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# Exact solution of the two-level system and the Einstein solid in the microcanonical formalism

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## Abstract

The two-level system and the Einstein model of a crystalline solid are taught in every course of statistical mechanics and they are solved in the microcanonical formalism because the number of accessible microstates can be easily evaluated. However, their solutions are usually presented using the Stirling approximation to deal with factorials. In this paper, those two models are solved without any approximation, using the gamma function and its derivatives. Exact values are calculated for the entropy, temperature and specific heat, and the relative error between our exact solution and the approximate one using the Stirling approximation. This error is significant for small systems, with a number of particles  $N \sim 100$ , as in studies of atomic clusters or nanoscale structures.

## 1. Introduction

The microcanonical formalism is an important topic in statistical mechanics courses; indeed, some textbooks [1–4] use it as the starting point for developing the subject. Typically, the relationship between ‘number of states’ and entropy is stated, and then some simple examples are considered. Amongst the most popular examples, the two-level system and the Einstein solid are solved using the Stirling approximation [5] and expressions for the entropy in terms of the relevant variables are found. The use of the Stirling approximation is justified since one is interested in the thermodynamics limit, i.e. when the number of particles gets very large. However, one may wonder what happens when the number of particles is small ( $10$ – $10^3$ ). This question is interesting for two reasons. On one hand, it is conceptually interesting to know the influence of the system size. On the other hand, there is a huge interest in small systems, including atomic clusters [6–9] and nanostructures [10, 11]. There are experimental

data for systems as small as  $10\text{--}10^3$  atoms and the usual formulae of statistical mechanics and thermodynamics are sometimes used without taking into account possible finite size corrections. The aim of this paper is to address the issue of finite system size solving both the two-level system and the Einstein solid exactly, i.e. without using the Stirling approximation, in the framework of the microcanonical formalism.

This paper is suitable for an upper undergraduate course in statistical physics and might also be of interest for a graduate course dealing with nanophysics.

The structure of this paper is as follows. After this short introduction, the Stirling approximation, the gamma function and its derivatives are discussed in section 2. Section 3 deals with the two-level system while section 4 is devoted to the Einstein solid. Finally, the results are summarized in section 5, with a discussion of their possible implications.

## 2. Stirling approximation, the gamma function and its derivatives

Counting the number of states at constant energy usually requires the evaluation of expressions including  $\ln N!$ , where  $N$  is a positive integer. The usual trick is to write the factorial in terms of the Stirling approximation, which is obtained by the series expansion of the function gamma:

$$\ln(N!) = \ln(\Gamma(N+1)) = \left(N + \frac{1}{2}\right) \ln(N) - N + \frac{1}{2} \ln(2\pi) + \frac{1}{12N} + \dots \quad (2.1)$$

Expression (2.1) is then simplified, and only the most relevant terms are kept:

$$\ln(N!) \simeq N \ln N - N \quad (2.2)$$

or directly

$$\ln(N!) \simeq N \ln N. \quad (2.3)$$

If one calculates  $\ln(N!)/(N \ln N - N)$  or  $\ln(N!)/(N \ln N)$ , it becomes clear that the ratios go to 1 as  $N \rightarrow \infty$ , although the second ratio has a much slower convergence, as shown in figure 1. From figure 1(a) it is clear that, for  $N > 1000$ , the first approximation—equation (2.2)—is in excellent agreement with the exact value. This approximation is used in the standard textbooks to solve the two-level system. The second approximation, (2.3), usually applied when dealing with the Einstein solid, is less satisfactory and even for  $N = 10^8$  it still differs by about 10% from the exact value, as seen in figure 1(b). Our purpose is to solve both physical systems without employing these approximations.

