

Critical behavior of a 3D anharmonic solid

G. CIOBANU

Department of Physics, University of Bucharest, 405 Magurele Str., Magurele 077125

The critical behavior of a rectangular lattice of quantum anharmonic (quartic) oscillators, in two and three spatial dimensions, is investigated, using a mean-field approach. Even if the quantum case is the only one studied in detail, the classical limit can be easily taken, in the final results. The model describes well structural phase transitions. The critical temperature is obtained via the formula of the dielectric susceptibility. In order to get analytic results, the polynomial potential is replaced with a symmetric double well square one. The results agree qualitatively with those obtained for other two well potentials, and with the Monte Carlo simulations.

(Received October 16, 2012; accepted October 30, 2012)

Keywords: Quantum square well, Resonant cavity, Normal modes, Transcendental equations

1. Introduction

The anharmonic solid - and especially, a solid with ψ^4 anharmonicities - attracts much interest, for both fundamental and practical reasons. There are at least two approaches of such solids - one of them, starting with the Ginzburg-Landau functional of the free energy [1], and another one, starting with a polynomial Hamiltonian [2], [3]. The statistical behavior of a n -dimensional solid described by a Ginzburg - Landau functional can be obtained through the transfer matrix theory [4], from the first energy levels of an associated $n-1$ -dimensional quantum Hamiltonian, with quartic anharmonicities. So, a classical statistical mechanical system, in n spatial dimensions, is equivalent to a quantum system, in $n-1$ dimensions. These two systems, sometimes called dual systems, describe quite similar objects - aggregates of classical or quantum oscillators. A well-known example of a study of such aggregates is that done by Stoeckly and Scalapino [5], [6], where the evaluation of the partition function of a planar array of classical quartic oscillators is reduced to the study of a chain of quantum quartic oscillators. This one-dimensional Hamiltonian can be transformed, for weak coupling between neighbor oscillators, to a fermionic Hamiltonian, similar to that used by Schultz, Mattis and Lieb [7] in their study of Ising model, to Luttinger models or other 1D systems [8], [9]. These 1D systems provide interesting theoretical and experimental applications, besides other atomic [10] and magnetic [11] exactly solvable models. In this way, the ψ^4 anharmonic solids can be linked to large classes of very well studied models of condensed matter theory, including the Ising model.

After remarkable theoretical progress done in the '70s (for a review, see for instance [12]), the next decenniums have been dominated by numerical investigations [13], [14], [15] - to mention only some few ones. More recently, other authors used both numerical and analytical

approximations [16], [17], for getting a deeper understanding of these systems. An attempt of extending the Ginzburg-Landau theory beyond the linear chain approximation has been generalized for systems with next-neighbor interaction [18]. Transfer matrix theory was applied to the analytical studies of thermal and quantum phase transitions in low dimensional systems, with or without external fields [19]. These results have been critically reviewed by Lungu [20].

If the analytical results mentioned in the previous paragraph refers essentially to low dimensional systems, the 3D anharmonic solids have to be investigated with less accurate theoretical methods, the most popular of these being the mean field theory. However, these models give good predictions of structural phase transitions [2], [3]. The model to be considered in this paper is a d -dimensional square lattice of quantum anharmonic (quartic) oscillators, interacting through elastic forces between near neighbors. In principle, the model can be developed for any value of d , but for $d = 1$, it gives, in general, inaccurate results, including a spurious phase transition. Even if the model is a quantum one, the classical case can be easily obtained, taking the $\hbar \rightarrow 0$ limit.

The physics described by this model (we shall consider in this paper only the case of a real order parameter) is quite simple. In an 1D picture, the particle situated in a lattice point can be placed in one of the two wells of the anharmonic potential, "at the left" or "at the right", if they are deep enough, with respect to the energy of thermal fluctuations. The preference for one position means an ordered state, and the equivalence of both positions - a disordered state. For shallow wells, the system can become "polarized", in the sense that the atoms "slide" in the same direction: we have a soft-mode transition, which shows up at a certain temperature. For deep wells, the systems shows up an order-disorder transition, and is equivalent to an Ising model. The

interplay between temperature, particle mass, dimensionality and potential strength determines the critical equation.

The main goal of this paper is to obtain an analytical approximation for the critical equation describing a model of 3D quantum anharmonic solid. We shall follow a mean-field approach [16], [17], and use, for the determination of the critical temperature, a formula which involves the dielectric susceptibility of the model [21]. In order to apply this formula, we need the knowledge of the wave functions and of the energy levels of a quartic (two wells) anharmonic oscillator. It is well known that, in spite of its apparent simplicity, this problem defies an exact solution; more than that, the Rayleigh - Schrodinger perturbation series - in the coefficient of the quartic term of the potential - for all levels of energy eigenvalues are divergent [22]; for a review of modern developments of this issue, see [23]. So, the quartic potential must be replaced with a tractable one; we choose to use the symmetric double square well. It is not, evidently, exactly soluble, even if there are some semi-quantitative descriptions of its behavior [24], but analytical approximations for its eigenvalues can be obtained, used a simple approach proposed by the present authors. It is fortunate that, for this model, with a piecewise-defined, locally constant functions, the knowledge of eigenenergies makes possible the knowledge of eigenfunctions. As the case of deep wells is well understood, due to its equivalence with an Ising model, the most interesting case to be studied is that of shallow wells; this case will be addressed in the present paper.

