Thermal fluctuations in a realistic ionic-crystal model

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Abstract

We investigate the thermal fluctuations of the ionic motions in a Born model of ionic crystals, namely, a model in which the electrons are eliminated, being replaced by suitable effective potentials among the ions. The model is studied in its classical version, computing the Newtonian trajectories of the ions. The general motivation is that, although being an essential ingredient within Green-Kubo linear response theory, thermal fluctuations apparently were not studied systematically by molecular dynamics methods, as was done instead for the approach to equilibrium in the Fermi-Pasta-Ulam problem. The time evolution of the fluctuations is studied in terms of the time-changes of the mode-energies of the system. The stages of the "regression" of the fluctuations are described, from a first stage of strong time-correlations up to a final decorrelation, and a comparison with the process of approach to equilibrium is performed. Finally, the dependence on specific energy is investigated.

keyword: relaxation times — ionic crystal model — long–range interactions.

1 Introduction

In the present paper we investigate a modified version of the classical Fermi-Pasta-Ulam problem, somehow an extension of it. Indeed, instead of studying how equilibrium is attained starting from a non-equilibrium state, we study thermal fluctuations, namely, how fluctuations evolve at equilibrium. Here, by equilibrium state we just mean a "generic" one in the sense of Khinchin [1], namely, one in which the mode-energies are Maxwell-Boltzmann

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distributed, with a mean equal to the specific energy ε of the system. Thus we leave aside any subtler question of ergodic type concerning the motions occurring at equilibrium, discussed for example in the papers [2, 3, 4, 5], and [6, 7, 8, 9].

"Thermal fluctuations" (see [10], chapter 12) are a constitutive ingredient of the Green-Kubo linear response theory [11, 12, 13] and of the previous Onsager theory [14, 15, 16], and thus were much investigated in connection with *macroscopic* quantities of physical interest. Recent works are for example [17, 18, 19] for thermal conductivity in variants of the FPU model, and [20, 21, 22] for infrared spectra in a realistic model of ionic crystals. Here, instead, the fluctuations are investigated for *microscopic* quantities, namely, the energies E_i of the normal modes, which constitute the basic, prototype microscopic quantities for all crystals, and are the ones considered in the FPU work.

However, the study is performed for the realistic FPU-like model of ionic crystals mentioned above, which, as shown by Fig. 1, could reproduce in a surprisingly good way the experimental infrared spectra, in terms of the Newtonian trajectories of the ions. There, the relevant quantity for the spectra was the electric polarisation $\mathbf{P}(t) = [\sum e_i \mathbf{x}_i(t)]/V$ (where e_i and $\mathbf{x}_i(t)$ are charges and position vectors of the ions, while V is the volume), and here our aim is to frame the thermal fluctuations of such a quantity within the fluctuations of the prototype microscopic quantities E_i.

In order to investigate the time-fluctuations of the mode energies E_i, we start considering their *time-changes* after a time-increment τ, as functions of τ, i.e., the functions

$$\Delta E_i(\tau) = E_i(\Phi^{t+\tau} z) - E_i(\Phi^t z) \ , \tag{1}$$

where $\Phi^t z$ denotes the evolved point at time t of an initial point z in phase space. These are random functions, since they depend on the initial datum z and on the current time t along an orbit, conceived as parameters over which they can be sampled (in the second case, for example, through a time-average).

It is clear that the energies E_i at times t and $t+\tau$, being equal for $\tau = 0$, are strongly correlated for τ small, whereas they are expected to become independent after a certain relaxation time. Now, such a relaxation time might be estimated by studying the time-auto correlations of the energies $E_i(t)$. However, one can also use a different quite elementary tool, of which we are unable to quote a previous reference.[1] By the way, such a tool has the merit of allowing one to compare in some natural way the process of "regression of the thermal fluctuations" to that of approach to equilibrium from a non equilibrium state, analogously to what was done by Onsager in connection with macroscopic quantities.

[1] Such a tool was proposed by the third author (A. C.) as the subject for an undergraduate thesis in Physics at the Milan University [23].

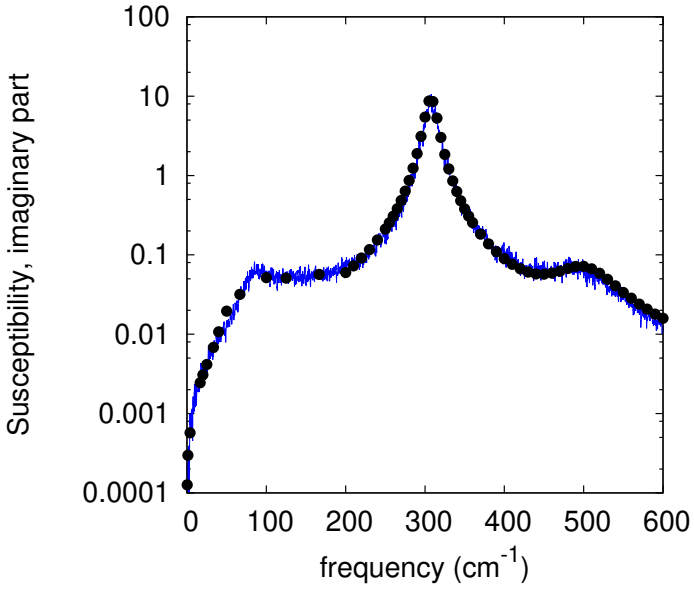

Figure 1: Imaginary part of susceptibility vs frequency at room temperature. Comparison between calculations (solid line) and experimental data (taken from E. Palik, *Handbook of optical constants of solids*, Academic Press, Amsterdam, 1998). This is Fig. 1 of [21]: see also Fig. 2 of that paper

