

**ON THE SPECIFIC HEAT
OF FERMI–PASTA–ULAM SYSTEMS,
AND THEIR GLASSY BEHAVIOR**

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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. It is found that there exists a “freezing” critical temperature below which the relaxation times to equilibrium between FPU system and calorimeter become relevant, so that the system presents aging and hysteresis features very similar to those familiar in glasses and spin glasses. In particular, in the frame of such a point of view involving finite long times, the specific heat appears to vanish for vanishing temperatures.

Key Words: Fermi–Pasta–Ulam; specific heat; glasses.

1. Introduction. It is very well known that systems of Fermi–Pasta–Ulam type present an energy threshold E_{eq} for equipartition among the normal modes (see for example [1–5]). Moreover, E_{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 $u_{\text{eq}} = E_{\text{eq}}/N$ which should not vanish in the thermodynamic limit^[6,7]. So one is confronted with the problem of deciding whether the specific energy threshold u_{eq} is relevant or not for statistical thermodynamics, typically for the specific heat.

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 temperatures, 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 are given for the specific heat measurement. In either work one makes use of the familiar formula relating specific heat to energy fluctuations: one considers an isolated FPU system, the temperature of which is defined through the initial data, and one looks at the energy fluctuations of a suitable small subsystem. The difference is that the subsystem is defined through pure configuration space localization in [8], and through pure momentum space localization in [9]; namely, the subsystem is in [8] a group of nearby particles (actually, averages were taken over several such groups), and in [9] a group of normal modes of the global system with nearby frequencies (actually, with exactly equal frequencies, in virtue of a degeneration occurring in the particular model considered). It is not clear to us which choice for the subsystem should be preferred; for example an intermediate choice was made in the celebrated paper known under the name of *dreimännerarbeit* [10], where the isolated system was a linear string. A reconsideration of the theoretical basis for the formula relating specific heat and energy fluctuations for energies lower than the equipartition threshold seems thus to be in order, and we hope to come back to this interesting problem in the future.

In any case, a confrontation with such a general question led us to the main idea underlying the present work: namely, to cope with the problem of choice of the subsystem in a very drastic and quite natural way, by making recourse, for the definitions of temperature and of specific heat, to the familiar calorimetric ones, involving the interaction of the system whose specific heat has to be measured with an external calorimetric substance. This idea was implemented through a one-dimensional model (inspired by the classical works [11,12] and [13] of Poincaré and Kelvin) where the calorimetric substance is an ideal gas adjacent to the FPU system (mimicking a crystal); the energy exchanges between crystal and gas occur through the extreme crystal’s particle adjacent to the gas, which is left free to interact, through a realistic potential, with all gas particles (the other extreme particle of the crystal is instead kept fixed). In such a model the calorimetric substance then acts also as a thermometer, the temperature being defined through the average kinetic energy of the gas, as in [12]; in turn, the specific heat C_V of the crystal is just defined by $C_V = \frac{\partial U}{\partial T}$, where U is the time average of the energy E of the FPU system. This mathematical model for the implementation of a specific heat measurement seems to be more realistic. In particular it takes into account the fact that in the traditional specific heat measurements one never makes reference to the energy of the crystal, and the only observed quantity

is the temperature of the calorimetric substance; analogously, in our case, the variations of the crystal energy can be inferred, through energy conservation, from the variations of the gas energy, so that we too are in principle considering as observable quantity only the temperature of the calorimetric substance.

Now, it turned out that in actually dealing with such a model we were somehow forced to take conscience of a question of principle concerning to specific heat measurements, related to the relevance of the dependence of the results on the observation time. This led us to discover an analogy with the phenomenology of glasses and spin glasses, involving aging and metastability, which perhaps constitutes the main contribution of the present paper. 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^[14], which had some influence on our work. The reason for such an analogy is that in our model a high nonuniformity in the time required to reach equipartition between calorimetric substance and crystal is manifested as temperature T is decreased (or a characteristic frequency ω of the system is increased). Indeed, in the extremely simplified version of the model (which we call the Poincaré model - see [11]) where the FPU system is reduced to just one linear spring and the calorimeter to just one gas particle, it is very well known that the relaxation time τ has an exponential-like dependence on ω and on $1/T$;^[15] moreover analytical estimates of such a type were also proven for models involving N equal frequencies, with some parameters independent of N .^[16]