Its structure is the following. In Section 2, our model of anharmonic solid is shortly presented. In Section 3, a formula of the dielectric susceptibility, to be used in the evaluation of the critical temperature, is obtained. Section 4 is devoted to a detailed study of the symmetric double square well. In Section 5, the critical equation is obtained. Final comments are exposed in Section 6.

2. The model

A simple model of an anharmonic solid, used since the early days of ferroelectricity (see [25 – 27]), is a lattice of anharmonic oscillators, connected by near neighbor elastic forces. It is described by the Hamiltonian:

$$H = \sum_n \frac{p_n^2}{2M} - \frac{A}{2} \sum_n X_n^2 + \frac{B}{4} \sum_n X_n^4 + \frac{C}{2} \sum_{n,n'} \sigma'_{n,n} (X_n - X_{n'})^2 \quad (1)$$

where $\sigma'_{n,n} = 1$ for near neighbors and 0 otherwise. It can be used both in the study of the classical and quantum case; in this paper, we shall consider the quantum one. In order to avoid irrelevant complications, only the isotropic case is considered; the inclusion of anisotropy can be easily done. The system presents a second order phase

transition if the dimensionality of the system is greater than 1, $d > 1$.

It is convenient to introduce dimensionless quantities, as follows:

$$X = \sqrt{\frac{B}{A}} x, \quad t = \frac{B}{AC} T, \quad m = \frac{CA^2}{\hbar^2 B^2} M \quad (2)$$

and also the dimensionless parameter

$$a = \frac{A}{C} \quad (3)$$

It characterizes the ratio between the on-site and inter-site potential; small values of a correspond to shallow wells - the case investigated in this paper. For large values of a , there are several analytical approximations for the energy levels of the deep wells, including the WKB approach.

For both shallow and deep wells, the area of each of the well and of the barrier (in the $x - V(x)$ plane) are comparable. This is why we shall approximate, later on, the polynomial potential with a symmetric double square well one, having also the wells and the barrier, of comparable areas.

3. The dielectric susceptibility

In this section, we shall obtain a formula for the electric susceptibility of a system which, in the mean field approximation, will give the critical equation and, in particular, the critical temperature of the phase transition occurring in the anharmonic solid described by (1).

For the beginning, let us consider that the Hamiltonian of a system can be written as an exactly solvable one, H_0 , and a perturbation, V :

$$H = H_0 + V \quad (4)$$

The eigenstates and the eigenvalues of H_0 will obey the equation:

$$H_0 |n\rangle = E_n^{(0)} |n\rangle. \quad (5)$$

In the second order of the perturbation theory, the energy of the Hamiltonian H is:

$$E_n = E_n^{(0)} + \langle n | V | n \rangle + \sum_{m \neq n} \frac{|\langle n | V | m \rangle|^2}{E_n^{(0)} - E_m^{(0)}}. \quad (6)$$

If

$$V = -Fx \quad (7)$$

is the energy of a particle in an electric field F , eq. (6) will take the form:

$$E_n = E_n^{(0)} - F \langle n | x | n \rangle + F^2 \sum_{m \neq n} \frac{|\langle n | x | m \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \quad (8)$$

and the quantum average of the dipolar momentum is:

$$P_n = - \frac{\partial E_n}{\partial F}. \quad (9)$$

The dielectric susceptibility is given by:

$$\chi = \frac{\partial P_n}{\partial F} = - \frac{\partial^2 E_n}{\partial F^2} = -2 \sum_{m \neq n} \frac{|<n|x|m>|^2}{E_n^{(0)} - E_m^{(0)}}. \quad (10)$$

Its statistical average is:

$$\chi = \frac{1}{Z_0} \sum_{m \neq n} \exp(-\beta E_n^{(0)}) \frac{2|<n|x|m>|^2}{E_m^{(0)} - E_n^{(0)}} \quad (11)$$

with Z_0 - the partition function for the Hamiltonian H_0 :

$$Z_0 = \sum_n \exp(-\beta E_n^{(0)}) \quad (12)$$

At $T=0$, this formula takes a simpler form. If $T \rightarrow 0$, the canonical distribution function $\rho(E_n)$:

$$\rho(E_n) = \frac{1}{Z} \exp(-\beta E_n) = \exp[\beta(F - E_n)] \quad (13)$$

where $F = U - TS = -T \ln Z$ is the free energy, U - the internal energy and S - the entropy, can be written as:

$$\rho(E_n) = \exp \left[-S(T) + \frac{U - E_0}{T} + \frac{E_0 - E_n}{T} \right] \quad (14)$$

