Tsallis distributions, their relaxations and the relation $\Delta t \cdot \Delta E \simeq h$, in the dynamical fluctuations of a classical model of a crystal

A. Carati$^a$ L. Galgani$^a$ F. Gangemi$^b$ R. Gangemi$^b$

August 4, 2020

Abstract

We report the results of a numerical investigation, performed in the frame of dynamical systems’ theory, for a realistic model of a ionic crystal for which, due to the presence of long–range Coulomb interactions, the Gibbs distribution is not well defined. Taking initial data with a Maxwell-Boltzmann distribution for the mode-energies $E_k$, we study the dynamical fluctuations, computing the moduli of the the energy-changes $|E_k(t) - E_k(0)|$. The main result is that they follow Tsallis distributions, which relax to distributions close to Maxwell-Boltzmann ones; indications are also given that the system remains correlated. The relaxation time $\tau$ depends on specific energy $\varepsilon$, and for the curve $\tau$ vs $\varepsilon$ one has two results. First, there exists an energy threshold $\varepsilon_0$, above which the curve has the form

$$\tau \cdot \varepsilon \simeq h,$$

where, unexpectedly, Planck’s constant $h$ shows up. In terms of the standard deviation $\Delta E$ of a mode-energy (for which one has $\Delta E = \varepsilon$), denoting by $\Delta t$ the relaxation time $\tau$, the relation reads $\Delta t \cdot \Delta E \simeq h$, which reminds of the Heisenberg uncertainty relation. Moreover, the threshold corresponds to zero-point energy. Indeed, the quantum value of the latter is $h\nu/2$ (where $\nu$ is the characteristic infrared frequency of the system), while we find $\varepsilon_0 \simeq h\nu/4$, so that one only has a discrepancy of a factor 2. So it seems that lack of full chaoticity manifests itself, in Statistical Thermodynamics, through quantum-like phenomena.

$^a$Dipartimento di Matematica, Università di Milano, Via Saldini 50, 20133 Milano, Italy. E-mail: andrea.carati@unimi.it
$^b$DMMT, Università di Brescia, Viale Europa 11, 25123 Brescia, Italy.
1 Introduction. A modified version of the original FPU problem

As pointed out by several authors\(^1\) simple large deviation arguments of Boltzmann type show that the distribution of the normal-mode energies of a system of weakly coupled oscillators is generically a Maxwell–Boltzmann one. In other terms, the region of a constant-energy surface presenting a distribution different from Maxwell-Boltzmann, has negligible measure.

This however is not sufficient for the aims of Statistical Thermodynamics, since many quantities of interest are expressed in terms of correlations of suitable observables (see \([2]\)), computed from initial data of generic type (i.e., with a Maxwell-Boltzmann distribution), and not just in term of averages of the normal-mode energies. An example is given in the works \([3, 4]\), where the electric susceptibility of Lithium Fluoride (LiF) was computed through the Fourier transform of the auto-correlation of the optical normal-mode amplitudes, for generic initial data, and the infrared spectra thus obtained were found to agree very well with the experimental ones at several temperatures (more details will be given later).

In other words, the dynamical properties of the considered system are relevant, beyond the occurrence of Maxwell-Boltzmann distributions. So, leaving aside questions of ergodic type (see \([5, 6, 7]\)), we decided to investigate whether significant properties of some general character may be found to occur for the dynamical fluctuations in systems of coupled oscillators, still working on the Lithium Fluoride model, which allows a comparison to be made between computational results and experimental data.

The problem is then to choose the significant quantities to be investigated, and our choice was to study the probability distributions for the moduli \(|E_k(t) - E_k(0)|\) of the energy-changes of the normal modes. This was inspired to the following naive argument.\(^2\) Assume that, starting from a point \(x_0\) in phase space, the evolved point \(x_1 \overset{\text{def}}{=} \Phi^t x_0\) at time \(t\) may be considered as “independent” of \(x_0\), in the sense that the normal-mode energies may be considered as random variables independent of their initial values. Then it will turn out that a Maxwell-Boltzmann distribution occurs not only for the normal-mode energies, both in \(x_0\) and in \(x_1\), but also (as a simple calculation shows - see Section 3) for the moduli of the

\(^1\)The first one known to the present authors is Khinchin in his book ref. [1], Section 20.

\(^2\)Such an argument was conceived by the first author about ten years ago, and some preliminary unpublished results for a standard Fermi-Pasta-Ulam model were illustrated in the thesis [8] of M. Dubrovich, with the first two authors as advisors. The results concerned the energy-changes of single normal modes, whose distribution was found to depend on mode-frequency. Tsallis distributions were not taken into consideration, and no comparison with experimental results was possible, so that no interpretation of the results could be advanced.
By an inversion of the argument, our choice was to try to establish whether the distribution of such moduli of the energy-changes converges to a Maxwell-Boltzmann one, and on which time scale. This actually constitutes what we call a modified version of the original FPU problem, inasmuch as the latter is concerned with a relaxation of the distribution of the mode-energies themselves[^2] rather than of their changes. Our choice may also be looked upon in the following way. As particularly stressed by Nernst [12], energy changes and not energies themselves, are the relevant quantities for Statistical Thermodynamics. Now, in systems of weakly coupled oscillators, as are the Fermi-Pasta-Ulam ones, the prototypes of the energy-changes are the mode-energy changes, whose moduli lead, by averaging, to correlations. These are indeed the quantities we decided to investigate.

