Relaxation times and ergodicity properties in a realistic ionic–crystal model, and the modern form of the FPU problem

Andrea Carati[a] Luigi Galgani[a] Alberto Maiocchi[a]
Fabrizio Gangemi[b] Roberto Gangemi[b]

March 12, 2019

Abstract

It is well known that Gibbs' statistical mechanics is not justified for systems presenting long–range interactions, such as plasmas or galaxies. In a previous work we studied a realistic FPU–like model of an ionic crystal (thus involving long–range interactions), and showed that it reproduces the experimental infrared spectra from 1000 K down to 7 K, provided one abandons the Gibbs identification of temperature in terms of specific kinetic energy, at low temperatures. Here we investigate such a model in connection with its ergodicity properties. The conclusion we reach is that at low temperatures ergodicity does not occur, and thus the Gibbs prescriptions are not dynamically justified, up to geological time scales. We also give a preliminary result indicating how the so–called "nonclassical" q-statistics show up in such a model. How to formulate a consistent statistical mechanics with the corresponding suitable identification of temperature in such nonergodicity conditions, remains an open problem, which apparently constitutes the modern form of the FPU problem.

Keywords: classical Gibbs statistics, equipartition principle, FPU model, ionic crystal model, infrared spectra.

[a]Dep. Mathematics, Università degli Studi di Milano, Via Saldini 50, 20133 Milano – Italy.
[b]DMMT, Università di Brescia, Viale Europa 11, 25123 Brescia – Italy.

1 Introduction

The present paper originates from questions of ergodicity type that naturally arise in connection with a previous paper of ours [1] (see also the review [2], where the connections with the FPU problem were pointed out). Paper [1] was devoted to a theoretical computation of the infrared spectra of the ionic crystal LiF (Lithium Fluoride) in a classical frame. The results, obtained through Molecular Dynamics computations of the ionic polarization $\mathbf{P}(t)$ for a realistic model, turned out to reproduce pretty well the experimental infrared spectra in a range of temperatures from 1000 K down to 7 K. Now, the relevant quantity that determines the spectra, i.e., the electric susceptibility $\chi(\omega, T)$ at temperature T, is the Fourier transform of essentially the time–autocorrelation function of polarization. On the other hand correlations are in principle defined as expectations with respect to a given invariant measure, and so one has to decide which measure should be used in the computations, at any temperature T. In practice, however, the expectations were computed as time–averages up to a certain final time, for a little number of random initial data, extracted in a suitable way at temperature T.

This fact, of substituting time–averages for phase–averages, already raises some questions, that were indeed posed to us by a referee of our previous paper. Namely, does one actually observe a relaxation? And how does the relaxation time depend on the dynamical quantity considered? So we started investigating relaxation times, and actually: 1) the time required for the vanishing of relevant time–correlations (usually called relaxation time in the literature on dynamical systems theory): 2) the time required to attain equipartition of normal–mode energies, starting from exceptional initial data (usually called the relaxation time in the FPU literature); and finally, 3) the time required for the stabilization of the computed spectra, which is the original question raised to us by the referee. In such a way, the relaxation times for the three mentioned cases were found to be, for example at room temperature, of order 1 picosecond, 10 picoseconds and 1 nanosecond respectively.

Such results naturally raise further questions of ergodic type for the LiF system. Indeed it is well known (see [4] [5]) that for strongly mixing systems the relaxation times for smooth functions do not depend on the function, being essentially related to the maximal eigenvalue of the Perron–Frobenius operator of the dynamical system. So the mentioned results appear to indicate that the LiF model is not strongly mixing.

On the other hand, there is a deeper reason for discussing the ergodicity

properties of the model, because lack of ergodicity at low temperatures is necessary for its physical consistency. Indeed, as will be recalled later, in paper [1] the agreement between theoretical and experimental spectra could be extended to low temperatures only if one assumes that at such temperatures the relation between specific kinetic energy $K/3N$ and temperature T is different from that dictated by the Gibbs statistics, i.e, two thirds the mean kinetic energy per particle:

$$k_B T = \frac{2}{3} \frac{K}{N} \ . \tag{1}$$

So, the existence of some dynamical obstructions to ergodicity is necessary for the physical consistency of the LiF model.

In the present paper it will be shown that in such a model ergodicity does not occur up to geological time scales, so that the Gibbs prescriptions are not justified up to such times. The arguments used clearly indicate that the same conclusion holds for all realistic models of solids, and perhaps for the whole domain of atomic physics.

The numerical results on the relaxation times are illustrated in Section 2, the relation between temperature and specific energy dictated by the agreement of experimental and computed spectra is shortly recalled in Section 3, the ergodicity properties are discussed in Section 4, and some open problems, including the possible relevance of "nonclassical" q–statistics, are shortly discussed in Section 5. The conclusions follow in Section 6. For details on the model and on the results already available the reader is referred to paper [1]. We are confident, however, that the rather quick recollection given below may suffice to make the present paper self contained.

2 Numerical results for the relaxation times

The LiF ionic–crystal model is defined in the standard way of solid state physics. Namely, we consider a system of point particles describing the two species of ions (with positive or negative charge), in a "working cell" containing an even number N of particles (typically, $N = 512$ or 4096), with periodic boundary conditions. The interactions among the ions are the Coulomb ones (cared for their long range feature through the well–known Ewald procedure), plus a two–body short range phenomenological potential. The latter is introduced, following Born (see [3], Chapter I), in order to implicitly take into account the role of the electrons, whose degrees of freedom don't show up in the model. In the same Born's spirit one also

introduces "effective charges" which are substituted for the true charges of the ions in the expression of the mutual Coulomb forces. So the model is defined by the Hamiltonian

$$H = \sum_{j,s} \frac{\mathbf{p}_{j,s}^2}{2m_s} + \sum_{j,j',s,s'} V_{s,s'}\big(|\mathbf{x}_{j,s} - \mathbf{x}_{j',s'}|\big) \ , \tag{2}$$

where $s = 1, 2$ denotes the ionic species (of mass m_s), while $\mathbf{p}_{j,s}$, and $\mathbf{x}_{j,s}$, are the momentum and position of the j-th ion of the s species. For the interaction potential $V_{s,s'}(r)$ we choose, in addition to the Coulomb one, the phenomenological Buckingham potential, so that the total potential has the form

$$V_{s,s'}(r) = a_{s,s'} e^{-b_{s,s'} r} + \frac{c_{s,s'}}{r^6} + \frac{e_s^{\text{eff}} e_{s'}^{\text{eff}}}{r} \ .$$

The values of the constants $a_{s,s'}$, $b_{s,s'}$, $c_{s,s'}$, and of the effective charges e_s^{eff} are taken from paper [1]. Notice that, due to the periodicity conditions, for what concerns the potential the sum extends to all points of the infinite lattice, although a cutoff of 5 Å was introduced for the phenomenological potential.

Having fixed a lattice step (which we take, at any temperature, from the experimental data), and thus a volume V of the working cell, one can check that, with the chosen values of the parameters of the potential[1], the system has an equilibrium point, in which the particle positions form a face–centered cubic lattice. Thus, at sufficiently low energies the particles oscillate about their equilibrium positions, and the model can be considered as a three–dimensional realistic variant of the standard one–dimensional FPU model.