Taking the limit of this expression for $T \rightarrow 0$, noticing that $\lim_{T \rightarrow 0} U(T) = E_0$ and, according to the third principle of thermodynamics, $S(0) = 0$, we get for the distribution function the following form:

$$\lim_{T \rightarrow 0} \rho(E_n) = \rho(E_0) = C \delta_{E_0 - E_n, 0} \quad (15)$$

where δ is the Kronecker function:

$$\delta_{E_0 - E_n, 0} = \begin{cases} 1, & E_0 = E_n \\ 0, & E_0 \neq E_n, \end{cases} \quad (16)$$

and C - a constant, which can be obtained from the normalization condition, $\sum_n \rho(E_n) = 1$. This gives $C = 1/g_0$, with g_0 - the degeneracy of the ground state, which has always the value $g_0=1$. The physical meaning of (15) is the following: if $T \rightarrow 0$, the canonical distribution tends to the microcanonical distribution, corresponding to the ground state.

Finally, the formula for the susceptibility is:

$$\chi(T=0) = \sum_m \frac{2|<n|x|m>|^2}{E_m^{(0)} - E_0^{(0)}} \quad (17)$$

It is, as it should, a positive quantity, as $E_m^{(0)} - E_0^{(0)} > 0$ for any $m > 0$.

3.1 The susceptibility and the phase transition

The Hamiltonian can be put in the form:

$$H = -\frac{1}{2m} \sum_n \nabla_n^2 + \left(2d - \frac{a}{2}\right) \sum_n x_n^2 + \frac{a}{4} \sum_n x_n^4 - \sum_n (\sum_m x_n \sigma_{nm}) \quad (18)$$

In the mean-field approximation, one makes the replacement:

$$\sum_m x_n \sigma_{nm} \rightarrow 4d \langle x \rangle \equiv F \quad (19)$$

where F is the effective field, which acts as an external (electric) field. So, (15) becomes a sum of non-interacting Hamiltonians:

$$H = \sum_n \left[-\frac{\nabla_n^2}{2m} + \left(2d - \frac{a}{2}\right) x_n^2 + \frac{a}{4} x_n^4 - F x_n \right]. \quad (20)$$

We can write this formula in the form $H = H_0 - Fx$ with

$$H_0 = \sum_n \left[-\frac{\nabla_n^2}{2m} + \left(2d - \frac{a}{2}\right) x_n^2 + \frac{a}{4} x_n^4 \right] \quad (21)$$

and the physics of the system can be obtained from the one-particle Hamiltonian:

$$H_{MF} = -\frac{\nabla^2}{2m} + \left(2d - \frac{a}{2}\right) x^2 + \frac{a}{4} x^4 - Fx \quad (22)$$

with

$$H_{MF}^{(0)} = -\frac{\nabla^2}{2m} + \left(2d - \frac{a}{2}\right) x^2 + \frac{a}{4} x^4. \quad (23)$$

The average value of the reduced coordinate x is given by:

$$\langle x \rangle = \frac{1}{Z} \text{Tr}[-\beta(H_0 - Fx)] = \frac{1}{\beta} \frac{\partial \ln Z}{\partial F} \quad (24)$$

with

$$Z = \sum_n \exp(-\beta E_n) \quad (25)$$

The condition (24) is a self-consistent equation for $\langle x \rangle$, as this quantity appears in the expression of Z also. The phase transition is given by the condition $\langle x \rangle = 0$. It will be put in a convenient form in the subsequent paragraph.

Taking the derivative with respect with $\langle x \rangle$, in the both sides of (22) we have:

$$1 = \frac{1}{\beta_c} \left[\frac{\partial^2 \ln Z}{\partial \langle x \rangle \partial F} \right]_{\langle x \rangle = 0} \quad (26)$$

where we replaced, according to (19),

$$F = 4d \langle x \rangle \quad (27)$$

In the same time:

$$\begin{aligned} \left[\frac{\partial^2 \ln Z}{\partial F^2} \right]_{\langle x \rangle = 0} &= \beta^2 \left[\frac{1}{Z} \frac{\partial^2 Z}{\partial F^2} - \left(\frac{1}{Z} \frac{\partial Z}{\partial F} \right)^2 \right]_{\langle x \rangle = 0} = \\ &= [\langle x^2 \rangle - \langle x \rangle^2]_{\langle x \rangle = 0} = \beta^2 \langle x^2 \rangle_{\langle x \rangle = 0} \end{aligned} \quad (28)$$

Consequently, the critical equation (26) will take the form:

$$1 = 4d\beta_c \langle x^2 \rangle_{\langle x \rangle = 0} \quad (29)$$

Restoring the extra-factor AC/B , and replacing the reduced coordinate x with the physical one X , one gets:

$$1 = \frac{4d}{T_c} C \langle X^2 \rangle |_{\langle X \rangle = 0} \quad (30)$$

with T_c - the critical temperature of the phase transition.