Some derivatives of the gamma function  $\Gamma$  appear in the following sections; they are designated as  $\psi^n(z)$  and they are defined as [12]

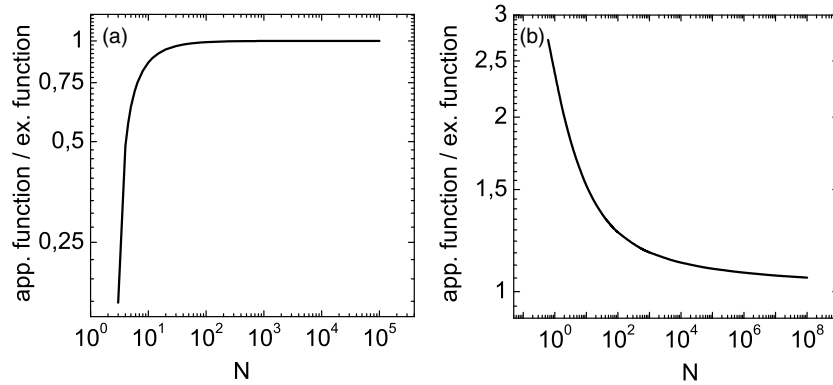
$$\psi^n(z) = \frac{d^{n+1}}{dz^{n+1}} \ln[\Gamma(z)]. \quad (2.4)$$

These derivatives cannot be expressed in terms of elementary functions, but they can be evaluated numerically and are included in computer packages like Mathematica [13].

## 3. Two-level system

### 3.1. Entropy

This is the simplest example studied in a statistical physics course. There are  $N$  particles and each one can be in one of two quantum states: the fundamental state with zero energy, or an excited state with energy  $\varepsilon$ . In the microcanonical formalism, one needs to know the number of states  $\Omega$  with energy  $U$  that are available to the system. The energy  $U$  is given by  $U = M\varepsilon$ ,



**Figure 1.** Log–log plots showing the Stirling approximation ( $\ln N! \cong N \ln N - N$ ) compared with the exact function in equation (2.1). (a) The ratio between  $(N \ln N - N)$  and  $\ln N!$  is shown as a function of  $N$ . For a system size as small as  $10^3$  the approximation is still extremely good, giving  $\approx 0.1\%$  difference. (b) Sometimes the exact function is simplified to  $\ln N! \cong N \ln N$ . The log–log plot of  $(N \ln N)/(\ln N!)$  is shown in terms of  $N$ . For  $N = 10^8$  the exact and approximated values are still different by  $\approx 10\%$ . Despite this difference, this approximation is usually applied to solve the Einstein model in most textbooks.

i.e.  $M$  is the number of energy quanta and it can be thought of as a dimensionless energy. Two-level systems are used as simplified models for a number of more complex scenarios, including paramagnetism in solids [14] and aspects of disordered systems [15].

In many textbooks—see for example [1]—it is shown that

$$\Omega = \frac{N!}{M!(N-M)!}. \quad (3.1)$$

The entropy of the system is given by the well-known relationship due to Boltzmann [1]:

$$S = k_B \ln \Omega, \quad (3.2)$$

where  $k_B$  is the Boltzmann constant.

Replacing (3.1) in (3.2), the exact value  $S_{\text{ex}}$  of the entropy for the two-level system is

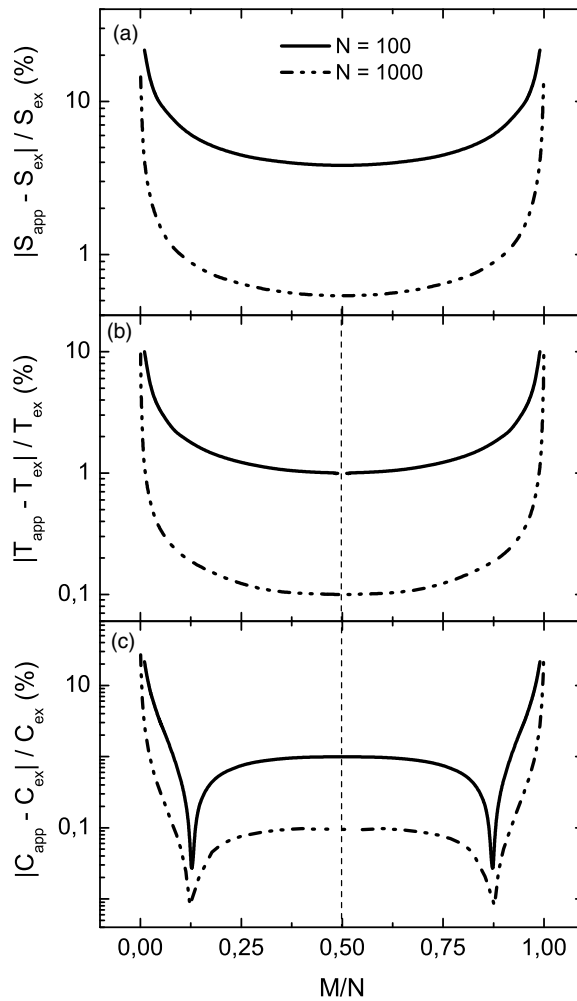
$$S_{\text{ex}} = k_B \ln \frac{N!}{M!(N-M)!}. \quad (3.3)$$

