

THE CHAIN OF CLASSICAL ANHARMONIC OSCILLATORS IN AN EXTERNAL FIELD

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Abstract. The polarization and the susceptibility of a chain of classical oscillators with quartic anharmonicities, interacting through near-neighbor elastic forces, are calculated through the transfer matrix technique, using recent results obtained for the ground state energy of a quantum anharmonic oscillator in an external field. The comparison with 1D Ising model in a magnetic field gives some guidance in the physical interpretation of the results. The method can be easily extended to the mean-field study of 2D and 3D anisotropic arrays of classical anharmonic oscillators.

1. INTRODUCTION

The chain of classical anharmonic oscillators is of central importance for understanding a number of physical systems, from atomic chains [1] to ferroelectric polymers [2]. In this paper, we shall focus our attention to a 1D system of classical oscillators, with two-well, quartic in-site potential, interacting through elastic, near-neighbor forces. Our goal will be to investigate the effect of an electric field on such a system, i.e. to evaluate its polarization and electric susceptibility. The results will be compared to those obtained for the 1D Ising model in magnetic field.

We shall use the transfer matrix method, as formulated by Scalapino, Sears and Ferrell [3], which reduces the evaluation of the free energy of a 1D system, to the calculation of the ground state energy of an associated Schrodinger equation. In our case, this equation describes a quantum quartic oscillator. The Hamiltonian of the chain will be treated in the continuum approximation, following the classical paper of Krumhansl and Schrieffer [4].

The quantum anharmonic oscillator in an external field is important not only for the exact treatment of a 1D system of classical anharmonic oscillators, but also for a mean-field treatment of 1D systems of quantum anharmonic oscillators [5] and of very anisotropic 2D and 3D systems of classical anharmonic oscillators [6].

In spite of the simple aspect of its potential, the Schrodinger equation for quartic oscillators cannot be solved exactly not even in the simplest case – the “pure quartic” – to say nothing about a two-well quartic potential and, so much the less, in the case when an external field is added. For instance, Koehler and Gillis [5] obtained approximate analytic results in the case of very deep wells, and Bishop and Krumhansl [6] – numerical results.

In the last years, remarkable progress has been made in the investigation of both one-well [7] and two-well [8-11] quartic anharmonic oscillators. However, only the ground state, and in some cases, some few low excited states wave functions have been obtained; consequently, a satisfactory development of a perturbation theory, in order to evaluate the effect of the external field, could not be done.

An interesting contribution to this subject is due to Van der Straeten and Naudts, who combined the analytical results of Jafarpour and Afshar [13] and the numerical ones of Bishop et al. [14], in order to obtain some hybrid – partly numerical, partly analytical – results concerning the ground state energy of a two-well, quartic anharmonic oscillator in an electric field.

The original part of this paper consists in the application of these results to the evaluation of the polarization and susceptibility of the chain of classical anharmonic oscillators in electric field. The finite-size effects have been also evaluated.

The paper is organized as follows. In Section 2, we give a short description of the transfer matrix technique, adapted to our problem. In Section 3, we expose the main results recently obtained for the ground state energy of a double-well anharmonic oscillator. Section 4 is a reminder of the 1D Ising model in magnetic field. Section 4 contains our original results. The last section contains some conclusions and suggestions for further work.

2. THE STATISTICAL MECHANICS OF THE ANHARMONIC CHAIN: A TRANSFER MATRIX APPROACH

We shall describe the chain of classical anharmonic oscillators using the standard Hamiltonian [4]:

$$H_{cl} = \sum_{i=1}^N \frac{1}{2} m_i \left(\frac{du_i}{dt} \right)^2 + \sum_{i=1}^N \left[\left(\frac{1}{2} A u_i^2 + \frac{1}{4} B u_i^4 \right) + \sum_{j=1}^N \frac{1}{2} c_{ij} (u_i - u_j)^2 \right], \quad (1)$$

$$c_{ij} = 0 \quad \text{for} \quad j \neq i \pm 1$$

where i, j indicate lattice sites; u_i – displacements of displacing atoms with respect to some heavy ions or reference lattice. Periodic boundary conditions are assumed. The coefficient A is defined by the attractive interactions of the mobile atom with the reference lattice, B – by short-range repulsive interactions, and c_{ij} – by elastic

interactions between displacing atoms. If (1) describes a lattice which is unstable against a displacive transition, $A < 0$, $B > 0$, $c_{ij} > 0$. In this situation, the potential energy on site appearing in (1) has two minima, at $\pm u_0$, where

$$u_0 = \left(\frac{|A|}{B} \right)^{1/2}. \quad (2)$$

We shall replace the discrete Hamiltonian (1) with a continuum representation:

$$H_{cl} = \int \frac{dx}{l} \left[\frac{1}{2m} p(x)^2 + \frac{A}{2} u(x)^2 + \frac{B}{4} u(x)^4 + \frac{1}{2} m c_0^2 \left(\frac{du}{dx} \right)^2 \right], \quad (3)$$

where l is the lattice spacing, c_0 – the sound velocity, and $x_j = jl$ locates an atom in the continuum representation.