The susceptibility of this system can be obtained as the derivative of $\langle X \rangle$ with respect to the effective field F . We get from (22):

$$\chi = \left[\frac{\partial \langle X \rangle}{\partial F} \right]_{F=0} = \beta_c \langle X^2 \rangle |_{F=0} \quad (31)$$

As the condition $F = 0$ is equivalent to $\langle X \rangle = 0$, from (28), (29) we get the condition:

$$4dC\chi = 1 \quad (32)$$

This relation is remarkable due to the fact that the phase transition in the system described by (18) can be obtained using only the "non-perturbed", simpler Hamiltonian H_0 , defined in eq. (21).

However, even the problem of obtaining the eigenvalues and the eigenfunctions (needed for the evaluation of the matrix element in (11)) of this "simpler" Hamiltonian is not an easy issue, as no exact solution is available, and approximate solutions treat only the deep well case. For shallow wells, which are essential for understanding the phase transitions in ψ^4 systems, the only way of obtaining analytical results from (11) is to use an exactly solvable two well potential, and the most convenient case is the symmetric two-well rectangular potential.

4. The symmetric double square well

We define the potential considering that the $E = 0$ level is situated on the bump:

$$V(x) = -V, \quad V > 0 \quad (33)$$

for $-a - \left(\frac{b}{2}\right) < x < -\left(\frac{b}{2}\right) \cup \left(\frac{b}{2}\right) < x < (b/2) + a$, and zero otherwise. As the potential is symmetric, the eigenstates will have well-defined parity. The states with negative energies ($E < 0$) and the states with positive energies ($E > 0$) must be discussed separately.

4.1. $E < 0$: even states, wave functions and energies

The wave function for even states is:

$$\psi_e(x) = A_e \sin k_e \left(a + \frac{b}{2} - x \right), \text{ for } \frac{b}{2} < x < a + \frac{b}{2}$$

$$k_e^2 = 2m(-|E| + V)/\hbar^2 \quad (34)$$

and

$$\psi_e(x) = B_e \cosh q_e x, \text{ for } 0 < x < \frac{b}{2}$$

$$q_e^2 = 2m|E|/\hbar^2 \quad (35)$$

It has the property:

$$\psi_e(x) = \psi_e(-x) \quad (36)$$

It is convenient to use for the potential, alternatively with V , the quantity v , defined

$$k_e^2 + q_e^2 = v^2 = \frac{2mV}{\hbar^2}, \quad V > 0 \quad (37)$$

The continuity of the wave function and of its derivative in $x = b/2$ gives:

$$A_e \sin k_e a = B_e \cosh q_e \frac{b}{2} \quad (38)$$

$$-A_e k_e \cos k_e a = q_e B_e \sinh q_e \frac{b}{2} \quad (39)$$

and the eigenvalue equation for energy has the form:

$$\frac{1}{k_e} \tan k_e a = -\frac{1}{q_e} \coth q_e \frac{b}{2} \quad (40)$$

The wave function is normalized if:

$$\frac{1}{B_e^2} = \frac{a}{2} + \frac{b}{4} + \left(1 + \frac{q_e^2}{k_e^2} \right) \left(\frac{1}{4q_e} \sinh b q_e + \frac{a}{2} \sinh^2 \frac{b q_e}{2} \right) \quad (41)$$

and:

$$\frac{1}{A_e^2} = \frac{1}{B_e^2} \frac{\sin^2 k_e a}{\cosh q_e \frac{b}{2}} = \frac{1}{B_e^2} \frac{k_e^2}{q_e^2 \sinh^2 \frac{b q_e}{2} + k_e^2 \cosh^2 \frac{b q_e}{2}} \quad (42)$$

4.2. $E < 0$: odd states, wave functions and energies

Similarly,

$$\psi_o(x) = A_o \sin k_o \left(a + \frac{b}{2} - x \right),$$

$$\text{for } \frac{b}{2} < x < a + \frac{b}{2} \quad (43)$$

and:

$$\psi_o(x) = B_o \sinh q_o x, \text{ for } 0 < x < \frac{b}{2} \quad (44)$$

Also:

$$\psi_o(x) = -\psi_o(-x) \quad (45)$$

The continuity relations give:

$$A_o \sin k_o a = B_o \sinh q_e \frac{b}{2} \quad (46)$$

$$-A_o k_o \cos k_o a = q_o B_o \sinh q_o \frac{b}{2} \quad (47)$$

and the eigenvalue equation is:

$$\frac{1}{k_o} \tan k_o a = -\frac{1}{q_o} \tanh q_o \frac{b}{2} \quad (48)$$

The wave function is normalized if:

$$\frac{1}{B_o^2} = -\frac{a}{2} - \frac{b}{4} + \left(1 + \frac{q_o^2}{k_o^2} \right) \left(\frac{1}{4q_e} \sinh b q_o + \frac{a}{2} \cosh^2 q_o \frac{b}{2} \right) \quad (49)$$

and:

$$\frac{1}{A_o^2} = \frac{1}{B_o^2} \frac{k_o^2}{q_o^2 \sinh^2 \frac{bq_o}{2} + k_o^2 \cosh^2 \frac{bq_o}{2}} \quad (50)$$

