ON THE SPECIFIC HEAT OF FERMI–PASTA–ULAM SYSTEMS

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ABSTRACT

The specific heat of Fermi Pasta Ulam systems was up to now estimated through the energy fluctuations of a suitable subsystem, and opposite answers were apparently provided concerning its possible vanishing for vanishing temperatures. In the present paper a more "realistic" numerical implementation of the specific heat measurement is discussed, which mimics the interaction of the FPU system with a calorimeter. This is obtained through a model inspired by one already discussed by Kelvin and Poincaré in connection with the foundations of statistical thermodynamics. It is found that there exists a "freezing" critical temperature below which the relaxation times for equilibrium between FPU system and calorimeter become relevant, so that the system presents aging and hysteresis features very similar to those familiar in spin glasses theory. In particular, in the frame of such a point of view involving finite long times, the specific heat is found to vanish for vanishing temperatures.

Key Words: Fermi–Pasta–Ulam; specific heat; statistical thermodynamics.

1. Introduction It is very well known that systems of Fermi–Pasta–Ulam type present an energy threshold $E_{\rm eq}$ for equipartition among the normal modes: one looks at the energy spectrum, namely the distribution of energy (in time average) among the normal modes as a function of frequency, and after a sufficiently long time one finds that for $E > E_{\rm eq}$ the spectrum is flat (equipartition) irrespective of the initial datum, while it depends on the initial datum for any energy $E < E_c$ (see for example [1], [2], [3], [4], [5]). Moreover, the critical energy $E_{\rm eq}$ appears to be extensive, i.e. proportional to the number N of degrees of freedom, so that there is defined a specific critical energy $u_{\rm eq} = E_{\rm eq}/N$ which should not vanish in the thermodynamic limit ($N \to \infty$, $E \to \infty$, with specific energy $u = E/N$ constant; see for example [6]–[7]).

So one is confronted with the important problem of deciding whether the specific energy threshold $u_{\rm eq}$ is relevant or not for statistical thermodynamics, typically for the specific heat. Indeed it is almost obvious that the specific heat should have the "classical" Dulong–Petit value in the equipartition regime, i.e. for $u > u_{\rm eq}$, and the open problem is to understand what happens for lower energies, where the system seems not to present a thermodynamic behaviour almost by definition. Indeed the zeroth law itself, which requires that equilibrium be attained at least for "long" finite times, independently of the details of the initial data, is thereby not satisfied, and therefore it is not at all obvious how the relevant thermodynamic functions should be defined..

This problem was already addressed in two papers, where opposite answers were apparently given: according to [8] the specific heat would be insensitive to the equipartition threshold, i.e. would essentially keep the constant "classical" Dulong–Petit value even at low energies, while it would tend to zero for vanishing temperatures according to [9]. The reason for the difference of the results is not completely clear. Apparently, in the two papers different implementations (to be recalled below) are given for the specific heat measurement, both based on the familiar formula relating specific heat to energy fluctuations. In the present paper we produce a concrete implementation which in our opinion more faithfully corresponds to an actual laboratory measurement. The result we find is in agreement with [9], inasmuch as we confirm that in systems of FPU type the specific heat vanishes at low temperatures, although different estimates for the temperatures are in general given. But the main contribution of the present paper consists perhaps in pointing out the general occurrence, below threshold, of metastable or aging situations, bearing a strong analogy to the phenomenology of spin glasses theory. And in fact the figures reported below to illustrate our results bear a strong resemblance to some figures drawn by Parisi, during a conference on spin glasses [10], which had some influence on our work.

Let us recall which are the implementations of the specific heat measurements proposed in the two quoted papers. In both of them one starts out considering at first an isolated FPU system, the temperature of which is defined through the initial data, in two different but essentially equivalent ways: namely, in [8] (up to multiplication by Boltzmann's constant k_B) as twice the average (over time and over the particles) kinetic energy of each particle, and in [9] as the temperature entering a Maxwell–Boltzmann distribution used in extracting the initial data. The essential equivalence of such two definitions of temperature is due to the well known fact that the kinetic energy of each particle, being a local quantity [11], behaves for not too small systems as if the system were ergodic [12], so that its time average coincides, for large enough systems and for generic initial data, with the canonical temperature. Thus, recalling that the harmonic part of the potential energy too is a local quantity, it is clear that in both cases the system's mechanical energy (in the harmonic approximation) turns out to be proportional to temperature itself, defined in any of the two said ways, and consequently the specific heat of the global isolated system is constant, i.e. insensitive to the energy threshold $E_{\rm eq}$.

In consideration of this, having in mind the fundamental formula of classical statistical mechanics relating the specific heat to the energy fluctuations of a small subsystem, in [8] the idea was introduced of addressing the attention to the energy of a small subsystem of the global isolated FPU system: in fact the subsytem was taken to be a spatially localized one, namely a group of nearby particles (actually, averages over several such groups were performed), and the specific heat was then found to be essentially constant, even below the equipartition threshold. The same idea was followed in [9], with however the difference that the subsystem was not a spatially localized one, being instead constituted by a group of normal modes of the global system with nearby frequencies (actually, with exactly equal frequencies, in virtue of a particular characteristic of the special two–dimensional model there considered, following the paper [13]), and the specific heat was then found to tend to zero for decreasing temperatures.