The numerical investigations were performed by integrating the equations of motion through the Verlet algorithm with a time step of 2 femtoseconds, for times up to 2 nanoseconds.

2.1 Decay–time of correlations, as a function of specific energy

With the aim of studying the relaxation times for relevant observables, we start considering the ionic polarization $\mathbf{P}$, which is defined by

$$\mathbf{P} = \frac{1}{V} \sum_{j,s} e_s \mathbf{x}_{j,s}$$

[1]The parameters were chosen by optimizing the agreement between experimental and computed spectra at room temperature, and were not changed at the other temperatures. We leave for a future work the task of a better choice of the parameters, by optimizing the agreement for the whole set of available spectra at different temperatures.

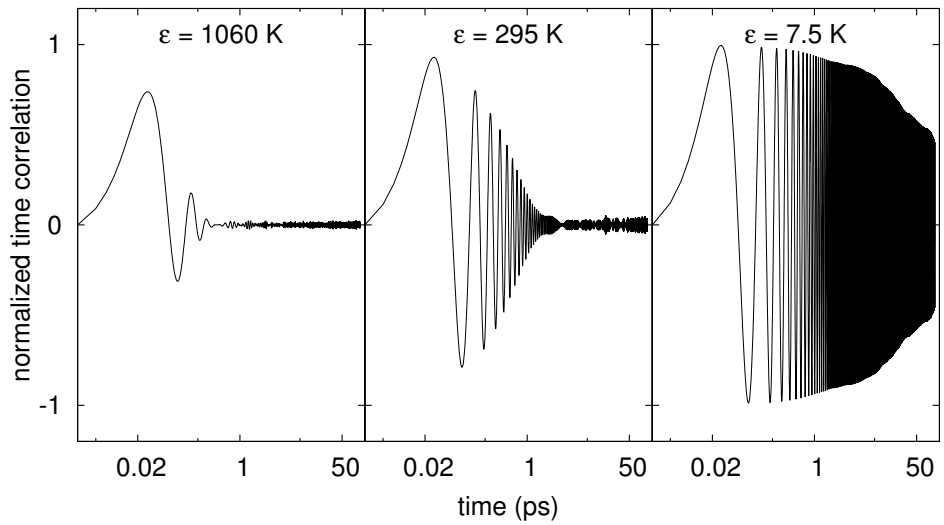

Figure 1: Normalized correlation between polarization and its time derivative versus time, for three different values of the specific energy ε (in Kelvin units). Figure taken from [1]. N=4096

(where e_s is the *actual* charge of the s species of ions), and investigate the decay of the correlation[2]

$$\overline{\mathbf{P}(t)\cdot\dot{\mathbf{P}}(0)} \stackrel{\text{def}}{=} \lim_{t_{fin}\to+\infty} \frac{1}{t_{fin}} \int_0^{t_{fin}} \mathbf{P}(s+t)\cdot\dot{\mathbf{P}}(s)\,\mathrm{d}s$$

between ionic polarization and its time–derivative, which is the key quantity determining the spectra of the crystal in the infrared region (see below). If the system were mixing, one would have $\overline{\mathbf{P}(t)\cdot\mathbf{P}(0)} \to 0$ as $t\to\infty$, for almost every initial datum.

The numerical results found in [1] are reported in figure 1, in which the time–correlation is given versus time for three different values of the specific energy ε. Here, and in the rest of the paper, energy is defined as the difference between the value E of the Hamiltonian H (determined for example by the initial data) and its minimum value E_{min} (i.e., the minimum

[2] In principle one should consider the correlation tensor involving products of the cartesian components P_i and $\dot{P}_j$. However, for LiF one deals with an isotropic case, and it turns out to be sufficient to consider only the scalar product $\mathbf{P}\cdot\dot{\mathbf{P}}$.

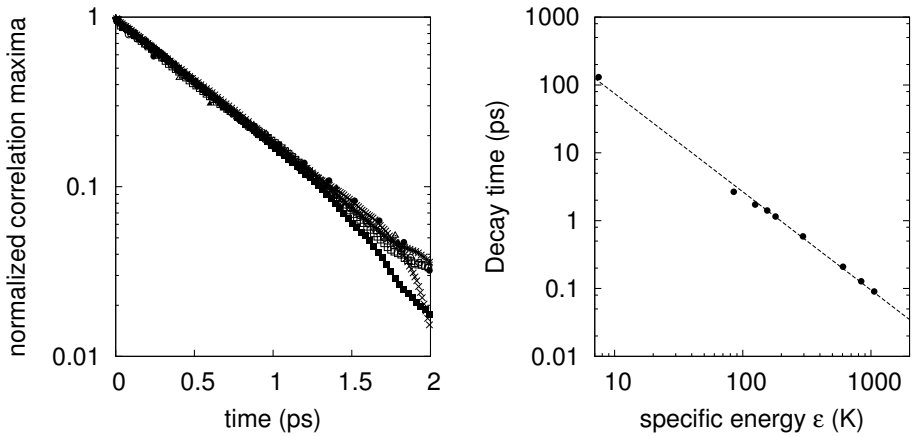

Figure 2: Left: the sequences of maxima of the normalized correlation function C^{ε} versus the rescaled time, for 7 different values of the specific energy ε. Right: Decorrelation time of polarization versus specific energy ε.

V_{min} of the potential energy), so that the specific energy (per degree of freedom) ε is defined as[3]

$$\varepsilon = \frac{E - E_{min}}{3N} \ .$$

In this paper we chose to express the specific energy ε in Kelvin: so, when we say for example that we have $\varepsilon = 295$ K we just mean that $\varepsilon/k_B = 295$.[4]

Every curve in figure 1 was obtained as an average over 10 different initial data, computed up to a finite time $t_{fin} = 200$ picoseconds. As one sees, the three correlations seem to vanish for suitable large times, but the decay–rate decreases with the specific energy ε. To give a quantitative estimate of

[3]As E_{min} is the minimum of the potential, ε differs very little from the specific energy of the normal modes of the quadratic approximation H_{harm} of the Hamiltonian about the equilibrium point. In this way, it becomes possible to compare our results with those obtained in the standard FPU model, which are usually expressed as a function of energy per mode (to which the specific energy ε reduces in the case $E_{min} = 0$).

[4]In our previous paper, instead of making reference to ε we were making reference to $2K/3N$ (K being the kinetic energy), which coincides with k_BT according to the Gibbs prescription. Thus its value, expressed in Kelvin, was called "effective temperature" (while it is called "kinetic temperature" in the papers of the Tsallis group – see below). Actually, the difference between the effective (or kinetic) temperature and the specific energy ε (expressed in Kelvin) is very small, actually a few percent even at rather large temperatures as 1000 K.

the decay–time we proceed as follows: for each value of ε we consider the absolute value of the normalized correlation, i.e., of the function

$$C^{\varepsilon}(t) \stackrel{\text{def}}{=} \frac{\left|\overline{\mathbf{P}(t)\cdot\dot{\mathbf{P}}(0)}\right|}{\left(\overline{\mathbf{P}^2(0)}\;\overline{\dot{\mathbf{P}}^2(0)}\right)^{1/2}} \;,$$

and determine the sequence $C^{\varepsilon}(t_n)$ of its maxima. Taking the values at $\varepsilon = 295$ K as reference, one finds that, for each specific energy, there exists a rescaling factor $r(\varepsilon)$ of time, such that the plot of the sequence of maxima as a function of the rescaled time $t/r(\varepsilon)$ overlaps to the others. This is exhibited in figure 2 (left), where the rescaled sequences for 7 different values of ε are reported in semilog scale. One can notice not only that the different sequences superpose, but also that they decrease exponentially[5] with a decay time $\tau_d(\varepsilon)$ that is estimated to be 0.6 picoseconds at $\varepsilon = 295$ K.