The equilibrium thermodynamics of the 1D model can be obtained from the classical partition function:

$$Z = \int \mathcal{D}u \mathcal{D}p e^{-\beta \mathcal{H}(u,p)}, \quad (4)$$

where, as usual,

$$Z_p = (2\pi k_B T)^{N/2}, \quad (5)$$

and

$$Z_u = e^{-N\beta\epsilon_0}, \quad (6)$$

with ϵ_0 – the ground state energy of the Schrödinger equation:

$$\left(-\frac{1}{2m^*} \frac{d^2}{du^2} + \frac{A}{2} u^2 + \frac{B}{4} u^4 \right) \Psi_n(u) = \epsilon_n \Psi_n(u), \quad (7)$$

$$m^* = m \frac{c_0^2}{l^2 k_B T^2}. \quad (8)$$

The free energy F is:

$$F = -k_B T \ln Z_p Z_u = F_p + F_u \quad (9)$$

but, in fact, only the “interaction term”, F_u ; produces interesting physical effects. The free energy per particle is:

$$f_u = \epsilon_0. \quad (10)$$

In the presence of an electric field, a term

$$-\mathcal{E}qu_i = -pu_i$$

is added to the on-site energy (the notation used in the r.h.s. intends to compromise with that used in [12]), and the quantum Hamiltonian from (7) becomes:

$$H_q = -\frac{1}{2m^*} \frac{d^2}{du^2} + \frac{A}{2} u^2 + \frac{B}{4} u^4 - pu. \quad (11)$$

So, the average value of the displacement can be written as:

$$\langle u \rangle = -\frac{\partial \epsilon_0(p)}{\partial p}, \quad (12)$$

where $\epsilon_0(p)$ is the ground state energy of H_q .

As it is wellknown, the eigenvalues of (11) cannot be obtained exactly. An approximate expression for $\epsilon_0(p)$ has been obtained in [12]. We shall use this expression in order to find the polarization and the electrical susceptibility of the chain of classical anharmonic oscillators.

In the next section, we shall briefly expose the deduction of $\epsilon_0(p)$, in order to properly understand its validity and its limitations.

3. THE QUANTUM DOUBLE WELL ANHARMONIC OSCILLATOR IN AN EXTERNAL .ELD

We shall briefly describe the results obtained recently by Van der Straeten and Naudts [12] on this subject. The Hamiltonian:

$$H = \frac{P^2}{2m} + \sum_{i=0}^I \lambda_i Q^i \quad (13)$$

is written in terms of annihilation and creation operators a , a^+ of the ordinary harmonic oscillator with mass m and frequency ω_0 : Defining

$$r^2 = \frac{\hbar}{m\omega_0} \quad (14)$$

and using a formula for normal ordering derived in [13], the Hamiltonian (1) takes the form:

$$H = -\frac{\hbar^2}{4mr^2} (a - a^+)^2 + \sum_{i=0}^I \lambda_i \left(\frac{r}{\sqrt{2}} \right)^i \sum_{k=0}^{\lfloor \frac{i}{2} \rfloor} \frac{i!}{2^k k!} \sum_{j=0}^{i-2k} \frac{(a^+)^{i-2k-j} a^j}{j!(i-2k-j)!} \quad (15)$$

The expectation value of (15) in a certain state $|\psi_t\rangle$, depending on a parameter t , will be minimized

$$\frac{\partial}{\partial r^2} \langle \psi_t | H | \psi_t \rangle = 0 \quad (16)$$

in order to obtain an equation which can determine the parameter t .

For a quartic oscillator in an external field, $\lambda_1 = -p$, $\lambda_2 = \frac{\alpha}{2}$, $\lambda_3 = 0$, $\lambda_4 = \frac{\beta}{4}$, $I = 4$, and (15) becomes:

$$(2t+1) \left(2\lambda_2 r_0^4 - \frac{\hbar^2}{m} \right) + 6\lambda_4 r_0^6 (2t^2 + 2t + 1) = 0. \quad (17)$$

If t is known – or, equivalently, if the choice of the state vector $|\psi_t\rangle$ has been done – eq. (17) will give the value of r_0 ; this cubic equation has indeed one real root, if the potential has two wells ($\alpha < 0$). The choice of t has no clear physical significance. The authors adopt the variant $t = N/2$; where N is the value at which the $|\psi_t\rangle$ basis is truncated, for reasons of rapid convergence of numerical calculations. ω is also fixed numerically. The choice of a shallow well, with $\alpha = 2\lambda_2 = -2$, $\beta = 4\lambda_4 = 1$, transforms (17) in an equation with numerical coefficients, which gives a numerical value for r_0 .

