

The Einstein model and the heat capacity of solids under high pressures

N. Aquino

*Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa,
Apartado Postal 55-534, 09340 México, D.F.,
e-mail: naa@xanum.uam.mx*

V. Granados and H. Yee-Madeira

*Departamento de Física, Escuela Superior de Física y Matemáticas del Instituto Politécnico Nacional,
Edif. 9, Unidad Prof. “Adolfo López Mateos”, Col. San Pedro Zacatenco, México D.F. 07738, México.*

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We use the Einstein model to compute the heat capacity of a crystalline solid where the effect of high pressures is simulated through a confined harmonic oscillator potential. The partition function and the heat capacity are calculated in terms of the box size (pressure), finding a clear tendency of the latter quantity to diminish as the pressure increases. For a strong confinement regime (high pressures) the heat capacity increases monotonically with the temperature, whereas at moderate and low pressures, it attains a maximum and asymptotically becomes that corresponding to a set of free (non-interacting) particles in a box. At high temperatures we find that the specific heat value of a crystalline solid under high pressures departs from that predicted by the Dulong-Petit model.

Keywords: Schrödinger equation; confined quantum systems; heat capacity; high pressure.

Se usa el modelo de Einstein para calcular el calor específico de un sólido cristalino sometido a altas presiones donde el efecto de la alta presión se simula usando un potencial de oscilador armónico confinado. La función de partición y la capacidad calorífica se calculan en términos del tamaño de la caja de confinamiento (presión), encontrándose una clara tendencia del calor específico a disminuir cuando la presión aumenta. En el régimen de confinamiento fuerte (alta presión) el calor específico aumenta monótonicamente con la temperatura, mientras que a presiones moderadas y bajas alcanza un valor máximo, y después tiende asintóticamente al calor específico correspondiente a un conjunto de partículas libres (no-interactuantes) dentro de una caja. A altas temperaturas se encuentra que el calor específico de un sólido cristalino sometido a altas presiones se aparta del valor predicho por el modelo de Dulong-Petit.

Descriptores: Ecuación de Schrödinger; sistemas cuánticos confinados; capacidad calorífica; alta presión.

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1. Introduction

One century ago, Albert Einstein proposed a simple model to calculate the heat capacity of solids [1] where the interaction between neighboring molecules was assumed to be given by a harmonic potential. He considered a solid composed of N_A molecules, each oscillating freely with the same frequency along a given direction in the three-dimensional space, around a fixed center. Thus, this problem is equivalent to the motion of $3N_A$ one-dimensional harmonic oscillators of frequency ν . He assumed that the energy of a one-dimensional harmonic oscillator is not a continuous variable but rather a discrete value equal to an integer times $h\nu$ (Planck's quantum), computing through his model the average energy of $3N_A$ one-dimensional oscillators and their specific heat.

Einstein considered the lattice vibrations only, which is a reasonable assumption, since it is well known that in most solids the energy arising from lattice vibrations yields the main contribution to the specific heat. In fact, in non-magnetic isolates, it is the only one, whereas in metals there are other contributions due to conduction electrons, and in the case of magnetic materials they are due to magnetic ordering.

In this paper, we use the Einstein model to calculate the heat capacity of solids under high pressures. One way to

simulate pressure exerted by the surrounding matter on a molecule is by means of an impenetrable potential surface that physically plays the role of a repulsive potential. In our case, the latter is represented by a confined harmonic oscillator (CHO) potential. This idea is not new, having first been used by Kaplan and Corson [2], in 1946. Michels *et al.* [3] were the first to use the idea of introducing an impenetrable wall to simulate the action of an external force. Since then, the use of a confined quantum system to simulate high pressures has been successfully applied to the computation of electronic properties of atoms and molecules [3-6]. The present method can be adapted for the computation of specific heats of quantum dots, among other spatial confined systems [5,6].