4.3. $E > 0$: even states, wave functions and energies

In this case, instead of (32-34), we have:

$$\psi_e(x) = A_e \sin k_e \left(a + \frac{b}{2} - x \right), \text{ for } \frac{b}{2} < x < a + \frac{b}{2}$$

$$k_e^2 = \frac{2m(E+V)}{\hbar^2}, \quad E > 0 \quad (51)$$

$$\psi_e(x) = B_e \cos q_e x, \text{ for } 0 < x < \frac{b}{2} \quad (52)$$

$$q_e^2 = \frac{2mE}{\hbar^2}$$

The continuity conditions give:

$$A_e \sin k_e a = B_e \cos q_e \frac{b}{2} \quad (54)$$

$$A_e k_e \cos k_e a = q_e B_e \sin q_e \frac{b}{2} \quad (55)$$

and the energy eigenvalue equation is:

$$\tan k_e a = \frac{k_e}{q_e} \cot q_e \frac{b}{2} \quad (56)$$

The wave function is normalized if:

$$\frac{1}{B_e^2} = \frac{b}{4} + \frac{a}{2} + \left(\frac{\sin q_e b}{4q_e} - \frac{2 \sin^2 q_e \frac{b}{2}}{a} \right) \cdot \left(1 - \frac{q_e^2}{k_e^2} \right) \quad (57)$$

$$\frac{1}{A_e^2} = \frac{1}{B_e^2} \frac{1}{\cos^2 q_e \frac{b}{2} + \frac{q_e^2}{k_e^2} \sin^2 q_e \frac{b}{2}} \quad (58)$$

4.4. $E > 0$: odd states, wave functions and energies

Similarly:

$$\psi_o(x) = A_o \sin k_o \left(a + \frac{b}{2} - x \right),$$

$$\frac{b}{2} < x < a + \frac{b}{2} \quad (59)$$

and:

$$\psi_o(x) = B_o \sinh q_o x, \text{ for } 0 < x < \frac{b}{2} \quad (60)$$

$$\psi_o(-x) = -\psi_o(x) \quad (61)$$

The continuity conditions:

$$A_o \sin k_o a = B_o \sinh q_o \frac{b}{2} \quad (62)$$

$$-A_o k_o \cos k_o a = q_o B_o \sinh q_o \frac{b}{2} \quad (63)$$

and the eigenvalue equation is:

$$\tan k_o a = -\frac{k_o}{q_o} \tanh q_o \frac{b}{2} \quad (64)$$

The wave function is normalized if:

$$\frac{1}{B_o^2} = \frac{a}{2} + \frac{b}{4} + \left(-1 + \frac{q_o^2}{k_o^2} \right) \left(\frac{1}{4q_o} \sinh bq_o + \frac{a}{2} \cosh^2 q_o \frac{b}{2} \right) \quad (65)$$

and:

$$A_o = B_o \frac{\sin q_o \frac{b}{2}}{\sin k_o a} \quad (66)$$

4.5. Approximate solutions for a shallow well

Considering this problem from the perspective of applications in statistical mechanics, it is important to have a correct description of the occurrence of the first negative energy level. We shall find the solutions of the eigenvalue equations, for this case. We shall investigate firstly the negative energy states, and later on the positive energy states.

4.5.1. Negative energy states

It is easy to see that the eigenvalue equation for negative energy has solutions only if

$$v > v_{min} = \frac{\pi}{2a} \quad (67)$$

With

$$z = \frac{q_e}{v} \quad (68)$$

and

$$v = \frac{\pi}{2a} + \varepsilon, \quad \varepsilon \ll 1 \quad (69)$$

the eigenvalue equation for negative energy is:

$$\tan a \left(\frac{\pi}{2a} + \varepsilon \right) \sqrt{1 - z^2} = -\frac{\sqrt{1 - z^2}}{z} \coth \frac{zb}{2} \left(\frac{\pi}{2a} + \varepsilon \right) \quad (70)$$

As the root of the equation occurs at very small z , and the argument of \coth is quite insensitive near $\pi/(2a)$:

$$\tan a \left(\frac{\pi}{2a} + \varepsilon \right) = -\cot a \varepsilon = -\frac{1}{z} \coth \frac{\pi b z}{4a}$$

Keeping only the first term in the series expansion:

$$z^2 = \frac{4a^2}{\pi b} \varepsilon = \frac{q_e^2}{v^2}, \quad q_e^2 \cong \frac{\pi}{b} \varepsilon$$

So:

$$q_e^2 = \frac{\pi}{b} \varepsilon = \frac{\pi}{b} \left(v - \frac{\pi}{2a} \right), \quad (71)$$

and:

$$q_e^2 = \frac{2m|E|}{\hbar^2}, \quad E = -\frac{\hbar^2 \pi}{2m b} \varepsilon = -\frac{\pi^2 \hbar^2}{4abm} - \frac{\pi \hbar}{b\sqrt{2m}} \sqrt{V} < 0 \quad (72)$$

The minimum value of the potential V , after which a state of negative energy occurs, is:

$$v_{min} = \frac{\pi}{2a}, \quad V_{min} = \frac{\hbar^2 v_{min}^2}{2m} = \frac{\hbar^2 \pi^2}{8ma^2} \quad (73)$$

It might be compared to the first level in an infinite square well of length $L = 2a + b$:

$$E_1^{(\infty)} = \frac{\hbar^2 \pi^2}{2m(2a + b)^2}$$

Consequently:

$$\frac{V_{min}}{E_1^{(\infty)}} = \left(1 + \frac{b}{2a}\right)^2 \quad (74)$$

So, the potential which produces the first state of negative energy is comparable to (in fact, slightly larger than) the first level of the infinite well.