The simple underlying idea for such a tool, is that the product $E_i(\Phi^{t+\tau}z)\cdot E_i(\Phi^t z)$, which is the key ingredient of a time-correlation, although not appearing in the expression (1) of the energy changes, appears however in its square. Then the parallel with the standard FPU approach is even stronger, if one considers the modulus (instead of the square) of the energy changes, i.e., one introduces the positive quantities

$$|\,\Delta E_i(\tau)\,|\ . \tag{2}$$

Indeed it is easily seen that, when relaxation did occur, i.e., when τ is large enough for the variables $E_i(\Phi^{t+\tau}z)$ to become independent of the variables $E_i(\Phi^t z)$, then the quantities (2) are Maxwell-Boltzmann distributed, with the same mean as the energies E_i, namely, as the specific energy ε of the system.[2] Thus one is reduced to study how the quantities $|\Delta E_i(\tau)|$ relax to a MB distribution with mean ε, in analogy to how, in the ordinary FPU

[2]Consider the paradigmatic case of two positive random variables x, y which are independent, and Maxwell-Boltzmann distributed with the same mean. Then for the proba-

problem, one studies the relaxation of the energies $E_i(t)$ themselves to a MB distribution, starting from a non equilibrium state.

In particular, the statistics of the quantities $|\Delta E_i(\tau)|$ can be studied in terms of the two simplest tools, i.e., mean and standard deviation. Thus, recalling that in the exponential distributions mean and standard deviation are equal, we will find that the relaxation occurs in three stages. In the first stage (presenting a strong time-correlation) the probability distribution of the random variables $|\Delta E_i(\tau)|$ is far from exponential; in the second stage the distribution is exponential, but with a mean smaller than the equilibrium one; eventually the mean relaxes to the equilibrium value, so that the Maxwell-Boltzmann distribution is attained. We also compare the results for the fluctuations with those for the approach to equilibrium. Finally we investigate the dependence on energy, which will be seen to open possibly interesting perspectives.

In section 2 is described the particular Born-type ionic-crystal model used, in section 3 the results are illustrated, and some further comments are reported in the conclusive section.

2 The Born model for ionic crystals

The model

We now recall what is the Born model that is commonly used for dealing with the motions of the ions in ionic crystals. Such crystals are considered to be the simplest, somehow the paradigm, of crystals (see for example the handbook by Seitz [24]), and among them Lithium Fluoride (LiF), which we study here, is the prototype, playing for crystals a role analogous to that of Hydrogen for atoms. The reason is that the electronic configurations of the ions (Li^+ and F^- in our case) have the same stability as that of noble gases (He and Ne respectively). Thus, as pointed out by Born since almost a century, to a very good approximation the ions can be dealt with as a system of point charges, in which the degrees of freedom of the electrons could be eliminated. Indeed, due to the large mass difference between ions and electrons, in the spirit of the adiabatic principle the screening effect due to the

bility $P(|x-y|>\Delta E)$ one has

$$P(|x-y|>\Delta E)=\beta^2\int_{|x-y|>\Delta E} e^{-\beta(x+y)}\mathrm{d}x\,\mathrm{d}y\ .$$

Performing the change of variables $X=x+y$, $Y=x-y$, the integral becomes

$$P(|Y|>\Delta E)=\beta^2\int_{\Delta E}^{+\infty} e^{-\beta X}\mathrm{d}X\int_{\Delta E}^{X}\mathrm{d}Y=e^{-\beta\Delta E}\int_0^{+\infty} ze^{-z}\mathrm{d}z=e^{-\beta\Delta E}\ ,$$

having defined $z\stackrel{\mathrm{def}}{=}\beta(X-\Delta E)$. This shows that $|x-y|$ too is MB distributed, with the same mean as x an y.

electrons can be taken into account through 1) the introduction of "effective charges" entering the Coulomb potentials, and 2) the introduction of a further "effective potential" acting among the ions. We want to emphasize that this "effective potential", either calculated in quantum mechanical terms or introduced in a phenomenological way, implicitly introduces Planck's constant in our model. This fact is responsible for the explicit showing up of a such a constant in one of the results for the Born model, dealt with as a classical dynamical system. In this paper, we use the phenomenological Buckingham potential which proved to produce the remarkably good infrared spectra shown in Figure 1, namely,

$$V_{ss'}(r) = a_{ss'}e^{-b_{ss'}r} + \frac{c_{ss'}}{r^6} \ , \tag{3}$$

where $s = 1, 2$ and $s' = 1, 2$ denote the ionic species. The values of the constants $a_{ss'}$, $b_{ss'}$ and $c_{ss'}$ and of the effective charges can be found in the work [21], Table I. It is a fact (shown by Figure 1) that, with such a choice for the parameters, the experimental infrared spectra were reproduced in an impressively good way. However, it is also true that in the procedure followed there remains an element of arbitrariness, which might particularly influence the dependence of the results on specific energy.[3]