In the usual treatment [1], the Stirling approximation (2.2) is applied to evaluate the logarithm in (3.3) and an approximated expression for the entropy  $S_{\text{app}}$  is obtained:

$$S_{\text{app}} = k_B [N \ln N - M \ln M - (N - M) \ln(N - M) - N + M + (N - M)]. \quad (3.4)$$

As shown in figure 1(a), the Stirling approximation is justified for large values of  $N$ , but for  $N < 10^3$ , the approximate value differs considerably from the exact one. Consequently, one expects differences between  $S_{\text{ex}}$  and  $S_{\text{app}}$  for small systems. It is useful to rewrite (3.3) using the gamma function for further use. One needs to evaluate derivatives of  $S_{\text{ex}}$  to get the temperature and the specific heat, and the derivatives of the gamma function are well defined. Equation (3.3), which is written in terms of factorials, cannot be used because the derivative of a factorial is not defined:

$$S_{\text{ex}} = k_B \{ \ln [\Gamma(N + 1)] - \ln [\Gamma(M + 1)] - \ln [\Gamma(N - M + 1)] \}. \quad (3.5)$$



**Figure 2.** The relative errors of the entropy (a), temperature (b) and specific heat (c) are shown for the two-level system in terms of the energy per particle  $M/N$ . Two sizes have been considered:  $N = 100$  (solid line) and  $N = 1000$  (dash line). Note that the absolute values have to be used to plot the errors in a log scale. The odd behaviour of the specific heat is an artifice due to the use of the absolute value. The error is negative below  $M/N \cong 0.125$  (or above  $M/N \cong 0.875$ ) and becomes positive above (below) that value. A plot in a linear scale of the specific heat relative error shows a monotonically increasing value as  $M/N$  goes from 0 (or 1) to 0.5 and the error sign changes at  $M/N \cong 0.125$  (or  $M/N \cong 0.875$ ). It is clear that for  $N = 100$  the relative errors of the entropy and temperature are significant in the full range. The dashed vertical line at  $M/N = 0, 5$  indicates a discontinuity in the functions.

The relative error  $(S_{\text{app}} - S_{\text{ex}})/S_{\text{ex}}$  is shown in figure 2(a) as a function of the energy per particle  $M/N$  for two different sizes ( $N = 10^2$  and  $N = 10^3$ ). For the smaller system, the difference between the approximated and exact values is relevant in all the energy range. This means that the value shown in textbooks is inaccurate for  $N \leq 100$ . For the larger system ( $N = 1000$ ), the error is lower but it is still relevant for low ( $M/N < 0.1$ ) and high ( $M/N > 0.9$ ) energies.

### 3.2. Temperature

The temperature evaluation is our next step and the well-known thermodynamics definition should be used:

$$\frac{\partial S}{\partial U} = \frac{1}{T}. \quad (3.6)$$

The usual temperature  $T_{\text{app}}$  obtained using the Stirling approximation is [1]

$$T_{\text{app}} = \ln \left( \frac{N}{M} - 1 \right)^{-1} \frac{\varepsilon}{k_B}. \quad (3.7)$$

On the other hand, if one uses the exact value of the entropy (3.5) in (3.6), the exact temperature  $T_{\text{ex}}$  is

$$T_{\text{ex}} = [\psi^0(N - M + 1) - \psi^0(M + 1)]^{-1} \frac{\varepsilon}{k_B}. \quad (3.8)$$

The function  $\psi^{(0)}$  is defined by (2.4).

In figure 2(b), the relative error between  $T_{\text{app}}$  and  $T_{\text{ex}}$  is shown in terms of  $M/N$ . Once again, the error is large for very low or very high energies.

