The Cercignani Conjecture About a Classical Zero-Point Energy, and Its Confirmation for Ionic Crystals

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Abstract A characteristic feature of Quantum Mechanics is that it predicts the existence of zero-point energy, i.e., of states with a nonvanishing kinetic energy at zero temperature. This is a fact that is experimentally verified and is considered to be inconceivable in a classical frame. In the year 1972 Carlo Cercignani advanced the idea that a classical zero-point energy may be conceived, if one understands the corresponding motions as characterized by being (in the terminology used at those times) of "ordered" rather than of "chaotic" type. Here we illustrate how the Cercignani idea is actually implemented for an ionic crystal model which was already shown to be of such a realistic character as to reproduce in a remarkably good way, in terms of the Newtonian trajectories of the ions, the experimental infrared spectra.

1 Introduction

The existence of "zero-point energy" or ZPE (which in German means zero-temperature energy) was first conceived in 1911 by Planck [1], within an attempt at understanding his blackbody formula in classical terms (as also did Nernst in the year 1916 [2]). Einstein and Stern in 1913 were able to confirm the existence of ZPE in diatomic molecules, making use, in a rather astonishing way, of the experimental data on specific heats [3]. ZPE manifests itself particularly in crystals, as exhibited by the Debye–Waller B-factors, which describe the fluctuations of atoms around their equilibrium positions, measured, e.g., by X-ray diffraction. It is observed that, when absolute temperature T tends to zero, the values of the B-factors don't vanish,

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P. Barbante et al. (eds.), *From Kinetic Theory to Turbulence Modeling*, Springer
INdAM Series 51, https://doi.org/10.1007/978-981-19-6462-6_10

tending instead to finite values [4]. Thus, it is an experimental fact that atoms present a residual mechanical energy at zero temperature.

Since the first paper of Planck, the occurring of a zero-point energy was explicitly associated with the idea that it should correspond to a transition from chaotic to ordered motions. So, the internal energy at temperature T was thought of as the sum of a "thermal energy" and of a residual zero-point energy. In fact such a superposition of two terms came out somehow "automatically" in the frame of quantum mechanics after Heisenberg and Schrödinger. But the idea that zero-point energy should have some kind of ordered character didn't find any explicit implementation in dynamical terms. The only qualitative distinction was of a thermodynamic character, since zero-point energy corresponds to a state of vanishing entropy (which is the "quintessence of the hypothesis of quanta," in Planck's words (see the preface of [5])).

In the year 1972 the idea that zero-point energy may exist in a classical frame, and actually as corresponding to a transition from chaotic to ordered motions, was advanced by Carlo Cercignani, in a joint paper with L. Galgani and A. Scotti [6]. A Fermi–Pasta–Ulam (FPU) model was considered, namely a chain of particles with nearest-neighbor interactions, the latter being taken of Lennard-Jones type with realistic parameters of atomic physics, a fact that implicitly introduces Planck's constant $\hbar$ into the problem.[1]

So one deals with a system of "weakly coupled" harmonic oscillators (the normal modes of the chain, of angular frequencies ω_j), to which a quantum zero-point energy $\sum \hbar\omega_j/2$ can be associated. The Cercignani conjecture was that such a quantum zero-point energy should be of the order of magnitude of the "stochasticity threshold" from chaotic to ordered motions that had been found in the FPU problem.[2] And this was actually checked to be the case.

In the present paper we will illustrate how ZPE naturally appears in a classical model of an ionic crystal, Lithium Fluoride (LiF), which was shown to reproduce with a surprisingly good accuracy experimental measurements of infrared spectra [8, 9]. It is just in terms of such spectra that ZPE comes in. Indeed the spectra are available at many different temperatures ranging from a few K up to values close to the melting point. Now, one of the peaks appearing in these spectra is of an anharmonic origin, since it doesn't correspond to any normal-mode frequency of the system. Thus its relative intensity would be expected to vanish at low temperatures,

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[1] As pointed out in the previous paper [7], this occurs through the known relation $\sqrt{m\epsilon\sigma} = 2Z\hbar$, where ϵ and σ are the familiar parameters of the Lennard-Jones potential, while m and Z are the mass and the atomic number of the particles.