So the model consists of an *even* number N of point charges (the pairs of ions) located inside a cubic "working cell", the side L of which determines the density of the system. In our computations we took a density, 2.713 g/cm^3, which is the experimental one extrapolated to zero temperature at atmospheric pressure. For example, for the case of 512 particles, which is the one considered in this paper, it corresponds to $L = 1.596$ nm. In order to simulate a macroscopic system, with the long-range character of the Coulomb forces somehow taken into account, the standard procedure is used of imposing periodic boundary conditions. Thus the Hamiltonian is given by

$$H = \sum_{j,s} \frac{p_{j,s}^2}{2m_s} + \sum_{\mathbf{n}\in\mathbf{Z}^3} \sum_{j,j',s,s'} \Big[V_{ss'}\big(|\mathbf{x}_{j,s} - \mathbf{x}_{j',s'} + \mathbf{n}L|\big) + \frac{e_{\text{eff}}^{(s)} e_{\text{eff}}^{(s')}}{|\mathbf{x}_{i,s} - \mathbf{x}_{j,s'} + \mathbf{n}L|} \Big] \ , \tag{4}$$

with the sum over j running from 1 to $N/2$. In fact, a question of principle remains open in the model, in connection with the long range character of the Coulomb interaction. Indeed, as it stands, the Hamiltonian function only has a formal character, since the series involving the Coulomb potential is

[3]The point is the following. The experimental spectra are measured at given temperatures T, while the theoretical ones are computed at given specific energies ε. The pragmatic choice we made was to optimize the parameters of the potential by reproducing the spectrum at $T = 300$ K through computations at the same value of specific energy, i.e., with $\varepsilon = T$ (in units of Boltzmann's constant). On the other hand, it is not clear which should be the relation between specific energy (as defined by us) and the experimental internal energy, so that the above mentioned choice is questionable. We plan to come back to this point in the future.

not absolutely convergent. In this connection we take the pragmatic attitude of completing the definition of the model by the usual prescription 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.[4]

The normal modes and the characteristic time of the system

Hamiltonian (4) turns out to admit a stable equilibrium configuration, which is a minimum of the potential energy, and is taken as defining the vanishing value of energy. The corresponding ionic positions $\mathbf{x}^0_{j,s}$ form a face-centered cubic lattice, which indeed is the structure of the LiF crystal.[5] For not too large specific energies (say, below 1060 K),[6] [7] the ions are found to oscillate about such equilibrium positions, thus reproducing the oscillating crystal structure of the solid. The normal modes related to the chosen minimum are then defined, each of them being determined by one of the six branches $\rho = 1, \ldots, 6$ of the dispersion relation, and by a suitable wave vector $\mathbf{k}$ of the reciprocal lattice. The normal-mode energies $E_{\mathbf{k},\rho}$ will be simply denoted by E_i. The corresponding angular frequencies ω_i are located in the infrared range, extending from about 100 to about 600 cm^{-1}, where the nonphysical lower limit is due to the smallness of the number N of ions amenable to computer simulations. The main peak in the spectrum ($\simeq 300$ cm^{-1}) corresponds to a frequency of $\simeq 10^{13}$ Hz, so that the characteristic time of the crystal is about 0.1 ps. The numerical computations were performed by a standard Verlet method, with a typical integration step of 2 fs (about one fiftieth of the characteristic period).

The initial data

As in our previous investigations concerned with the spectra, the initial data with a given energy E_{tot} were chosen in the following way (apart from one exception that will be mentioned later). One sets the ions in the positions corresponding to the chosen minimum of the potential energy, and gives to the single ions velocities extracted from a Maxwell-Boltzmann distribution, with a total kinetic energy equal to the desired total energy E_{tot}. In such a

[4] For the Ewald method, see the original German work [25], or the recent one [26], or our work [27].

[5] Obviously, there also exist the other configurations obtained by permutations of the ions of the same species.

[6] As in the previous papers, we measure the energies in Kelvin, so that for example a specific energy (per degree of freedom) $\varepsilon = E_{tot}/3N$ of 300 K means $\varepsilon/k_B = 300$ where k_B is the Boltzmann constant.

[7] The experimental melting temperature of the LiF crystal is 1118 K. Indeed, in our model (see [22]), for specific energies up to 1300 K the ions kept oscillating, whereas at specific energy 1450 K some ions began to jump from their site to another one.