Now, it might not be completely clear a priori which choice for the subsystem should be preferred: are the energies of the particles or the energies of the modes the physical relevant quantities for the specific heat? Should the subsystem be spatially localized or not? Or should even the result be independent of the choice of the subsystem? Just in order to point out how the problem is far from trivial, it may be of interest to recall that also in the celebrated paper [14] known under the name of *Dreimänner–Arbeit*, a similar problem of energy fluctuations for a subsystem was investigated; the complete system was a linear string, and the choice made for the subsystem (probably following Lorentz [15]) was somehow intermediate between the two ones mentioned above, because the subsystem was a subset of normal modes (of nearby frequencies) of a spatially localized portion of the string. A reconsideration of the theoretical basis for the formula relating specific heat and energy fluctuations for energies lower that the equipartition threshold would then be in order, and we hope to come back to this interesting problem in the future.

In any case, a discussion of this point led us to the main idea underlying the present work, namely to cope with the problems of choice for the subsystem in a very drastic and quite natural way, by making recourse for the definitions of temperature and of specific heat to the ones given in the handbooks of calorimetry, which involve the interaction of the system with an external calorimetric substance. Now, the simplest model for a calorimetric substance seems to be that of an ideal gas, namely [16] a system of point particles which have no mutual interaction, but interact instead through a realistic potential with the boundary particles of the solid (the FPU system). An andvantage of this model is that the calorimetric substance then acts at the same time as a thermometer; indeed one lets the compound system (solid+ gas) go to equilibrium (or at least to a practical one), and the temperature T of the FPU system is just defined as coinciding with that of the ideal gas, which in turn is defined in the familiar way as twice the average kinetic energy per particle of the gas (here and in the following, temperature units are used such that $k_B = 1$, where

k_B is Boltzmann's constant). For what concerns the internal energy U of the FPU system, to start out we just define it (as usual, but not at all obvious, as will be discussed below) as coinciding with its (average) mechanical energy E, with no need of distinguishing between energy of particles and energy of modes. The specific heat of the FPU system is then in principle defined in agreement with the classical calorimetric use (see the Appendix), namely as the rate of growth of energy with respect to temperature, i.e. as $C_V = \frac{\partial E}{\partial T}$. But the situation is in fact rather complicated, because one meets with a question of principle, concerning the times actually required to reach equilibrium. Indeed in order to estimate $\frac{\partial E}{\partial T}$ one should look at the global energy ΔE which the FPU system actually exchanges with the gas, if the gas temperature is initially altered by an amount ΔT. The problem is then how much time is one allowed to wait, so that one has in general a dependence of the results on the "measuring time" (see also [17]). This crucial point is at the heart of the present work, and will be discussed in detail below. Another minor problem is related to the fact that, in general, a contribution to ΔE also comes from the mechanical work performed by the gas on the boundary FPU particles, but for simplicity's sake we did limit ourselves to situations in which such an external mechanical work is negligible, so that the exchanged energy ΔE can in practice be identified with the exchanged heat ΔQ.

The measurement process sketched above is implemented in the present paper through a one–dimensional model consisting of two adjacent subsystems, namely an FPU–system (i.e. the solid) and an ideal gas (i.e. the calorimetric substance), which we choose to have the same number N of moving particles. The FPU system (the solid) consists of $N+1$ particles $P_0, \cdots, P_N$ on a line interacting through nonlinear springs, with P_0 fixed at say the origin, while the last one P_N (say to the right) is free to move on the line; the N gas particles move to the right of P_N with no mutual interaction among them, up to a fixed wall (say a distance L from the origin), from which they are reflected, while they suffer smooth collisions with the boundary FPU particle P_N; more details are given below. By the way, it may be of interest to point out that this model seems to be a generalization of a model with three degrees of freedom introduced by Kelvin [18], and discussed as a dynamical system by Poincaré [19] (see also [20]), just in connection with the equipartition problem and the foundations of classical statistical mechanics, and which apparently is not usually mentioned in the scientific community (with the exception of [21], where however a critical examination is still lacking). We hope to have the opportunity to come back to such classical papers on another occasion.

The most impressive result we find is the existence of a "freezing energy" threshold E_f (or equivalently of a "freezing temperature" T_f), in principle independent of the equipartition threshold E_{eq}, with the property that the specific heat has the "classical" Dulong–Petit value for larger temperatures, and a lower value for lower temperatures, decreasing then to zero for vanishing temperatures. But actually below T_f the situation turns out to be much more complicated, particularly because hysteresis phenomena occur, and in general the results appear to depend very much on the observation time. Our opinion is that here one should openly take a position, where the dependence of the results on the observation time is accepted as a physically meaningful fact, as is usual for example in spin glasses theory. In our case, there appears to exist a relaxation time τ characterizing the interaction of the system with the calorimeter, presenting a huge jump at the freezing temperature T_f, below which metastable or aging phenomena are observed. In physically meaningful cases it turns out that the two thresholds $E_{\rm eq}$ and E_f are of comparable orders of magnitude, but they are in principle independent.