The calculation of the specific heat of crystalline solids through the Einstein model is an obligatory topic in courses such as Introduction to Modern Physics and Introduction to Solid State Physics, among others. In this work we make use of knowledge of this topic to explore the variation of the specific heat of crystalline solids subjected to very high external pressures. In this work, a relationship is established between two areas of Physics; Statistical Mechanics and quantum confined systems. The latter have recently become more relevant due to a growing interest, theoretical as well as experimental, in quantum points, wells and wires.

TABLE I. 1D confined harmonic oscillator energy eigenvalues as a function of the box size ($L = 2R$). Lengths and energies are given in units of $\sqrt{\hbar/m\omega}$ and $\hbar\omega$, respectively. The exact results were obtained by a method described in Ref. 7 and 12.

R	E_1 [Eq. (5)]	E_1 (exact)	E_2 [Eq. (5)]	E_2 (exact)	E_5 [Eq. (5)]	E_5 (exact)	E_{20} [Eq. (5)]	E_{20} (exact)
0.5	4.951	4.951	19.775	19.775	123.411	123.411	1973.96	1973.96
1.0	1.299	1.298	5.076	5.076	31.005	31.005	493.647	493.647
1.5	0.695	0.689	2.511	2.505	14.074	14.075	219.699	219.699
2.0	0.570	0.537	1.799	1.765	8.361	8.369	124.036	124.036
2.5	0.606	0.505	1.673	1.551	5.951	5.978	79.997	80.000

This report is organized as follows: In Sec. 2 we describe a method to obtain approximate eigenvalues of the one-dimensional confined harmonic oscillator. In Sec. 3 the specific heat is formulated in terms of the partition function, while in Sec. 4 our results and conclusions are given.

2. The one dimensional confined harmonic oscillator

The one-dimensional (1D) confined harmonic oscillator (CHO) has been widely discussed in the literature for more than sixty years [4-12]; however, few papers have been devoted to the study of confined quantum systems from the academic point of view [11,13-18]. The energy eigenvalues of this problem cannot be calculated in a closed analytical way (in terms of elementary functions); instead, their approximate values are obtained by a variety of methods, either algebraic or numerical. Recently, Montgomery *et al.* [7] computed energy eigenvalues and eigenfunctions of 1-D CHO with very high accuracy.

In this work, we use a simple method to obtain analytical results for the energy levels of a CHO. The energies were obtained using first-order Perturbation Theory (PT) [11].

The Hamiltonian of the one-dimensional symmetrically confined harmonic oscillator of mass m and angular frequency ω is given by

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 + V(x), \quad (1)$$

where

$$V(x) = \begin{cases} 0 & \text{if } |x| < R \\ \infty & \text{if } |x| > R \end{cases}. \quad (2)$$

The time-independent Schrödinger equation of this system is given by

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \left[\frac{1}{2}m\omega^2x^2 + V(x) \right] \psi = E\psi, \quad (3)$$

with boundary conditions:

$$\psi(x = \pm R) = 0. \quad (4)$$

In order to apply the PT, it is convenient to take the unperturbed Hamiltonian as the one corresponding to a particle

in an impenetrable box of length $2R$, and the harmonic oscillator potential as the perturbation [9,11]. It is also convenient to write the Schrödinger equation in the harmonic oscillator dimensionless variables. A straightforward calculation gives the energy values with corrections up to first order in perturbation theory [11]:

$$E_n = \left(\frac{n^2\pi^2}{8R^2} + \frac{R^2}{6} - \frac{R^2}{n^2\pi^2} \right). \quad (5)$$

The energies are given in units of $\hbar\omega$. In this equation, instead of the typical harmonic oscillator energy, there appears a term corresponding to the energy of a free particle in a box plus correction terms that are proportional to R^2 . Accordingly, when the box size increases beyond bounds, the energies diverge, thereby preventing recovery of the harmonic oscillator energy levels. Equation 5 approximates well the exact results for boxes in the range $R \leq 2.0a$ ($a = \sqrt{\hbar/m\omega}$ is the length unit), as shown in Table I.