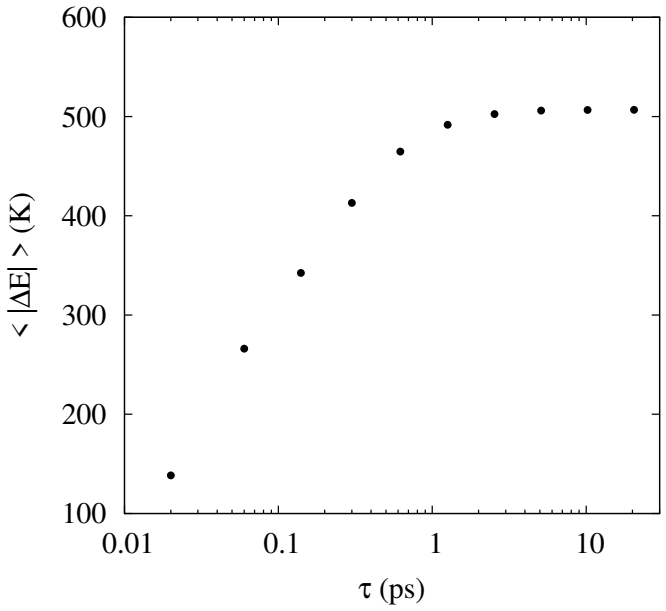

Figure 2: Mean value of the random variable $|\Delta E(\tau)|$ vs time-increment τ. Number of ions $N = 512$ (here and in the whole paper), specific energy $\varepsilon = 500$ K

way the normal-mode energies E_i too (in addition to the particles' velocities) turn out to present a MB distribution, albeit with phases far from random, since they are all equal. Then one waits a time of 10 ps, which we know (and will be seen here) to be amply sufficient to reach thermal equilibrium (i.e., for randomization of the phases too) at the considered specific energies.

It may be worth recalling that, due to the non linearity of the dynamical system, the harmonic energy (sum of the normal mode energies) presents a fluctuating character, its difference with respect to the constant total energy being typically of two percent. When speaking of the specific energy ε of the system, we will usually refer to the total energy (non linearity included) per degree of freedom. In one occasion, in connection with Figs. 7 and 8, we will make reference to the *harmonic* specific energy ε_{harm}, i.e., total *harmonic* energy per mode.

3 Results

Regression of the fluctuations

The object of our investigation is the random function $|\Delta E|(\tau)$, i.e., the modulus of a mode-energy change as a function of the time-increment τ.

For any given τ, the random variable $|\Delta E|$ depends on the mode i, on the initial datum z of a trajectory, and on the current (discretized) time t of a trajectory.[8] The first statistical tools we consider are mean and standard deviation, namely,

$$< |\Delta E| > \quad \text{and} \quad \sigma_{|\Delta E|} \ .$$

The corresponding averages are performed over all modes i, over all discretized times t of a trajectory (which amounts to performing a time average), and over the different trajectories (i.e., the initial data z). Ten different trajectories were taken, each of them lasting 2 ns. The time-increment τ was taken in the interval 0.02 to 30 ps (i.e., from 10 integration steps up to 300 characteristic times). All results of this paper were obtained for a number of ions $N = 512$

The result for the mean is reported in Fig. 2, for a specific energy $\varepsilon = 500$ K. Recall that $|\Delta E|$ starts from 0 at $\tau = 0$, and that its distribution is expected to relax to a Maxwell-Boltzmann one, i.e., to an exponential distribution with mean equal to the given specific energy ε. One sees that after 10 integration steps (one fifth of the characteristic time) the mean has already made a jump to one fifth of the final expected value. Then one has an apparent sequence of logarithmic growths, with a final relaxation to the expected value, which is essentially attained at a time of about 10 ps. One may notice that, as expected in virtue of non linearity, the final value $\simeq 506$, which refers to the normal-mode energies, does not exactly coincide with the specific energy 500 K if the system.

We now give more details on how the relaxation develops. This is illustrated in Fig. 3 and Fig. 4. The two panels of Fig. 3 report the evolution of both mean and standard deviation (left) and of their ratio (right). Recall that for an exponential distribution such two quantities are equal. Now, the left panel clearly shows that such two quantities are different for small values of τ, while becoming equal at larger times. The right panel then shows that equalization occurs at about 4 ps. Thus one concludes that there is an initial stage in which the distribution of $|\Delta E|$ is not exponential. A second stage with an exponential distribution then occurs for times larger than 4 ps. However, this is not yet the equilibrium stage since, as the left panel shows, mean and standard deviation are still increasing. Eventually, the necessary condition (exponential distribution with mean equal to the specific harmonic energy) for the full regression of the fluctuation is satisfied at about 10 ps. In fact such a Maxwell-Boltzmann distribution is actually attained, as exhibited by the histograms of $|\Delta E|$ reported below.