In fact, the occurrence of jumps in the characteristic relaxation times are quite familiar in the framework of the adiabatic invariants theory, where it is shown (both by the method of Nekhoroshev [22,23] and that of Landau–Teller [24] (see also [25]–[26])) that such times increase exponentially fast as certain parameters are varied; a typical example is that of the energy exchanges between translational and vibrational degrees of freedom in diatomic molecules, where the parameters to be varied are the translational energy and the vibrational frequency. One has thus a strong analogy with the present problem, where the centers of masses of the diatomic molecules correspond to the gas particles on one side, while the oscillations of the diatomic molecules correspond to the FPU system on the other side. Such an analogy suggests that also for a perfectly harmonic solid, where no reference to any equipartition threshold $E_{\rm eq}$ can be made at all, there should exist a freezing energy threshold E_f (or a freezing temperature threshold T_f), below which the energy exchanges with the gas are essentially frozen; the specific heat would then correspondingly be lowered, tending to zero exponentially for vanishing temperatures. So one would be tempted to extend to the present case the analytical estimates known for the diatomic molecules; but we prefer to refrain from this at the moment, leaving this suggestion for possible future work, and we limit ourselves here to a purely phenomenological numerical approach. Thus the two processes, that of internal equipartition (characterized by $E_{\rm eq}$) due to the internal nonlinearity in the FPU system, and that of equipartition with the external gas (characterized by T_f), should in principle be independent phenomena, both influencing the specific heat. In this paper we limit ourselves to the consideration of cases in which both such processes are present, i.e. the normal mode energies are influenced both by the interaction with the gas and by the internal nonlinearities in the FPU system, both interactions being due to "realistic" potentials.

In conclusion, we study numerically the one–dimensional model described above, where the nearest–neighbour interaction potential in the FPU system as a function of distance r has the familiar form

$$V_1(r) = \frac{1}{2}\kappa r^2 + \frac{1}{3}\alpha r^3 \ , \tag{1}$$

with positive parameters κ and α, while the interaction potential between the boundary particle P_N of the solid and the gas molecules is given by

$$V_2(r) = \epsilon\, \frac{e^{-2(r/\sigma)^2}}{r/\sigma} \ , \tag{2}$$

with positive parameters ϵ and σ, constituting the characteristic energy and length of the system. We take units in which $\epsilon = \sigma = m = 1$, where m denotes the mass of the particles (assumed to be the same for the gas and the solid). However, in order to mimic "realistic" situations, for the parameters κ and α entering the FPU potential V_1 we take rather large values, precisely $\kappa = 400$ and $\alpha = 3742$, which in particular imply that the FPU springs are not at all "soft". Indeed the requirement we impose is that the interaction potential V_1 coincide with a third order expansion about the minimum of a Lennard–Jones potential

$$V(r) = 4\epsilon\Big[(\sigma/r)^{12} - (\sigma/r)^6\Big] \tag{3}$$

having the same parameters ϵ and σ as the "external" potential V_2.

The final Hamiltonian is thus

$$H = \sum_{i=1}^{N}\left[\frac{p_i^2}{2} + V_1(x_{i-1} - x_i) + \frac{\pi_i^2}{2} + V_2(y_i - x_N)\right] \ ,$$

where x_i, p_i denote position and momentum of the i–th particle of the solid, y_i, π_i position and momentum of the i–th particle of the gas; these all are real variables with the constraints $x_0 = 0$, $x_N < y_i < L$, $(i = 1, \cdots, N)$, where $L > 0$ denotes the position of the wall enclosing the gas, with which reflecting collisions of the gas molecules occur.

For future reference, we recall that in the FPU system there is defined a characteristic time $t_{\rm min}$, namely

$$t_{\rm min} = 2\pi/\omega \ ,$$

where ω is the maximum among the frequencies ω_k of the linearized system,

$$\omega_k = \omega\,\sin(\frac{k}{N}\frac{\pi}{2}) \ , \quad k = 1, \cdots, N \ , \qquad \omega = 2\sqrt{\kappa}\,\frac{1}{\sigma}\sqrt{\frac{\epsilon}{m}} \ . \tag{4}$$

2. Results. To start out we determined, in the familiar way recalled above, the equipartition threshold $E_{\rm eq}$ in the isolated FPU system with nearest neighbour interaction potential (1). By integrating the equations of motion up to a fixed time $t^* = 10^7 t_{\rm min}$ for $N = 200$ particles, we found $u_{\rm eq} \equiv E_{\rm eq}/N \simeq 5 \cdot 10^{-3}\epsilon$. This is of the order of 1/10 the first estimate ever produced, namely [1] $u_{\rm eq} \simeq \epsilon/15$, which was found for an FPU system with Lennard–Jones interaction potential.

Then we investigated our model, with the FPU system in contact with an ideal–gas calorimeter, implemented as described above, with typically $N = 200$. The "macroscopic" state of the system was described by a pair (T, u) where T is the temperature (i.e. twice the specific energy of the gas) and u the solid's (i.e. the FPU–system's) specific energy. The initial data too were characterized by a pair (T, u), because for the gas particles the positions were just taken randomly from a uniform distribution in the interval (x_N, L), while the velocities were taken randomly from a gaussian distribution with zero mean and suitable standard deviation; instead, the initial data for the FPU particles were taken in such a way that the normal modes had all the same energy u. By the way, in the considered range of energies the anharmonic contribution to the FPU system energy was usually negligible.

First of all we checked that above the equipartition threshold everything goes as expected in classical statistical mechanics. Indeed, by taking initial data T_0 and u_0 greater than $u_{\rm eq}$, we found that after rather short times there was equipartition between gas and solid, namely one had $u \simeq T$, where $u = E/N$, E being the (time–averaged) harmonic energy of the FPU system and T twice the (time–averaged) specific energy in the gas. Thus it is consistent to interpret u as the thermodynamic internal energy per particle of the FPU system and T as its temperature. Consequently, for the specific heat per particle $c_V = \frac{\partial u}{\partial T}$ of the FPU system we found above the equipartition threshold the "classical" Dulong–Petit value $c_V = 1$ (namely twice the specific heat c_V^{gas} of the gas, which in the used units has the value $c_V^{gas} = 1/2$).