The dependence of the decay–time $\tau_d(\varepsilon)$ on specific energy is exhibited in figure 2 (right), where the values found are reported in logarithmic scale. As one sees, a straight line with a slope near to -1.5 gives a good interpolation. One can thus infer for the decay–time τ_d a law of the form

$$\tau_d(\varepsilon) = \frac{C}{\varepsilon^{3/2}} \tag{3}$$

with a suitable C.

2.2 Equipartition time, as a function of specific energy

We come now to the equipartition times, i.e., the times needed for attaining equipartition among the normal–mode energies, starting from an initial condition in which just a few modes of nearby frequencies are excited. Precisely, we excite only the whole packet of modes (in the number of 15 out of 512) which have exactly the lowest frequency, the modes having the same energy but random phases,

We use two methods. The first one is standard in studies of the FPU model (see for example [7]). Denoting by E_k the energy of the k–th normal mode (the definition of normal modes, and a discussion of their properties will be given in Section 4), one defines the so–called spectral entropy $\eta(t)$

[5] At least for not too small values of the correlation. On the other hand, it is very difficult to reliably compute correlations below a certain threshold, because it would require an exceedingly long stretch of trajectory of the system. So we discard the tail in our considerations.

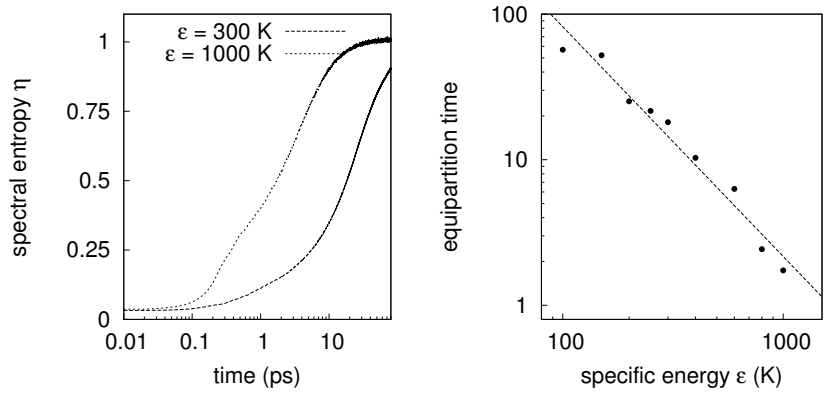

Figure 3: The approach to equipartition by spectrtal entropy $\eta(t)$. Left: Spectral entropy versus time for three different specific energies. Right: equipartition time τ_{eq} vs specific energy ε (points) in logarithmic scale, together with the regression line.

by

$$\eta(t) = \frac{1}{3N} \exp\left(-\sum \frac{\overline{E_k}(t)}{E_{harm}} \log\left(\frac{\overline{E_k}(t)}{E_{harm}}\right)\right) ,$$

where $\overline{E_k}(t)$ is the time–average of E_k up to time t, while E_{harm} is the total harmonic energy (i.e., the sum of the mode energies).[6] The spectral entropy turns out to be very small (of order $1/N$) when just a few modes share the energy E_{harm} , becoming 1 when equipartition occurs (with $\overline{E_k} = \varepsilon$ for $k = 1, \ldots, 3N$). So the attainment of equipartition corresponds to finding $\eta(t) \simeq 1$ for a large enough t. It is usually supposed that the attainment of equipartition flags the attainment of thermal equilibrium. This, however, is a delicate point on which we will come back later. To give a quantitative estimate of the equipartition times, the following convention is usually adopted in the FPU literature: for any given value of the specific energy one defines the equipartition time τ_{eq} as the time at which the curve $\eta(t)$ attains a certain value, for example the value 1/2.

The results for the spectral entropy are reported in figure 3. In the left panel we report the curves $\eta(t)$ corresponding to three different values of ε. Each such curve was determined by averaging the curves corresponding to

[6] Actualy, E_{harm} too is a function of time. However, as will be shown in Section 4, for the values of ε we are considering it simply presents small oscillations about the value $3N\varepsilon$. Here we just neglect such oscillations.

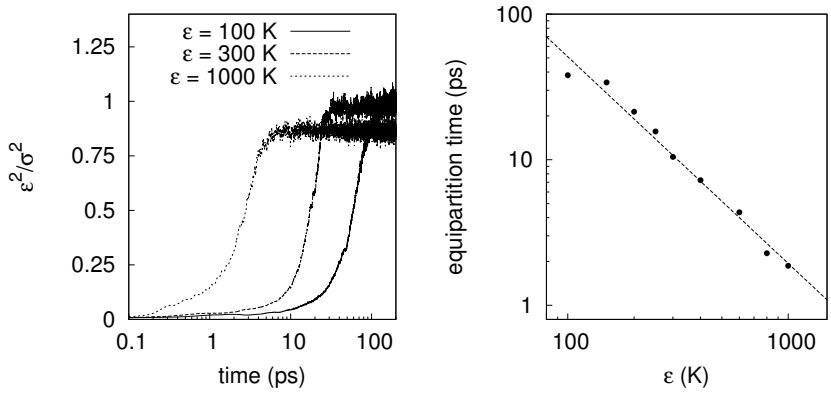

Figure 4: The approach to equipartition by energy variance σ^2. Left: Inverse of the normalized energy variance versus time. Right: equipartition time versus specific energy (points) in logarithmic scale, together with the regression line.

five different initial data, defined through a different choice of the random phases of the excited modes. In agreement with the FPU case, one finds that the function η increases monotonically towards the value 1, with a decreasing rate as ε is decreased. The corresponding values of $\tau_{eq}(\varepsilon)$ are reported in figure 3, right panel, in logarithmic scale. One sees that a straight line with a slope not far from -1.5 gives a good interpolation of the data.

In order to overcome the conventional character of the procedure in which a value such as $\eta = 1/2$ is chosen for flagging the attainment of equipartition (which is somehow necessary, since the "final" value 1 is never attained), we devised a second method. This is based on the idea that, by the attainment of equipartition of the time–averaged mode energies, the system might have actually attained also the Maxwell–Bolztmann distribution for the instantaneous values of the mode energies. If this occurs, the variance $\sigma^2(t) = \frac{1}{3N}\sum_k \left(E_k(t)\right)^2 - \left(\frac{1}{3N}\sum_k E_k(t)\right)^2$ should converge to ε^2, and quite naturally the relaxation time τ_{eq} could be defined as the first time at which $\sigma^2(t)/\varepsilon^2 = 1$. However, in order to be coherent with the first method, and also to save computation time, we define the equipartition time $\tau_{eq}(\varepsilon)$, still conventionally, as the time at which $\sigma(t) = 2\varepsilon$.