### 3.3. Specific heat

The next step is to evaluate the exact specific heat  $c_{\text{ex}}$  and to compare it with the approximated value  $c_{\text{app}}$  given in textbooks (see for example [1]):

$$c_{\text{app}} = \frac{N\varepsilon^2}{k_B^2 T^2} (e^{\varepsilon/2k_B T} + e^{-\varepsilon/2k_B T})^{-2}. \quad (3.9)$$

The temperature in (3.9) can be replaced by the value given in (3.7) to obtain

$$c_{\text{app}} = k_B \left[ \ln^2 \left( \frac{N - M}{M} \right) \right] \frac{M}{N} (N - M). \quad (3.10)$$

To calculate the exact value of the specific heat, it is convenient to start from (3.8) and obtain

$$\frac{dM}{dT} = -\frac{1}{T^2} \frac{\varepsilon}{k_B} [-\psi^1(N - M + 1) - \psi^1(M + 1)]^{-1}, \quad (3.11)$$

and from the definition of the specific heat

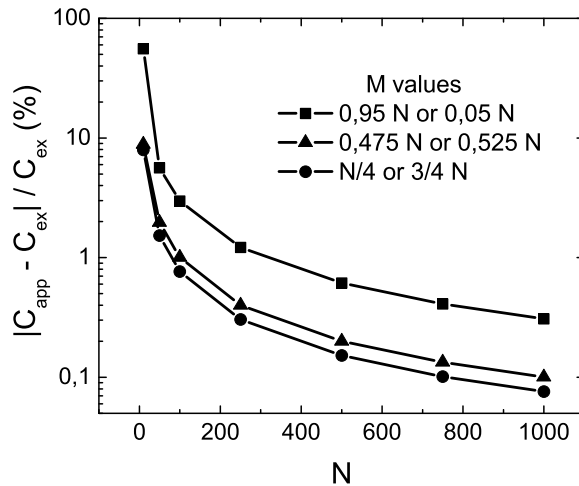
$$c = \frac{\partial U}{\partial T} = \frac{\partial U}{\partial M} \frac{dM}{dT} = \frac{\varepsilon^2}{T^2 k_B} [\psi^1(N - M + 1) + \psi^1(M + 1)]^{-1}. \quad (3.12)$$

As defined in (2.4),  $\psi^1$  is the second derivative of the gamma function, which can be evaluated numerically. The final step is to replace the value of  $T$  given by (3.8) into (3.12) to obtain the exact value of the specific heat:

$$c_{\text{ex}} = \frac{k_B [\psi^0(N - M + 1) - \psi^0(M + 1)]^2}{\psi^1(N - M + 1) + \psi^1(M + 1)}. \quad (3.13)$$

The relative error of the approximate specific heat is shown in figure 2(c) for two different system sizes. Note that in the  $N = 100$  system the error is around 1% for  $M/N \rightarrow 0.5$  and it becomes larger for very low or very high energies. The error is much lower for the  $N = 1000$  case.

In figure 3, the relative error is shown in terms of the system size for different values of the energy  $M$ . It becomes clear that for sizes smaller than  $10^2$  the difference between the approximated and exact specific heat can be significant. For instance, it is  $\approx 5\%$  for  $N = 100$  and  $M/N$  very large or very small.



**Figure 3.** The specific heat relative error of the two-level system in terms of the system size  $N$ . The different curves are for different values of the energy: upper curve for  $M = 0.05N$  (or  $M = 0.95N$ ); middle curve for  $M = 0.475N$  (or  $M = 0.525N$ ) and the lower one for  $M = 0.25N$  (or  $M = 0.75N$ ). For systems smaller than  $N = 100$  there is an appreciable difference between the approximated and the exact value of the specific heat.