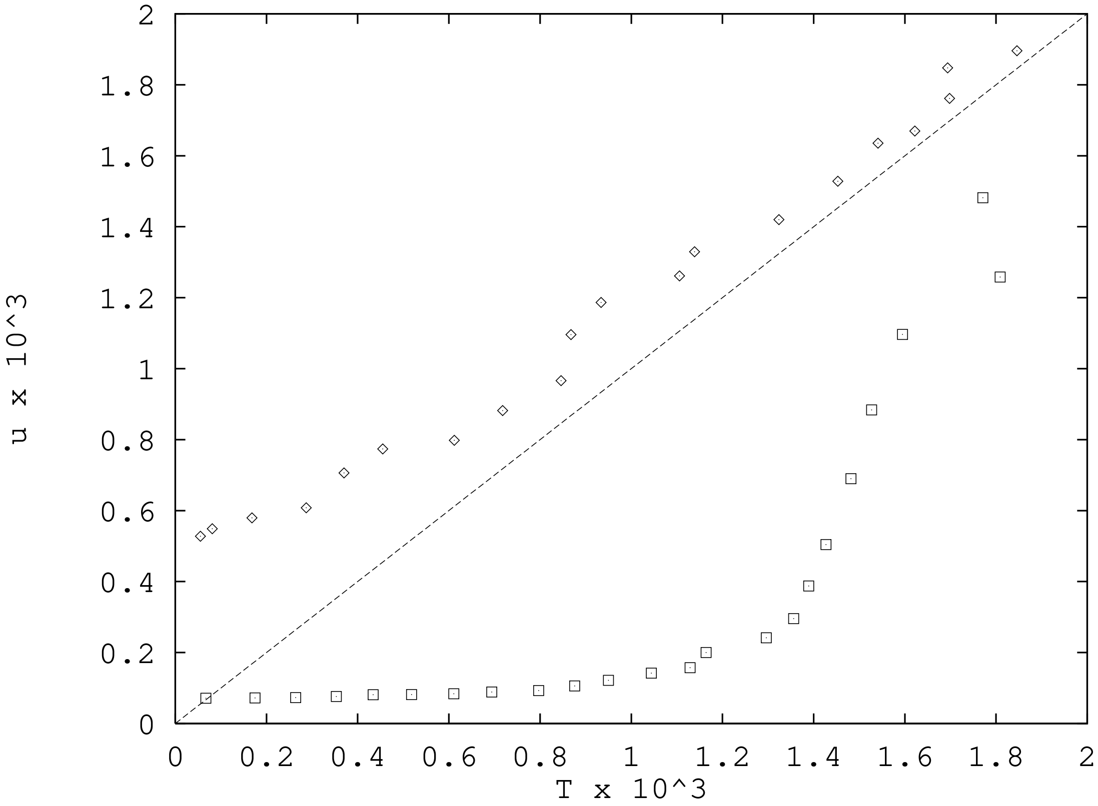

Fig. 1. *The energy of the FPU system versus temperature T (i.e twice the gas energy) for a cooling process starting from equipartition (upper curve) and for a heating process starting from the origin (lower curve).*

Our main purpose is then to extend the curve of u versus T to a range below $u_{\rm eq}$, where metastable phenomena are expected, with a corresponding dependence of the results on the observation times. We organized the computations as follows. First of all, the observations were made up to a fixed observation time t^*, to be considered as a parameter. We start with the complete system (gas + solid) in a given initial state characterized by data $(\tilde{T}_0, \tilde{u}_0)$ in the sense described above, and let the complete system evolve up to time t^*, registering the "final" or "equilibrium" state (T_1, u_1). Then we take new "initial" data

$(\tilde{T}_1, \tilde{u}_1) = (T_1 + \Delta T, u_1)$ with a given ΔT (i.e. we change the gas temperature, while keeping for the solid's specific energy the previous "final" value), and let again the complete system relax up to the observation time t^*, registering the final values (T_2, u_2); the procedure is then iterated, so building up a sequence of "final" states (T_i, u_i), $i = 1, ..., n$. One has thus an ideal curve $u = u(T)$ interpolating such points (T_i, u_i) in the (T, u) plane, which gives the putative curve expressing the "thermodynamic internal energy" u as a function of temperature T for the FPU system; the derivative $c_V(T) = \frac{\partial u}{\partial T}(T)$ then gives the corresponding specific heat. More precisely, borrowing the terminology from spin glasses phenomenology [27], we say that the curve and the specific heat thus found correspond in fact to a definite *process*, characterized by the parameters t^*, T_0, u_0 and ΔT. In the case $\Delta T < 0$ one speaks of a uniform *cooling process*, and the quantity $|\Delta T|/t^*$ is called the *cooling rate*; *heating processes* and *heating rates* are analogously defined.