The ground state eigenenergy in the presence of an electric field, $\epsilon_0(p)$, is determined for small, moderate and large values of the field. For small fields,

$$\epsilon_0(p) \approx \epsilon_0(0) - |c_1| p^2 \quad (18)$$

and for moderate values of p ,

$$\epsilon_0(p) \approx \epsilon_0(0) - |Q_{01}| p. \quad (19)$$

The authors proposed an interpolation formula:

$$\epsilon_0(p) \approx \epsilon_0(0) - |a| p \tanh \omega p, \quad (20)$$

which could cover both cases. The coefficients c_1 , Q_{01} are determined numerically:

$$c_1 \approx -3.39, \quad |Q_{01}| \approx 0.853, \quad a \approx -0.93, \quad \omega = \frac{c_1}{a}. \quad (21)$$

Their “exact” value depends on the truncation of basis functions $|\psi_t\rangle$.

For large fields,

$$\epsilon_0(p) \simeq A + B_p^{4/3}. \quad (22)$$

4. THE 1D ISING MODEL IN EXTERNAL FIELD: A REMINDER

There is a deep connection between anharmonic solids and the Ising model, as noticed since early, 60s [15]. For $D > 1$, they have the same critical behaviour; for $D = 1$, where no phase transition occurs, the Ising model is useful because its thermodynamics can be evaluated exactly, and it can provide a guidance for the physical behaviour of our system under scrutiny – the chain of classical anharmonic oscillators.

We shall write the Ising Hamiltonian

$$\mathcal{H}_I = -E_1 \sum_{k=1}^N \sigma_k \sigma_{k+1} - H \sum_{k=1}^N \sigma_k \quad (23)$$

using the notations of McCoy and Wu [16]. The free energy is:

$$F = -E_1 - \frac{1}{\beta} \ln \left\{ \cosh \beta H + \left(\sinh^2 \beta H + e^{-4\beta E_1} \right)^{1/2} \right\} \quad (24)$$

and the magnetization:

$$M = -\frac{\partial F}{\partial H} = \sinh \beta H \cdot \left(\sinh^2 \beta H + e^{-4\beta E_1} \right)^{1/2}. \quad (25)$$

We have $M(H = 0) = 0$, so there is no magnetization in the absence of an external field. In the plane (H, M) , $M(H)$ increases monotonically from $H = 0$ to a saturation value, for $H \rightarrow \infty$. Consequently, the magnetic susceptibility decreases continuously, from $H = 0$, to larger values of H :

$$\chi(H) = \frac{\partial M}{\partial H} = \beta \cosh \beta H \frac{e^{-4\beta E_1}}{\left(\sinh^2 \beta H + e^{-4\beta E_1} \right)^{3/2}}. \quad (26)$$

Its maximal value is

$$\chi(0) = \beta e^{2\beta E_1}, \quad (27)$$

and the minimal one:

$$\chi(H \rightarrow \infty) = 0.$$

5. THE CHAIN OF CLASSICAL ANHARMONIC OSCILLATORS IN AN EXTERNAL FIELD

Now we are prepared to evaluate the polarization and the electric susceptibility of the chain. This reduces to the evaluation of the ground state energy of a quantum anharmonic oscillator moving in a symmetric, two-well potential:

$$V_s(x) = \frac{\alpha}{2}x^2 + \frac{\beta}{4}x^4 \quad (28)$$

superposed with a linear potential, due to the electric field, which creates a total, asymmetric, potential:

$$V_{as}(x) = \frac{\alpha}{2}x^2 + \frac{\beta}{4}x^4 - px. \quad (29)$$

The “electric” term favors one of the two wells; this one becomes deeper, while the other one – more shallow, disappearing when the electric field is larger than a certain critical value p_c . It is easy to find p_c by analyzing the extremum points of $V_{as}(x)$, which are the roots of the equation:

$$\frac{dV_{as}(x)}{dx} = \beta x^3 + \alpha x - p = 0, \quad (30)$$

where $\alpha < 0$, $\beta > 0$, $p > 0$. This equation may have one or three real roots, according to the sign of the discriminant, proportional to the expression:

$$-\frac{|\alpha|^3}{27\beta} + \frac{p^4}{4},$$

which changes its sign at the critical value:

$$p_c = \left(\frac{4}{27} \frac{|\alpha|^3}{\beta} \right)^{1/4}. \quad (31)$$

If we presume a Landau-type temperature dependence of the parameter α , i.e. $\alpha = \alpha'(T - T_c)$, then the critical field has also a T -dependence, of the form:

$$p_c = p_{c0} |T - T_c|^{3/4}, \quad (32)$$

where we have used the standard notations of the Landau theory of phase transitions (see for instance [17]).