The results concerning the second method are better understood if one reports, as a function of t, the inverse $\varepsilon^2/\sigma^2(t)$ of the normalized variance,

They are reported in figure 4, left panel, for the same simulations of figure 3. One sees that $\varepsilon^2/\sigma^2(t)$ increases monotonically towards the value 1, again with a decreasing rate as ε is decreased, then oscillating about such a value. The values of the equipartition $\tau_{eq}(\varepsilon)$ are reported in logarithmic scale in figure 4, right panel. Again, a straight line with a slope not far from -1.5 is found to give a good interpolation.

So the equipartition times τ_{eq} seem to follow a law of the form

$$\tau_{eq}(\varepsilon) = \frac{C'}{\varepsilon^{3/2}} \ , \tag{4}$$

with a suitable C'. Such a law seems to be in rather good qualitative agreement with the law (3) for the relaxation time of the correlation of polarization, but the quantitative agreement is not that good. For example, at $\varepsilon = 295$ K the relaxation time for polarization was of only 0.5 picoseconds, while the relaxation time for equipartition is about 10 picoseconds.

In any case, the previous results seem to show that the time needed for time-averages to relax to their asymptotic values is larger than the time needed for decorrelation to occur. In the next subsection it will be seen that much larger times are needed in order to reproduce the spectra, which means that the attainment of equipartition doesn't flag the attainment of thermal equilibrium. This was already pointed out in the papers [8] (see Figure 6), [9] (Figure 3) and [10], and discussed in [2]. Eventually, this fact will be strongly supported by the results illustrated here in Section 4.

2.3 Relaxation times for the spectra

In the two previous subsections we were dealing with indicators which don't correspond to any real, physically observable, quantity. As the two relaxation times there found differ by at least one order of magnitude, it is of interest to determine the relaxation time for a quantity that is physically observable. So we deal here with reflectivity, the prototype of the measured quantities in connection with spectra: we want to determine up to what final time t_{fin} should an orbit be computed in order that reflectivity be determined in a reliable way. Let us recall that the reflectivity $R(\omega)$ is connected to the (complex) refractive index $n(\omega)$ by the relation (see Born's handbook [11])

$$R(\omega) = \left| \frac{1 + n(\omega)}{1 - n(\omega)} \right|$$

In turn, the refractive index $n(\omega)$ is the square root of the dielectric "constant" $\epsilon(\omega)$, which eventually is determined theoretically (see the next sec-

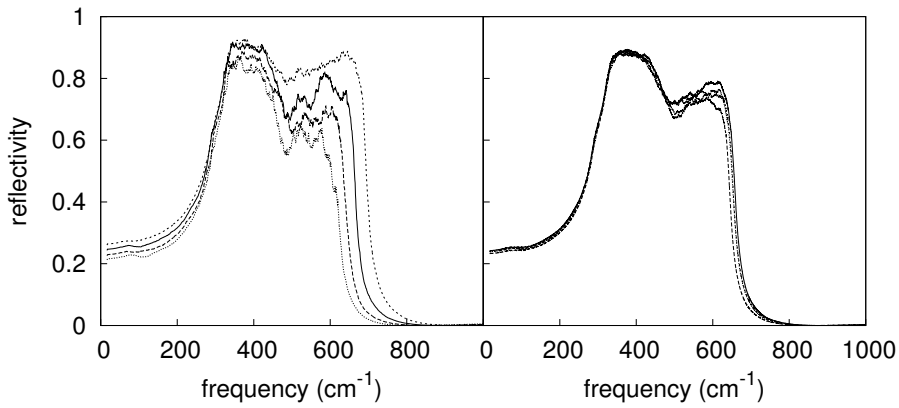

Figure 5: Reflectivity curves computed for different stretches of a trajectory at $\varepsilon = 295$ K. Left panel: four curves corresponding to tracts of 40 picoseconds. Right panel: four curves corresponding to tracts of 400 picoseconds. Compare with Figure 6, which involves an average over ten trajectories of 200 picoseconds.

tion) from the Fourier transform of the correlation $\overline{\mathbf{P}(t) \cdot \dot{\mathbf{P}}(0)}$, which involves the ionic polarization, i.e., the positions of the ions.

So we would like to know the time neeeded for the time–average $\overline{\mathbf{P}(t) \cdot \dot{\mathbf{P}}(0)}$, and thus reflectivity, to settle down to its asymptotic value. One might conjecture that this time coincides with the time required for the variance $\sigma^2(t)$ of the normel mode energies to attain the Maxwell–Boltzmann value ε^2. For example, from figure 4 (left panel) one sees that, for $\varepsilon = 295$ K, this time is less than 40 picoseconds (perhaps being of the order of 10 picoseconds). So we take a trajectory computed for a sufficiently long time t_{max} (2 nanoseconds), and subdivide it into stretches of length 40 picoseconds. Then we compute the correlations $\overline{\mathbf{P}(t) \cdot \dot{\mathbf{P}}(0)}$ as time–averages over any single stretch, thus obtaining distinct reflectivity curves (i.e., values $R^i(\omega)$ for for each ω in the domain of interest). From figure 5 one sees that such curves differ greatly from each other for tracts of 40 picoseonds (left panel), and much less for tracts of 400 picoseconds (right panel), although a satisfactory stabilization was not yet attained. This means that such stretches of the trajectory stick in different regions of phase space, which actually give rise to qualitatively different spectra. By trial and error we found that, at

$\varepsilon = 295$ K, times of the order of 2 nanoseconds are needed for the computed spectra to stabilize. As the latter time is larger than that needed to attain equipartition, and much larger than the decay–time of the correlation, this result shows that the attainment of equipartition doesn't correspond to the attainment of thermal equilibrium. It appears that, notwithstanding the occurrence of decorrelation and of equipartition, partial times of 400 picoseconds are not sufficient for the partial orbits to explore the whole region actually explored in 2 nanoseconds, which is sufficient for the orbit to produce a spectrum agreeing with the experimental one.

Now, by analogy with the two relaxation times previously investigated, one is naturally led to try to estimate how the stabilization time for reflectivity too depends on specific energy ε. However, unexpectedly, we met with serious difficulties in implementing a method providing a reliable quantitative answer to this question. At first sight it seems that the latter time doesn't depend sensibly on specific energy ε, but at the moment we content ourselves with the mentioned result, which refers to $\varepsilon = 295$ K.

In any case one is quite naturally led to conjecture that, in analogy with what was found here in the two previously discussed cases and was always found in the FPU literature, also for the spectra the relaxation times diverge as $\varepsilon \to 0$- This, however, would make a theoretical computation of the spectra at low temperatures impossible. In the next section we will show that, even if the relaxation times did diverge as $\varepsilon \to 0$, a computation of the spectra is nevertheless at hand, because the relaxation times are actually bounded, keeping microscopic values. This is due to an unexpected fact, discovered in paper [1], which concerns the identification of temperature in terms of specific energy.