The main results concerning the region below $u_{\rm eq}$ are reported in Fig. 1, where two "curves" u versus T are given, for $N = 200$, $t^* = 6 \cdot 10^6 t_{\rm min}$ and $\big|\Delta T\big| = 10^{-4}\epsilon$ or $\big|\Delta T\big| = 1.35 \cdot 10^{-4}\epsilon$ respectively. The upper curve refers to a uniform cooling process starting from the equipartition curve $u = T$, while the lower one corresponds to a uniform heating process starting from near the origin ($T_0 = 0, u_0 = 0$). The most relevant features seem to be that:

1) the two curves, instead of essentially coinciding with the equipartition curve $u = T$ as for high temperatures, are here ostensively distinct, so that one is in presence of a kind of hysteresis phenomenon; notice in particular that on the upper (cooling) curve there exists a nonvanishing "residual" energy $E_0 = E(0)$, with $E_0 \simeq 0.5 \cdot 10^{-3}\, N\, \epsilon$. Thus we can say that in our FPU system there exists an analogue of what in spin glasses theory is called the freezing temperature T_f, which moreover for realistic systems (and with the present choice for the parameters t^* and ΔT) is about one order of magnitude less than the equipartition threshold $T_{\rm eq}$.
2) Concerning the specific heat, on both curves it appears to tend to zero for vanishing temperatures, while tending to the "classical" Dulong–Petit value at higher temperatures. Moreover, while decreasing steadily on the upper (cooling) curve, it seems to present a rather huge jump on the lower (heating) curve. Actually, concerning the jump region of the heating curve, in several instances we observed "S–shaped" curves of the type familiar in elementary phase transitions, but we do not insist on this point here.
3) Concerning temperature, looking at situations as those of the lower (heating) curve of Fig. 1, in which the energy of the FPU system is much smaller than temperature, it is clear that the temperature as defined in this paper, namely as coinciding with that of the "calorimeter–thermometer", can be substantially different from the temperature defined in the works [8,9], i.e. essentially as the average kinetic energy of the FPU particles. Which definition should be chosen is then an interesting question of principle.

The results for three further uniform heating processes starting from the equipartition curve $u = T$ in the low temperature region are reported in Fig. 2.

It is thus clear that, within the given observation time t^*, one can distinguish in the (T, u) plane between a "classical" thermodynamic domain, above the freezing temperature

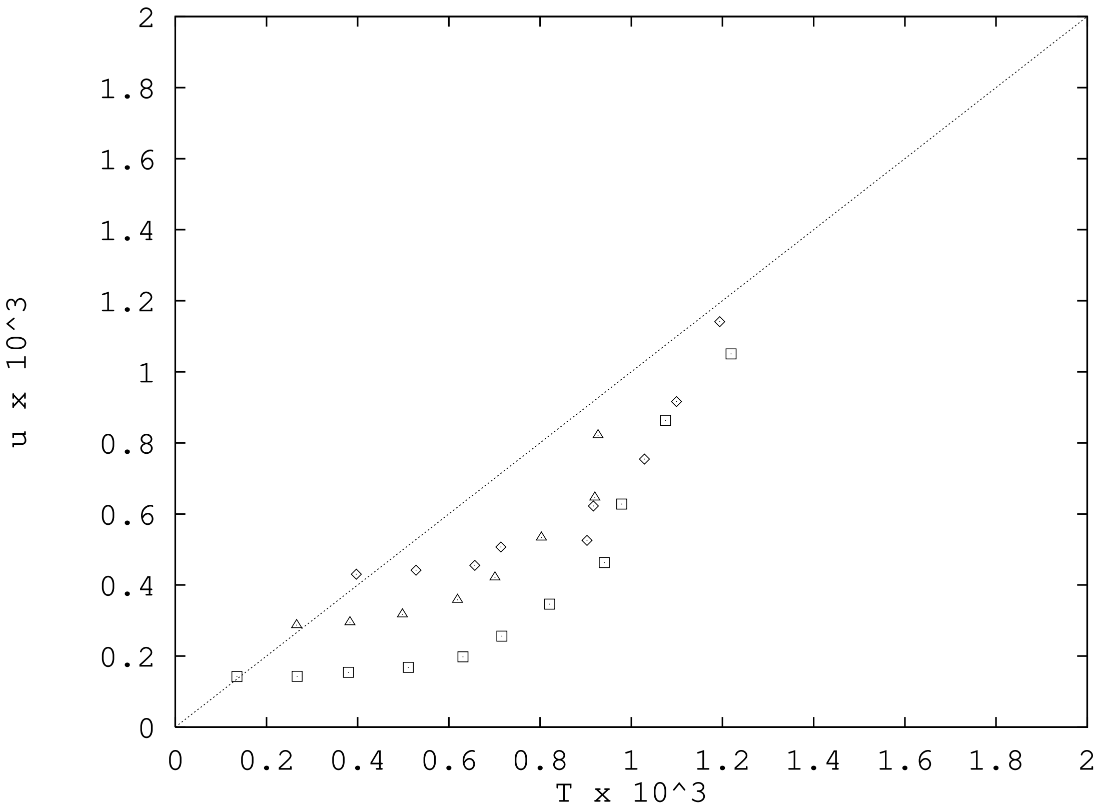

Fig. 2. *Three heating processes starting from equipartition in the low energy region; t^* and ΔT same as in the lower curve of Fig. 1*

T_f, and a "nonclassical" one below T_f, the latter being characterized by the fact that the temperature T does not uniquely define the internal energy u. This should correspond to the fact that in the latter region one has effective nonergodicity (or "broken ergodicity", in the standard spin glasses terminology [28]), in the sense that the energy surfaces appear to be subdivided into domains that are invariant up to the considered observation time t^*.