The force acting on each wall is defined by [3]

$$F = -\frac{dE_1}{dR}, \quad (6)$$

where E_1 refers to the ground state energy.

3. The specific heat of a solid under high pressure

We consider one mole of a solid consisting of N molecules, each one oscillating around a fixed center (the equilibrium position). For small displacements around it, we may regard the vibrations as given by a harmonic oscillator attractive potential. Pressure effects arising from the surrounding matter on a molecule can be simulated by means of a confined harmonic oscillator (CHO) potential, as discussed in the previous section. The walls are symmetrically located along each direction around the equilibrium position and we assume that all oscillators vibrate with the same frequency ω in each direction.

This problem is thus equivalent to $3N$ one-dimensional confined harmonic oscillators, each of frequency ω . The specific heat of a solid can be calculated in a straightforward way [19-23].

The one-dimensional partition function is given by

$$Z = \sum_{n=0}^{\infty} \exp(-\beta E_n) \quad (7)$$

where $\beta = 1/kT$, and the average energy is

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta}. \quad (8)$$

In order to compute this quantity numerically, it is convenient to write it as

$$\bar{E} = \frac{\sum_{n=0}^{\infty} E_n \exp(-\beta E_n)}{\sum_{n=0}^{\infty} \exp(-\beta E_n)} = \hbar\omega. \quad (9)$$

The total internal energy U for $3N$ oscillators is given by

$$U = 3N \bar{E}, \quad (10)$$

out of which, the specific heat at constant volume is obtained as

$$C_v = \frac{dU}{dT}. \quad (11)$$

By substituting Eqs. (5) and (7) into Eq. (8) it follows that

$$C_v = 3Nk \left(\frac{\hbar\omega}{kT} \right)^2 \left[\frac{1}{Z} \sum_{n=0}^{\infty} E_n^2 e^{-\beta E_n} - \frac{1}{Z^2} \left(\sum_{n=0}^{\infty} E_n e^{-\beta E_n} \right)^2 \right]. \quad (12)$$

The specific heat can be computed in terms of the Einstein temperature θ

$$\hbar\omega = k\theta, \quad (13)$$

where ω and k refer to the oscillator frequency and the Boltzmann constant, respectively.

The pressure acting on the cube walls (Fig. 1) is obtained in the usual way [3] where the force exerted on each (Eq. 6) is divided by the corresponding surface area A^2 .

$$P = \frac{F}{A^2} = -\frac{1}{A^2} \frac{dE_1}{dR}, \quad (14)$$

where E_1 denotes the ground state energy.

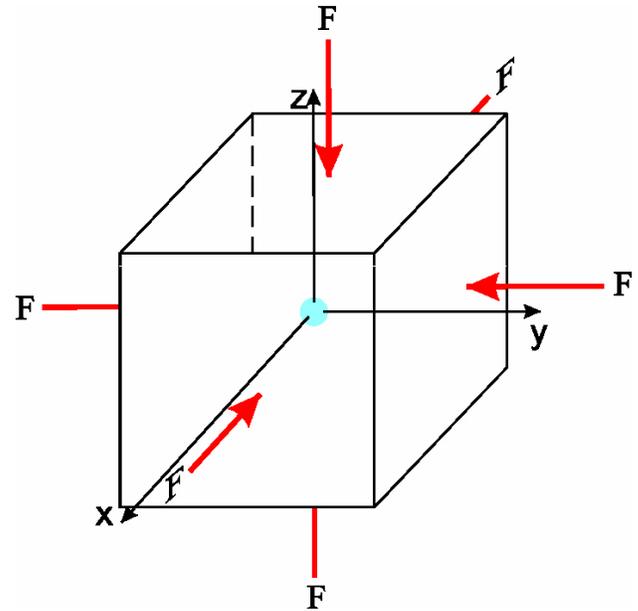


FIGURE 1. A particle (molecule) at the cube center oscillates with frequency ω around axes x, y and z . The motion of the particle is constrained within impenetrable walls of length $L = 2R$. An external force F is acting on each of the cube faces.