3 Behavior of the relaxation times at low temperatures

So we illustrate how the problem of the divergence of the relaxation times as $\varepsilon \to 0$ is overcome, by making reference to the computation of a physical quantity actually susceptible of comparison with experimental data. i.e, the infrared spectrum, in its dependence on temperature T. We summarize here results of our previous paper [1].

The theoretical quantity relevant for the spectra is the electric susceptibility tensor χ_{ij} as a function of frequency ω at a given temperarure T. In the case of LiF, due to isotropy, one finds that it is sufficient to deal with the trace $\chi = (1/3)\sum_i \chi_{ii}$. The contribution of the electrons to the permittivity

$\epsilon(\omega)$ in the infrared can be taken into account through a constant χ^∞, so that one finally has

$$\epsilon(\omega) = 1 + 4\pi\big[\chi^{ion}(\omega) + \chi^\infty\big] \ .$$

where χ^{ion} is the contribution due to the ions. Through permittivity one can compute all quantities of interest as the refractive index, the absorption coefficient and the reflectivity (see the Born's handbook [11]). We concentrarte on reflectivity, which is the quantity for which the largest set of actually measured data is available.

In the Green–Kubo approach the macroscopic response $\chi^{ion}(\omega)$ of the ions is expressed by a formula which, in the semiclassical approximation, at least formally reduces to the Fourier transform of a time–correlation involving polarization, i.e., to the formula

$$\chi^{ion}(\omega, T) = \frac{V}{k_B T} \int_0^{+\infty} e^{-i\omega t} \, \frac{\langle \mathbf{P}(t) \cdot \dot{\mathbf{P}}(0) \rangle}{3} \, \mathrm{d}t \ , \tag{5}$$

in which the average $\langle \cdots \rangle$ is computed in principle according the classical Gibbs ensemble at temperature T.

Now, in our paper [1] we were unable to implement formula (5). The reason is that the Gibbs measure is ill defined for long–range potentials: one should for example impose a cutoff, and then take the limit in which the cutoff tends to infinity. We chose instead to perform the Ewald summation in which, by the way, energy is somehow renormalized. The relations between such two methods is not studied in the literature.

However, a formula for the ionic susceptibility analogous to (5) can also be deduced in a completely classical frame, as was actually done in [12]. The only relevant difference in such a classical approach is that any reference to ensembles is avoided, as only time–averages are introduced. Indeed, the analogue of formula (5) reads

$$\chi^{ion}(\omega) = \frac{V}{\sigma_p^2} \int_0^{+\infty} e^{-i\omega t} \, \frac{\overline{\mathbf{P}(t) \cdot \dot{\mathbf{P}}(0)}}{3} \, \mathrm{d}t \ , \tag{6}$$

where σ_p^2 is the variance of the momenta of the ions, and thus involves their kinetic energy K, through $\sigma_p^2 = 2K/3N$. Obviously, if the time–average coincides with the Gibbs average, one has $\sigma_p^2 = k_B T$, and formula (6) reduces exactly to (5).

So, quite naturally we started our computations by identifying temperature T with kinetic energy through the Gibbs prescription (1), i.e., essentially through $\varepsilon = k_B T$. The results of the numerical simulations are

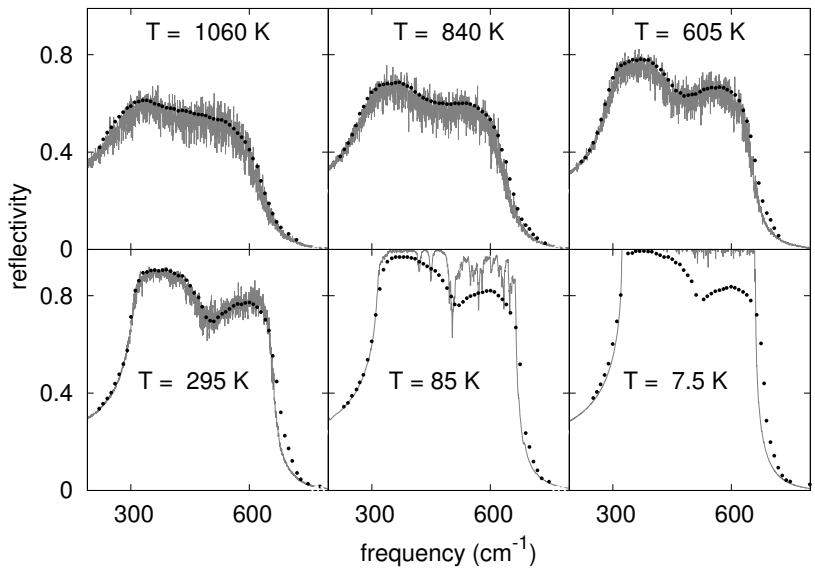

Figure 6: Reflectivity curves of LiF as a function of frequency at six temperatures. Results from calculations (solid line) are compared with experimental data (points). Figure taken from [1]. For any temperature T the simulations were performed at a apecific energy $\varepsilon = k_B T$, and this leads to a disagreement at the two lower temperatures.

shown in figure 6, where the computed spectra are reported together with the experimental data, for six different values of T.

One sees that a good agreement is found at room temperature and at the higher ones, actually 605 K, 840 K and 1060 K (just below melting). Instead, the agreement is seen to be partially lost at 85 K, and even more so at 7.5 K, where the secondary peak appears to be completely reabsorbed in the main peak, the computed reflectivity sticking to the value 1.[7] However, it occurred to us to find that a pretty good agreement between experimental

[7]This fact is quite peculiar. Indeed, at variance with the main peak, the frequency of the secondary one does not show up among the normal mode frequencies. So the secondary peak seems to be due to the nonlinearity, and its visibility should decrease with decrearing energy, whereas the contrary is seen to occur.

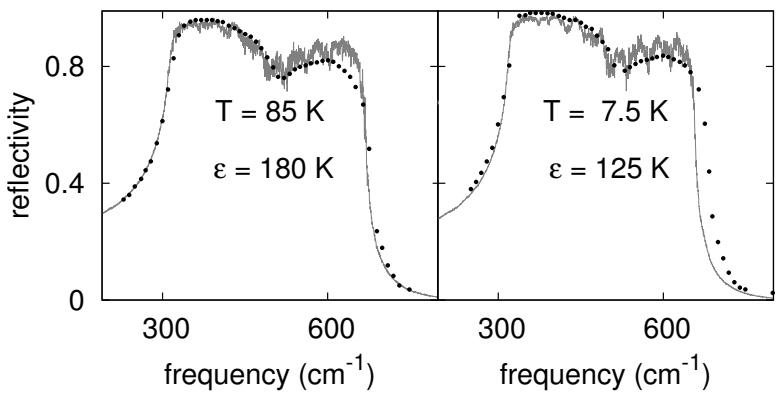

Figure 7: Same as Fig. 6, for the two temperatures 85 K and 7.5 K, with calculations performed at specific energies $\varepsilon = 180$ K and $\varepsilon = 125$ K, rather than 85 and 7.5 respectively.

and computed spectra is recovered at the two low temperatures of 85 K and 7.5 K too, if one chooses for ε the values 180 K and 125 K respectively. This is shown in Fig. 7.

