



Classical infrared spectra of ionic crystals and their relevance for statistical mechanics

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HIGHLIGHTS

- Classical computation of IR spectra as analogue of the FPU problem.
- Applicability of classical statistical mechanics and chaos-order transition.
- Changes in statistical treatment: identification of temperature through kinetic energy.
- Good reproduction of experimental spectra through classical realistic model.

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ABSTRACT

It was recently shown that the experimental infrared spectra of ionic crystals at room temperature are very well reproduced by classical realistic models, and here new results are reported on the temperature dependence of the spectra, for the LiF crystal. The principal aim of the present work is however to highlight the deep analogy existing between the problem of spectra in ionic crystal models on the one hand, and that of energy equipartition in the Fermi–Pasta–Ulam model, on the other. Indeed at low temperatures the computations of the spectra show that the dynamics of the considered system is not completely chaotic, so that the use of the Boltzmann–Gibbs statistics is put in question, as in the Fermi–Pasta–Ulam case. Here, however, at variance with the equipartition problem, a first positive indication is given on the modifications that should be introduced in a classical statistical treatment: the new results at low temperatures show that it is indeed the Clausius identification of temperature that has to be modified. In fact, at very low temperatures the theoretical spectra fail to reproduce the experimental ones, if the temperature is taken as proportional to mean kinetic energy, but agreement is recovered through the only expedient of introducing a suitable temperature rescaling. Analogous results are also found in connection with thermal expansion.

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1. Introduction

The present paper reports new results concerning classical theoretical estimates of infrared spectra of ionic crystals. In two previous papers (see [1] and [2]) the estimates were given for spectra at room temperature, and here the temperature dependence of the estimates is investigated, particularly at low temperatures, for the Lithium Fluoride (LiF) crystal.

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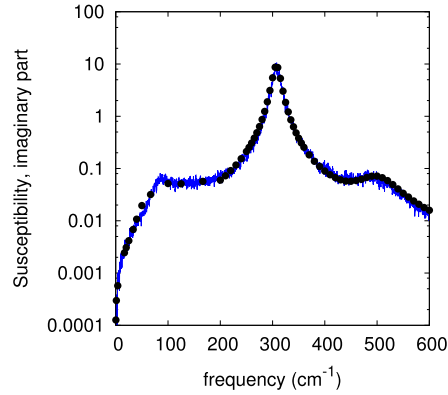


Fig. 1. Imaginary part of susceptibility vs frequency, at room temperature. Comparison between calculations (solid line) and experimental data taken from [3] (points). Here, as in all following figures but Fig. 7, the computations are performed at a kinetic energy proportional to temperature according to the Clausius identification (1).

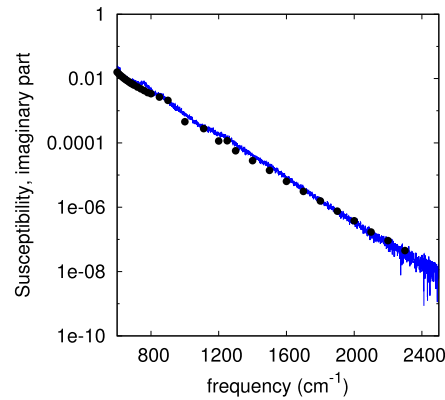


Fig. 2. High frequency behavior of the imaginary part of susceptibility vs frequency (at room temperature) compared with experimental data.

Thus stated, the problem seems to be one of interest for solid state physics, which indeed is the case. However, in this paper it is pointed out that we are actually meeting here with quite general problems of statistical mechanics. First of all, we are meeting with the problem of the relations between quantum statistical mechanics and its classical counterpart, if not between quantum and classical physics altogether. Because the theoretical spectra discussed here reproduce well the experimental data, as shown by Figs. 1 and 2 (for the LiF crystal at room temperature), while they are computed in purely classical terms involving solutions of Newton equations for the ions' motions, with no reference at all to energy levels and corresponding jumps.

Furthermore, we are meeting with a problem concerning the dynamical foundations of classical statistical mechanics. Indeed it will be seen that, as temperature is diminished, the dynamics of the considered model becomes less and less chaotic, so that the use of the Boltzmann–Gibbs statistical mechanics becomes less and less justified, as in the FPU case. On the other hand, a first positive indication is also provided here, because it is shown that what should be modified in a statistical treatment, is the Clausius identification of temperature T in terms of mean kinetic energy $\langle K \rangle$, namely, the relation

$$\langle K \rangle = \frac{3}{2} N k_B T, \quad (1)$$

where N is the number of particles and k_B the Boltzmann constant. Indeed it will be seen that, using the Clausius identification, at low temperatures the theoretical spectra fail qualitatively in connection with a certain feature of the spectrum. However, agreement is recovered if, at each of the two low temperatures considered (85 K and 7.5 K), the initial data are taken at a suitable value of the mean kinetic energy, which, through the Clausius identification, would correspond to a much larger “effective temperature” (180 and 125 K respectively). Analogous results are also obtained in connection with the thermal expansion.

The plan of the paper is as follows. In Section 2 we illustrate some general features concerning realistic ionic crystal models, in particular how they can be considered as evolutions of the FPU model, and how ionic spectra can be dealt with in a classical statistical mechanical frame. In Section 3 we give details on the concrete model used for the LiF crystal actually

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