Clearly, a feature which is characteristic of the metastable or aging situations occurring in the "nonclassical domain" is that the curves obtained by heating or cooling processes depend on the observation time t^*, and should tend to align themselves on the equipartition curve $u = T$ as t^* increases. This is exhibited in fig. 3 in the following way. We perform n different runs corresponding to different initial data $(T_{0,i}, u_{0,i})$, $i = 1, \cdots, n$ all on a curve parallel to the equipartition curve, namely on the curve $u = T + a$ with a constant a ($= 0.4$ in the figure), and let the system evolve, for each of such initial data, up to a sequence of increasing times $t_k = k\, t^*$, $k = 1, \cdots, K$. The "final" values $(T_{k,i}, u_{k,i})$ are reported in the figure for $t^* = 1.5 \cdot 10^6 t_{\min}$ (namely 1/4 than in Figs. 1 and 2), and $K = 8$ (the initial data on the curve $u = T + a$ are not reported), and the expected phenomenon seems to be clearly exhibited.

We also performed some other computations with different values for the parameters

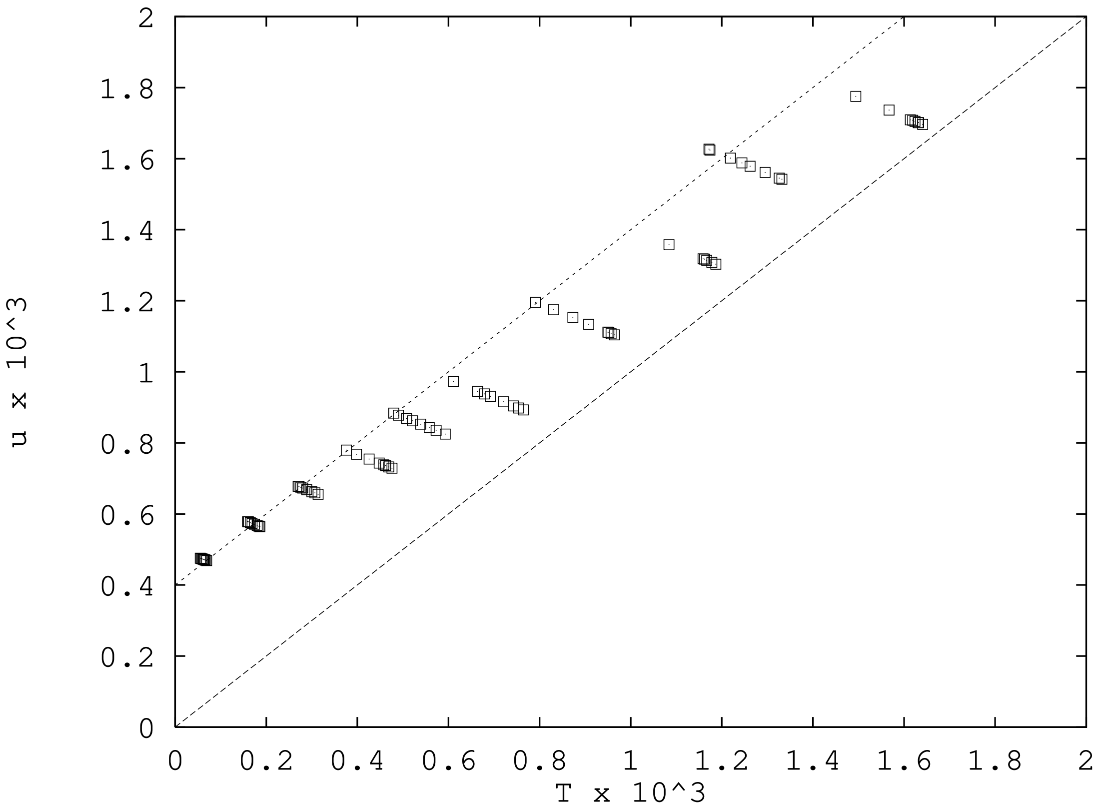

Fig. 3. *Illustrating how the rate of approach to equipartition depends on temperature. The initial data (not reported in the figure) were on the curve* $u = T + 0.4$*, and the "final" states are reported for times* $t_k = kt^*$*,* $k = 1, \cdots, 8$*, with* t^* *having a value* $1/4$ *than in Figs. 1, 2.*

κ and α entering the "internal" interaction potential (1) of the FPU system. It turned out that the freezing temperature T_f depends rather strongly on them. This means that the two critical temperatures $T_{\rm eq}$ and T_f are in general independent from each other, and that their orders of magnitude are comparable when "realistic" interaction potentials are considered. We mention also in passing that for $\kappa = 1$ the FPU system is so "soft" that its compressions and dilatations (and so also the external work) under the gas influence are relevant; consequently the internal energy u actually depends on the volume occupied by the FPU system, so that the identification of C_V is not trivial. It took to us some time to make this point clear.

Finally, the dependence of the results on the common number N of particles of gas and solid was also investigated, but not in a systematic way; the impression we got from our preliminary results is that the freezing temperature T_f should be intensive (i.e. independent of N) for large enough N. We plan to come back to this important problem at an analytical level.