[2] At those times the question of interest was what Fermi had called his "little discovery," i.e., a lack of attainment of energy equipartition starting from an initial non-equipartition state. In the following years it was found that the Fermi discovery corresponds to a metaequilibrium state, since a final equipartition state is always attained, however small the energy of the system be. On the other hand, a transition from ordered to chaotic motions still persists in a suitable sense. To this point we will come back later.

where the crystal vibrations tend to become harmonic, whereas experimental data show that the peak keeps a significant intensity even at the lowest temperatures.

Tentative interpretations of this phenomenon were suggested in the context of quantum mechanics (see, for example, [10]). We show here that, in a classical model of ionic crystals, such a phenomenon can be interpreted as a manifestation of a state function or equation of state $\varepsilon(T)$, internal energy versus temperature (at fixed room pressure), with the property that $\lim_{T\to 0}\varepsilon(T) \neq 0$, i.e., a ZPE exists.

At the present stage of our investigations the relation between ε and T can only be obtained through an empirical procedure, in which the value of the (specific) internal energy ε corresponding to a given temperature T is chosen so as to give the best fit of the calculated spectrum to the experimental one. As a result of this procedure, the value of internal energy per vibrational mode ε^0 corresponding to $T = 0$ can be estimated to be[3] $\varepsilon^0 \approx 120$ K, which differs by about a factor 2 from the quantum mechanical one. From the description of the procedure used it will appear that it contains an empirical element, a better choice of which might perhaps remove such a discrepancy.

In Sect. 2 the model is presented, in Sect. 3 the results of the numerical simulations for the spectra are illustrated, and are then discussed in Sect. 4 in connection with ZPE. The conclusions follow.

2 The Ionic Crystal Model

The model of LiF we adopt treats each ion as a point charge with a mass equal to the experimental value. Electrons are not explicitly present in the model. However, following a tradition going back to Born, their effect is assumed to be responsible for two features, namely: (1) the value of an "effective charge" e_i for each ion i, which is one of the free parameters in the model, and (2) the production, through their distribution around the ions (in the spirit of Born's adiabatic principle), of a short-range "effective potential" V^{SR} acting among the ions. The pairwise interaction potential among the ions, with a suitable choice for V^{SR}, is thus given by

$$V_{ij}(r) = \frac{e_i e_j}{r} + V_{ij}^{SR}(r), \qquad V_{ij}^{SR}(r) = A_{ij} e^{-B_{ij} r} - \frac{C_{ij}}{r^6} \, . \tag{1}$$

Simulations are performed on a cubic cell of N ions (with N between 512 and 4096) with periodic boundary conditions, so that the system has infinite size. The short-range interactions are calculated for pairs within a cutoff $r \leq 5$ Å, while the familiar Ewald summation method is applied for the Coulomb long-range forces.

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[3] Here and in the following we report energy values divided by the Boltzmann constant k_B, so that they are expressed in kelvin.

By means of the Green–Kubo linear response theory applied to dispersion in dielectric media, along the lines of ref. [11] one can show that the electric susceptibility of a system of charges is given by

$$\chi_{ij}(\omega) = \frac{3V}{2\langle K\rangle}\int_0^{+\infty} e^{-i\omega t}\left\langle P_i(t)\dot{P}_j(0)\right\rangle dt\,, \tag{2}$$

$$\mathbf{P}(t) = \frac{1}{V}\sum_j e_j \mathbf{x}_j(t) \qquad \text{microscopic polarization,} \tag{3}$$

where $\mathbf{x}_j$ is the position vector of charge e_j, V is the volume of the integration cell, K the kinetic energy, and the notation $\langle\ldots\rangle$ indicates phase averages. The latter are actually replaced by time averages. We perform molecular dynamics (MD) simulations at constant energy and volume,[4] integrating the equations of motion by means of the Verlet integration method with 2 fs integration step. Moreover, in order to enhance phase-space sampling, we average over multiple trajectories with independent initial conditions.