4. Results and discussion

Computation of the specific heat is performed via Eq. (12), in which use is made of the analytical relation for energies [see Eq. (5)]. For small temperatures and high pressures (small R), only a few terms of the series in Eq. (12) are required to ensure convergence. The specific heat can be calculated with the aid of a spreadsheet or even of a pocket calculator. However, due to the availability of computational resources such as high-level languages and programs that combine analytical handling of expressions and numerical calculation techniques (some well-known examples are Mathematica, Maple and Derive), we decided to use one of them. Programs like Mathematica simplify the work, where no special algorithms are required to obtain the value of a series, since these programs have built-in routines to compute it involving a large number of terms. The present calculations were carried out by using the command **Sum[]** of Mathematica to compute the series in Eq. (12).

In Fig. 2 we show the specific heat $C_v/(3Nk)$ as a function of T/θ (θ is the Einstein temperature), for five different box sizes or pressures (Eq. 14). As seen in Fig. 2, at very low temperatures ($T/\theta \rightarrow 0$) all specific heat curves fall off to zero; however, one should bear in mind that the temperature dependence of the specific heat is a function of the pressure. As mentioned above, Einstein's theory fails at low temperatures; therefore, we only expect a qualitative agreement in comparison to experimentally observed behaviour (whenever experiments under such conditions can be carried out).

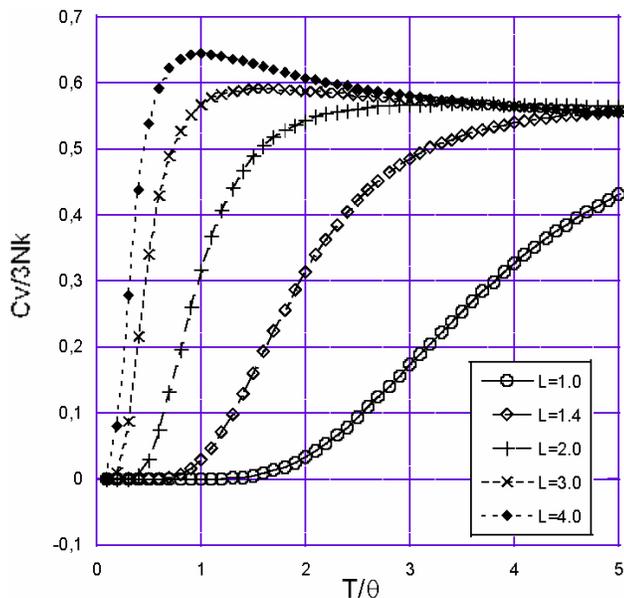


FIGURE 2. Specific heat for a few values of the confinement as a function of T/θ (box radius $L=2R=1.0, 1.4, 2.0, 3.0,$ and 4.0 . Length units are given by $a = \sqrt{\hbar/m\omega}$).

Toward the high confinement (pressure) regime, the specific heat curve $C/3Nk$ increases smoothly with the temperature. At a high temperature, $C/3Nk \rightarrow 1/2$, which is the value that corresponds to the specific heat of an ideal gas. For moderate and small confinement regimes the specific heat increases with the temperature, rising over 0.5, and subsequently decreases slowly, approaching back to 0.5 again. For box sizes $R=4$ length units a clearly defined maximum is discerned. This behaviour is, however, not completely unexpected, where a maximum of similar features is found for the specific heat of a rotor [21], also in a two-energy level system [23], as well as in a Bose-Einstein gas [24]. In addition, it is in agreement with the specific heat behaviour for a particle in a box, as shown by Rosenstock [21] and Granados and Aquino [22].

As temperature T/θ increases to approximately 5.0, the specific heat $C_v/(3Nk)$ approaches 0.5, which is the value predicted by the classical equipartition principle for a mono atomic ideal gas. In our case, the specific heat at high temperatures does not approach 1.0 - as predicted by the Dulong-Petit model - because the dominant behaviour stems from the free particle in a box, rather than due to a typical harmonic oscillator contribution, which may occur in the absence of or for vanishingly small-external pressures.