Two such histograms are given in Fig. 4, at times $\tau = 0.02$ ps (left) and $\tau = 20$ ps (right), corresponding to the non exponential stage and to the fully relaxed stage respectively. Each histogram was obtained by collecting, from all the available time steps of all runs, the modes whose $|\Delta E_i|$ belongs

[8] The values of the energies were collected every 0.02 ps, i.e., every ten integration steps

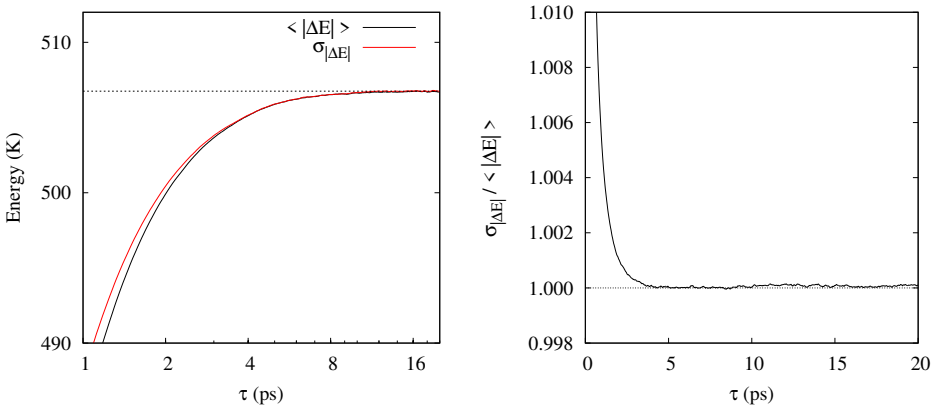

Figure 3: Color online. Mean (black) and variance (red) of $|\Delta E|$ (left panel) and their ratio (right), versus time increment τ. The straight line in the left panel corresponds to 506 K, which is the value of the specific harmonic energy.

to each bin, and reporting their number divided by the bin width, so that the integral is normalized to 1. The bin width, equal to the maximum observed value of $|\Delta E|$ divided by 1000, is approximately 10 K.

The left panel shows that at short times one already has an exponential distribution, but only in the tail, whereas one meets with a full exponential (with the correct equilibrium parameter) in the fully-relaxed stage (right panel). However, one could exhibit figures with fully exponential histograms already at times larger than 4 ps, with parameters which relax to the equilibrium value for increasing time.

The non fully exponential character of the distributions at short times plays a relevant physical role, inasmuch as it contributes to determining the correct form of physically significant fluctuations, as occurs for the fluctuations of polarization in the case of infrared spectra. Here we just limit ourselves to mention that, if one excludes the data with $|\Delta E| < 200$ K, the histogram is pretty well fitted by a modified Tsallis distribution (with three parameters, apart from the normalization factor C) [28], defined by

$$\rho(x) = \frac{C}{\left(1 - \frac{\lambda}{\mu} + \frac{\lambda}{\mu} e^{(q-1)\mu x}\right)^{\frac{1}{q-1}}} \ .$$

Instead, the part with $|\Delta E| > 1500$ K is well reproduced by an exponential (although not yet with the equilibrium mean).

In the particular case of the the left panel, the fitting with the modified Tsallis distribution exhibited corresponds to $q = 1.56, 1/\lambda = 87.1$ K, and $1/\mu = 215$ K. Instead, the fitting with the exponential distribution for the

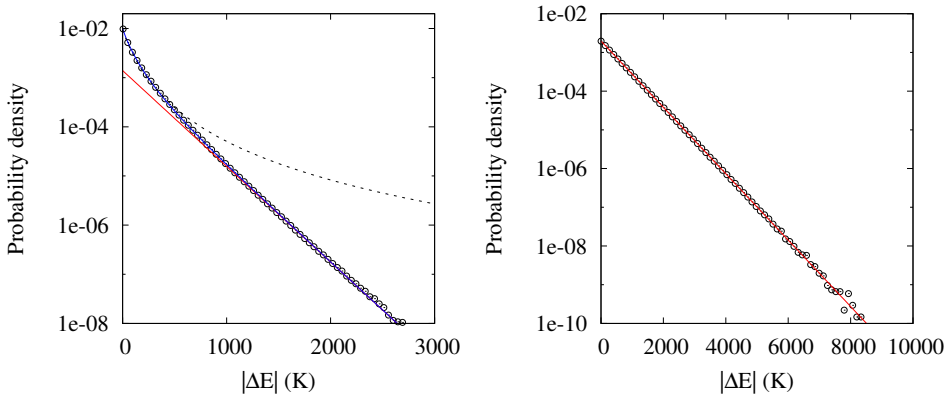

Figure 4: Color online. Histograms of the random variable $|\Delta E|$ (circles). *Left panel*: $\tau = 0.02$ ps (non exponential stage), *Right panel*: $\tau = 20$ ps (full relaxation). The fits are as follows. *Left panel*: blue line, best fit with the modified Tsallis distribution function (see text), restricted to data above 200 K; red line, best fit with exponential distribution, for data restricted above 1500 K. *Right panel*: best fit with exponential distribution over all data (red line).

tail corresponds to a mean value of 223 K. One is naturally led to conjecture that one in general meets with a crossover between exponential and modified Tsallis distribution, which for increasing time shifts to the left, leading to a full exponential. See ref. [29], ref. [30] Figure 8, and ref. [31] Figure 2.

Comparison with the process of approach to equilibrium

We now compare the process of "regression" of the thermal fluctuations, just illustrated, to the process of approach of the mode energies E_i to equilibrium, starting from a non equilibrium state, which is the process studied in the standard FPU problem. We consider two types of initial conditions, illustrating the corresponding results in the two next figures, Fig. 5 and Fig. 6.