From electric susceptibility one obtains the permittivity tensor

$$\epsilon_{ij}(\omega) = \delta_{ij}\epsilon_\infty + 4\pi\chi_{ij}^{(ions)}(\omega)\,, \tag{4}$$

where the constant ϵ_∞ takes into account the electronic contribution and is obtained from experimental data. For isotropic materials such as LiF, one simply has $\epsilon_{ij}(\omega) = \epsilon(\omega)\delta_{ij}$. Once the permittivity is known, the quantities observed in the experiments can be easily calculated: the refractive index is given by

$$n(\omega) = \sqrt{\epsilon(\omega)}\,, \tag{5}$$

while the reflectivity is

$$R(\omega) = \left|\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\right|\,. \tag{6}$$

3 The Computed Spectra

A comparison between calculated and measured spectra at room temperature ($T = 295$ K) is shown in Fig. 1. The very good agreement with data is the result of accurate determination of the parameters of the potential, by fitting the

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[4] As will be further discussed in the following, the lattice spacing, and thus the density, is suitably chosen at each temperature T, according to the experimental data on thermal expansion at fixed room pressure. In this sense, one may consider that the crystal is simulated at constant pressure.

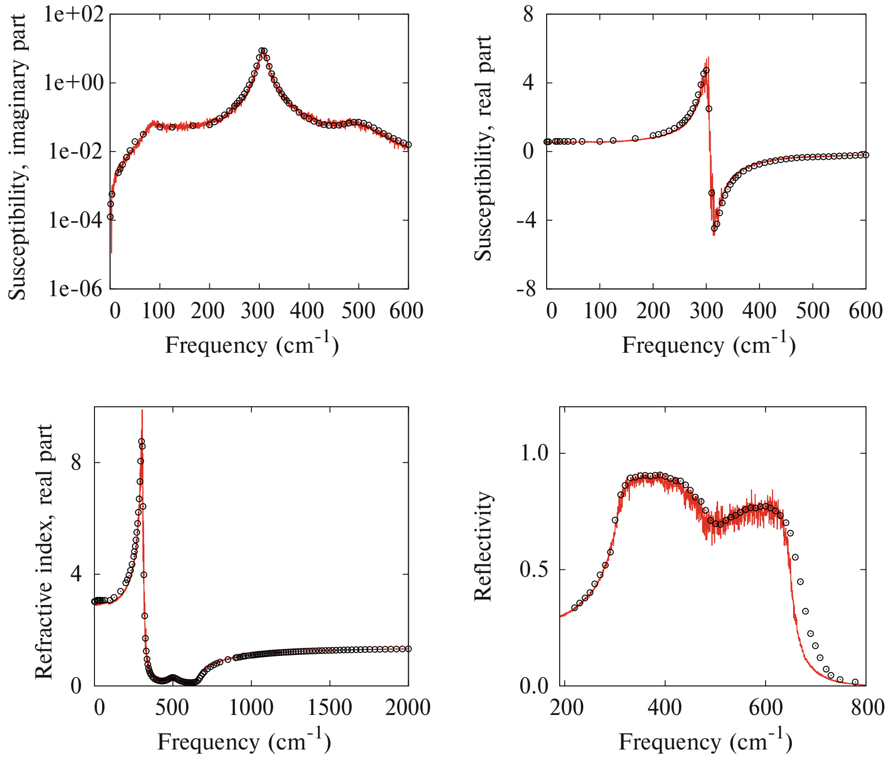

Fig. 1 Comparison between calculated (line) and experimental (circles) values of optical properties at room temperature. Upper left: imaginary part of susceptibility. Upper right: real part of susceptibility. Lower left: refractive index. Lower right: reflectivity. Experimental data are taken from [12] (lower right panel) and [13] (all the other panels)

calculated dispersion relations to the experimental ones. The resulting curves are in better agreement with data than quantum calculations available in the literature [14]. Notice that the fitting was performed within the familiar assumption of MD simulations that $T = 295$ K should correspond to $\varepsilon = 295$ K. On this point we will come back later.