The dependence of the results on the observation times is manifested in the following way. To implement a specific heat measurement, first of all we let the compound system (crystal + gas) go to equilibrium (or at least to a practical one), and the temperature of the crystal is just defined as coinciding with that of the gas. Then, in order to estimate $\frac{\partial U}{\partial T}$ one has to 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, and in general how the results depend on the “measuring or waiting time”. 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 E_{eq} , although comparable to it in realistic cases), with the property that the specific heat has the “classical” Dulong–Petit value for larger temperatures, and a lower value for lower temperatures, apparently decreasing to zero for vanishing temperatures. Namely, while above T_f equipartition is obtained quite independently of the waiting time, below T_f the results depend very strongly on it. Moreover, phenomena analogous to hysteresis, metastability and aging are observed.

One should then understand whether such a glassy behavior for crystals is an artifact of our model or has a physical counterpart. This is a very interesting open problem, which can be investigated both from an experimental and from an analytical point of view.

Our results are described in the next section, which also contains some more details on the model, and a brief discussion then follows.

2. The model and the results. The FPU system (crystal) and the gas are taken with the same number N of moving particles, all of the same mass m , on a line. The FPU

system consists in fact of $N + 1$ particles P_0, \dots, P_N , the extreme particle P_0 being fixed at say the origin, while the other extreme 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 . The interaction in the FPU system is of nearest neighbor type due to nonlinear springs, the interaction potential as a function of distance r being of the familiar form $V_1(r) = \frac{1}{2}\kappa r^2 + \frac{1}{3}\alpha r^3$ with positive parameters κ and α ; the interaction potential between the boundary particle P_N of the crystal and the gas molecules is instead taken as

$$V_2(r) = \epsilon \frac{e^{-2(r/\sigma)^2}}{r/\sigma} , \quad (1)$$

with positive parameters ϵ and σ , which we consider as constituting the characteristic energy and length of the system. 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 $\alpha = 3742$; these values are determined by the condition that the interaction potential V_1 coincide with a third order expansion about the minimum of a Lennard–Jones potential $V(r) = 4\epsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right]$ 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 crystal, y_i, π_i position and momentum of the i -th particle of the gas; these all are real variables with the constraints $x_0 = 0$, $x_N < y_i < L$, ($i = 1, \dots, N$), 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_{\min} , namely $t_{\min} = 2\pi/\omega$, where ω is the maximum among the frequencies ω_k of the linearized system,

$$\omega_k = \omega \sin\left(\frac{k}{N} \frac{\pi}{2}\right) , \quad k = 1, \dots, N , \quad \omega = 2\sqrt{\kappa} \frac{1}{\sigma} \sqrt{\frac{\epsilon}{m}} . \quad (2)$$

We take mechanical units in which $\epsilon = \sigma = m = 1$; temperature units are used such that $k_B = 1$, where k_B is Boltzmann’s constant. We will be concerned with energy exchanges ΔE between gas and crystal, and in general a contribution to ΔE also comes from the mechanical work performed by the gas on the boundary FPU particle; 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 .

We come now to a description of the results. To start out we determined, in the familiar way, the equipartition threshold E_{eq} in the isolated FPU system, and we found

$u_{\text{eq}} \equiv E_{\text{eq}}/N \simeq 5 \cdot 10^{-3}\epsilon$; this is of the order of 1/10 the first estimate ever produced, namely^[1] $u_{\text{eq}} \simeq \epsilon/15$, which was found for an FPU system with Lennard–Jones interaction potential. The integrations were performed for $N = 200$ and up to a fixed time $t^* = 10^7 t_{\text{min}}$. Such a choice for N and t^* was dictated just by our available computing power.

Then we investigated our model, 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 time-averaged specific energy of the gas) and u the crystal’s time-averaged 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; 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_{eq} , we found that after rather short times there was equipartition between gas and crystal, namely one had $u \simeq T$. Consequently, for the specific heat per particle $c_V = \frac{\partial u}{\partial T}$ of the crystal 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 $c_V^{gas} = 1/2$).