Some interesting results were found. The first one is that at all times the moduli of the energy-changes seem to follow a well defined distribution, i.e., a Tsallis one (see [13]). Such a fact is not completely unexpected, since Tsallis distributions are known to show up in models involving long-range forces, either Coulomb ones [14] (as the ionic crystal considered here), or gravitational ones (see [15] [16]). As is known, Tsallis distributions are characterized by two parameters: \( q \) (the so-called Tsallis entropic index, related to the decay of the tail of the distribution), and \( \beta \), which determines the specific energy per degree of freedom \( \varepsilon \). Such distributions have the form

\[
\rho = C [1 - (1 - q)\beta E]^{1 - q}, \tag{1}
\]

\( C \) being a normalization factor, and reduce to the Maxwell-Boltzmann one, \( C' \exp(-\beta E) \), in the limit \( q \to 1 \) (which implies that \( \varepsilon \) tends to \( 1/\beta \)). The dynamical reason for the occurring of a Tsallis distribution in the frame of dynamical systems is not clear to us, at the moment. However, as pointed out for example in the work [17], one might surmise that such an occurrence could be related to the “dimension” of the orbits in phase space, i.e., to their tendency to invade sets with dimensions smaller than that of the energy surfaces, as if some remembrance remained of the integrals of motion of the linearized system.

In our computations the parameters \( q \) and \( \beta \) were found to change with time, presenting some final relaxation for large enough times. At first sight, the relaxation might appear to lead to a Maxwell-Boltzmann distribution, but a more accurate inspection shows that the results depend on the number \( N \) of ions. Thus, for \( N = 4096 \) (and specific energy per degree of freedom \( \varepsilon \)).

[^2]: After about fifty years of harsh debates (see for example refs. [9] [10] [11]) the scientific community eventually came to agree that, in models of Fermi-Pasta-Ulam type, equipartition, and possibly also a Maxwell-Boltzmann distribution, would be attained for the normal-mode energies, even if one starts from exceptional initial data.
freedom $\varepsilon = 500$ Kelvin\footnote{All along the present work, the specific energies are expressed in Kelvin, i.e., as their ratios with respect to the Boltzmann constant $k_B$. This will be seen to make a comparison with the experimental data easier.}, the relaxed distribution turns out not to coincide with Maxwell-Boltzmann, being however rather close to it, since one finds $q = 1.014$. This indicates that some kind of correlation persists even after relaxation.

Then, the dependence of the relaxation time $\tau$ on the specific energy $\varepsilon$ per degree of freedom was investigated. Here, two further significant results were found. First of all, there exists a specific energy threshold $\varepsilon_0$, at about 100 K, distinguishing between two behaviors: a quick relaxation above threshold, and a slower one below it. An analogous behavior was observed long ago for the Fermi-Pasta-Ulam model, first by Bocchieri, Scotti and Loinger \cite{18}, then by Casartelli et al. \cite{19} as a vanishing of the maximal Lyapunov exponent, and eventually, by Pettini and Landolfi in the work \cite{20}, still in terms of the Lyapunov exponent in a way very similar to the one found here, actually as a knee in the curve Lyapunov exponent versus specific energy. Concerning such a threshold, already in the paper \cite{21}, along the lines of \cite{22}, the idea was advanced by Carlo Cercignani that it should correspond to zero-point energy. This is indeed essentially confirmed here, since it turns out (see later) that, denoting by $\nu$ the characteristic infrared frequency of Lithium Fluoride, for the threshold energy $\varepsilon_0$ one has $h\nu/2 \simeq 2\varepsilon_0$, where $h$ is Planck’s constant, so that, up to a factor 2, $\varepsilon_0$ coincides with the quantum zero-point energy.

Finally, above threshold another result was met, and again a rather peculiar one. Indeed the relaxation time was found to be inversely proportional to specific energy, through a proportionality constant, an action, which again turns out to be nearly the Planck constant (actually, about three times larger), so that one has\footnote{More precisely, one has $\tau(\varepsilon) \simeq 3.5h/\varepsilon$ so that, with $\varepsilon_0 \simeq h\nu/4$, for the largest relaxation time $\tau_{\max} \simeq 3.5h/\varepsilon_0$ one finds $\tau_{\max} \simeq 1/\nu$, i.e., the maximal relaxation time is equal to the period of the characteristic infrared frequency.}

\begin{equation}
\tau(\varepsilon) \simeq \frac{h}{\varepsilon} \quad \text{i.e.,} \quad \tau \cdot \varepsilon \simeq h . \tag{2}
\end{equation}

Now, every mode-energy is always Maxwell-Boltzmann distributed, so that for its standard deviation $\Delta E$ one has

\begin{equation}
\Delta E = \varepsilon . \tag{3}
\end{equation}

Thus, the result \cite{2} for the relaxation time can be phrased in the following suggestive way: *The product of the uncertainty of a mode–energy by the relaxation time is nearly equal to $h$,*

\begin{equation}
\tau \cdot \Delta E \simeq h . \tag{4}
\end{equation}
which closely reminds of the Heisenberg uncertainty principle.

We are well aware that the problems on the foundations of Statistical Thermodynamics are very difficult and complex. However it seems to us that the above mentioned results, although obtained in a quite elementary way, may present a certain interest.

