Egypt. J. Sol., Vol. (23), No. (2), (2000)

Specific heat, Energy Fluctuation and Entropy of Isotropic Harmonic and Anharmonic Oscillators

Samy H. Aly

Department of Physics, Faculty of Science at Demiatta,
University of Mansoura, P.O.Box 89, New Demiatta, Egypt

In this article a study of the specific heat, energy fluctuation and entropy of 1D, 2D, 3D harmonic and 1D anharmonic oscillators is presented. The effect on the thermodynamic properties of considering a finite number of the quantum states, involved in evaluating the partiton function, is analyzed. In the case of the anharmonic oscillator we calculate the contribution of the anharmonicity to these properties and compare (or contrast) with their counterparts in the harmonic case.

Introduction

The harmonic and anharmonic oscillators are well known to have an important place in physics both at the fundamental and practical levels. The specific heat of solids, for example, is well explained in terms of the harmonic vibrations of the atomic oscillators [1] . Anharmonic contributions, however, to the specific heat have been reported [2]. There are, in addition, a number of other physical properties which cannot be accounted for using a strictly harmonic model. Examples of these in solids are: the thermal expansion, the finite thermal conductivity and the temperature dependence of elastic constants [1]. The anharmonicity, also, causes the existence of soft modes which provide the mechanism for displacive phase transitions [3]. In quantum crystals, the role of anharmonicity is even more important for a reasonable description of these crystals [4]. In the field of magnetism, the lattice anharmonicity presents a mechanism for the phonon-induced contribution to the magnetocrystalline anisotropic constants [5].

Recently, the specific heat of several one-dimensional classical and quantum potentials was analyzed by Pizarro et al [6]. They showed that the classical limit of the specific heat of a 1D simple harmonic oscillator is reached at moderate temperatures if a relatively small number of quantum levels (<<100) is considered. The specific heats of simple harmonic oscillators of two-level, n-level and infinite number of levels were investigated in more detail by Styer [7].

A guiding motive of the present work is to analyze the effect of anharmonicity on the specific heat, energy fluctuation and entropy of a 1D anharmmonic oscillator and compare (or contrast) with their counterparts in the 1D harmonic oscillator case. It is also instructive to study the evolution of these properties with increasing the number of quantum states, used in evaluating the partition function, of these two different oscillators.

The partition functions of the isotropic 2D and 3D harmonic oscillators are simply related to that of their 1D counterpart. Their thermodynamic properties (e.g. specific heat and entropy) are, therefore, simply related to those of the 1D oscillator. It may be of some pedagogical value, however, to study how the dimensionality and the number of quantum states of these n-level degenerate oscillators affect their properties.

In section 2, we present calculations of the specific heat and energy fluctuations of n-level harmonic, and anharmonic oscillators of different anharmonicity strength. Section 3 presents a study of the entropy of these oscillators in particular their low and high temperature limits. General conclusions of this study are drawn in section 4.

Specific Heat And Energy Fluctuation

a) The 1D simple harmonic oscillator :

The partition function Z_1 of this oscillator is well known to be[8]:

$$Z_1 = \sum_0^{\infty} e^{-(n+\frac{1}{2})x} = \frac{1}{2\sinh\frac{x}{2}} \tag{1}$$

where x = ħωβ and β = 1/kT.

The specific heat at constant volume, normalized to k, is related to the partition function by:

$$\frac{C_v}{k} = x^2\left(\frac{\partial^2 \ln Z_1}{\partial x^2}\right) = \frac{x^2}{(4\sinh^2\frac{x}{2})} \tag{2}$$

From now on, for the sake of simplicity, we will drop the subscript ν (which stands for the volume) and use the symbol C_1, in the text , to mean the specific heat at constant volume *normalized* to Boltzmann constant k. The low and high temperature limits of C_1 are : $C_1 \approx x^2 e^{-x}$ and $C_1 \approx 1$ respectively.