Experimental data on reflectivity are available at many different temperatures, and, in particular, in ref. [12] they are given in a range from 7.5 K to 1060 K. In order to make a comparison with calculated data one has to define what is temperature in a classical model of a system different from a gas. The common prescription used in molecular dynamics studies consists in identifying temperature with a quantity proportional to the average kinetic energy per atom in the system, according to the well known Clausius relation $< K >= \frac{3}{2}k_B T$, assumed to hold at all temperatures, not only for ideal gases but also for other aggregation states. The results shown in Fig. 2, corresponding to four values of temperature, were obtained by applying such a prescription: moreover, since all experimental data are at room pressure,

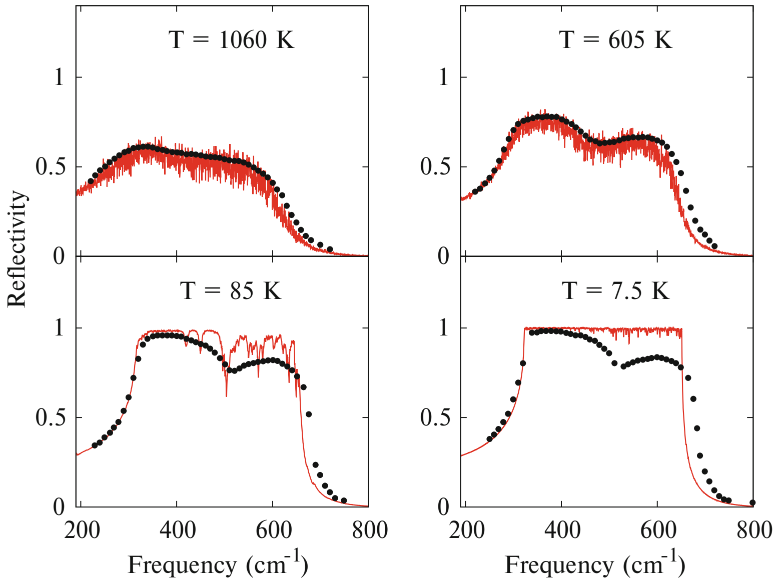

Fig. 2 Comparison between calculated (solid line) and experimental (circles) reflectivity at four different temperatures. Simulations are based on the prescription $< K >= \frac{3}{2}k_B T$. Data are taken from [12]

and each simulation is performed at constant volume and energy, the density of the system was changed at each temperature by adjusting the lattice spacing according to the available experimental data on thermal expansion. The figure shows that the agreement of calculated spectra with experimental data essentially persists at high temperatures, whereas at low temperatures a strong disagreement is found.

A detailed analysis of the LiF reflectivity spectra is needed to better understand these results. The reflectivity curve is determined by susceptibility as shown in Eqs. 4–6, and its features can be interpreted in terms of the peaks of susceptibility, as shown in Fig. 3, where experimental data of both quantities are shown for $T = 295$ K. In the range from 200 to 800 cm^{-1}, where reflectivity data are collected, there are two peaks in the susceptibility curve: one at a frequency $\simeq$ 310 cm^{-1}, of harmonic origin, and one at $\simeq$ 500 cm^{-1}, of anharmonic origin, since no optically active normal mode is found at this frequency. The reflectivity curve consists of a rising part at low frequencies that reaches its maximum approximately at the position of the first peak of susceptibility, followed by a plateau. The height of this plateau is related to the width of the susceptibility peak: the higher the width, the lower is the plateau, while for a vanishing width the plateau tends to 1. At the position of the second susceptibility peak one has a local minimum in the reflectivity plot and then almost a second plateau, lower than the first one. The height of this plateau is related to the width of the second susceptibility peak in the same way as discussed for the previous one. Now, the second peak in susceptibility should disappear when