In Section 2 the Lithium Fluoride model is briefly described, and are recalled the relevant previous results on electric susceptibility which motivated the present study. In particular it is recalled how the results on the infrared spectra naturally make zero-point energy emerge in a classical frame. Section 3 is instead devoted to illustrating the new numerical results. In Section 4 the results obtained are summarized and briefly discussed, commenting in particular how should one understand the occurring of Planck’s constant in a purely classical model, while some conclusions are drawn in the last Section.

2 The model, the infrared spectra, and the idea of a classical way to zero-point energy

We briefly recall the ionic-crystal model investigated, and the relevant results available in the literature. In the studies on the dynamics of the ions in an ionic crystal, following Born one usually works in the so-called adiabatic approximation, in which the dynamics of the electrons can be ignored, and the ions are dealt with as point particles. Indeed, the screening effect of the electrons is implicitly taken into account both through a suitable interaction potential acting among the ions, and through an effective charge for the ions in place of the true one. In such an approximation the following model can be introduced. One considers a system of an even number $N$ of point particles $x_{i,s}, i = 1, \ldots, N/2$ of two suitable ionic species $s = 1, 2$ such as Lithium and Fluorine (with masses $m_s$ and charges $e^{(s)}$), located inside a cubic cell of side $L$. Such points interact both through Coulomb forces, and through a Buckingham potential of the form

$$V_{ss'}(r) = a_{ss'} e^{-b_{ss'} r} + c_{ss'} r^{-6}. \quad (5)$$

The values of the constants $a_{ss'}, b_{ss'}$ and $c_{ss'}$ and of the effective charges can be found in the work [3], Table I, and were determined by optimizing

\[\text{at variance with ref. [3], in which we worked at fixed pressure, now we work at fixed volume at all energies, with a lattice step } L = 1.995 \text{ Å.}\]

\[\text{This is a modern modification of the potential } V(r) = C/r^6, \text{ first proposed by Born, which contains just one free parameter. This potential was used in our first paper on LiF, and indeed it too turned out to produce spectra in good agreement with experiment, although not as good as with the Buckingham potential.}\]
the dispersion relations and the spectra at 300 K. Finally, as usual, periodic boundary conditions are introduced, so that the model turns out to be defined by the Hamiltonian

$$H = \sum_{j,s} \frac{p_{j,s}^2}{2m_s} + \sum_{n \in \mathbb{Z}^3} \sum_{j,j',s,s'} \left[ V_{ss'}(|x_{j,s} - x_{j',s'} + nL|) + \frac{e_{\text{eff}}^{(s)} e_{\text{eff}}^{(s')}}{|x_{i,s} - x_{j,s'} + nL|} \right].$$

(6)

Actually, such a definition of the model only has a formal character, inasmuch as the series involving the Coulomb potential is not absolutely convergent. The definition is completed by prescribing that such a series be summed according to the Ewald method, which transforms it into the sum of two rapidly absolutely convergent series, of which one is defined over the direct lattice, and the other one over the reciprocal lattice. For the Ewald method one can consult, in addition to the original german work [23], also the recent one [24], or our work [25].

The first interesting point is that such a Hamiltonian admits a stable equilibrium configuration (which is chosen as defining the energy minimum), in which the ionic positions $x_{j,s}^0$ form a face-centered cubic lattice, which indeed is the structure of LiF. Furthermore, for not too large kinetic energies (say, below 1060 K)⁸ the ions are found to oscillate about such equilibrium positions, thus reproducing the oscillating crystal structure of the solid.

Let us now come to the infrared spectrum. In this connection the motion of the electrons can be essentially ignored, since it is known to contribute to susceptibility (in such a domain) only through a constant. Thus, having obtained, through numerical computations, the solutions of the equations of motion of the ions corresponding to the Hamiltonian (6), the dielectric susceptibility tensor $\chi_{ik}(\omega)$ due to the ions is computed in the following way. One defines the (microscopic) polarization as

$$\mathbf{P}(t) \overset{\text{def}}{=} \frac{1}{V} \sum_{j,s} e_j^{(s)} (x_{j,s}(t) - x_{j,s}^0)$$

(7)

with $V = L^3$, and the susceptibility is then given by the (Green–Kubo) formula (see [27])

$$\chi_{jk}(\omega) = \frac{1}{\sigma} \int_0^{+\infty} dt e^{i\omega t} < P_j(t) \dot{P}_k(0) > ,$$

(8)

where $\sigma^2$ is the variance of the kinetic energy, while by $< >$ we have denoted a phase average, which concretely was computed as the mean of time–averages over several trajectories. Thus, in words, the electric susceptibility

---

⁸The melting temperature is 1118 K.

⁹We recall that the dielectric tensor $\epsilon_{i,j}$ is a thermodynamic quantity, and is equal to the Hessian of the Gibbs free energy of the crystal with respect to the electric field intensity, i.e., one has $\epsilon_{i,j} = \partial^2 G/\partial E_i \partial E_j$ (see [26]).
is computed essentially as the Fourier transform of the time auto-correlation of polarization. In the terminology of dynamical systems, it is computed in terms of the spectrum of the considered dynamical system.

In order to perform a comparison with the experimental data, one is confronted with the problem of identifying temperature, inasmuch as the experimental measures are performed at a given temperature, whereas in our model the computations are performed at a given specific energy. If one makes use of the familiar identification of temperature as proportional to mean kinetic energy, the susceptibility thus computed is found to be in remarkable agreement with the experimental measures at room temperature and at larger ones, up to 1000 K. Instead, the agreement is not so good at 85 K, and a complete disagreement is found at 7.5 K.