The first case is the analogue of that considered in the very FPU paper, in which only a small fraction of modes, with small frequencies, were initially excited. This is indeed the case in which, in the words attributed by Ulam to Fermi (see the preface to the reproduction [32] of the paper in the Collected Papers of Fermi, vol. 2), the authors were faced with an apparent "little discovery", inasmuch as the system appeared not to attain a state of energy equipartition, and thus not to attain a Maxwell–Boltzmann distribution. As is well known, about fifty years of studies were needed to ascertain that instead, after a sufficiently long time the equilibrium Maxwell–Boltzmann

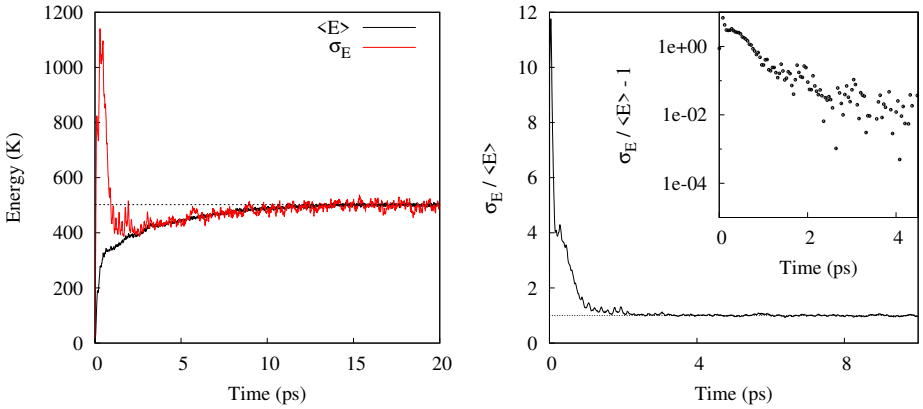

Figure 5: Approach to equilibrium from an initial condition of FPU type, with only the 12 lowest-frequency modes initially excited. The evolution of the initially unexcited modes only is illustrated, through both mean $< E >$ and standard deviation σ_E (left panel), and through their ratio (right panel). The same three stages as for the fluctuations are observed, with characteristic times of the same order of magnitude.

distribution of the mode energies is eventually attained.

So we consider an initial condition in which the only modes excited are the ones having the same frequency, the smaller one present in the system ($\omega = 95.8\ \mathrm{cm}^{-1}$), which are in number of 12 (over a total of $3\times512-3 = 1533$ modes). The total energy, corresponding to a specific energy $\varepsilon = 500$ K (the same one considered here for the thermal fluctuations), was equally distributed among them, and the phases were taken at random. Such a kind of FPU initial condition is particularly suited for a close comparison of the evolution of the mode-energies $E_i(t)$ with the evolution of their time-changes $|\Delta E_i|\,(\tau)$. Indeed, in the present case we study the evolution of the fluctuations *only for the modes not initially excited*. Thus in both cases one meets with quantities that start initially form zero, and are expected to attain a Maxwell–Boltzmann distribution.

In fact, as in the standard FPU problem, here too we find that the Maxwell–Boltzmann equilibrium state is attained, and actually through an evolution essentially analogous to that of the thermal fluctuations. This is illustrated in Fig. 5. The left panel shows that one initially meets with a non exponential distribution for the mode energies E_i, followed by an exponential distribution at a specific energy ε lower than the equilibrium one, until the Maxwell–Boltzmann distribution with the equilibrium mean of $\simeq 500$ K is eventually attained. Moreover, the times involved are of the same order of magnitude as for the thermal fluctuations, since the first and the second stages terminate at about 2 ps and 15 ps respectively.

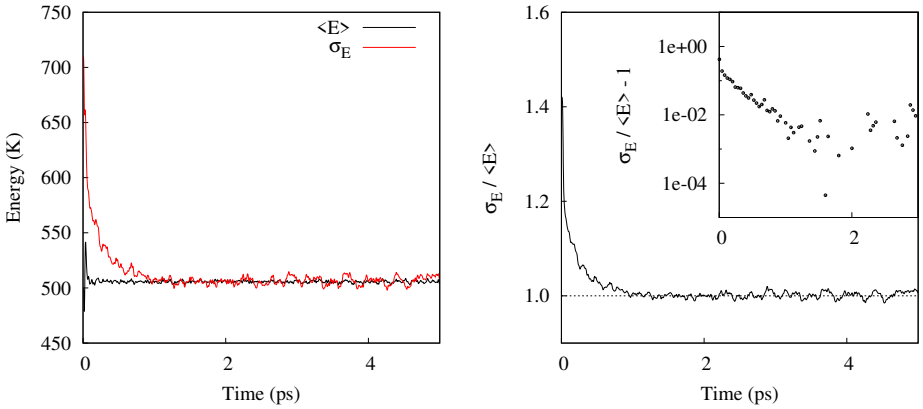

Figure 6: Same as Fig. 5, but for an initial condition with all atoms in equilibrium position, and their velocities generated according to a Maxwell distribution. In this case the averages are performed over all modes.