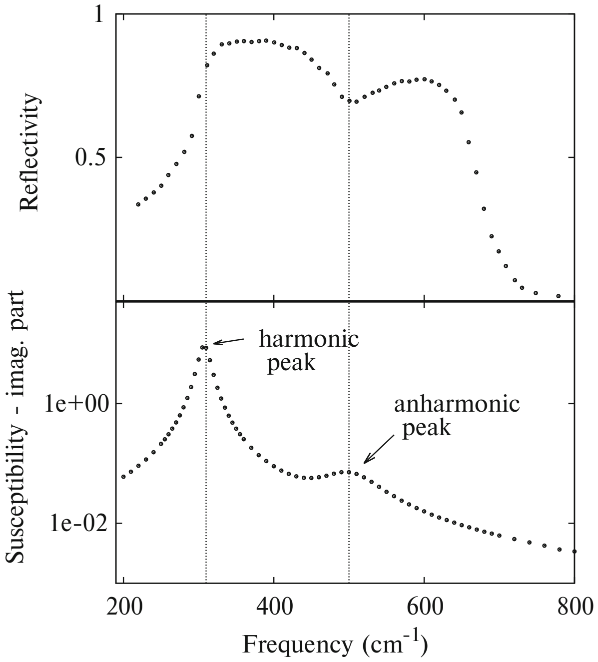

Fig. 3 Analysis of the main features of experimental data on reflectivity (upper panel) and on the imaginary part of susceptibility (lower panel)

the vibrational energy of the crystal vanishes, since the anharmonic interactions between modes vanish. This is what is actually observed in the calculated curve in the lower right panel of Fig. 2, but not in the experimental data. This fact suggests that the specific energy of the crystal doesn't vanish when temperature tends to zero. Indeed a good agreement between calculated and experimental spectra is restored if the values of internal energy of the crystal are suitably chosen in an empirical way, abandoning the Clausius relation between kinetic energy and temperature. The plots shown in Fig. 4 were obtained by means of simulations with average energy per mode $\varepsilon = 180$ K in the case of $T = 85$ K and $\varepsilon = 125$ K in the case of $T = 7.5$ K.[5]

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[5] It should be noticed that the parameterization of the potential was done by assuming $\epsilon = 295$ K at $T = 295$ K, which is not consistent with the values of ε obtained at lower T. A more realistic curve $\varepsilon(T)$ should be obtained by a different suitable choice of the ε value corresponding to $T = 295$ K. This we leave for possible future work.

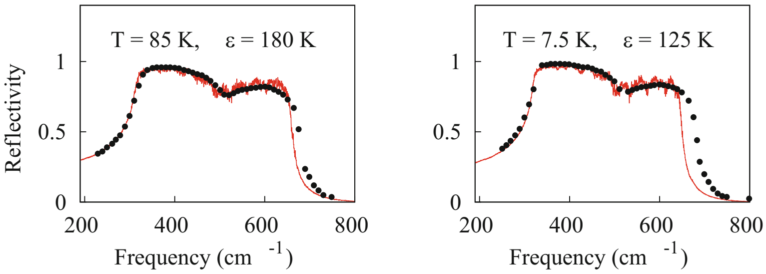

Fig. 4 Comparison between calculated (solid line) and experimental (circles) reflectivity at the two lowest temperatures of Fig. 2. Calculated spectra are fitted in this case to the experimental data by choosing a suitable value ε of specific energy for each temperature T

4 Discussion of the Results

The results shown in Fig. 4 may be interpreted as an empirical determination of the relation $\varepsilon(T)$ between internal energy and temperature for LiF. This clearly indicates that $\lim_{T\to 0}\varepsilon(T) \approx 120$ K, i.e., that a ZPE exists.

In other words, the persistence of the second peak at very low temperatures (down to 7.5 K) could be justified by assuming that, due to ZPE, the total energy of the crystal even at $T = 0$ is sufficiently large to produce significant anharmonic effects as those involved in the generation of the secondary peak.

Although the role of ZPE to explain the behavior of experimental spectra of LiF at low T was invoked by other authors in the framework of quantum calculations, we point out that the model considered here is completely classical as far as the motions of the ions (the only particles entering the model) are concerned. So it is of interest to investigate whether suitable dynamical properties of the system can be found, which reveal the existence of some energy threshold separating two qualitatively different regimes, along the lines of the original Cercignani's conjecture that a transition may occur from chaotic to ordered motions.