The polarization is proportional to the average displacement; according to (12),

$$\langle Q \rangle = -\frac{\partial \epsilon_0(p)}{\partial p}. \quad (32)$$

So, for small fields, using (18),

$$\langle Q \rangle = 2|c_1|p \quad (33)$$

and for intermediate ones,

$$\langle Q \rangle = |Q_{01}|. \quad (34)$$

Accordingly, the susceptibility

$$\chi = \frac{\partial \langle Q \rangle}{\partial p} \quad (35)$$

is:

$$\chi = 2|c_1|, \quad \text{small } p, \quad (36)$$

$$\chi = 0, \quad \text{intermediate } p. \quad (37)$$

Using the formula (20), proposed in [12] to interpolate between these two regimes, one obtains:

$$\langle Q \rangle = \tanh \omega p + \frac{\omega p}{\cosh^2 \omega p}, \quad p < p_c. \quad (38)$$

For small fields,

$$\langle Q \rangle = \omega p (1 + \dots) \quad (39)$$

and, comparing with the magnetization of the Ising model, (25), for small fields,

$$M = \beta H e^{2\beta E_1} + \mathcal{O}(\beta^2 H^2),$$

we can identify the coefficient ω as

$$\omega = \beta e^{2\beta \epsilon_0^*}. \quad (40)$$

Qualitatively, (38) has a correct critical behaviour, in the sense that it is a monotonically increasing function of p , which saturates asymptotically. Also, the comparison with the Ising model gives some insight on the physical significance of numerical constants entering in the solutions obtained in [12].

With (38), we find for the susceptibility:

$$\chi = \frac{2\omega}{\cosh^2 \omega p} \left(1 - \frac{\omega p \tanh \omega p}{\cosh \beta p} \right), \quad p < p_c. \quad (41)$$

Let us examine now the situation for large fields. It is worth mentioning that Bronzan and Sugar [18] obtained, for the k -th excited state of a Hamiltonian with potential energy

$$V(x) = A_0 x + x^4, \quad (42)$$

the following asymptotic expression:

$$E_k = E_{k0} - 3 \left(\frac{A_0}{4} \right)^{4/3} + (2k+1) \left(\frac{A_0}{4} \right)^{1/3} + \mathcal{O}(A_0^{-2/3}) \quad (43)$$

assuming $A > 15$. This expression is similar to (22), and allows us a determination of the constant B , from this equation.

So, using the same formulae as for weak and moderate fields, we get for large ones:

$$\langle Q \rangle \sim p^{1/3}, \quad p > p_c, \quad (44)$$

$$\chi \sim p^{-2/3}, \quad p > p_c. \quad (45)$$

This regime has no analogue in the Ising model, because, in this case, the potential has only one well.

The analogy with the Ising model, for $p < p_c$, allows us to make some comments on the finite-size effects in anharmonic chains. We shall examine here the difference between cyclic and free ends conditions [16]. They might have some relevance for low T , and also influence the way the thermodynamic limit is reached, in each case. The partition function for free ends and N particles is, for $T \rightarrow 0$,

$$Z^{free}(N) \approx 2e^{\beta|E_1|(N-1)} \quad (46)$$

and, for cyclic conditions,

$$Z^{cyclic}(N) \approx 2e^{\beta|E_1|N} \quad (47)$$

with $E_1 = \frac{1}{2}cu^2$, with $u \sim u_0$. The ratio

$$\frac{Z^{free}(N)}{Z^{cyclic}(N)} \approx e^{-\beta|E_1|} \quad (48)$$

may be significant for an atomic chain, at low T .

Even if, in both cases, the free energy per particle is the same, in the thermodynamic limit, $\frac{1}{N} \ln Z^{cyclic}(N)$ approaches this value exponentially in N ,

while $\frac{1}{N} \ln Z^{free}(N)$ approaches it at the much slower rate of N^{-1} .

6. CONCLUSIONS

Using the most recent results of the studies of a quantum anharmonic oscillator in an external field, we obtained the polarization and the electric susceptibility of a chain of classical anharmonic oscillators, interacting through near-neighbor elastic interaction, in an external field. This system simulates the behaviour of atomic chains or ferroelectric polymers in electric fields. The comparison with the exact solution of the Ising model in an external field gives some insight of the physical significance of the numerical coefficients of the solution of the asymmetrical anharmonic oscillator.

The theory exposed in this paper can be easily applied to the mean-field treatment of anisotropic 2- and 3D arrays of classical anharmonic oscillators [6]. Also, the Hsue-Chern approach [19] may be extended to describe the effect of an external field.

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