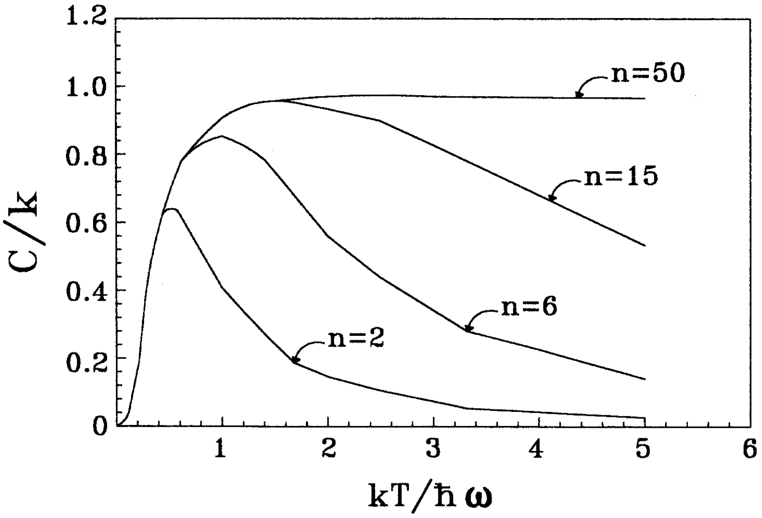

Fig. (1) Specific heat of a 1D simple harmonic oscillator for n = 2, 6, 15 and 50 as function of kT/ħω.

Recently [6,7] it has been shown that the high temperature limit of C_1 is obtained for relatively small quantum numbers (<<100). In Fig.1 we generate few specific heat plots using n=2,6,15 and 50. The plot for n=50 is identical to the one generated using the full (i.e. summed from zero to infinity) partition function of equation (1). Our calculation is in agreement with those of refs. 6 and 7).

It is of interest now to compare the specific heat with the relative energy fluctuation f defined by:

$$f = \frac{\sqrt{< E^2 > - < E >^2}}{< E >} \tag{3}$$

The quantity f measures the thermal stability of the system and is related to the specific heat by the equation :

$$f = \frac{kT\sqrt{C_1}}{< E >} \tag{4}$$

The low and high temperature limits of equation(4) are f~ $e^{-x/2}$ and f~1 respectively. At these two limits C_1 is almost identical to f, however for x=1, for example, the percentage difference between C_1 and f is ~10%. For small quantum numbers C_1 drops quickly to zero at high temperatures while the fluctuation nearly saturates.

b) The 2D and 3D isotropic simple harmonic oscillators:

It is evident that the partition functions of the 2D and the 3D harmonic oscillators have the same temperature dependence as that of the 1D oscillator and that the zero-point energies of these oscillators do not, as well, contribute to their specific heats. The difference lies in the degeneracy of the energy levels of the 2D and 3D oscillators. The energy spectrum of the 2D oscillator is: $E_n=(n+1)\hbar\omega$ and the partition function Z_2 is easily evaluated to be[8]:

$$Z_2 = \sum_{0}^{\infty} (n+1)\, e^{-(n+1)x} = \frac{1}{4\sinh^2 \frac{x}{2}} = Z_1^2 \tag{5}$$

Similarly the partition function of the 3D oscillator is (footnote 1):

$$Z_3 = 0.5\sum_{0}^{\infty} (n+1)\,(n+2)\, e^{-(n+\frac{3}{2})x} = \frac{1}{8\sinh^3 \frac{x}{2}} = Z_1^3 \tag{6}$$

From Eqs. 5 and 6 it is evident that the specific heats of the 2D and 3D oscillators are respectively twice and thrice that of the 1D oscillator.

Unlike the Debye oscillators which have different temperature dependencies in their low-temperature specific heats, namely C~T^d where d is the dimensionality (d= 1, 2 and 3 for the 1D, 2D and 3D oscillators respectively), the Einstein oscillators have the same temperature dependence in their low-temperature specific heats namely $C_d \approx dx^2 e^{-x}$.