A first attempt can be made, using an extremely naive procedure, as follows. In Fig. 5 are reported the projections, on some chosen single normal modes phase planes, of two phase-space trajectories generated by numerical simulations at $\varepsilon =$ 300 K (upper row) and at $\varepsilon = 10$ K (lower row): points are taken at 0.02 ps intervals along the trajectories. One sees that, at 10 K, in most cases the projections exhibit a character that might be considered ordered, whereas they become completely disordered at 300 K. This seems to be in agreement with the hypothesis that the value $\varepsilon \simeq 120$ K of internal energy indicated through the spectra as corresponding to $T = 0$ might correspond to a threshold from partially ordered to completely disordered motions.

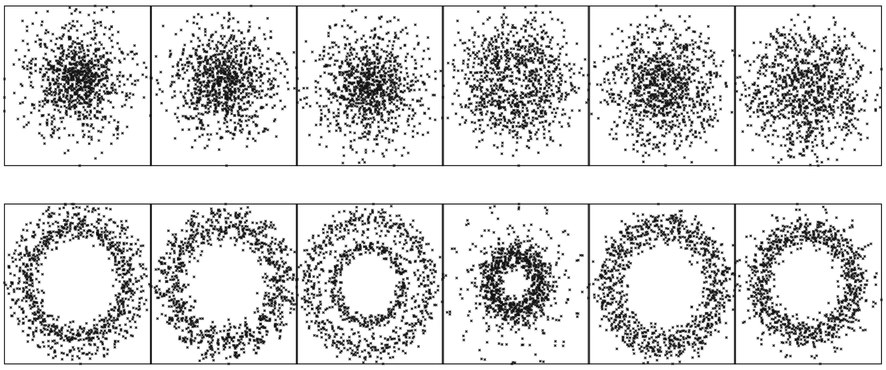

Fig. 5 Projections of simulated phase-space trajectories onto selected normal-mode phase planes for $\varepsilon = 300$ K (upper row) and $\varepsilon = 10$ K (lower row). Points are taken at 0.02 ps intervals from trajectories of 20 ps. Notice that the scales of the different plots are different, being just chosen in order to produce a common size

5 Conclusions

The existence of a zero-point energy (an energy below which motions occur at zero temperature) is considered to be a typical quantum phenomenon, but already in the year 1972 Carlo Cercignani proposed that it may be conceived also in a classical frame. A result supporting such a conjecture was reported here, on the basis of numerical computations performed in a classical Born-like model of ionic crystal, for which the rather astonishing result was already obtained that it reproduces fairly well the infrared spectra in terms of the Newtonian trajectories of the ions. The existence of a zero-point energy was exhibited by extrapolating to zero temperature the state function $\varepsilon(T)$, specific energy versus temperature. In turn, the latter was obtained by the empirical procedure of finding, for each T, the value of ε which gives the best fit of the calculated spectrum to the experimental one. Moreover, such a zero-point energy appears to correspond to a qualitative change in the chaoticity character of the motions, along the lines of the original Cercignani conjecture.

Although it was not yet possible for us to find a rationale for the existence of a zero-point energy within classical statistical thermodynamics,[6] it was for us a gratifying experience to produce the preliminary supporting arguments illustrated above, almost exactly fifty years after the idea of a classical zero-point energy was conceived, in the form of a startling invention, by our dear late friend Carlo.

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[6] The key point is to understand why temperature might vanish at all below an energy threshold. Here arguments mimicking the familiar ones of Khinchin should be considered. One should, however, take into account that the microcanonical or the canonical ensembles cannot be used, due to lack of ergodicity in the case of crystals. Indeed the arrangement of the atoms in a crystal is just one among the $N!$ ones a priori available and, as long as a crystal is a crystal, most of the remaining $N! - 1$ arrangements are not dynamically attained.

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