## 4. The Einstein model of a crystalline solid

### 4.1. Entropy

The Einstein solid [1, 4] is another example used to illustrate the microcanonical formalism because the accessible microstates are easily counted. In this model the solid is an assembly of  $N$  atoms that can oscillate in the three spatial dimensions, i.e. there are  $3N$  independent quantum oscillators with a frequency  $\nu$ . If the total energy is  $E$ , the number of energy quanta is  $M = E/h\nu$ . It is easy to show [1] that the number of accessible microstates  $\Omega$  is

$$\Omega = \frac{(3N - 1 + M)!}{(3N - 1)!M!}. \quad (4.1)$$

For large  $N$  this expression is usually simplified to

$$\Omega \simeq \frac{(3N + M)!}{(3N)!M!}. \quad (4.2)$$

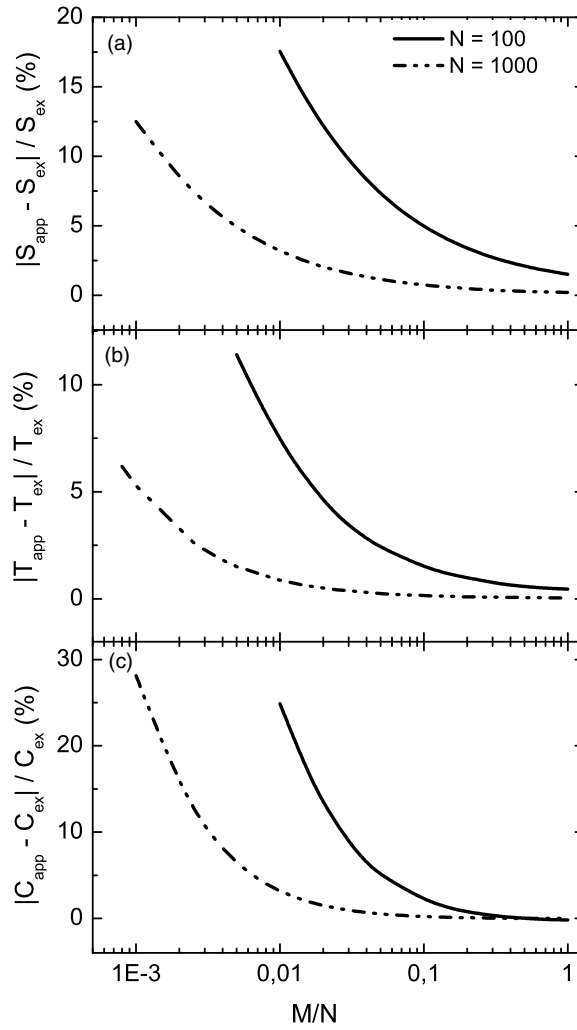
From (4.2) and using the Stirling approximation (2.3), one obtains the approximated expression for the entropy  $S_{\text{app}}$ :

$$S_{\text{app}} = k_B \left\{ 3N \left( 1 + \frac{M}{3N} \right) \ln \left[ 3N \left( 1 + \frac{M}{3N} \right) \right] - 3N \ln (3N) - M \ln M \right\}. \quad (4.3)$$

The exact value of the entropy is obtained from (4.1) and replacing the factorial by the gamma function:

$$S_{\text{ex}} = k_B \{ \ln [\Gamma(M + 3N)] - \ln [\Gamma(M + 1)] - \ln [\Gamma(3N)] \}. \quad (4.4)$$

In figure 4(a), the relative error between the approximated and the exact entropy values is shown in terms of the dimensionless energy  $M$  for two different system sizes. For the smaller system ( $N = 100$ ) the difference between the two values is  $\approx 5\%$  at intermediate energy values and is larger than  $15\%$  at low energies. Even for the larger system ( $N = 1000$ ) the difference is  $\approx 10\%$  at low energies.



**Figure 4.** The relative error of the entropy (a), temperature (b) and specific heat (c) for the Einstein model of a solid in terms of the energy per particle  $M/N$ . The solid line corresponds to  $N = 100$  and the dashed line to  $N = 1000$ . Note that for  $N = 100$ , the entropy error is larger than 1% even for  $M/N \cong 1$  and larger than 15% for  $M/N \cong 0.01$