4.5.2. Positive energy states

Even states

In the new variable z , the eigenvalue equation (54) is:

$$\tan av\sqrt{1+z^2} = \frac{\sqrt{1+z^2}}{z} \cot \frac{vzb}{2} \quad (75)$$

Numerical investigations of this equations show that it can be replaced, with minor loss in the precision of the solutions, with its "asymptotic form", i.e. considering that:

$$\frac{\sqrt{1+z^2}}{z} \cong 1 \quad (76)$$

and that (75) can be replaced with:

$$\tan av\sqrt{1+z^2} = \cot \frac{vzb}{2} \quad (77)$$

Looking for solutions near $v_{min} = \frac{\pi}{2a}$, we have:

$$\tan \frac{\pi}{2} \sqrt{1+z^2} = \cot \frac{\pi zb}{2a} = \tan \frac{\pi}{2} \left(1 - \frac{zb}{2a}\right) \quad (78)$$

which gives the quantization condition:

$$\frac{\pi}{2} \sqrt{1+z^2} - \frac{\pi}{2} \left(1 - \frac{zb}{2a}\right) = n\pi \quad (79)$$

or:

$$\sqrt{1+z^2} = 2n + 1 - \frac{zb}{2a} \quad (80)$$

It can be written as:

$$\left(1 - \frac{b^2}{4a^2}\right) z^2 + 2z(2n+1) \frac{b}{2a} - 4n^2 - 4n = 0 \quad (81)$$

The root relevant for our discussion is:

$$z_n = (2n+1) \frac{b}{2a} \frac{\sqrt{1 + \frac{4n(n+1)4a^2 - b^2}{(2n+1)^2 b^2}} - 1}{1 - \frac{b^2}{4a^2}} \quad (82)$$

The factor

$$f(n) = \frac{4n(n+1)}{(2n+1)^2} \quad (83)$$

is very closed to 1, even for small n :

$$f(1) = \frac{8}{9}, \quad f(2) = \frac{24}{25}, \quad f(3) = \frac{48}{49}$$

and (82) can be replaced with:

$$z_n = (2n+1) \frac{2a}{2a+b} \quad (83a)$$

As $q_n = vz_n$, $E_n = z_n^2 V$ and:

$$E_n = (2n+1)^2 \frac{4a^2}{(2a+b)^2} V \quad (84a)$$

Also,

$$k_e^2 = \frac{2m(E+V)}{\hbar^2} = q_e^2 + v^2, \\ v^2 = \frac{\pi^2}{4a^2} + \varepsilon \frac{\pi}{a}$$

and

$$V = \frac{\hbar^2 \pi^2}{8ma^2} + \varepsilon \frac{\pi \hbar^2}{a 2m} \quad (84b)$$

Odd states

Following exactly the same steps as for even states, we get, instead of (83):

$$z_n = 2n \frac{2a}{2a+b} - \frac{1}{2n} \quad (85)$$

5. The critical equation

5.1. Dipole matrix elements

Due to symmetry, only the matrix elements of the coordinate x between the ground state (which is an even one) and odd states of positive energy are non-zero, so we have to evaluate:

$$\langle x \rangle_{e,n} = 2 \int_0^{a+\frac{b}{2}} x \psi^{(e)}(x) \psi_n^{(o)}(x) dx \quad (86)$$

where n labels the odd states. The previous notation (57) is slightly modified, being replaced with:

$$\psi_n^{(o)}(x) = A_n \sin k_n \left(a + \frac{b}{2} - x \right),$$

for $\frac{b}{2} < x < a + \frac{b}{2}$ (87)

and

$$\psi_n^{(e)}(x) = B_n \sin q_n x, \quad 0 < x < \frac{b}{2} \quad (88)$$

Also, for the even state:

$$\psi^{(e)}(x) = A \sin k \left(a + \frac{b}{2} - x \right),$$

for $\frac{b}{2} < x < a + \frac{b}{2}$ (89)

and

$$\psi^{(e)}(x) = B \cosh qx$$

for $0 < x < \frac{b}{2}$ (90)

In the lowest order in ε ,

$$q^2 = \frac{\pi}{b} \varepsilon; \quad k^2 = v^2 - q^2 = \left(\frac{\pi}{2a} \right)^2 + \varepsilon \pi \left(\frac{1}{a} - \frac{1}{b} \right)$$