So, it is a fact that agreement is recovered at low temperatures if one renounces to stick at the Gibbs prescription. This in particular implies that the specific energy ε keeps a nonvanishing value even at zero temperature, in qualitative agreement with the experimental fact that a nonvanishing zero–point energy exists. In turn, the nonvanighing of ε at vanishing temperature implies that the relaxation times, which would diverge as $\varepsilon \to 0$, remain instead bounded in the zero–temperature limit. In other words, at low temperatures the classical theoretical formulas implemented through ionic orbits obeying Newton's equations still apply, reproducing pretty well the experimental spectral curves, if one admits that Gibbs' statistical mechanics doesn't.

4 Ergodicity properties

Naturally, it is universally accepted that classical Gibbs statistics should be abandoned at low temperatures, due to the increasing relevance of purely quantum phenomena, not describable in a classical frame. In such a perspective the fact that, at a temperature as low as 7 K, in order to reproduce the spectra one has to work at a value of specific energy ε large as about 125

K, would be understood as corresponding to the existence of a nonvanishing zero–point energy. Nevertheless it seems that, apart from such a correction, classical dynamics is adequate to computing the relevant correlations. One might perhaps describe such a situation through the slogan: "At low temperatures the dynamics is classical, while the statistics is a quantum one". The reason for such a behaviour remains however obscure.

Thus we preferred to follow, so to say, an "internal" approach, trying to understand whether there exist reasons within classical physics itself which allow one to ascertain whether Gibbs statistics is justified for our model or not. This clearly is a problem concerning the ergodicity properties of our system, and so we presently start a discussion of this point. See also the mathematical contributions given by the Kozlov school [13, 14, 15, 16].

First of all it is immediate to conclude that, by the fact itself of being in a crystalline phase, the system is not ergodic. This should be obvious, as will be recalled in a moment, but in any case we exhibit it here through an elementary counterexample. Namely, using the Gibbs ensemble one finds that the phase–averaged particle positions all have the same value, i.e., one has $< \mathbf{x}_j >=< \mathbf{x}_l >$ for all j, l. Indeed, as the potential $\sum_{i,k} V(\mathbf{x}_k - \mathbf{x}_i)$ is invariant under the exchange $\mathbf{x}_j \leftrightarrow \mathbf{x}_l$, one has

$$\int_V \mathbf{x}_j \exp\big[-\beta \sum_{i,k} V(\mathbf{x}_k - \mathbf{x}_i)\big] \mathrm{d}\zeta = \int_V \mathbf{x}_l \exp\big[-\beta \sum_{i,k} V(\mathbf{x}_i - \mathbf{x}_k)\big] \mathrm{d}\zeta \ ,$$

However, in the crystalline phase, for $j \neq l$ one has, for averages computed over not too long times, $\overline{\mathbf{x}}_j = \mathbf{x}_j^0 \neq \mathbf{x}_l^0 = \overline{\mathbf{x}}_l$, where $\mathbf{x}_j^0$ and $\mathbf{x}_l^0$ are the lattice sites. So, there exist dynamical variables with time averages differing from the phase averages, and the system is not ergodic.

A more physical reason for the system not being ergodic is that at low temperatures the system's representative point in phase space remains confined in a small region about the initial equilibrium point. This can be seen by checking the value of H_{harm}, the second order truncation of the expansion of H about the equilibrium point. The function H_{harm} provides a distance in phase space, since its level surfaces are ellipsoids, centered about the equilibrium point. In fact, H_{harm} is a positive definite quadratic form in phase space, so that it can be put into diagonal form by a familiar change of variables, the new ones being exactly the normal modes coordinates discussed in Section 2.2.

Figure 8 (left) shows that, even at so large a specific energy as $\varepsilon = 1300$ K the value of H_{harm} remains bounded, presenting very limited fluctuations, thus indicating that the point is visiting a small region about the equilibrium

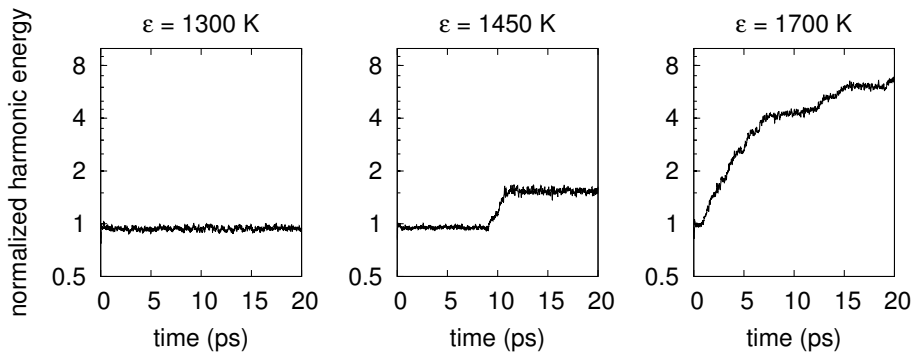

Figure 8: Normalized harmonic energy $H_{harm}/(H - E_0)$ as a function of time for a time interval of 20 picoseconds, at $\varepsilon = 1300$ K, $\varepsilon = 1450$ K and $\varepsilon = 1700$ K, from left to right. Semilogarithmic scale. One passes from a fluctuation about 0.95, to a jump from 1 to 1.6, and finally to a continuous increase from 1 to 7.

point. This fact is immediately clear if one recalls that our model, as any model of a crystal, actually presents $N!$ minima, which are obtained from the particular one we considered up to now, by permuting in all possible ways the particles. Moreover, such points are far away from each other in phase–space, so that the corresponding values of the function H_{harm} (which refers to the expansion of the Hamiltonian H about a definite particular minimum among the different $N!$ ones), takes on very large values when evaluated about one of the remaining minima (see the analogous phenomenon observed in [17]). On the other hand, for large enough N, at any fixed ε no "kinematic" obstacle exists to the exchange of adjacent particles, because the two particles just have to overcome a small finite energy barrier. So, if the system were ergodic, for increasing time one would observe a slow growth of the value of H_{harm} until the value $< H_{harm} >$ is attained, with a subsequent oscillation about it.

In fact the phenomenon of the ions diffusing along the lattice is actually observed at sufficiently high values of ε: for example in the central panel of figure 8, which was obtained for $\varepsilon = 1450$ K, one can see a sudden jump of the value of H_{harm}, which corresponds exactly, as could be visually exhibited, to an exchange of two adjacent particles of the lattice. However, as only two ions are involved, the phase point did not yet wander along a large part of the energy surface. Instead, in the right panel of figure 8, which refers to

$\varepsilon = 1700$ K, one finds a continuous growth of H_{harm}: evidently the point is free to wander in phase space, perhaps through the whole energy surface. So, an ergodic behaviour may be conjectured to occur in the latter case, but certainly not at lower energies: for $\varepsilon < 1300$ K one has $< H_{harm} > \neq \overline{H}_{harm}$, and the system is not ergodic, [8] at least up very long times. In a similar context it was shown that the time required for the system to jump out of the local minimum increases exponentially as a function of $1/\varepsilon$ (see [18]).