We have studied the dependence of the specific heat on temperature and quantum number n for the 2D and 3D oscillators. The same general conclusions regarding the behavior of the specific heat of the 1D oscillator are drawn here as well, namely that the specific heat is not saturated for relatively low values of the quantum number n but, rather, it develops a peak and drops slowly at high temperatures.

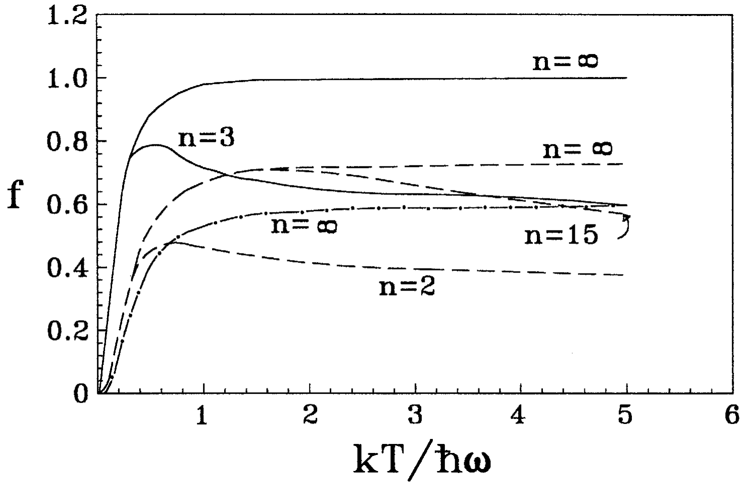

Fig. (2) Energy fluctuation as function of kT/ħω for simple 1D, 2D, 3D harmonic oscillators. The plots are for different values of n.

Fig.2 shows the dependence of the r.m.s. energy fluctuation f on temperature for the three oscillators. The r.m.s. energy fluctuation in the 2D and 3D cases reach values of, $1/\sqrt{2}$ and $1/\sqrt{3}$ at high temperatures, respectively [footnote 2] as compared to the value 1 for the 1D oscillator. Thus the degree of thermal stability of the harmonic oscillator goes as the square root of dimensionality. In the low temperature region, however, the energy fluctuation goes as $\sim e^{-x/2}$.

c) The 1D anharmonic oscillator:

The Hamiltonian of this oscillator is well known to be:

$$H = H_0 + \lambda x^4 \tag{7}$$

where H_0 is the unperturbed Hamiltonian and λ is a constant which indicates the strength of the perturbation. The energy levels are approximately given by[9]:

$$E_n \approx (n+\frac{1}{2})\hbar\omega + 3\lambda(\frac{\hbar}{2m\omega})^2 (2n^2+2n+1) \tag{8}$$

The partition function Z_a of the anharmonic oscillator, to first order in A, is related to Z_1 by[10] (see the appendix):

$$Z_a \approx Z_1(1 - Ax\coth^2\frac{x}{2}) \tag{9}$$

where $A=3\lambda\hbar/4m^2\omega^3$ is a dimensionless constant which characterizes the strength of the perturbation and we may call it the anharmonicity factor. The symbols m and ω are the mass and angular frequency respectively. The specific heat of the anharmonic oscillator, normalized to k, is related to C_1 by:

$$C_\alpha \approx C_1 + x^2 \frac{\partial^2 \ln(1 - Ax\coth^2\frac{x}{2})}{\partial x^2} \tag{10}$$

The term added to C_1 in this equation is the contribution, to first order in A, of the anharmonicity to the specific heat. For very small values of A one expects that $C_a \approx C_1$. We have found that this contribution is negative providing that A <0.04, and that its absolute value increases with increasing A, i.e. the anharmonicity diminishes the specific heat of the oscillator. Fig.3 shows the dependence of C_a on temperature as calculated from equation (10) for A=.001,.01,.02 and .04.