(91)

and

$$k = \frac{\pi}{2a} + \varepsilon \pi \left(\frac{1}{a} - \frac{1}{b} \right) \quad (92)$$

Also, in the lowest order in ε :

$$\begin{aligned} \cosh qx &= 1 + \frac{\pi}{2b} \varepsilon x^2 \quad (94) \\ \sin k \left(a + \frac{b}{2} - x \right) &= \\ &= \cos \frac{\pi}{2a} \left(\frac{b}{2} - x \right) + \varepsilon \pi \left(\frac{1}{a} - \frac{1}{b} \right) \cdot \left(a + \frac{b}{2} - x \right) \cdot \\ &\quad \cdot \sin \frac{\pi}{2a} \left(\frac{b}{2} - x \right) \quad (95) \end{aligned}$$

However, the ε -dependence of the matrix element is insignificant compared to the exponential factors, and the matrix element can be written as:

$$\frac{1}{2} \langle x \rangle_{e,n} = BB_n I_b + AA_n I_n \quad (96)$$

with:

$$\begin{aligned} I_b &= \int_0^{b/2} x \sin q_n^0 x \, dx \quad (97) \\ I_a &= \int_{b/2}^{a+b/2} x \cos \frac{\pi}{2a} \left(\frac{b}{2} - x \right) \sin k_n^0 \left(a + \frac{b}{2} - x \right) dx \quad (98) \end{aligned}$$

As the quantities $q_n^0 = q_n(\varepsilon = 0)$ and $k_n^0 = k_n(\varepsilon = 0)$ depend only on the geometry of the well (a and b), and not on the mass m , they are just numbers, playing a peripheral role in the expression of susceptibility. However, these formulas will not be used in the present paper, where only the dominant term in the expression of susceptibility will be taken into account.

5.1.1. The critical temperature

The susceptibility is given by the formula:

$$\chi = \frac{1}{Z} \quad (99)$$

$$\cdot \left\{ \sum_{n=1}^{\infty} \frac{2d_{no,e}^2 e^{-\beta E_n^{(o)}}}{E_n^{(o)} - E_e} + \sum_{n=2}^{\infty} \frac{2d_{no,1e}^2 e^{-\beta E_n^{(o)}}}{E_n^{(o)} - E_e} + \dots \right\}$$

where the upper index (o) refers to the odd levels. The first term:

$$\frac{2d_{no,e}^2 e^{-\beta E_n^{(o)}}}{E_n^{(o)} - E_e} \quad (100)$$

is the dominant one.

The partition sum can be approximated through the expression:

$$Z = \frac{1}{2} \left[\vartheta_3 \left(0, \frac{4a^2}{(2a+b)^2} \beta V \right) - 1 \right] \quad (101)$$

where ϑ_3 is the Jacobi elliptic function. In the lowest approximation,

$$\frac{1}{Z} \cong \exp \left(\frac{4a^2}{(2a+b)^2} \beta V \right) \quad (102)$$

With respect to the critical equation, we are merely interested in the connection between temperature, mass and potential - in our case, V . It is close to the value $\pi/2a$, so it can be written as: $v = \pi/2a + \varepsilon$. The dipole matrix element depends on geometry (i.e. on parameters a, b) only (not on mass or temperature; they enter in the expression of eigenenergies). Finally, we get the following expression for the critical equation:

$$dC \frac{\exp \left(-\frac{32a^2}{L^2} \beta V \right)}{\frac{36a^2}{L^2} V + \frac{\pi \cdot \hbar}{b\sqrt{2m}} \sqrt{V} - \frac{\pi^2 \hbar^2}{4abm}} = \text{const.} \quad (103)$$

It gives the connection between the temperature β , the mass m and the potential, V . The result is correct for $d = 2$ and $d = 3$, but must be not taken into consideration for $d = 1$, as in this case the mean-field theory gives inaccurate predictions.

In the classical limit, $\hbar \rightarrow 0$ and $m \rightarrow \infty$, so eq. (102) becomes:

$$\frac{1}{T} \sim \left| \frac{\ln V}{V} \right| \quad (104)$$

It bears a quite interesting resemblance with a similar result, obtained in the mean-field approximation, for a planar array of Ginzburg - Landau chains (the 3rd paper in [19], eq. (43)). A formula similar to (103) has been obtain for the first time by Scalapino, Imry and Pincus [28], using a different approach. Numerically, the result was firstly obtained by Bishop and Krumhansl [29]. It is also in qualitative agreement with more recent Monte Carlo simulations for a polynomial potential [13-15].

6. Conclusions

The critical equation describing the phase transition in a rectangular array of anharmonic (quartic) oscillators,

interacting through elastic forces, was obtained using a mean-field approximation of the statistical problem. Further on, the on-site polynomial (quartic) potential was replaced with a simpler one - the symmetric double square well potential. Original methods for obtaining its energy eigenvalues [30] have been developed - a contribution which presents interest in itself. A peculiarity of this potential is that, if the energy eigenvalues are known, the eigenfunctions are also known. In this way, it is possible to evaluate the electric susceptibility of the model, and to obtain the critical equation. A similar exercise could be repeated with another simpler model of the quartic potential - for instance, the so-called "two-center harmonic oscillator". The resemblance of the result obtained here for the critical temperature, with the result given by another mean-field approximations or numerical methods [31], suggests that the approach used in this paper is justified.