Our main purpose is then to extend the curve of u versus T to the range below u_{eq} , where metastable phenomena are expected, with a corresponding dependence of the results on the observation (or waiting) times. We organized the computations as follows. First of all, the observations were made up to a fixed waiting time t^* , to be considered as a parameter. We start with the complete system (gas + crystal) 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” 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 crystal’s specific energy the previous “final” value), and let again the complete system relax up to the waiting 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) , $i = 1, \dots, n$. 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^[17], 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_{eq} are reported in Fig. 1, where two “curves” u versus T are given, for $N = 200$, $t^* = 6 \cdot 10^6 t_{\text{min}}$ and $|\Delta T| = 10^{-4}\epsilon$ or $|\Delta T| = 1.35 \cdot 10^{-4}\epsilon$ 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

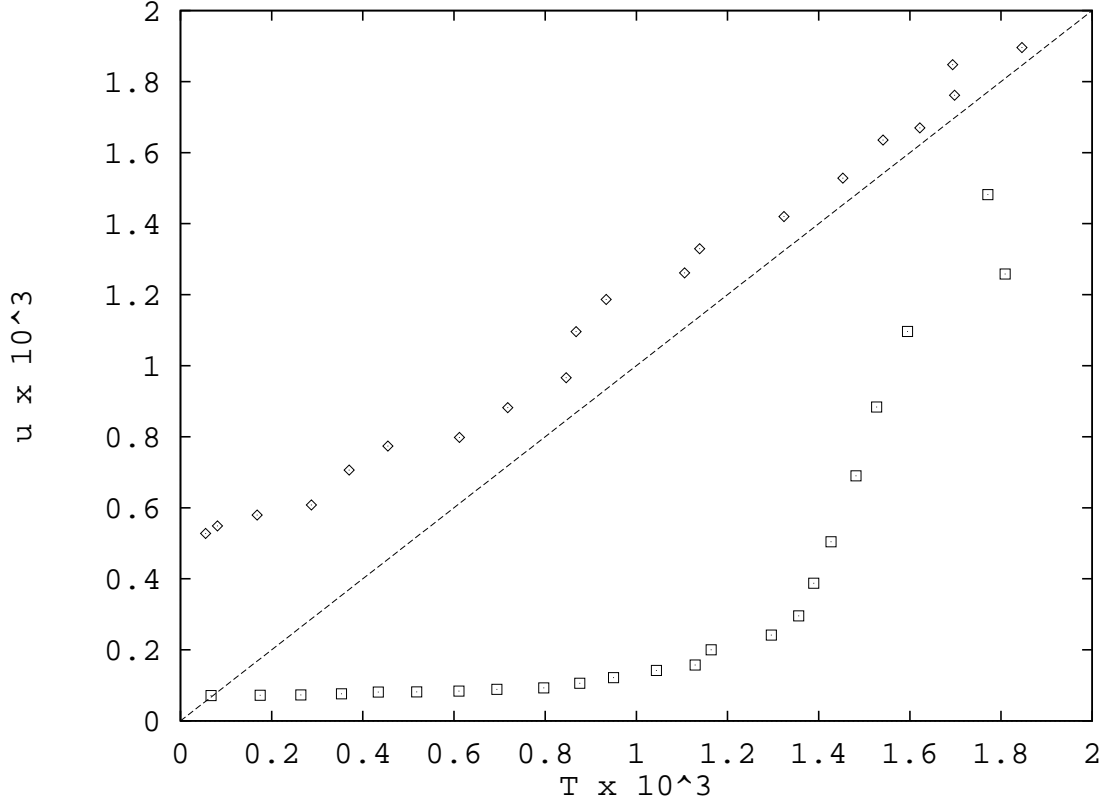


Fig. 1. *The energy of the FPU system versus temperature T (i.e twice the gas energy) for a cooling process starting from equipartition (upper curve) and for a heating process starting from the origin (lower curve).*

seem to be that:

- 1) the two curves, instead of essentially coinciding with the equipartition curve $u = T$ as for high temperatures, are here manifestly 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 non-vanishing “residual” energy $U_0 = U(0)$, with $U_0 \simeq 0.5 \cdot 10^{-3} N \epsilon$. 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_{eq} .
- 2) Concerning the specific heat below the freezing temperature, it clearly tends to zero for vanishing temperatures on the heating curve, and the same was found for all other heating curves we produced, not reported here. The situation is a little more complicated on the cooling curve, because the only visible thing is that the specific heat is lower than the classical Dulong–Petit value. The impression we got from several other cooling curves, not reported here, is that on all of them the specific heat actually tends to zero, although the available data are non completely conclusive;

indeed, in general, we found that the cooling curves present a form which is much more “fuzzy” than the heating curves, for some reason which is still unknown to us. Another interesting point concerning the heating curve is that the specific heat seems to present a rather huge jump in reaching the classical value. Actually, 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, in situations as those of the lower (heating) curve of Fig. 1 one sees that the energy of the crystal is much smaller than the temperature defined in this paper (namely as coinciding with that of the “calorimeter–thermometer”). So it is clear that the temperature here considered can be substantially different from that 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.

It is thus clear that, within the given waiting time t^* , one can distinguish in the (T, u) plane between a “classical” thermodynamic domain, above the freezing temperature T_f , and a “non-classical” 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, for the compound system, in the latter region one has effective non-ergodicity (or “broken ergodicity”, in the standard spin glasses terminology^[18]), in the sense that the energy surfaces appear to be subdivided into domains that are invariant, at least up to the considered waiting time. One might expect that the classical value of the specific heat would be obtained at any temperature for an infinite waiting time, but no proof of this is available. However, the analytical estimates mentioned in the introduction suggest that the waiting time required to get equipartition increases with an exponential-like behavior as temperature is decreased.

An illustration of the dependence of the results on the waiting time is given in Fig. 2. We performed n different runs corresponding to different initial data $(T_{0,i}, u_{0,i})$, $i = 1, \dots, n$, all on a curve parallel to the equipartition curve, precisely on the curve $u = T + 0.4$, and let the system evolve, for each of such initial data, up to a sequence of increasing times $t_k = k t^*$, $k = 1, \dots, K$. The “final” values $(T_{k,i}, u_{k,i})$ are reported in the figure for $t^* = 1.5 \cdot 10^6 t_{\min}$ and $K = 8$. These results show that, by increasing the waiting time from $1/4$ to twice that of Fig. 1, one essentially reaches equipartition for temperatures higher than 10^{-3} ; but such a time is not sufficient for lower temperatures, where moreover it appears that the data might be compatible with an exponential-like dependence of the relaxation time on $1/T$.

The dependence of the results on the common number N of particles of gas and crystal 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.