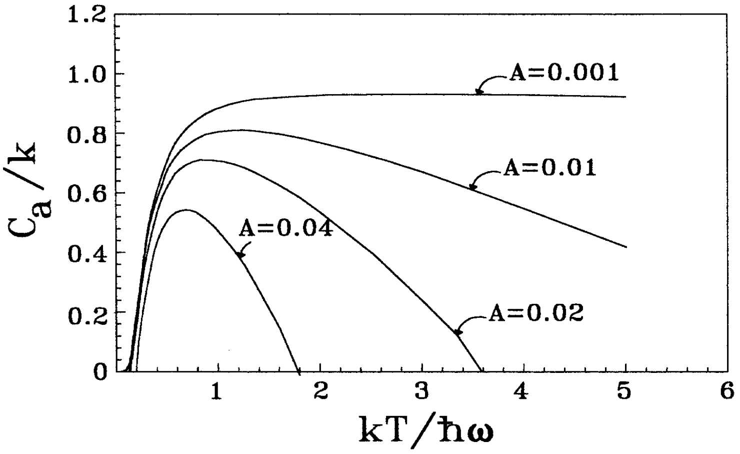

Fig. (3) Specific heat of anharmonic oscillator for A=0.001, 0.01, 0.02 and 0.04 as function of kT/ħω using equation (10).

Larger values of A did not result in generating well -behaved curves. Probably one has to consider higher order terms of A in Z_a. We find it more instructive, however, to study also the effect of varying the number of the quantum levels on the specific heat of this oscillator and compare (or contrast) with the harmonic case. Therefore we use the following partition function:

$$Z_a = \sum_{0}^{\infty} e^{-(n+\frac{1}{2})x - A(2n^2+2n+1)x} \qquad (11)$$

Fig.4 shows the specific heat as function of temperature for A=0.1 and n=2,6 and 15. The behavior of C_a shown in this figure is different from that of Fig.1 in the following aspects: firstly, for small quantum numbers the specific heat of the harmonic oscillator reaches a maximum then decreases at higher temperatures as a consequence of the limited number of the available quantum levels. In the anharmonic case, however, the same behavior is observed but with a less -steep drop of specific heat at high temperatures. Secondly, the specific heat of the harmonic oscillator saturates to the classical value (k) for n≥50. In the anharmonic case the saturation takes place for much less number of the quantum states (n~10). In addition, the saturated C_a is about 0.7 k. We have also checked this behavior for n=100 and found that it is identical to the case of n=15 shown in Fig.4. The effect of the anharmonicity is appreciable at higher temperatures as the mean position of the oscillator moves away from its equilibrium position. One, therefore, expects the thermodynamic properties of the anharmonic oscillator to reflect this behavior.

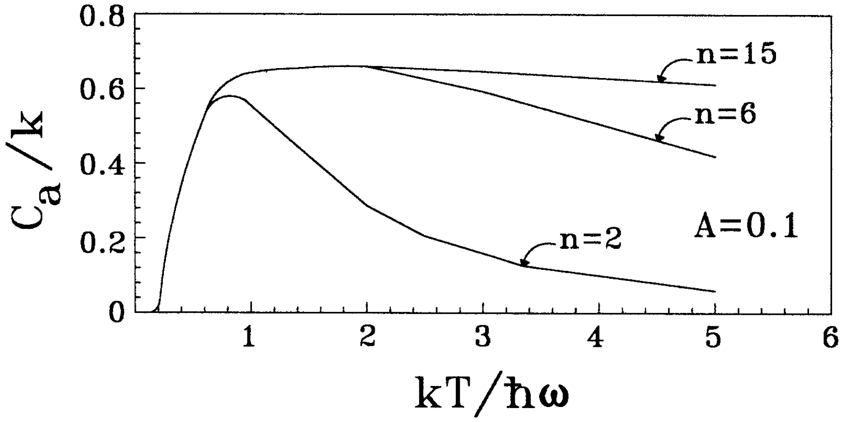

Fig. (4) Specific heat of anharmonic oscillator of A= 0.1 for n=2,6 and 15 as function of kT/ ħω.