The unexpected empirical result of the work [28] was that an agreement between experimental data and numerical computations at low temperatures can be restored, provided one abandons the familiar identification of temperature as proportional to mean kinetic energy. Indeed the experimental data at a temperature of 85 K are reproduced if one takes a specific energy $\varepsilon = 180$ K, and analogously for the data at 7.5 K if one takes $\varepsilon = 125$ K. One should notice that a procedure of such a type for constructing the relation between temperature and mechanical energy has a noble precursor in statistical mechanics since, in the case of dilute gases, Clausius obtained such a relation by comparing the theoretical expression of the product $pV$ in terms of kinetic energy, with the empirical expression in terms of temperature.

With respect to the case of dilute gases, in the case of crystals the qualitative difference is that a zero-point energy is empirically known to exist, namely, a finite kinetic energy of the ions is observed even for vanishing temperature, as proved by the Debye-Waller effect. Now, the existence of a zero-point energy in crystals is predicted by quantum mechanics, and one might be induced to think that at low temperatures one is entering an essentially quantum regime, irreducible to a classical one. On the other hand it is a fact that, through a suitable redefinition of temperature in mechanical terms, classical dynamics does reproduce the experimental spectra in an appropriate manner. Thus the problem seems rather to be one of statistical mechanics, namely, how should temperature be consistently defined for our system. This would be trivial if one could make use of the Gibbs measure. However, in our model we are in presence of long range potentials (even resummed through the Ewald procedure), so that the existence of the Gibbs measure is not even guaranteed. Furthermore, the use of the Gibbs measure would require that suitable ergodicity conditions be satisfied.

So it seems that the problem of defining temperature in classical statistical mechanics for a crystal, in a way consistent with dynamics, is still

\footnote{An analogous procedure could perhaps be used for crystals, by numerically computing pressure as a function of energy, and this indeed is an interesting subject for future work.}
open. This is indeed the original motivation of the present work, namely, to investigate the statistical properties induced by the dynamics, at several values of specific mechanical energy, for generic initial data. The aim was to check whether some sort of qualitative change in the dynamics may be found to occur for specific energies in the region where, according to the mentioned results on infrared spectra, zero-point energy should emerge, i.e., for specific energies of about 120 K. This indeed might advocate the necessity of identifying temperature, in mechanical terms, in a way different than the Clausius one, in that region of specific energy, for a LiF crystal. We will show in the next section that this is actually the case.

3 The Tsallis distributions for the moduli of the energy-changes, and their relaxation

To investigate the ergodicity properties of a system with a very large number of degrees of freedom is not a simple task since, due to the large deviation theorems, extremely numerous are the functions which are essentially constant on any given energy surface (i.e., coincide, apart from regions of negligible measure, with their phase average). This is essentially the same property that makes the Maxwell-Boltzmann distribution have an overwhelming probability. A positive use of this fact can be made, by trying to check whether a distribution different from the Maxwell-Boltzmann one can be observed for suitable variables, since this would indicate that the dynamics of the considered system presents peculiar properties.

In such a spirit we decided to look at the mode-energy-changes, defined in the following way. As explained in the previous section, the Hamiltonian admits a configuration of stable equilibrium and let the corresponding positions of the ions be denoted by $x_{j,s}^0$. By linearization about the equilibrium configuration one obtains a linear system, whose normal mode amplitudes $A_{k,\rho}$ can be determined, where $\rho = 1, \ldots, 6$ denotes one of the 6 branches of the dispersion relation, and $k$ is a suitable wave vector of the reciprocal lattice. The energy of any normal mode is then defined as

$$E_{k,\rho} = \frac{1}{2} \left( \dot{A}_{k,\rho}^2 + \omega_{k,\rho}^2 A_{k,\rho}^2 \right),$$

where $\omega_{k,\rho}$ is the corresponding oscillation frequency. Each $E_{k,\rho}$ is a constant of motion for the linearized system, whereas it behaves as a “slow” variable for the complete system.

\footnote{Actually the system admits $\approx N!2^N$ such configurations, which are obtained by permutations of particles of the same species. However, as already mentioned, starting near to one of such configuration the point will remain near to it for the whole actual integration time. Different minima can be visited only for temperatures above the melting one. Then the ions freely exchange positions, but the system behaves as a liquid, and no more as a solid.}
Take now, at random, a phase space point sufficiently near to a given equilibrium configuration, and consider the set of the corresponding normal-mode energies $E_{k,\rho}$, computed for such an initial datum. As mentioned in the introduction, according to a large deviation argument it turns out that, if one builds the corresponding histogram, i.e., one determines how many normal modes have energies in the interval between $E$ and $E + \delta E$, then the histogram will follow with a good approximation a Maxwell-Boltzmann law $C \exp(-E/\varepsilon)$, at least in the limit of large values for the number $N$ of particles. In the same way, if one takes two initial data at random on the same energy surface, still in a neighborhood of the given equilibrium point, and computes the normal-mode energies $E^0_{k,\rho}$ and $E^1_{k,\rho}$ corresponding to the first and the second point respectively, then the histogram of the moduli of the energy-changes $\left|E^1_{k,\rho} - E^0_{k,\rho}\right|$ will still follow a Maxwell-Boltzmann type law $C' \exp(-\Delta E/\varepsilon)$, as is easily checked.\footnote{If $x$ and $y$ are independent positive random variables, identically distributed according the Maxwell-Boltzmann distribution, then the probability $P(|x - y| > \Delta E)$ will be}