The relevant point is that this happens notwithstanding the fact that equipartition of the normal mode energies had previously been attained. Rather, it even turns out that the occurring of equipartition is a signal that ergodicity does not hold. Indeed, equipartition means $\overline{E_k} \simeq \varepsilon$, whereas ergodicity implies $\overline{E_k} \gg \varepsilon$. In conclusion: at low temperatures ergodicity does not hold up to geological time scales, so that the Gibbs identification of temperatures in terms of kinetic energy per particle is not justified.

5 Open problems

We point out that, in fact, the ergodic problem is not really relevant for quantities of a mechanical type, because a comparison with experimental data involves time–averages rather than phase–averages. This was amply illustrated in the discussion following the Einstein contribution to the first Solvay conference [19], and is also currently done in Molecular Dynamics simulations. The really hard problem is met when dealing with quantities of thermodynamic type, namely, temperature and entropy, because, for example, temperature is characterized as being an integrating factor of the heat exchanged with another system, and not as the average of some function in phase space. If expectations are implemented as averages with respect to the Gibbs measure, one proves that the Lagrange multiplier β is the required integrating factor, which moreover coincides, in classical statistical mechanics, with two thirds the mean kinetic energy per particle. If instead the expectations are computed as time–averages, the problem of finding an integrating factor is scarcely discussed in the literature, apart from the classical works of Boltzmann and Clausius (a review was given by Gallavotti in [20]); see however the recent paper [21]. So nobody knows what the in-

[8] The exact calculation of $\langle H_{harm} \rangle$ is not feasible. However the property $\overline{H}_{harm} \neq \langle H_{harm} \rangle$ can be shown as follows: on the one hand one obviously has $\overline{H}_{harm} \simeq 3N\varepsilon$, on the other hand one has $\langle H_{harm} \rangle \simeq \frac{1}{N!} \frac{1}{Z} \sum_i \int_{U_i} H_{harm} \exp(-\beta H) d\zeta$ where U_i is a suitable neighborhood of the i-th minimum, and the constant Z the partition function. Now, by symmetry the Gibbs weight is the same in all such neighborhoods, whereas H_{harm} is much larger than $3N\varepsilon$ in all of them, apart from the initially chosen one.

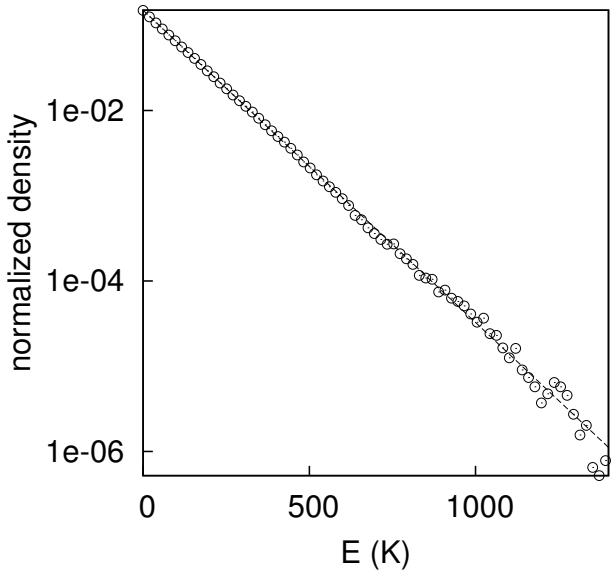

Figure 9: Histogram (in semilogarithmic scale) of the energies E (circles) of the modes not initially excited, at time $t = 200$ ps, after their equipartition is attained. Specific energy $\varepsilon = 120$ K. Solid line is the graph of the Maxwell–Boltzmann distribution function $\varepsilon \exp(-E/\varepsilon)$

tegrating factor is, nor whether it coincides with the time–average of some definite dynamical variable.

It seems that this problem could be solved if the expectations were implemented with respect to a suitable invariant phase–space measure (see for example [22]). So it is of interest to understand whether in our case it is possible to find a measure which reproduces the actually computed time–averages. To this end, following Kolmogorov, the first step consists in determining the marginal distributions and then checking their compatibility conditions. We just performed a preliminary work in this direction, which consists in computing the histograms of the mode energies, i.e. the marginals for a single variable. The results are illustrated in figure 9 in semilogarithmic scale, together with the fitting exponential curve (solid line), for specific energy $\varepsilon = 120$ K (points). The histogram was obtained as follows. One starts from initial data of FPU type, in the way previously illustrated, namely,

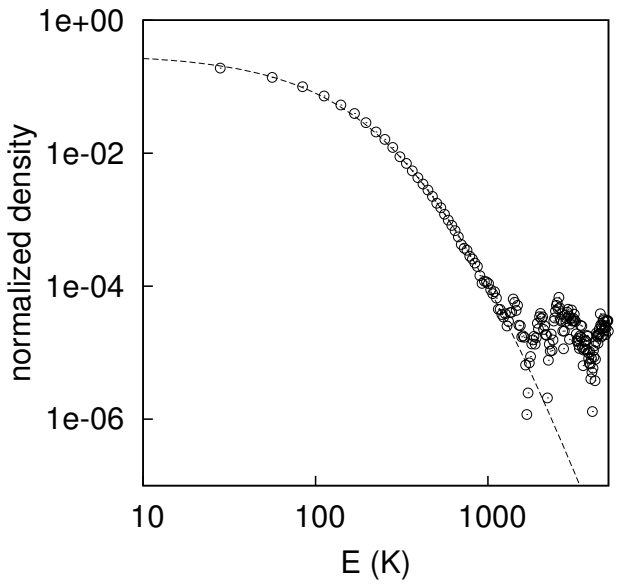

Figure 10: Histogram (in logarithmic scale) of the energies E (circles) of the modes not initially excited, at time $t = 20$ ps, for the same run of figure 9 at $\varepsilon = 120$ K. Solid line is the graph of the Tsallis distribution function $C(1 + \beta(q-1)E)^{1/(1-q)}$ for $q = 1.14$, $\beta^{-1} = 67.8$ K.

with energy given only to the packet of 15 normal modes (out of 512) having the lowest frequency, all with the same energy but with random phases, and then integrates an orbit up to 200 picoseconds, a time larger than the equipartition time (see figure 4, left panel). Then one just considers the set of all normal modes that were not initially excited (thus excluding only the 15 modes having the lowest frequency), and collects the values of the normal mode energies at times multiple of a time step of $\Delta t = 5$ femtoseconds. One sees that the histogram agrees very well with the Maxwell-Boltzmann distribution $\varepsilon \exp(-E/\varepsilon)$.

We address now a further problem, that came to our attention after a conversation with C. Tsallis. The problem is how are our researches situated with respect to a thesis often discussed in recent works. Namely, that in systems with long–range interactions the Maxwell–Boltzmann distribution should be attained only for very large times, whereas previously

quasi stationary states would be met, which present "nonclassical" distributions: moreover, the crossover should take place at times which increase systematically as the number N of particles is increased (see for example [23, 24, 25, 26, 27, 28]). The problem is thus whether such a phenomenon is met in our model, or more in general in the whole domain of atomic physics. Indeed, as particularly emphasized by Feynman, the whole domain of atomic physics is characterized by the presence of long–range electromagnetic forces, actually in their retarded form, involving also the radiation reaction force (see [29] [12]). Thus the deep question is whether the so–called q–statistics are relevant for atomic physics, and in particular for our realistic FPU–type, ionic–crystal model.