In addition to the previously mentioned remarks we notice that C_l is higher than C_a up to a certain temperature above which C_a exceeds C_l. This "temperature" for example is x= 0.5, 1.8 and 4.5 for n=2, 6 and 15 respectively. In Fig.5 we generated a family of curves for C_a in the case of A=.001, 0.01, 0.05, 0.1 and 0.2 for n=10. It is clear from this figure that increasing A leads to a tendency of C_a to saturate at high temperatures and that, in the saturated state, the specific heat decreases as the anharmonicity increases.

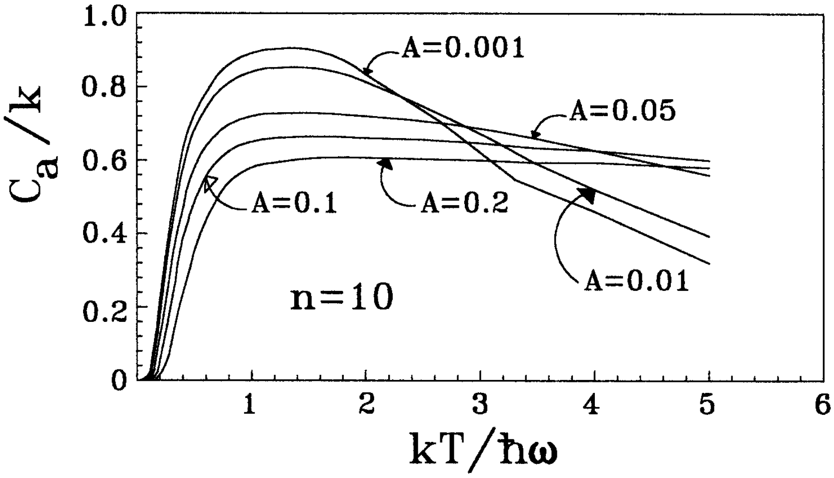

Fig. (5) Specific heat of anharmonic oscillator of A= 0.001, 0.01, 0.05, 0.1 and 0.2, for n=10 as function of kT/ ħω.

It is of interest now to study how the relative r.m.s energy fluctuation f changes with temperature and anharmonicity. Fig.6 shows these changes for A=0.01,0.05 and 0.1 in the case n=20. For relatively weak anharmonicities (~0.01) the fluctuation increases quickly with T then at relatively higher temperatures it tends to saturate. On the other hand when A>0.05 the fluctuation increases in the entire temperature range studied reaching values larger than unity. This demonstrates that the anharmonic oscillator becomes less thermally stable at high temperatures.

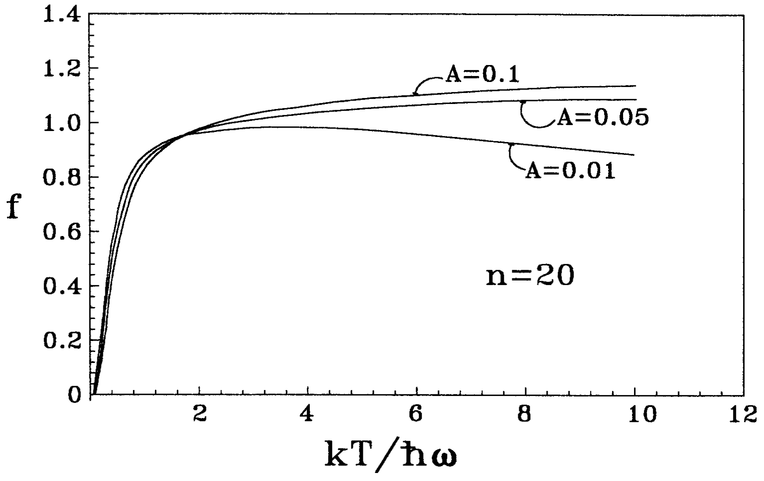

Fig. (6) Energy fluctuation as function of kT/ħω for anharmonic oscillator of A = 0.01, .05 and 0.1 for n = 20.