$$P(|x - y| > \Delta E) = \beta^2 \int_{|x-y|>\Delta E} e^{-\beta(x+y)} \, dx \, dy;$$

performing the change of variable $X = x + y$, $Y = x - y$, the integral will change into

$$P(|Y| > \Delta E) = \beta^2 \int_{\Delta E}^{+\infty} e^{-\beta X} \, dX \int_{\Delta E}^{X} \, dY = e^{-\beta \Delta E} \int_{0}^{+\infty} ze^{-z} \, dz = e^{-\beta \Delta E},$$

having defined $z \overset{\text{def}}{=} \beta(X - \Delta E)$. This shows that $|x - y|$ too is distributed according to Maxwell-Boltzmann.
Figure 1: Evolution of the histogram of the moduli of the energy-changes, for specific energy $\varepsilon = 150$ K and a cell with $N = 216$ ions, as time is increased: $t = 0.5$ picoseconds left, $t = 15$ picoseconds right.

Figure 2: Relaxation of Tsallis distributions to Maxwell-Boltzmann. Tsallis entropic index $q$ (left) and the parameter $1/\beta$ (right) vs. time, for $\varepsilon = 150$ K and $N = 216$. 
chooses a time increment $t$ and a sequence of times $t_n = n\delta t$, and computes the energy-changes $|E_{k,\rho}(t_n + t) - E_{k,\rho}(t_n)|$. The time interval $\delta t$ has to be taken sufficiently large that the sequence of positions $x_{j,s}(t_n)$ may be considered to produce a sample representative of the statistics. Thus the time interval has to be increased as the specific energy $\varepsilon$ is decreased: we took $\delta t = 5$ picoseconds for specific energies larger than 300 K, increasing it up to $\delta t = 100$ picoseconds at a specific energy of 10 K. Such a procedure was repeated for a number of 16 up to 48 different initial data.

In such a way a sample of the energy-changes was produced, and one can pass to build the histogram of their moduli. The result, for a system with a cell of $N = 216$ particles and specific energy $\varepsilon = 150$ K, is shown in Fig. 1 in log-log scale: the left panel refers to $t = 0.5$ picoseconds, and the right one to $t = 15$ picoseconds. The sample is constituted of $5 \cdot 10^6$ energy-changes. In the same figure are plotted both the curve corresponding to the Maxwell-Boltzmann distribution (dashed line) and the curve corresponding to a Tsallis distribution (continuous line) with $q = 1.11$ e $1/\beta = 63.8$ K for the left panel, and $q = 0.9995$ and $1/\beta = 152, 1$ K for the right panel. One notices that in the left panel the histogram clearly differs from Maxwell-Boltzmann, being remarkably well described by a Tsallis distribution. However, after a sufficient lapse of time the histograms, Maxwell-Boltzmann and Tsallis, do coincide: the system did relax. In all the different tests carried out, with several specific energies $\varepsilon$ and at several times $t$, the Tsallis distribution was always found to give a very good description of the histograms. As already said, the reason of such a fact remains at the moment unknown.

In order to study the relaxation times one can report the plots of the Tsallis entropic index $q$ versus time. This is shown in figure 2 for specific energy $\varepsilon = 150$ K, and $N = 216$, where the relaxation to Maxwell-Boltzmann is clearly exhibited. The computation can be repeated for other values of specific energy, checking whether one has convergence or not. The surprising result obtained is that all plots corresponding to $\varepsilon \geq 150$ K actually superpose if the entropic index $q$ is plotted as a function of $\varepsilon t$, or better of $\varepsilon t/h$, which is a dimensionless variable. This is shown in figure 3 (left panel). One visually “sees” that $q$ attains the value 1 in a dimensionless time of about 10. A less arbitrary characterization of the relaxation times can be obtained by referring to the right panel of the same figure, in which the entropic index $q$ is plotted as a function of $\varepsilon t/h$ in semilogarithmic scale. As one can check, the decay of $q$ to 1 follows with very good approximation a straight line with a slope of 0.28, which gives a characteristic dimensionless time of 3.5. Recalling that for a Maxwell-Boltzmann distribution the

\begin{footnotesize}
\begin{itemize}
\item[13] The choice of Planck’s constant $h$ may appear natural as the characteristic action of atomic physics. However, in our case the choice was induced by the fact that, having estimated the relaxation time $\tau$ for several values of $\varepsilon$, we found $\tau(\varepsilon) \simeq C/\varepsilon$ with a certain action $C$, and it turned out that one has $C \simeq 3h$.
\end{itemize}
\end{footnotesize}

11
Figure 3: Tsallis entropic index $q$ versus rescaled time $t\varepsilon/h$ (in units of $h$), for specific energies $\varepsilon$ between 150 and 1000 K, in linear scale (left) and in semilogarithmic scale (right). This is a main result of the paper, since all graphs are seen to superpose.

Figure 4: Same as Figure 3, for low specific energies, namely $\varepsilon = 10, 50$ and 100 K. Superposition no more occurs, through the previous rescaling.

standard deviation $\Delta E$ is equal to mean energy $\varepsilon$, the relation between relaxation time and energy fluctuation takes the form $\tau \cdot \Delta E \simeq h$, which reminds of the analogous uncertainty relation of quantum mechanics.