In order to estimate how much pressure these systems are subjected to, we shall assume that no changes on the harmonic oscillator vibration frequency occur as the pressure

increases. We consider the frequency and Einstein temperature of aluminium (Al) at 1 atmosphere (Atm). In Mandl's book [20] we found $\omega = 39.6 \times 10^{12} s^{-1}$ and $\theta = 303^\circ K$, bearing in mind that frequency and Einstein temperature are related via $\hbar\omega = k\theta$.

By using this value for the frequency, we find that the length unit $a = \sqrt{\hbar/m\omega} = 7.708 \times 10^{-12} m$ (where m is the aluminium mass = 27 amu). The confining box size is thus approximately 10^{-2} \AA . (It should be observed that a is **not** a lattice parameter.) The unit of pressure is therefore $\hbar\omega/a^3 = 9.0019 \times 10^7 \text{ Atm}$. Pressure as a function of the box size is shown in Table II.

These enormous pressures are well beyond any experimentally accessible with present-day technology; however, they can be found in stars or in planets whose mass outweighs that of Jupiter. Also, the frequency may not be completely invariant under pressure increments. Takayanagi *et al.* [25] performed experimental measurements of the specific heat for a single crystal of CeNi under pressures in the range 0.2-0.7 GPa, showing that the Debye temperature increases slightly when the applied pressure is raised. The Debye temperature is analogous to the Einstein temperature [Eq. (13)]; therefore, when the former increases, so does the frequency.

5. Conclusions

In this paper we have shown that the specific heat behaviour of a crystalline solid under high pressures can be predicted by using the Einstein model. It is well known that in the absence of external pressure, or when this is very small, the specific heat of most solids at low temperatures is proportional to T^3 ; however, no explanation for a feature of this type is provided by Einstein's theory. Along the same lines, the present model gives a qualitative description of the specific heat of solids at high pressures and low temperatures.

As in the case free of any confinement, the specific heat of the solid is determined by the pressure. These quantities are obtained from the interaction potential between the particles. In the present case this potential is given by the harmonic oscillator potential confined by impenetrable walls, which is the form commonly accepted in which the effect of the pressure on the system is included. A most realistic approximation would have to include penetrable walls.

Pavlov and Jojlov [26] assert that at temperatures lower than the Einstein temperature $T \ll \theta$, it is important to consider energy quantization, while at temperatures greater than the Einstein temperature $T \gg \theta$, the quantization becomes less important and can be substituted by classical representations. Stishov [27] has used this same idea to make a study in the opposite region, the specific heat of liquids and dense gases at low temperatures. Furthermore we must take into account the anharmonic term in the potential in the region $T \gg \theta$; this consideration is not too important in this work because this condition is not satisfied.

TABLE II. Pressure ($\times 10^6$ Atm) as a function of the box size (in units of a) for aluminium.

R (R=L/2)	0.5	0.7	1.0	1.5	2.0
P($\times 10^6$ Atm)	1771.013	329.246	56.338	8.686	3.078

It is also found that upon increase of pressure the specific heat falls off, which is a qualitative trend in agreement with the experimental results of Takayanagi *et al.* [25]. At very high pressures (reduced box radii) the specific heat grows monotonically with the temperature, while at moderate and low pressures it develops a well-defined maximum. By comparison, a similar behaviour has been observed in the rotor problem [21], a two-energy level system [23], Bose-Einstein gas [24] and a free particle in a box [21-22].

The energy levels given by Eq. (5) grow boundlessly when the confining box radius R goes to infinity, which prevents recovery of the free harmonic oscillator energy levels, therefore the value predicted by the Dulong-Petit law is thus not attained in this limit. Using the exact values of the

confined harmonic oscillator instead of the approximate ones (used in this work) could solve this problem.

This model represents a first step toward a deeper understanding of some of the properties of metals subject to very high pressures, as likely to be found in the core of giant gassy planets existing outside our solar system.

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