In terms of the time factor, this means that the anharmonic oscillator spends a good fraction of time, at high temperatures in a state where the deviation of the energy, from its mean value, is an appreciable fraction of the mean energy.

3. Entropy:

a) The 1D harmonic oscillator:

The entropy S_1 is obtained from the partition function using the equation:

$$\frac{S_1}{k} = \ln Z_1 - x\frac{\partial \ln Z_1}{\partial x} \qquad (12)$$

Using Z_1 from equation 1,we get:

$$\frac{S_1}{k} = \frac{x}{2}\coth\frac{x}{2} - \ln\left(2\sinh\frac{x}{2}\right) \qquad (13)$$

The high temperature limit of the entropy S_1 is:

$$S_1 \approx 1 - \ln x \qquad (14)$$

where we will use the symbol S_1 from now on instead of S_1/k .
On the other hand, the low- temperature limit of the entropy is:

$$S_1 \approx \frac{x}{2}\coth\frac{x}{2} - \frac{x}{2} \approx x\,e^{-x} \qquad (15)$$

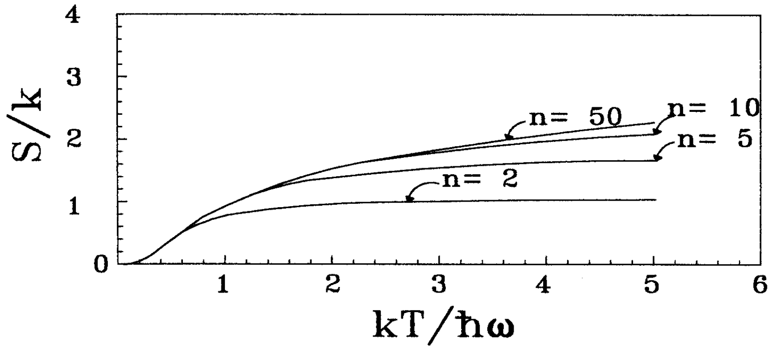

Fig. (7) Entropy as function of kT/ ħω for 1D harmonic oscillator for n = 2, 5, 10 and 50.

The high- temperature limit holds well for x values in the range 0.1 -0.6 with a relative percentage error<1%. For x>1,however, the percentage error is>4%. In the low-temperature limit the relative percentage error in equation 15 is < 2% for x in the range 7-10, but increases for smaller x values (x<4) to >5%. For the purpose of studying the entropy of a 1D harmonic oscillator with only limited number of quantum levels we have generated in Fig.7 the temperature dependence of the entropy for n=2, 5, 10 and 50. The curve with n=50 is almost identical to the curve with n=∞. For relatively small n the entropy increases very slowly at high temperatures, while for n>10 it increases obeying Eq.14. In the low temperature limit, however, all the curves follow Eq.15.

b) The 1D anharmonic oscillator:

Using the partition function Z_a we obtain the following approximate expression:

$$S_a \approx S_1 + \ln(1 - Ax\coth^2\frac{x}{2}) + \frac{\{Ax\,(2x - \sinh\frac{x}{2})\coth\frac{x}{2}\}}{\{1 + Ax + (Ax-1)\cosh x\}} \qquad (16)$$

This expression reduces to $S_a \approx S_1$ as A tends to zero.
The low temperature limit of S_a is:

$$S_a \approx xe^{-x} + \ln(1 - Ax) + \frac{Ax}{(1 - Ax)} \qquad (17)$$

The last two terms of Eq.17 represent the anharmonic contribution to the entropy. we have calculated this contribution for x values between 4 and 5 for different anharmonicity factors and found that this contribution is *positive* but only less than 1% of S_1 for A=0.01 and increases for larger values of A. On the other hand, the high temperature limit is :

$$S_a \approx 1 - \ln x + \ln(1 - 4\frac{A}{x}) + \frac{(2Ax - 4\frac{A}{x})}{(1 - 4\frac{A}{x})} \tag{18}$$

We have calculated the contribution of the anharmonicity to S_a for A between 0.01 and 0.04 and x in the range 0.2-1. The contribution is found to be *negative*. The negativity decreases with increasing x, i.e with decreasing temperature. In other words, the effect of a given anharmonicity on the entropy becomes more pronounced as the temperature increases, on the other hand, increasing A results in decreasing the entropy.