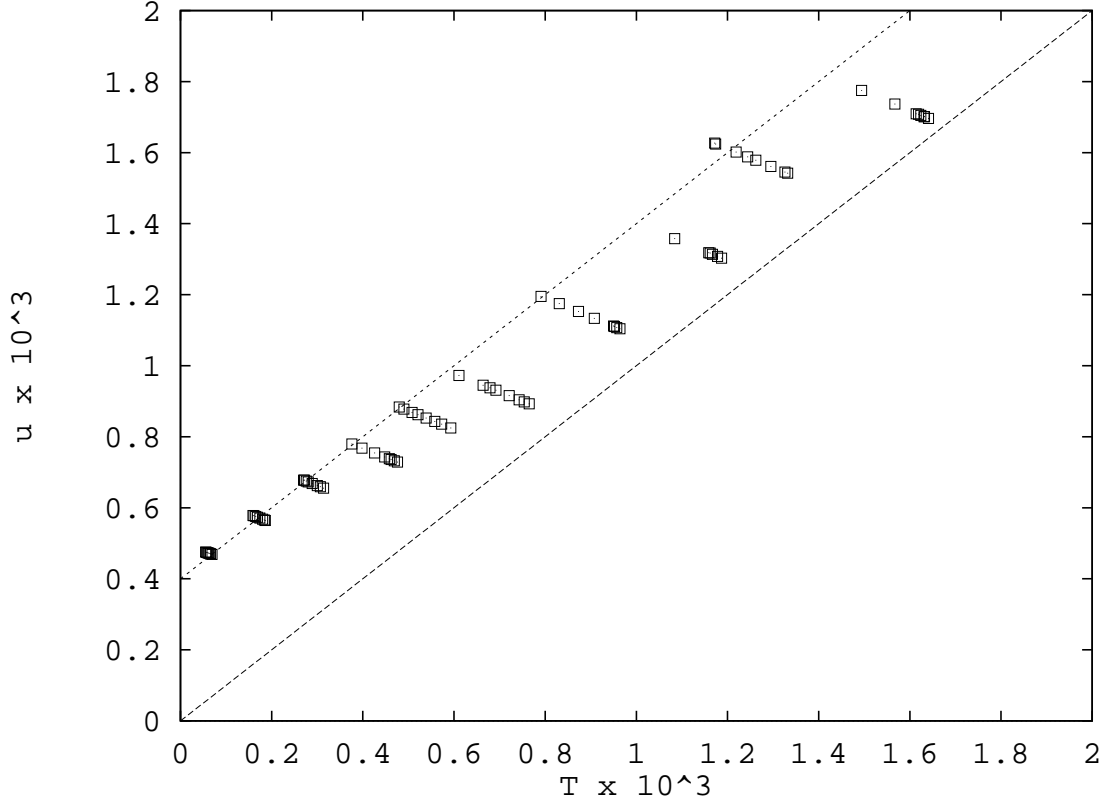


Fig. 2. *Illustrating how the rate of approach to equipartition depends on temperature. The initial data (not reported in the figure) were on the curve $u = T + 0.4$, and the “final” states are reported for times $t_k = kt^*$, $k = 1, \dots, 8$, with t^* having a value $1/4$ of that in Fig. 1.*

3. Discussion. In the present paper we pointed out that a realistic implementation of the specific heat measurement for FPU systems requires taking into account the interaction of the system with a calorimetric substance. To this end we introduced a simple model inspired by a classical one studied by Poincaré, and reported the results of some numerical computations. The main result we found is that the FPU system seems to present at low temperatures a behavior of glassy type, with its characteristic phenomena of aging and hysteresis, due to the largeness of the relevant relaxation times of equipartition between the system and the calorimetric substance. In particular, in the frame of the philosophy of finite observation or waiting times typical of glasses theory, the specific heat of the FPU system appears to vanish for vanishing temperatures.

Two main problems seem to remain open concerning the glassy behavior: whether analytical proofs can be produced, and whether it is observed in actual experiments. Concerning the first point, no strict analytical proof is presently available in the thermodynamic limit, although some partial results might appear to be promising.

Concerning the second point, no direct observation of glassy behaviour for crystals

in known to us. However, we would like to point out that the taking into account of the relaxation time to equilibrium between a system and a measuring apparatus 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 [19]), depending on the wave frequency, in fact depends on the waiting time; as a special case, the static specific heat corresponds indeed to infinite waiting 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 and Teller^[20], now so popular for the general study of adiabatic invariants^[21,15], was introduced. Similar concepts were applied repeatedly in plasma physics by a group around O’Neil^[22,23] (see also [24]). For spin glasses, phenomena analogous to the frequency dependence of the speed of sound are also familiar; for example, in [25] (see page 5) it is said that *“the freezing temperature turns out to depend on the frequency of the applied magnetic field”*, while in [17] 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”*.

Finally, as a comment of an historical type, we would like to recall that the deepest discussion of the relevance of relaxation times in defining the thermodynamic energy U , implying that in general the latter should be distinguished from the mechanical energy E and that a residual energy U_0 might be present at zero temperature, is probably due to Boltzmann himself^[26,27] (see also the works of Jeans [28]–[29], and [30]). 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. [31] for a model of diatomic molecules (see [16] for the analytical estimates), while a model of rotators, even nearer to Boltzmann’s example, was discussed in [32]. So, according to Boltzmann, in any concrete case one fixes a waiting time t^* , and then takes as internal energy U only that portion of the mechanical energy which is actually exchangeable within such fixed waiting time. And this is exactly what we were doing in the present paper.

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