3. Discussion. Let us recall which was the main idea underlying the present work. We were faced with the fact that two qualitatively different estimates were given in the literature for the specific heat of a FPU system as a function of temperature, namely, the specific heat would either be essentially constant [8], or tend to zero [9], for vanishing temperatures; in each case, the specific heat was estimated through the energy fluctuations of a subsystem, and the difference in the results was probably due to the different choice for the subsystem, namely a group of particles or a group of modes respectively. In lack of a clear argument in favour of any of such choices, particularly in the relevant phase space domain where the foundations themselves of statistical thermodynamics are under discussion, we decided to revert for the definition of the specific heat to the classical calorimetric one, involving as observable quantity just the temperature of a calorimetric substance; so we were naturally led to the study of a compound system consistituted of a solid (the FPU system) in interaction with an ideal gas, generalizing a classical model first investigated by Kelvin [18] and Poincaré [19] just in connection with the foundations of statistical thermodynamics. In such a way we came to a confirmation of the second of the quoted estimates, namely that the specific heat appears to vanish for decreasing temperatures. But this entailed the assessment of some rather subtle questions of principle concerning the mechanistic identification of the relevant functions appearing in statistical thermodynamics, to the discussion of which we now turn.

Indeed, as recalled in the Appendix, the classical definition of specific heat, which just involves as observable the temperature T of the calorimetric substance, is well known to be equivalent to the definition $C_V = \frac{\partial U}{\partial T}$, which involves instead the thermodynamic energy $U(T)$ of the solid as a function of temperature; so one is confronted with the problem of identifying the thermodynamic quantities U and T in mechanistic terms, a problem which is particularly delicate in situations such as the present one, where the dynamical properties usually assumed for the validity of statistical thermodynamics are indeed in question. For the temperature T, following all the classics we identify it just with the (average) energy of the gas, through the relation $E^{gas} = T/2$. This is however not so trivial, because the temperature thus defined can be substantially different from the average kinetic energy of each particle in the FPU system, which is often used as an alternative definition of temperature. For the internal energy U one generally makes the identification $U = E$, where E is the (time averaged) solid's mechanical energy; but this is indeed the main point of concern in the low energy region, where the times required to reach equilibrium between solid and gas can be much longer than the observation times, or equivalently the relaxation times can increase so fast with decreasing temperatures as to become by far larger than any fixed observation time. This led us to the consideration of cooling or heating processes, which led to curves $E = E(T)$ of the types reported in Fig. 1. Such curves turn out to coalesce for large temperatures, where they in fact essentially superpose to the equipartition curve $E = NT$, while there are as many of them as there are initial data, observation times t^* and temperature increments ΔT in the low energy, "nonclassical" region; correspondingly, aging and hysteresis features, in the way familiar in spin glasses theory, are exhibited in such a region. In particular, for cooling processes one finds out at zero temperature a residual energy $E_0 = E(0)$, which bears some analogy to the familiar "zero–point energy". Obviously such a residual energy would vanish in the limit in which larger and larger observation times were considered, and the relevant point is whether the times required for this might actually increase exponentially fast as temperature decreases, as the available analytical estimates *à la* Nekhoroshev [22] or Landau–Teller [24] seem to indicate. This is a very interesting open problem to which we plan to come back in the near future. But in any case the main contribution of the present paper just consists in pointing out that situations as those described above, with the thermodynamic functions not univocally defined as a function of temperature because of the largeness of the relevant relaxation times, should be considered as common facts in classical statistical thermodynamics at low temperatures (or high frequencies).

It is clear that such a state of affairs could appear somehow paradoxical, because it entails for example that the vanishining of the specific heats of solids should be ultimately due to the largeness of the time of relaxation to *equilibrium between solid and measuring apparatus* (i.e. in our case between FPU system and gas). But this seems indeed to be the case, at least in a classical framework. On the other hand, we would like to point out that the taking into consideration of situations of this type is not at all new, and is instead a rather common fact in applied physics. The main example we quote is just the measurement of the specific heat of diatomic molecules through measurements of the speed of sound at various frequencies. Indeed, the existence itself of sound dispersion just means that the "transfer of internal energy through collisions" in the molecules (see [29]), depending on the wave frequency, in fact depends on the observation time; as a special case, the static specific heat corresponds indeed to infinite observation times of the measuring apparatus, i.e. to zero frequency. This example is particularly relevant, because it was just in order to understand sound dispersion that the mathematical technique of Landau ant Teller [24], now so popular for the general study of adiabatic invariants [25,26], was introduced. Similar concepts were applied repeatedly in plasma physics by the group around O'Neil [30,31] (see also [32]). For spin glasses, phenomena analogous to the frequency dependence of the speed of sound are also familiar; for example, in [33] (see page 5) it is said that *"the freezing temperature turns out to depend on the frequency of the applied magnetic field"*, while in [27] page 302 one finds that *"the position of the jump occurs when the time scale τ for the molecular dynamics becomes comparable to the natural time scale of the experimentator"*.