The effect of anharmonicity on entropy is shown in Fig.8 for A=.01,0.05 and 0.1 and n=50. It is clear that the anharmonicity diminishes the entropy, in particular at higher temperatures. In order to study the entropy of n-level anharmonic oscillators, we generated plots for n=2, 5 and 50 and A=0.1 (Fig.9). The general behavior of entropy in the anharmonic case is similar to that of the harmonic oscillator in that the entropy increases very slowly with temperature for low-n states (when x>1). In this case the high-temperature limit of the entropy which is equal to k lnΩ, where Ω is the number of the microstates, is approached at moderate temperatures. The entropies of the 2D and 3D oscillators have the same temperature dependence as the 1D oscillator. It is quite clear that $S_2 = 2S_1$ and $S_3 = 3S_1$. The number of the isoenergetic levels in these degenerate systems grows with both the dimensionality and quantum number n of the degenerate level. It is also instructive to notice that the specific heat plots (e.g. Fig.1), are related to the temperature-derivative of the entropy via the relation: $C_V = T(\partial S/\partial T)_V$. This correlation is clear in particular for small-n systems.

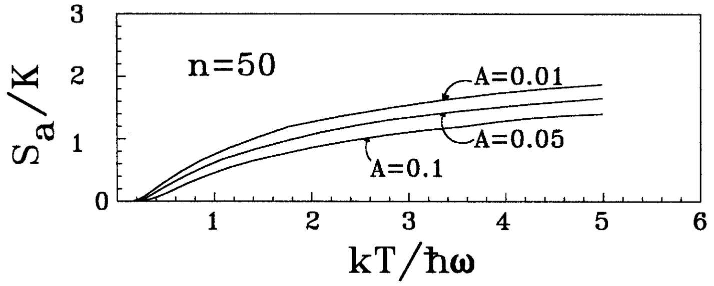

Fig. (8) Entropy as function of kT/ ħω for anharmonic oscillator of A= 0.01, 0.05 and 0.1 and n=50.

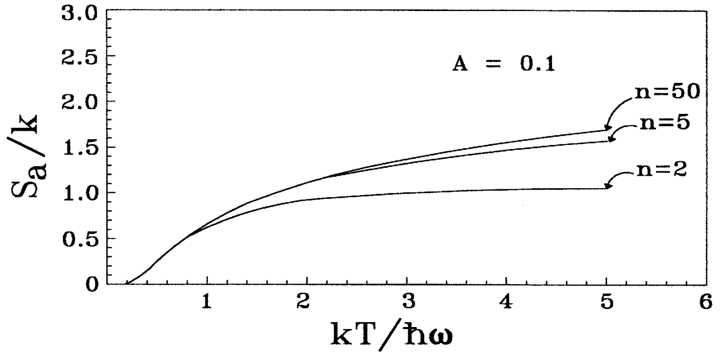

Fig. (9) Entropy for anharmonic oscillator with A=0.1 and n=2, 5 and 50 as function of kT/ ħω.