In fact, it gives the first analytic approximation for the case of shallow wells, contributing to a better understanding of structural phase transitions; indeed, till now, only the case of deep wells has been studied analytically. The results are in qualitative agreement with Monte Carlo simulations.

Acknowledgement

This work was supported by a grant of Romanian National Authority for Scientific Research, CNCS-UEFISCDI, project IDEI number 953 / 2008.

References

- [1] L. D. Landau, E. M. Lifshitz: *Physique statistique*, Ed. Mir, Moscou, 1972.
- [2] R. A. Cowley, *Adv. Phys.* **29**, 1 (1980).
- [3] A. D. Bruce, *Adv. Phys.* **29**, 111 (1980).
- [4] D. J. Scalapino, M. Sears, R. A. Ferrell, *Phys. Rev.* **B6**, 3409 (1972).
- [5] B. Stoeckly, D. J. Scalapino, *Phys. Rev.* **B11**, 205 (1975).
- [6] B. Stoeckly, *Phys. Rev.* **B14**, 1271 (1976).
- [7] T. D. Schultz, D. C. Mattis, E. H. Lieb, *Rev. Mod. Phys.* **36**, 856 (1964).
- [8] G. D. Mahan: *Many-particle physics*, Plenum Press, 1990.
- [9] V. Barsan, *Rev. Roum. Phys.* **30**, 775 (1985); *J. Phys.: Cond. Matter* **1**, 7961 (1989); **2**, 4815 (1990).
- [10] V. Barsan, S. Cojocaru, *Rom. Rep. Phys.* **58**, 123 (2006).
- [11] S. Cojocaru, V. Bârsan, A. Ceulemans, *physica status solidi B* **243** 1963 (2006); *J. Mag. Magn. Mat.* **307**, 62 (2006); V. Barsan, S. Cojocaru, A. Ceulemans, *Philos. Mag.* **86**, 4983 (2006).
- [12] V. Barsan, *St. Cerc. Fiz.* **35**, 124; **35**, 781 (1983).
- [13] R. Toral, A. Chakrabarti, *Phys. Rev.* **B42**, 2445 (1990).
- [14] W. Janke, T. Sauer, *J. Stat. Phys.* **78**, 759 (1995).
- [15] W. Loinaz, R. S. Willey, *Phys. Rev.* **D58** 076003 (1998).
- [16] V. V. Savkin, A. N. Rubtsov, T. Janssen, *Phys. Rev.* **B65**, 214103 (2002).
- [17] V. V. Savkin, A. N. Rubtsov, *J. Exp. Theor. Phys.* **91**, 1204 (2000); arXiv:cond-mat/0112429v2 (2002).
- [18] V. Barsan, *J. Phys.: Condensed Matter* **18**, 9275 (2006); **20**, 019701 (2008) *The Ramanujan Journal*, **20**, 153 (2009).
- [19] V. Barsan, *Philos. Mag.* **87**, 1043 (2007); **88**, 121 (2008); **91**, 477 (2011); *Rom. Rep. Phys.* **60**, 205 (2008); **62**, 219 (2010).
- [20] R. Lungu, *Optoelectron. Adv. Mater. - Rapid Commun.* **5**, 1223 (2011).
- [21] Yu. Ilinskii, L. V. Keldysh, *Electromagnetic response of material media*, Plenum Press (1994).
- [22] C. M. Bender, T. T. Wu, *Phys. Rev.* **184**, 1231 (1969); *Phys. Rev. D7*, 1620 (1973).
- [23] G. Ciobanu, V. Barsan, A. T. Mincu, *Rom. J. Phys.* **55**, 539 (2010).
- [24] E. A. Johnson, H. T. Williams, *Am. J. Phys.* **50**, 239 (1982).
- [25] R. Blinc, B. Zeks: *Soft modes in ferroelectrics and antiferroelectrics*, North Holland Publishing Company (1974).
- [26] A. Strukov, A. P. Levanyuk: *Ferroelectric phenomena in crystals*, Springer (1998).
- [27] K. Rabe, C. H. Ahn, J.-M. Triscone (Eds.): *Physics of ferroelectrics*, Springer (2007).
- [28] D. J. Scalapino, Y. Imry, P. Pincus, *Phys. Rev.* **B11**, 2042 (1975).
- [29] A. R. Bishop, J. A. Krumhansl, *Phys. Rev.* **B12**, 2824 (1975).
- [30] V. Barsan, *Rom. Rep. Phys.* **64**, 685 (2012); V. Barsan, R. Dragomir, *Optoelectron. Adv. Mater. - Rapid Commun.*, **6**, 917 (2012).
- [31] E. Van der Straeten, J. Naudts, *J. Phys.* **A39**, 933 (2006).

*Corresponding author: gciobanu2003@yahoo.com