A further interesting remark was pointed out to us by A. Ponno. Namely, that an analogue of the second stage just described for the regression of fluctuations was essentially observed also in the standard FPU problem with FPU-like initial conditions. Indeed, after a first stage in which one observed the formation of a meta stable smooth packet about the initially excited modes, with the higher-frequency modes still having essentially no energy, the approach to the final equilibrium phase occurred with an essential equipartition among the higher modes (which is compatible with an exponential distribution), at a specific energy increasing with time. See for example [33].

All these facts seem to confirm the general connection between irreversible processes and spontaneous fluctuations at equilibrium, that was proposed by Onsager and Machlup in the first lines of their work [16]. Namely, the " *postulate that the decay of a system from a non equilibrium state produced by a spontaneous fluctuation obeys, on the average, the (empirical) law for the decay from the same state back from equilibrium, when it is produced by a constraint which is then suddenly removed*".

We now come to the process of approach to equilibrium for a different type of initial condition, actually the same one we adopted in our previous investigations on the infrared spectra, and also in the investigations on thermal fluctuations reported above. Namely, an initial condition with the particles in their equilibrium positions (which we take as defining the zero value of energy) and their velocities extracted form a Maxwell distribution at a given kinetic energy, which defines the total energy E_{tot} of the system.

The results, still in terms of the evolution of mean and standard deviation of the mode-energies, are reported in Fig. 6. One sees that again

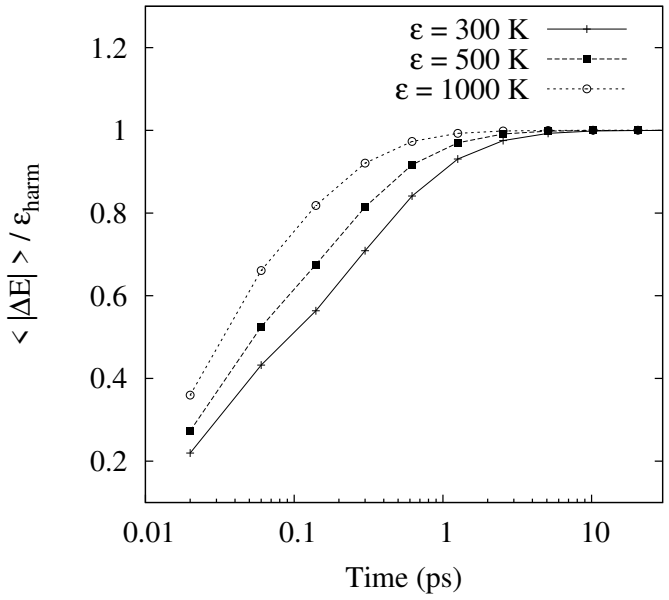

Figure 7: Mean $< |\Delta E| > /\varepsilon_{harm}$ of the normalized energy-change versus time-increment τ, at three different specific energies $\varepsilon = 300, 500, 1000$ K.

one has an initial non exponential stage. However, now there is no third stage at all since, when mean and standard deviation become equal, they already have the equilibrium value $\varepsilon = 500$. This is due to the special initial condition chosen for the particles, that induces for the mode-energies a Maxwell-Boltzmann distribution with the same mean ε. The phases however are not random, since they are actually all equal, and some time is then required for a full equilibrium to be established.

Dependence on specific energy: a challenge for the Born-like models

We finally come back to the main result on the regression of the fluctuations, and investigate its dependence on specific energy ε. To this end we complement the result at $\varepsilon = 500$ K, illustrated in Fig. 2 through the curve $< |\Delta E| >$ versus τ, and now consider also the cases at specific energies 300 and 1000 K.

The results for the three cases are collected in Fig. 7. In order to compare such different cases it is clearly expedient to normalize energies in such a way that they have a common range. This could be obtained by reporting $< |\Delta E| > /\varepsilon$. However, a more exact comparison (to which we are interested here) is obtained by reporting the data normalized in terms of the harmonic

specific energy ε_{harm}, which is just defined by $N\varepsilon_{harm} = \sum E_i$. The figure clearly exhibits a well expected property, namely, that the regression process slows down for decreasing energy.

It is then quite natural to try to determine some analytic features of the energy-dependence illustrated in the figure. Clearly this is a problem concerning specifically ionic-crystal models, and thus going somehow beyond the questions of a general character previously discussed. To this end we performed a preliminary investigation which, as will be seen, led to results having an interlocutory character. We decided however to give here a short account of them, since they appear to open some interesting perspectives.

We proceeded in the following way. A preliminary inspection gives indications that the relaxation time τ_{relax}, defined for example as the time at which the second stage begins, might be inversely proportional to the specific energy, say as $1/\varepsilon_{harm}$, so that the product $\tau_{relax} \cdot \varepsilon_{harm}$, which is an action, would be a constant, independent of ε_{harm}. Moreover, the value of such an action turns out to be of the order of magnitude of Planck's constant h, which might have been expected, since Planck's constant is implicitly involved in our model, through the effective Born-type potential. So we produced a new figure, with the time increment τ too rescaled, as $\tau\,\varepsilon_{harm}/h$. This led to Fig. 8, left panel. The figure shows that such a rescaling works not so badly for $\tau\,\varepsilon_{harm}/h$ larger than about 2. Instead, the dependence of τ on ε_{harm} seems to follow a different law for shorter times, when the distribution is not yet exponential. To understand what occurs for short times is an open problem.