4.Conclusions:

1) The specific heat of the 1D anharmonic oscillator reaches its classical limit using a number of quantum states less than what is needed for its harmonic counterpart to do so. The classical limit of the specific heat for the 1D harmonic oscillator is larger.
2) The effect of the anharmonicity on the specific heat is more pronounced at high temperatures. The specific heat diminishes with increasing the anharmonicity if a large-enough number of quantum states is made available to the oscillator.
3) The r.m.s. energy fluctuation of the anharmonic oscillator increases with increasing the anharmonicity in the high-T region, i.e. the oscillators with relatively stronger anharmonicity are less thermally stable.
4) The contribution of the anharmonicity to the entropy of the anharmonic oscillator is larger at higher temperatures. On the other hand the entropy reduces as the anharmonicity increases.
5) The partition function and, consequently, the specific heats, energy fluctuations, and entropies of the 1D, 2D and 3D harmonic oscillators are simply related through numerical factors which reflects the dimensionality of the isotropic 2D and 3D oscillators.

Acknowledgment

The author is indebted to Drs. S.Yehia, O. Fathi, F. Hashim and Eng. Hisham El-Masry for their kind assistance in producing the manuscript and figures of this work.

References:

1. C. Kittel, Introduction to solid state physics, 7th ed. 1996, Ch. 5, (John Wiley, 1996); H. P. Myers, Introductory Solid State Physics, Ch. 5, (Taylor and Francis 1990); H. Ibach and H. Lűth, Solid-State Physics, Ch. 5, (Springer – Verlag 1990); J. R. Hook and H. E. Hall, Solid State Physics, 2nd ed, Ch. 2, (John Wiley, New York, (1994).
2. L.Gill, M. A. Ramos, A. Bringer and U. Buchenau, Phys. Rev. Lett. 70, 182 (1993).
3. J.F.Scott, Rev. Mod. Phys. 46, 83 (1974).
4. T. R. Koehler, Dynamical Properties of Solids Vol. 2, Ch. 1, eds. G. K. Horton and A. A. Maradudin, (North-Holland Publishing, Amsterdam, 1975)
5. C. A. Bates and H. Szymczak, J. Magnt. Magnt. Mater.15, 563 (1980).
6. C. A. Pizarro, C. A. Condat, P.W.Lamberti and D.P.Prato, Am. J. Phys. 64, 736 (1996).
7. D. F. Styer, Am. J. Phys. 65, 974 (1997).
8. F. Reif, Fundamentals of Statistical and Thermal Physics, Ch 7, (McGraw-Hill, New York, 1965).
9. R. P. Feynman, Statistical Mechanics: A set of lectures, Ch.6 (Benjamin / Cumming, 1982).
10. Giorgio Parisi, Statistical Field Theory, Ch.17 (Addison Wesley, 1988).

Appendix

$$Z_a = e^{-\frac{x}{2}} \sum_0^{\infty} e^{-nx - A(2n^2 + 2n + 1)x} \qquad \text{(A1)}$$

In the case of very small A one can expand the exponent of equation (A1) retaining only terms linear in A:

$$e^{-A(2n^2 + 2n + 1)x} \approx 1\text{-}Ax\,(1 + 2n + 2n^2) \qquad \text{(A2)}$$

One may write Z_a in terms of Z_1 as follows:

$$Z_a \approx Z_1 - e^{-\frac{x}{2}}[A\sum_0^{\infty} x\, e^{-nx} + 2A\sum_0^{\infty} x\, n\, e^{-nx} + 2A\sum_0^{\infty} x\, n^2\, e^{-nx}] \qquad \text{(A3)}$$

After few steps one reaches the following expression:

$$Z_a \approx Z_1\left[1 - Ax\left\{1 + \frac{4e^{-x}}{(1-e^{-x})^2}\right\}\right] \qquad \text{(A4)}$$

$$Z_a \approx Z_1\left[1 - Ax \coth^2 \frac{x}{2}\right]$$

Which is equation (9) in the text.

Notes:

1. The derivation of the partition functions of the 2D and 3D oscillators, is easily done by evaluating the sum-over- the states. However, one can intuitively reach the result because each of the 2D and 3D isotropic harmonic oscillators could be considered as two and three independent 1D oscillators respectively.
2. The remark here is related to the previous footnote. It is well known that the r.m.s fluctuation is inversely proportional to $\sqrt{N}$, where N is the number of particles.