#### 4.2. Temperature

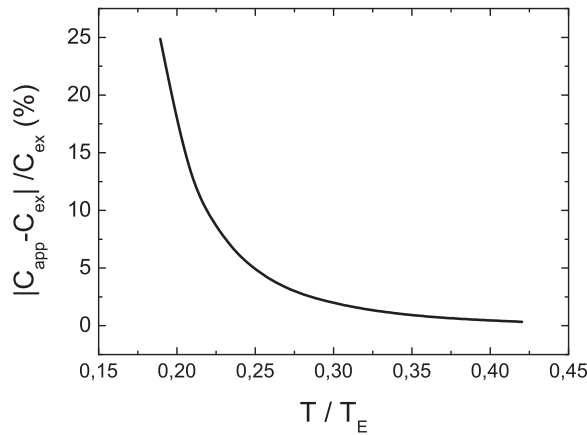
From (3.6) and (4.3) the approximated expression for the temperature  $T_{\text{app}}$  is

$$T_{\text{app}} = \frac{h\nu}{k_B} \left[ \ln \left( 1 + \frac{3N}{M} \right) \right]^{-1}. \quad (4.5)$$

From (4.4), one can obtain the exact value of the temperature  $T_{\text{ex}}$ :

$$T_{\text{ex}} = \frac{h\nu}{k_B} [\psi^0(M + 3N) - \psi^0(M + 1)]^{-1}. \quad (4.6)$$





**Figure 5.** The relative error for the specific heat of the Einstein solid as a function of the reduced temperature  $T/T_E$  where  $T_E$  is the Einstein temperature. For low temperatures, the error is quite large.

The relative error between the two temperatures for  $N = 100$  and  $N = 1000$  is shown in figure 4(b). As in the previous case, the difference between the two values is larger than 10% and 5% at low energies.

#### 4.3. Specific heat

The same steps as in the two-level system should be followed to evaluate the specific heat. The energy is calculated from (4.5) and, therefore, the approximated specific heat  $c_{\text{app}}$  is

$$c_{\text{app}} = \frac{h^2 \nu^2}{k_B T^2} \frac{e^{h\nu/k_B T}}{(e^{h\nu/k_B T} - 1)^2} 3N. \quad (4.7)$$

Using (4.5) in the previous expression, the approximated specific heat in terms of the dimensionless energy  $M$  is

$$c_{\text{app}} = k_B M \ln^2 \left( 1 + \frac{3N}{M} \right) \left( \frac{M + 3N}{3N} \right). \quad (4.8)$$

To obtain the exact value of the specific heat is slightly more complicated. From (3.12) and (4.6), one obtains

$$\frac{dM}{dT} = -\frac{1}{T^2} \frac{h\nu}{k_B} [\psi^1(M + 3N) - \psi^1(M + 1)]^{-1}. \quad (4.9)$$

It is clear that  $dE/dM = h\nu$  and the exact value of the temperature is given by equation (4.6). Finally, one obtains

$$c_{\text{ex}} = \frac{k_B [\psi^0(M + 3N) - \psi^0(M + 1)]^2}{\psi^1(M + 1) - \psi^1(M + 3N)}. \quad (4.10)$$

The relative error between the approximated and the exact values of the specific heat is shown in figure 4(c). The difference between the two values is appreciable for low energies, i.e. larger than 20%. The relative error in terms of a dimensionless temperature  $T_{\text{ex}}/T_E$  has been plotted in figure 5, where  $T_E$  is the Einstein temperature defined as  $T_E = h\nu/k_B$ . Note that the error is as large as 25% for  $T/T_E = 0.2$  and a 100-atom system. These results may be of interest in research about atomic clusters since clusters smaller than 100 atoms are often probed in such experiments [6, 16].

## 5. Conclusions

In this paper, two well-known examples taught in any statistical mechanics course have been exactly solved in the microcanonical formalism. The two-level system and the Einstein model have been always solved in the microcanonical formalism using the Stirling approximation. We have solved both examples without any approximations, using the gamma function and its derivatives to deal with the factorials in the equations.

The first conclusion we reach is that the Stirling approximation is an excellent one. For systems larger than  $N = 10^4$ , the differences between the exact values and the approximated ones for entropy, temperature and specific heat are negligible. However, for smaller sizes ( $N \sim 100$ ) the differences can be significant, as shown in figures 2 and 4. This is interesting from a conceptual viewpoint since a lower bound to the Stirling approximation has been found. Moreover, some results may be useful in the study of small atomic clusters or nanostructures.

In summary, we have proposed an interesting addition for a typical course in statistical mechanics and suggested some results that might be of interest to researchers working with few-body systems. Other properties of small systems described by the Einstein or two-level models, including Gruneisen-type corrections [17], are being studied and will be published elsewhere.

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