For smaller specific energies the rescaling previously illustrated doesn’t apply any more, as is seen from figure 4. In fact, the graphs of $q$ versus the rescaled time $t\varepsilon/h$, drawn for $\varepsilon = 10$ and 50 K, no more superpose each other, neither do they superpose with the previous ones (here drawn
Figure 5: Relaxation time vs specific energy in log–log scale, exhibiting a crossover at about 100 K. Here $N=216$.

for $\varepsilon = 100$). The right panel shows that the relaxation is at any rate well described, for any $\varepsilon$, by an exponential, so that one can determine the corresponding relaxation time. The values found are reported versus specific energy, in log–log scale, in figure 5. One sees that a sharp knee appears at $\varepsilon \simeq 100$ K: this might signal a change in the dynamics of the system.

All the results exhibited in the previous figures were obtained for a system with a cell of $N = 216$ ions. An obvious question is then what happens by increasing the number of ions. As we are dealing with a three-dimensional model involving long range interactions, increasing the number of ions implies a more than linear growth of the computational times, so that we were not in a position to perform a systematic study. Thus we limited ourselves to raising the number of ions for just one fixed value of specific energy, actually $\varepsilon = 500$ K. The computations were performed at $N = 216$, 1000 and 4096, and in all cases it turned out that the statistics of the fluctuations follows very well a Tsallis distribution. The entropic parameter $q$ obviously depends on time, and the three graphs of $q$ versus time are reported in figure 6.

In particular, in the left panel the plot of $q$ vs. time is reported in linear scale: it is apparent that one has a relaxation but, at least on the time scale investigated, the asymptotic value $q_0$ of $q$ depends on the number of ions. We are unable to say whether, at a larger time, one will finally get Maxwell-Boltzmann, but at any rate one can conclude that the time for attaining Maxwell-Boltzmann would grow for sure when the number of degrees of freedom is increased. This is at variance with what occurs for
Fermi-Pasta-Ulam models with next neighbors interactions, and is instead in agreement with the results found for systems with long range interactions. In particular, it is coherent with the findings of paper [29], which deals with a one-dimensional Fermi-Pasta-Ulam model with long range interactions: the entropic index relaxes to a metastable value, which lasts for a longer time as the number of particles is increased, until eventually attaining the Maxwell-Boltzmann value $q = 1$. By the way, for values of $q$ close to 1, our computations have a large margin of error, so that it seems to be premature to advance precise statements.

The right panel reports instead the entropic index $q$ minus the asymptotic value $q_0$ vs. time, in semi logarithmic scale, for different values of $N$: one sees that the points superpose well along a straight line. This implies that the relaxation to $q_0$ is exponential, and that the relaxation time doesn’t depend on $N$, at least at the specific energy $\varepsilon = 500$ K considered.

4 Discussion of the results

Let us now summarize and comment the results obtained for the moduli of the energy-changes occurring with initial data of generic type (i.e., with a Maxwell-Boltzmann distribution for the mode energies), for the Lithium...
Fluoride model. First of all, the moduli of the energy-changes follow time-dependent Tsallis distributions which present a relaxation after a rather well defined relaxation time \( \tau(\varepsilon) \). Concerning the nature of the distribution after relaxation, we don’t yet have a definitive answer, but the result obtained for 4096 ions seems not to exclude, as a possible conjecture, that for a large enough number \( N \) of ions, and perhaps even at the thermodynamic limit, the distribution still be a Tsallis one. If this feature were confirmed, one would be in presence of a relevant fact, since it would mean that classical statistical mechanics shouldn’t be the standard Gibbs one.

However, interesting phenomena already are found even for small numbers of ions, with the occurrence of quantum-like features involving a characteristic action of the order of Planck’s constant, within a wholly classical frame. Such features concern the form of the curve \( \tau(\varepsilon) \) of relaxation time versus specific energy, which indeed was shown to be pretty well defined in terms of the results available for a small value \( N \) of ions.

The first phenomenon, exhibited in figure 5, is the existence of a threshold (or a knee, or a crossover) \( \varepsilon_0 \), apparently at 100 K, i.e., rather near to the value of 120 K that would be expected from the results on the infrared spectra\(^{14}\). One may wonder which role be played by such a threshold. We already recalled how, for the threshold observed in the standard Fermi-Pasta-Ulam, already in the early years 70’s Cercignani put forward the suggestive hypothesis that it be the analogue of zero-point energy. That hypothesis actually produced a strong stimulus on the subsequent works on the Fermi–Pasta–Ulam problem, in view of its relevance for the relations between classical and quantum mechanics. Such a perspective appeared to have been frustrated when a general consensus was obtained on the fact that in systems of Fermi-Pasta-Ulam type equipartition is eventually attained, also starting from initial data faraway from it, since such a fact was interpreted as confirming the common opinion that classical mechanics fails at low temperatures. Things started changing, however, with the investigations on the realistic Lithium Fluoride model which, at variance with the standard Fermi-Pasta-Ulam model, allowed one to compare numerical computations with experimental data, for example in connection with polaritons (see ref. [30]) and with the infrared spectra.