This is indeed a very interesting question, that we plan to address more systematically in future studies, and here we limit ourselves to a preliminary result. What we can presently say is that the above described picture may not be inconsistent with the phenomena occurring in the realistic ionic crystal model. What we have available at the moment is illustrated in figure 10, where we report an histogram obtained for the same run of figure 9, but at time 20 (rather than 200) picoseconds. Now, the scale is logarithmic and the full curve is that of the q—distribution $C\,[1-\beta(q-1)E]^{1/1-q}$ (with $q = 1.14$ and $1/\beta = .92$ K). This result shows that, before the Maxwell–Boltzmann distribution is attained, a q–distributions is exhibited in our model too. Whether a persistence of the q–distribution for extremely long times with increasing N also occurs, we cannot say at the moment, due to the difficulty of working with large numbers of particles in our realistic three–dimensional model.

6 Conclusions

So we have shown that the realistic ionic–crystal model we investigated is not ergodic in the sense that, up to geological time scales, the phase space trajectories explore only a very small part of an energy surface. Nevertheless the time–averages of physical observables relax to asymptotic values within microscopic times, of the order of nanoseconds. In particular this allows one to compute theoretical infrared spectra, which moreover reproduce the experimental spectra, even at extremely low temperatures.

This fact seems at first sight to be in contrast with the picture one gets from the numerical experiments performed on one–dimensional FPU models, in which the relaxation times diverge as specific energy tends to zero. Such a contradiction is overcome through the empirical realization that tem-

perature should not be identified with kinetic xenergy per particle, as would be required by Gibbs statistical mechanics, if the latter were dynamically justified. Finally, a preliminary indication was given that "nonclassical" q-distributions may be significant for the realistic ionic–crystal model too, and presumably for the whole domain of atmoic physics.

How to formulate a consistent statistical mechanics, with the corresponding suitable identification of temperature, in such nonergodicity conditions is an open problem that seems to constitute the modern form of the original FPU problem.

References

[1] A. Carati, L. Galgani, A. Maiocchi, F. Gangemi, and R. Gangemi, *Classical infrared spectra of ionic crystals and their relevance for statistical mechanics*, Physica A **506**, (2018) 1-10.

[2] A. Carati, L. Galgani, A. Maiocchi, F. Gangemi, and R. Gangemi, *The FPU problem as a statistical mechanical counterpart of the KAM problem, and its relevance for the foundations of physics*, Regular and Chaotic Dynamics **23**, (2018) 704–719.

[3] M. Born, K. Huang, Dynamical theory of crystal lattices, Oxford U.P. (London, 1954).

[4] D. Ruelle, *Resonances of Chaotic dynamical systems*, Phys. Rev. Lett. **56**, (1986) 405-407.

[5] J.-P. Eckman. D. Ruelle. Ergodic theory of chaos and strange attractors, Rev. Mod. Physics, **57** (1985) 617—656

[6] L.D. Landau, *On the theory of phase transitions* (1937), in Collected Papers, n. 39, page 193.

[7] G. Benettin, A. Ponno, Time scales to equipartition in the FPU problem, finite size effects and thermodynamic limit, J. Stat. Phys. **144** (2011) 793–812.

[8] A. Giorgilli, S. Paleari, T. Penati, *Local chaotic behaviour in the Fermi-Pasta-Ulam system*, DCDS-B **5**, (2005) 991–1004.

[9] Danieli, C., Campbell, D.K. and Flach S., Intermittent FPU dynamics at equilibrium, *Phys. Rev.* E, 2017, Vol. 95, 060202.

[10] Mithun, T., Kati, Y., Danieli, C. and Flach, S., Weakly nonergodic dynamics in the Gross-Pitaevskii lattice, *Phys. Rev. Lett.*, 2018, Vol. 120, 184101.

[11] M. Born, Optik, Springer (Berlin, 1933).

[12] A. Carati, L. Galgani, *Classical microscopic theory of dispersion, emission and absorption of light in dielectrics*, Eur. Phys. J. D **68**, (2014) 307.

[13] Kozlov, V.V, Thermal equilibrium by Gibbs and Poincaré, 2002 (Idshevsk, Moscow), in Russian.

[14] Kozlov, V.V., Gibbs ensembles, equidistribution of energy of sympathetic oscillators and statistical models of thermostat, *Regular and Chaotic Dynamics*. 2008, 13, pp. 141–154.

[15] Kozlov, V.V., On justification of Gibbs distribution, *Regular and Chaotic Dynamics*. 2002, 1–10.

[16] Kozlov, V.V., Treshchev, D.V., Weak convergence of solutions of Liouville equation for non linear Hamiltonian systems, *Theor. and Math. Phys.*, 2003, 134, 339–350.

[17] A. Carati, A. Maiocchi, L. Galgani, G. Amati, *The FPU system as a model for glasses*, Math. Phys. Anal. Geom. **18**, 31 (2015).

[18] A, Carati, A. Ponno, Chopping time of the FPU -model, J. Stat. Phys. 170 (2018) 883–894.

[19] A. Einstein, Discussion following the lecture "On the present state of the problem of specific heats" at the first Solvay Conference, in Collected Papers, Vol. 3, pages 549–561, Princeton University Press (Princeton, 1993).

[20] G. Gallavotti, Ergodicity: a historical perspective. Equilibrium and Nonequilibrium, Europ. Physical J. H (1918) .

[21] A. Carati, *On the definition of temperature using time–averages*, Physica A **369**, (2006) 417-431.

[22] A. Carati, A. Maiocchi, L. Galgani, *Statistical thermodynamics for metaequilibrium or metastable states*, Meccanica **52**, (2017) 1295–1307.

[23] D. Badchi, C. Tsallis, Fermi–Pasta–Ulam–Tsingou problem: Passage from Boltzmann tp q–statistics. Physica A 491 (2018) 869–873.

[24] H. Christodoulidi, C. Tsallis, T. Bountis. FPU model with long–range interactions: Dynamics and thermostatistics, EPL 108 (2014) 40006.

[25] H. Christodoulidi, T. Bountis, C.Tsallis 3, L. Drossos, Dynamics and statistics of the FermiPastaUlam beta–model with different ranges of particle interactions, Jour. Stat. Mech.: Theory and Experiment, (2016) 1–13

[26] V. Latora, A. Rapisarda. C. Tsallis, Non-Gaussian equilibrium in a long-range Hamiltonian system. Phys. Rev. E **64** (2001) 056134.

[27] M. Antoni, H. Hinrichsen, S. Ruffo, On the microcanonical solution of a system of fully coupled particles, Chaos, solitons and fractals, 13 (2002) 393–399.

[28] A. Campo, P.-H. Chavanis, A. Giansanti, G. Morelli, Dynamical phase transitions in long–range Hamiltonian systems and Tsallis distributions with a time–dependent index, Phys. Rev. E**78** (2008) 040102.

[29] A. Lerose, A. Sanzeni, A. Carati, L. Galgani, Classical microscopic theory of polaritons in ionic crystals , Eur. Physical. J. D 68 (2014) 35.