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The Einstein specific heat model for finite systems

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HIGHLIGHTS

- Extension of the Einstein specific heat model for finite solids.
- Obtainment of the specific heat (χ) solving transcendental equations.
- Obtainment of the chemical potential (m) using a discrete Leibniz integral rule.
- Discontinuities of $\chi(\tau)$ and $\beta m(\tau)$ derivatives appear only for finite N.
- Achievement of BEC temperature has an inverse of harmonic series dependence on N.

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ABSTRACT

The theoretical model proposed by Einstein to describe the phononic specific heat of solids as a function of temperature consists of the very first application of the concept of energy quantization to describe the physical properties of a real system. Its central assumption lies in the consideration of a total energy distribution among N (in the thermodynamic limit $N \to \infty$) non-interacting oscillators vibrating at the same frequency (ω). Nowadays, it is well-known that most materials behave differently at the nanoscale, having thus some cases physical properties with potential technological applications. Here, a version of the Einstein model composed of a finite number of particles/oscillators is proposed. The main findings obtained in the frame of the present work are: (i) a qualitative description of the specific heat in the limit of low-temperatures for systems with nano-metric dimensions; (ii) the observation that the corresponding chemical potential function for finite solids becomes null at finite temperatures as observed in the Bose–Einstein condensation and; (iii) emergence of a first-order like phase transition driven by varying N.

1. Introduction

The Einstein model [1] encompasses basic principles of Thermodynamics, Quantum and Statistical Mechanics to describe the specific heat of solids. Whereas this model does not exhibit "perfect" quantitative performance [2], it is the very first realistic solid state model to consider the effect of the crystal lattice vibrations on the thermodynamic properties, see e.g. Refs. [3,4]. As a matter of fact, there are only a few realistic systems, whose multiplicities can be calculated using elementary methods, see e.g. Ref. [5] and references cited therein. Essentially, the model proposed by Einstein in 1907 [1] to describe the thermal properties of a simple crystalline solid, treating the solid as an array of atoms consisting of independent three-dimensional harmonic oscillators, is still of great interest [3,4].

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The aim of this work is to extend the model proposed by Einstein for the case of finite number of harmonic oscillators. To this end, mathematical functions describing analogous thermodynamic properties for finite solids such as the specific heat and the chemical potential were deduced. Although exhibiting, for $N \to \infty$, the thermodynamic behavior well-known from textbooks [6], such analogous functions have the advantage of being defined for any N, which allows one to explore how close to the thermodynamic behavior the properties of solids with low numbers of particles can be. In other words, the introduction of analogous thermodynamic functions extends the range of applications of thermodynamic, statistical and quantum mechanics, from macroscopic to microscopic scales.

Given the high interest in the physical properties of nano-materials, several models have been proposed to explain the peculiar properties of finite solids. Among them, it is worth mentioning reports taking into account surface effects [7–9], the form of the nanoparticles [10] and the presence of impurities [11]. Following Einstein's original framework, the model proposed here is based on how the total energy of the system of interest is distributed among their constituting oscillators, whose description is presented in the following. Initially, a closed-form function S, analogous to the thermodynamic entropy was obtained for systems with a finite number of particles (one-dimensional harmonic oscillators), see Section 2 for details. By taking the derivative of S with respect to the energy E, one obtains the analogous thermodynamic temperature as a function of E for finite systems, i.e. $\tau(E, N) = (\partial S/\partial E)^{-1}$. Then, by numerically differentiating $E(\tau, N)$ with respect to τ the specific heat as a function of N, namely $\chi(N)$, for finite systems is deduced. Similarly, by taking the derivative of the entropy in relation to N, and employing a discrete form of the Leibniz integral rule (see Appendix B), the function m, analogous to the chemical potential for finite systems, was obtained.

Essentially, the main findings achieved in the present work are: (i) for different finite N, the χ vs. τ curves reproduce qualitatively the experimental behavior observed in the limit of low τ; (ii) $m(\chi)$ converges quickly (upon increasing N) on the thermodynamic behavior of chemical potential (specific heat) even for low values of N; (iii) while the thermodynamic chemical potential is null only for $\tau \to 0$, the function m for finite N can be null even at finite temperatures (τ_0), with $\frac{\tau_0 k_B}{\hbar\omega}$ being numerically equals to the inverse of the harmonic series, which converges slowly to zero as N grows; k_B and $\hbar$ are, respectively, the Boltzmann and Planck constants, ω stands for the oscillators vibrational frequency. Furthermore, the present model can represent a bridge between finite systems and the thermodynamic limit by considering different values of N. Yet, the model can be employed in the description of the phononic specific heat of small clusters or nano-systems. Before starting with the theoretical discussion we stress that the physical quantities to be derived for finite systems are analogous to those well-known from text-books for the thermodynamic limit. The same holds true for the discussion about the phase transition like behavior to be discussed in Section 3.4. Yet, we stress that the present approach can be employed for one-, two- and three-dimensional systems as well, since that in the frame of the Einstein model the oscillators are uncoupled and thus the dimensionality and the arrangement of the system are no longer relevant.

2. Theory

The number of accessible eigen-states, Ω, in a solid can be obtained by considering the sharing of $M(=E/\hbar\omega - N/2)$ energy quanta among N non-interacting oscillators. This approach is frequently discussed in the literature [6] and it is given by:

$$\Omega(E, N) = \frac{(M + N - 1)!}{M!\,(N - 1)!} = \frac{\left(\frac{E}{\hbar\omega} + \frac{N}{2} - 1\right)!}{\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)!\,(N - 1)!}. \tag{1}$$

For $N \geq 2$, $\ln(\Omega)$ can be reorganized exactly as (see Appendix A for generic $M = F(E)$):

$$\ln(\Omega(E, N)) = \sum_{i=1}^{N-1} \ln\left(\frac{\frac{E}{\hbar\omega} - \frac{N}{2} + i}{i}\right). \tag{2}$$

The analogous to the energy and entropy per particle functions in the thermodynamic limit are readily obtained from the definitions $u \equiv E/N$ and $s \equiv S/N$, respectively. By considering $S = k_B \ln(\Omega)$, it turns out that:

$$s \equiv S/N = \frac{k_B}{N} \sum_{i=1}^{N-1} \ln\left(\frac{\frac{u}{\hbar\omega} - \frac{1}{2} + \frac{i}{N}}{\frac{i}{N}}\right). \tag{3}$$

Using the relation $\partial s/\partial u = \partial S/\partial E = 1/\tau$, an expression can be found for the intensive function τ, analogous to the thermodynamic temperature:

$$\frac{1}{\tau} = \frac{k_B}{\hbar\omega} \sum_{i=1}^{N-1} \left(\frac{E}{\hbar\omega} - \frac{N}{2} + i\right)^{-1} = \frac{k_B}{N\hbar\omega} \sum_{i=1}^{N-1} \left(\frac{u}{\hbar\omega} - \frac{1}{2} + \frac{i}{N}\right)^{-1}. \tag{4}$$

The functions $E = E(\tau, N)$, or $u = u(\tau)$, cannot be obtained analytically by simple inversion of the Eq. (4) for $N > 4$ since it involves polynomials of fifth or higher degree. However, numerical techniques for root finding problem as, for instance, Newton–Raphson can be used to obtain these functions with arbitrary precision. s and u are given in Table 1 for different values of N. It is worth mentioning that u cannot be less than $\frac{\hbar\omega}{2}$ since the zero point energy is the lowest value possible, namely the entropy goes to zero when $u = \frac{\hbar\omega}{2}$. The behavior of $u_N(\tau)$ for various values of N is depicted in Fig. 1.