In the present paper a further comparison, leading support to the Cercignani hypothesis, is made possible, since one finds that the threshold \( \varepsilon_0 \) agrees with the quantum zero-point energy, albeit up to a factor 2. The simplest way to see this fact, is to proceed as Einstein did in his work on specific heats, namely, by assimilating the crystal to a system of oscillators all of the same frequency \( \nu \), equal to the characteristic infrared frequency of

\(^{14}\)Our impression is that such a discrepancy should be due to the fact that the results on the spectra were obtained at fixed pressure, whereas the results presented here were obtained at fixed volume.
the crystal. In the Lithium Fluoride case this means the spectral line at 300 cm\(^{-1}\) (i.e., \(\nu = 300 \, c \, cm^{-1}\), where \(c\) is the speed of light). In fact, recalling that one has \(hc/k_B = 1.4\), if one assumes \(\varepsilon_0 = 100 \, K\) one immediately gets

\[
\frac{1}{2} h\nu = 2\varepsilon_0 ,
\]

i.e., \(\varepsilon_0\) is just one half the quantum value \(h\nu/2\). Essentially the same result is obtained also if one sums the zero-point energies of all the single normal modes of the model.

The second phenomenon, in addition to the first one on the existence of the threshold \(\varepsilon_0\), is the law for the relaxation time observed above it, which, as was previously pointed out, reminds of the time-energy uncertainty relation of quantum mechanics, and still exhibits a characteristic action, very close to Planck's constant.

So the problem arises of understanding how is it possible at all that Planck's constant shows up in a purely classical system. Now, it would seem obvious that Planck's constant appears in our model through the coefficients of the phenomenological Buckingham potential, which takes implicitly into account the forces among ions due to the electrons, in the adiabatic hypothesis. Thus the occurring of Planck's constant would eventually be a manifestation of the quantum character of the dynamics of the electrons. In such a way one may understand why Planck's constant shows up not only in the zero-point energy, but also above the knee, in the rescaling of the relaxation times through specific energy \(\varepsilon\). More in general, the occurring of a characteristic action of the order of Planck's constant through the effective potential might explain why classical dynamics may reproduce the experimental result, as it actually does so well in our model, for the infrared spectra.

In fact, however, the situation is more complex, as exhibited typically by the result obtained in the paper [31], concerned with the \(H^+\) ion. Such an ion is the simplest case in which an effective potential due to electrons occurs, since one has just one electron which produces a chemical bond between two protons. In such a case, an effective potential can be computed in quantum mechanical terms, thus involving Planck's constant in an obvious way. However, in the mentioned paper we showed how in the \(H^+\) ion the binding through an effective potential is explained also in classical terms in the three-body purely Coulomb model, which involves no free parameter at all. The relevant point is that the binding occurs\(^{15}\) only if the motion of the system is sufficiently regular rather than chaotic; otherwise no confinement can occur, which is indeed the core of the adiabatic principle in a classical

\(^{15}\)As is well known, in systems with pure Coulomb forces the equilibrium points are always unstable. In our case, instead, the bond is produced by the attractive action of the electron, which continues to bounce back and forth between the protons, and turns out to prevail on the repulsion between the two protons.
frame. In particular it is found that the binding occurs only if the angular momentum of the electron about the axis through the protons is sufficiently large, actually of the order $\hbar$. So, in the case of the $H_2^+$ ion, Planck’s constant enters as a chaoticity threshold, in a purely classical frame. Perhaps, an analogous situation may be found to occur also for the phenomenological inter-ionic potential in the general case involving more than just one electron.

5 Conclusions

The numerical investigation performed in the present work does not allow one to answer in a conclusive way the main question addressed in this paper. Namely, whether the necessity of introducing temperature values different from those of specific energy in order to reproduce the susceptibility data at low temperatures, originates from the intrinsically quantum character of the dynamics, or rather from a lack of sufficient chaoticity in the classical dynamics. Indeed, Figure 6 shows that the results depend on the number $N$ of ions constituting the system. This dependence is very strong, because the exponent in the Tsallis distribution, i.e., $1/(1-q)$, changes from $\infty$, to 500 and 70 by just multiplying by 4 the particles’ number $N$ (with the asymptotic value $q_0$ passing from 1 to 1.002 and 1.014), so that is not clear what occurs at the thermodynamic limit.

This notwithstanding, a fixed point seems to have been established, namely, that the Tsallis distribution plays a relevant role for our system and more in general, we believe, for ionic crystals. Which might be the dynamical properties (apart from a reduced chaoticity) inducing the occurrence of such distributions, is not clear. Neither are clear the implications such distributions may have for the expected values of the thermodynamic variables. By the way, one might recall in this connection that, as previously mentioned, the relevant quantities in Statistical Thermodynamics actually are not the energies themselves, which follow Maxwell-Boltzmann distributions, but rather, as particularly stressed by Nernst [12], the exchanged energies, i.e., the energy-changes, whose moduli were here shown to follow Tsallis distributions. In any case, certainly chaoticity diminishes for decreasing specific energy, as witnessed by the occurring of the knee in the graph of relaxation time versus specific energy. It would be interesting to establish what happens as the number of ions is increased, namely, whether the marked tendency for a diminishing of chaoticity with increasing $N$, exhibited at the higher temperatures, persists also below the threshold $\varepsilon_0$. For our program, addressed at explaining the phenomenology of Lithium Fluoride in purely classical terms, this is is crucial point, on which we hope to come back in the near future.

As a final remark, we would like to point out that we are well aware of the difficulties of such a program; but it is not excluded that it may be im-
plemented. In such a case, the relations between classical and quantum mechanics would appear under a new light, with quantum mechanical features occurring as a manifestation of lack of full chaoticity. The present paper, however, shows at least that the relations between classical and quantum mechanics are more complex than is commonly believed.