The deepest discussion of the relevance of relaxation times in defining the thermodinamic energy U, implying that in general it should be distinguished from the mechanical energy E and that a residual energy E_0 might be present at zero temperature, is probably due to Boltzmann himself [34,35] (see the works of Jeans [36]–[37], and also [38]). Let us recall that Boltzmann's preferred example was his beloved model of rigid spheres, whose energy is constituted of a translational and of a rotational part. Due to the mutual collisions, the translational part is in general quite rapidly exchanged and equally shared among the different spheres, but in general this is not the case for the rotational part, which for example is not at all exchanged for perfectly smooth spheres, thus remaining equal to the initial one; there is instead an exchange in the case of rough spheres, but the actually exchanged amount depends on the particular model. A modern illustration of a similar effect involving centers of mass and vibrational energies was given in ref. [39] for a model of diatomic molecules (see [40]–[41] for the analytical estimates), while a model of rotators, even nearer to Boltzmann's example, was discussed in [42]. So, according to Boltzmann, in any concrete case one has to fix an observation time t^*, and then to take as internal energy U only that portion of the mechanical energy E which is actually exchangeable within the time t^*; the residual mechanical energy E_0, not actually exchangeable within the given observation time, thus plays essentially the role of a kind of "zero–point energy". In our case, it might be of interest to compare the value of the residual energy E_0 estimated from Fig. 1 with that of the quantum zero–point energy $E_0^q = \frac{1}{2}\sum_{k=1}^{N} \hbar\omega_k$, where $\hbar$ is the reduced Planck's constant. This can be done exactly as in refs. [43,44] (see also [45] page 204, and the comments in [5]), by introducing Planck's constant in the molecular parameters through the well known phenomenological relation $\sqrt{m\epsilon}\,\sigma \simeq 2Z\,\hbar$, or equivalently $\epsilon \simeq \frac{Z}{\sqrt{\kappa}}\,\hbar\,\omega$ where Z is the atomic number, and one finds $E_0 \simeq \frac{Z}{16}\,10^{-3}E_0^q$. Notice however that one should take into account the fact that the value of the residual energy E_0 depends on the parameters defining the cooling process, especially on the observation time t^*, so that it is not clear how a comparison with E_0^q should be made.

We close with two more comments.

1) For what concerns the interaction between the gas molecules and the boundary particle of the solid, the assumption of smoothness made in this paper turns out to play an essential role. Indeed, it is very well known (see [46,47]) that the metastable or aging phenomena discussed in this paper disappear in the case of hard collisions, essentially because the freezing phenomena occur only for frequencies higher than a characteristic frequency depending on the interaction potential, which in turn is infinite in the case of hard collisions. So, we follow here the familiar attitude of considering the results holding for models involving hard collisions as approximations describing only the low frequency–high temperature regime (with absence of metastable or aging phenomena) for realistic smooth interaction potentials.
2) The fact that thermodynamics can arise from mechanics only after some relaxation times are elapsed is of course discussed in the standard treateses. Particularly interesting is the discussion given by Planck in section 3 of his celebrated *Wärmestrahlung*[48] (see also page 152 of the german edition), where it is stated that one should wait many typical periods of the involved oscillators in order that the "*dependence on the phases*" be eliminated, and a thermodynamical behaviour show up. We plan to come back in the future to this fundamental problem, basing our considerations on the presently available analytical estimates[42,26]. Indeed from these it appears that the time required for a thermodynamic behaviour, i.e for a washing out of the phase dependence, might rather increase essentially in an exponential way with the ratio ω/T, and this would give a solid theoretical basis to the present phenomenological work.

APPENDIX

We recall here how the definition $C_V = \frac{\partial E}{\partial T}$ for the specific heat, namely as the rate of growth of the solid's mechanical energy E with temperature T, is usually justified making reference only to quantities which are in principle observable, i.e. the temperatures T of the calorimetric substance; in our case, these are just the perfect gas temperatures, which are identified by $T = 2E^{gas}$ (i.e. we are taking by definition $C_V^{gas} = 1/2$). By the way, also the heat ΔQ exchanged between the solid and the calorimetric substance (the gas) turns out to be defined in terms of the temperature of the calorimetric substance, because one has by definition

$$\Delta Q = \Delta E^{gas} = \frac{1}{2}\Delta T \ .$$

Now, how is in principle a measurement of the specific heat C_V of the solid performed? One first of all takes the solid at a certain temperature T_1, i.e. one lets the composed system gas + solid go to an equilibrium (or to an apparent one), and defines T_1 as the corresponding temperature of the calorimetric substance (the gas); in our case one will have $T_1 = 2E_1^{gas}$, while the solid will have an energy E_1, not observed . Then one immerses the solid into a gas at a different temperature, say T_3; in our case, one will alter by hand the gas energy, putting it equal to a new value $E_3^{gas} = T_3/2$, while keeping unaltered the solid's energy. Finally one lets the composite system evolve to a new apparent equilibrium, which will have a certain temperature $T_2 = 2E_2^{gas}$, intermediate between T_1 and T_3, while the solid will have a certain energy E_3, not observed. The specific heat of the solid is then defined as the limit of the ratio

$$\overline{C}_V = \frac{|\Delta Q|}{|T_1 - T_2|} = \frac{1}{2}\frac{|T_2 - T_3|}{|T_1 - T_2|}$$

of the heat exchanged between gas and solid in the transition $3 \to 2$ over the corresponding temperature variation of the solid. The latter relation is the one where only observable quantities (gas temperatures) are involved, as in the dear old books of calorimetry (the only difference is the factor $1/2$, due to the fact that in our units one has $C_V^{gas} = 1/2$). On the other hand the heat $|\Delta Q| = |\Delta E^{gas}|$ exchanged in the transition $3 \to 2$ just coincides with the energy $|\Delta E| = |E_3 - E_2|$ exchanged by the solid in the same transition, which in turn is also equal to $|E_1 - E_2|$ because in the transition $1 \to 3$ only the gas temperature was altered. So one has

$$\overline{C}_V = \frac{E_2 - E_1}{T_2 - T_1} \ ,$$

which in the limit $T_2 \to T_1$ just gives $\frac{\partial E}{\partial T}$.

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