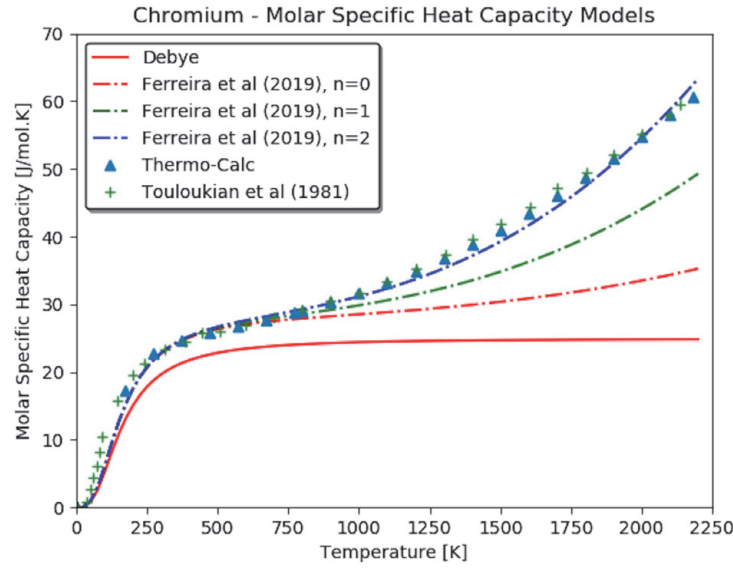


Figure 1.

Comparison of the molar heat capacity of pure chromium by applying Debye, Thermo-Calc, and Ferreira et al. [15, 16], and Touloukian et al. [17].

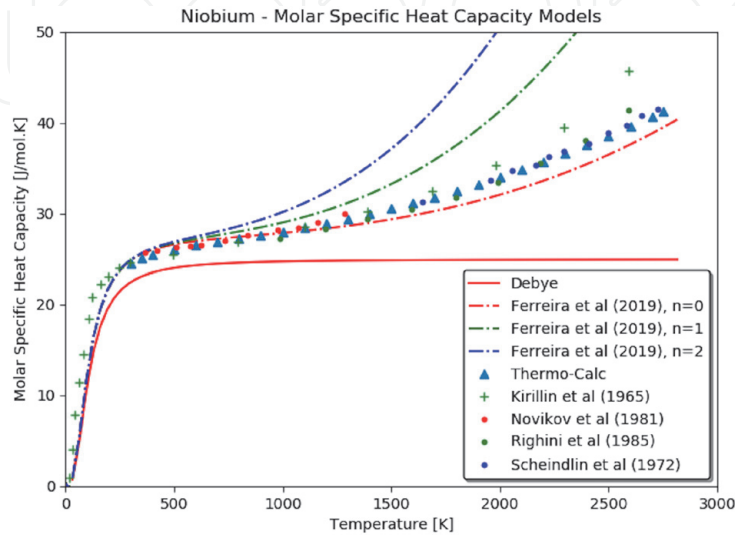


Figure 2.

Comparison of the molar heat capacity of pure niobium by applying Debye, Thermo-Calc, and Ferreira et al. [15, 16], and Kirillin et al. [18], Novikov et al. [19], Righini et al. [20] and Scheindlin et al. [21].

to 2180 K. The proposed model agrees, for low and high temperatures, with the experimental data of Touloukian et al. [17].

Figure 2 shows model calculations for Niobium compared with calculations performed with Thermo-Calc, and four experimental data sets [18–21]. In the literature, experimental values of molar heat capacity at high temperatures (for which measurements are complicated) generally overestimate the heat capacity. On the other side, at low temperatures, where measurements are difficult to control, the experimental values underestimate this property [22]. Furthermore, observations of the thermophysical properties of Nb applied in the model predictions, such as surface tension, Debye’s temperature, atomic radius, the density of solid at the melting point, latent heat of fusion, among others, should be carefully compared with those from different authors, as values for the thermophysical properties found in the literature differ from author to author, and they could also be a likely source of the slight deviation observed in the predicted curve. The equivalent