Acknowledgements: Research carried out with the support of resources of Big and Open Data Innovation Laboratory (BODaI-Lab), University of Brescia, granted by Fondazione Cariplo and Regione Lombardia.

References

[1] A. Khinchin. Mathematical foundations of statistical mechanics. Dover, New York, 1949.

[2] A. Carati, L. Galgani, and A. Maiocchi. Statistical thermodynamics for metaequilibrium or metastable states. Meccanica, 52:1295–1307, 2017.

[3] F. Gangemi, A. Carati, L. Galgani, R. Gangemi, and A. Maiocchi. Agreement of classical Kubo theory with the infrared dispersion curves $n(\omega)$ of ionic crystals. EPL, 110:47003, 2015.

[4] 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, 506:1, 2018.

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

[6] T. Mithum, Y. Kati, C. Danieli, and S. Flach. Weakly nonergodic dynamics in the gross-pitaevskii lattice. Phys. Rev. Lett., 120:184101, 2018.

[7] V.V. Kozlov. On justification of gibbs distribution. Reg. Chaotic Dynamics, 7:1, 2002.

[8] M. Dubrovich. Sul paradosso di Fermi, Pasta e Ulam - Studio numerico delle variazioni delle energie armoniche. Master’s thesis, Corso di Laurea triennale in Fisica, Università di Milano, 2009.

[9] G. Gallavotti. The Fermi-Pasta-Ulam Problem: A Status Report, volume 728 of Lecture Notes in Physics. Springer–Verlag, Berlin, 2008.

[10] D. Campbell, P. Rosenau, and G.M. Zavlinky. The FPU problem - The first fifty years. Chaos, 15:015101, 2005.
A. Carati, L. Galgani, and A. Giorgilli. The FPU problem as a challenge for the foundations of physics. *Chaos*, 15:015105, 2005.

W. Nernst. *The new heat theorem*. Dover, New York, 1969.

C. Tsallis. Possible generalization of boltzmann-gibbs statistics. *J. Stat. Phys.*, 52:479–487, 1988.

A. Carati, L. Galgani, F. Gangemi, and R. Gangemi. Approach to equilibrium via tsallis distributions in a realistic ionic-crystal model and in the FPU model. *Eur. Phys. J. Spec. Top.*, 229:743–749, 2020.

V. Latora, A. Rapisarda, and C. Tsallis. Non-gaussian equilibrium in a long-range hamiltonian system. *Phys. Rev. E*, 64:056134, 2001.

M. Antoni, H. Hinrichsen, and S. Ruffo. On the microcanonical solution of a system of fully coupled particles. *Chaos Solitons & Fractals*, 13:393, 2002.

A. Carati. On the fractal dimension of orbits compatible with the tsallis statistics. *Physica A*, 387:1491–1503, 2008.

P. Bocchieri, A. Scotti, B. Bearzi, and A. Loinger. Anharmonic chain with lennard-jones interaction. *Phys. Rev. A*, 2:2013, 1970.

M. Casartelli, E. Diana, L. Galgani, and A. Scotti. Numerical computations on a stochastic parameter related to the kolmogorov entropy. *Phys. Rev. A*, 13:1921, 1976.

M. Pettini and M. Landolfi. Relaxation properties and ergodicity breaking in nonlinear hamiltonian dynamics. *Phys. Rev. A*, 41:768, 1990.

C. Cercignani, L. Galgani, and A. Scotti. Zero-point energy in classical non-linear mechanics. *Phys. Lett. A*, 38:403–404, 1972.

L. Galgani and A. Scotti. Planck–like distributions in classical nonlinear mechanics. *Phys. Rev. Letts.*, 28:1173, 1972.

P. P. Ewald. Die berechnung optischer und elektrostatischer gitterpotentiale. *Ann. der Phys.*, 64:253, 1921.

P. Gibbon and G. Sutmann. Long-range interactions in many-particle simulation. In J. Grotendorst, D. Marx, and A. Muramatsu, editors, *Quantum Simulation of Complex Many–Body Systems: from Theory to Algorithms*, volume 10 of *NIC Series*, pages 467–506. NIC-Directors, 2002.

A. Carati, F. Benfenati, A. Maiocchi, M. Zuin, and L. Galgani. Chaoticity threshold in magnetized plasmas: Numerical results in the weak coupling regime. *Chaos*, 24:013118, 2014.
[26] J. Grindlay. *An introduction to the phenomenological theory of ferroelectricity*. Pergamon Press, Oxford, 1970.

[27] A. Carati and L. Galgani. Classical microscopic theory of dispersion, emission and absorption of light in dielectrics. *Europ. Phys. Journal D*, 68:397, 2014.

[28] A. Carati, L. Galgani, F. Gangemi, and R. Gangemi. Relaxation times and ergodic properties in a realistic ionic-crystal model, and the modern form of the FPU problem. *Physica A*, 532:121911, 2019.

[29] E. Cristodoulidi, C. Tsallis, and T. Bountis. Fermi-Pasta-Ulam model with long range interactions. *EPL*, 108:40006, 2014.

[30] A. Lerose, A. Sanzeni, A. Carati, and L. Galgani. Classical microscopic theory of polaritons in ionic crystals. *Eur. Phys. J. D*, 68:35, 2014.

[31] A. Carati, L. Galgani, F. Gangemi, and R. Gangemi. Electronic trajectories in atomic physics: the chemical bond in the $\text{H}_2^+$ ion. *Chaos*, 30:063109, 2020.