In any case, the rescaling observed for large times allows one to conclude that any relaxation time τ_{relax} defined with reference to such a domain of the curve satisfies a relation of the form

$$\tau_{relax} \cdot \varepsilon_{harm} \sim h \ , \quad \text{or equivalently} \quad \tau_{relax} \cdot \sigma_E \sim h \ , \tag{5}$$

the latter of which (obtained using $\varepsilon_{harm} = \sigma_E$) has the formal aspect of the Heisenberg time-energy uncertainty relation. For example, if the relaxation time is defined as that for which one has $|\Delta E|/\varepsilon_{harm} = 0.75$, then the proportionality constant is about 2.

Now, this might be a completely fortuitous fact. Or, perhaps, it might have a physical significance. The latter possibility is conceivable, after all, since the present Born-like model dealing with Newtonian trajectories of the ions, already proved to work pretty well in such a typically quantum domain as that of infrared spectra. Here, the question at hand is the reliability of the rescaling introduced above, with its linear dependence on specific energy, which ultimately is responsible for the Heisenberg-like relation (5). Indeed, the possible physical significance of such a relation could be taken into serious consideration if the linear rescaling would lead, for the three curves in question, to a superposition much neater than exhibited in the left panel. That a neater superposition is altogether possible through a

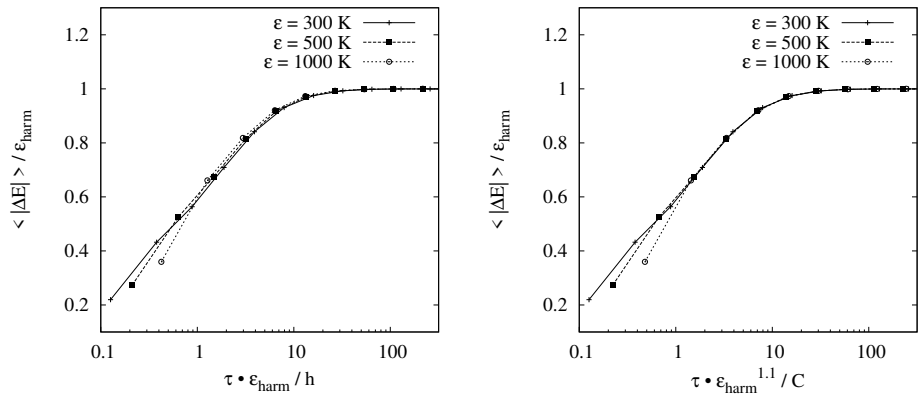

Figure 8: Same as Fig. 7 with τ rescaled as $\tau \cdot \varepsilon_{harm}/h$ (left panel), and as $\tau \cdot \varepsilon_{harm}^{1.1}/C$ with $C = 0.046$ erg$^{0.1} \cdot h$ (right panel), where h is Planck's constant

suitable *ad hoc* rescaling is clearly exhibited by the right panel, where, just to give an example, a rescaling with specific energy raised to a power 1.1 was performed. Now, as mentioned in passing when describing the model, we are aware that the choice of the parameters entering the effective potential contains an element of arbitrariness, which moreover might have an impact on the dependence of the results on specific energy.

So, the preliminary results just reported for the dependence of the regression of thermal fluctuations on specific energy, seem to pose a challenge for future research on ionic crystals, namely, to ascertain whether the significance of the Heisenberg-like relation (5) can be confirmed. This would be the case if a consistent choice of the parameters of the effective potential turned out to produce by itself, for large times, an actually linear rescaling of time with respect to specific energy.

4 Conclusions

So, by considering a particular ionic-crystal model, we have shown how the classical Fermi-Pasta-Ulam problem of the approach to equilibrium can be investigated in an extended form, in connection with evolution and regression of thermal fluctuations. In particular, we reported results confirming the general property postulated by Onsager and Machlup [16], about the analogy between approach to equilibrium from a non equilibrium state and regression of a spontaneous fluctuation.

If the expectations raised by the "little discovery" of the original FPU work (lack of approach to energy equipartition) may have been frustrated by the realisation that equilibrium is attained starting from a non equilibrium

state, we point out that nevertheless thermal fluctuations (so important for physics in the frame of linear response theory) are still there, just when equilibrium was attained. If such a fact was not taken into consideration by Fermi, Pasta and Ulam, since it was emphasized by Kubo and Green after the FPU work (and after Fermi's death), it is quite possible that the original key idea underlying the FPU problem (i.e., to disclose unexploited potentialities of classical statistical mechanics) may remain still alive today, in connection with thermal fluctuations. A significant example seems to be that of ionic crystals, whose experimental infrared spectra were reproduced in a surprisingly good way (Fig. 1), by just applying a naive classical version of Green-Kubo's theory [34], in terms of the Newtonian trajectories of the ions in the Born model.

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