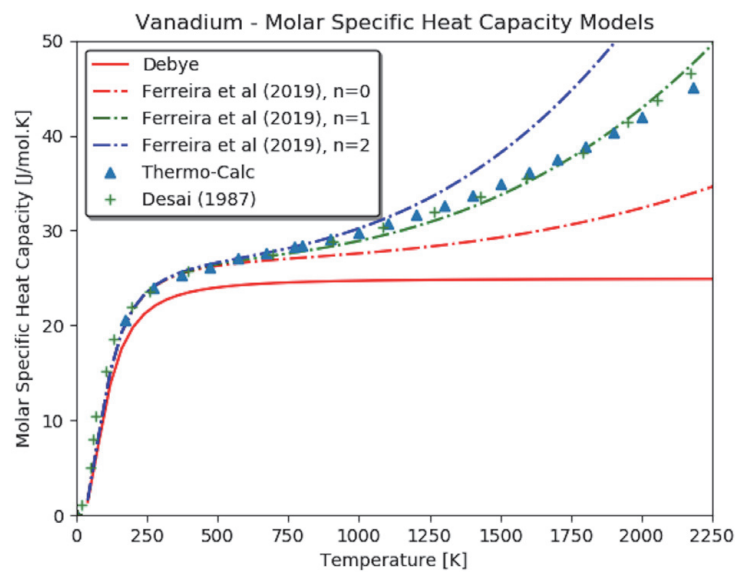


Figure 3.
Comparison of the molar heat capacity of pure Vanadium by applying Debye, Thermo-Calc, and Ferreira et al. [15], and experimental data Desai [23].

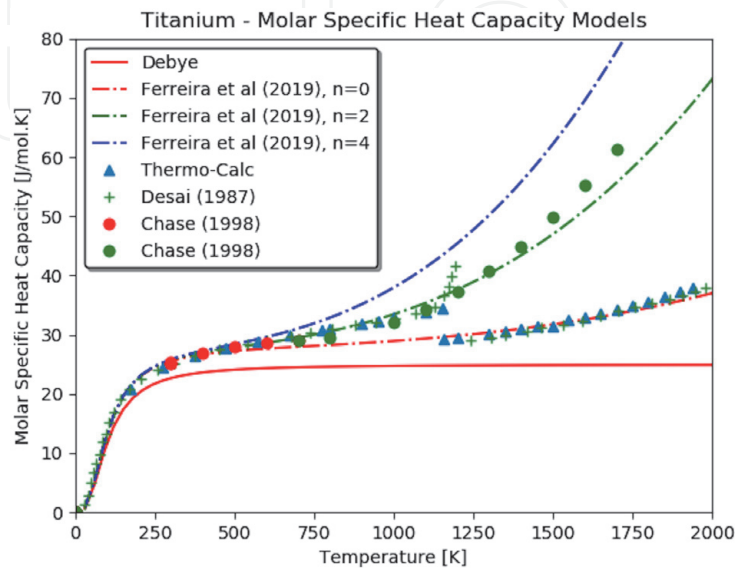


Figure 4.
Comparison of the molar heat capacity of pure titanium by applying Debye, Thermo-Calc, and Ferreira et al. [15, 16], and experimental data Desai [23] and Chase [24].

wavevectors simulated are $n = 0, 1$, and 2 . The experimental data are close to the theoretical calculations for $n = 0$.

Figure 3 shows the experimental scatter for Vanadium from the absolute zero to the melting point, Thermo-Calc and Ferreira et al. model's calculations [15, 16]. The predictions for $n = 1$ agrees, for the whole temperature range, with the experimental data, and Thermo-Calc.

Figure 4 shows the molar specific heat for Titanium, the experimental data from Chase [24] and found in Desai [23]. Chase experimental data, in green, follow $n = 2$ for the whole temperature range. In this case, Chase's experiment's thermodynamic conditions allow concluding that no phase transition at $T = 1156K$ takes place, which configures a non-fundamental state specific heat. On the other hand, after the transition temperature, Desai's [23] experimental data and Thermo-Calc agree with the theoretical model for $n = 0$ from 1156 to 1941 K, configuring a fundamental state specific heat.

4. Conclusions

The model previously proposed by Ferreira et al. [15, 16] based on the critical radius of phase nucleation to determine the total numbers of modes, and consequently, the Density of State successfully predicted the molar specific heat capacity of transitional elements. In Cr and V, the experimental data follow the theoretical prediction curves with $n = 2$ and $n = 1$, respectively. Furthermore, the model's calculation for Nb agrees with the experimental data except for the set found in Kirillin et al. [18]. The thermophysical properties of Niobium at high temperatures and experimental difficulties might be the reasons responsible for the slight deviation observed between the predictions and experimental data at high temperatures. For Titanium, non-fundamental states and fundamental state molar heat capacity were predicted experimentally and theoretically, as Chase's experiments follow the model's theoretical predictions for $n = 2$.

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