Quantization *à la* Nernst for the Plane Rotator.

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(ricevuto il 7 Febbraio 1984)

PACS. 03.65. – Quantum theory; quantum mechanics.

Summary. – We extend to the case of classical plane rotators the quantization procedure *à la* Nernst that was recently applied to harmonic oscillators. At variance with that case, we find now that the thermodynamic energy as a function of temperature does not coincide with the one given by quantum mechanics, but the qualitative trend is very similar and even quantitative differences are small.

As in classical dynamics it was realized in recent times that one has typically coexistence of ordered and chaotic motions (1), so correspondingly in statistical mechanics it was recently proposed (2,3) (see also ref. (4)) that one could have a possible understanding of Planck's law in a classical framework. This was obtained just by exploiting the old suggestion of Boltzmann (5) that, in any mechanical interpretation of thermodynamics, one should neglect those motions which, having characteristics of order or of stability, are to be considered as frozen, *i.e.* do not exchange energy within some

(1) M. HENON: in *Cahotic behaviour of Deterministic Systems*, edited by G. IOOS and R. G. H. HELLEMAN Les Houches, Course 36 (Amsterdam, 1983).
(2) L. GALGANI: *Lett. Nuovo Cimento*, **31**, 65 (1981); *Nuovo Cimento B*, **62**, 306 (1981).
(3) L. GALGANI and G. BENETTIN: *Lett. Nuovo Cimento*, **35**, 93 (1982); L. GALGANI: *Ann. Fond. L. de Broglie*, **8**, 19 (1983).
(4) C. CERCIGNANI, L. GALGANI and A. SCOTTI: *Phys. Lett.*, **38**, 403 (1972); L. GALGANI and A. SCOTTI: *Phys. Rev. Lett.*, **28**, 1173 (1972); L. GALGANI and A. SCOTTI: *Riv. Nuovo Cimento*, **2**, 189 (1972).
(5) L. BOLTZMANN: *Nature*, **51**, 413 (1895); see also *Vorlesungen über Gastheorie* (Leipzig, 1896-1898); english translation: *Lectures on Gas Theory* (Berkeley, 1964), p. 87 and 91.

typical observation time. In fact, such deduction of Planck's law turned out to be exactly equivalent to a previous deduction given by NERNST (6) in the year 1916.

In the latter work, combining the idea of Planck (7) on the existence of a zero-point energy with his own understanding of degenerate motions (where the third principle applies) as ordered motions, NERNST came to conceive that for a system of weakly coupled oscillators of frequency ν there should exist an energy threshold $\varepsilon(\nu)$ such that any oscillator has ordered or chaotic motions according to whether its instantaneous energy is lower or greater than $\varepsilon(\nu)$, respectively. Then, as usual, just on the basis of the general Wien's law for a black body, $\varepsilon(\nu)$ is shown to be equal to $h\nu$, where h is a suitable action to be possibly identified with Planck's constant.

It is then quite natural to ask whether a similar quantization procedure also works for the plane rotator, which was indeed the first case considered in the history (8) of quantum mechanics after the linear oscillator. In such a case, many difficulties were encountered, just because of the nonlinearity of the Hamiltonian, which has the form $H(p, \theta) = p^2/2$ (the moment of inertia having been put equal to 1), the variables being the (cyclic) angular co-ordinate θ and the corresponding conjugate momentum (or angular momentum) p; in the case of the linear oscillator one has instead, in terms of action-angle variables p, θ, the linear Hamiltonian $H(p, \theta) = \omega p$, where ω is a constant.

In quantum-statistical mechanics, for the plane rotator, whose energy levels are given by $E_n = n^2\hbar^2/2$ ($\hbar$ being the reduced Planck's constant $h/2\pi$), one defines the partition function $Z(\beta) = \sum_{n=0}^{\infty} \exp[-\beta E_n]$ ($\beta = 1/kT$ being the usual inverse absolute temperature) and then the internal energy $U(\beta)$ turns out to be given by

$$U(\beta) = -\frac{\partial \ln Z}{\partial \beta} = \frac{\sum_{n=0}^{\infty} E_n \exp[-\beta E_n]}{\sum_{n=0}^{\infty} \exp[-\beta E_n]} . \tag{1}$$

Coming now to the procedure *à la* Nernst, first of all one distributes the rotators in the phase space of a single rotator according to the generalized Maxwell-Boltzmann law; due to the symmetry with respect to rotations in the phase plane and to reflexions around the origin in the momentum variable, it is sufficient to consider then the probability density ϱ as a function of the positive variable p only, and defined by

$$\varrho(p) = \frac{\exp[-\beta H(p)]}{\int_0^{\infty} \exp[-\beta H(p)]\, dp} . \tag{2}$$

One has then the relations

$$\int_0^{\infty} \varrho(p)\, dp = 1 , \qquad \int_0^{\infty} \frac{p^2}{2}\, \varrho(p)\, dp = \frac{1}{2\beta} , \tag{3}$$

(6) N. NERNST: *Verh. Dtsch. Phys. Ges.*, **18**, 83 (1916), especially p. 87 and 91.

(7) M. PLANCK: *Ann. d. Phys.*, **37**, 642 (1912); *Waermestrahlung*, 2nd edition (1913), english translation: *The Theory of Heat Radiation*, Part 4, Chapt. 3.

(8) F. HUND: *Geschichte der Quantentheorie* (Zurich, 1975); italian translation: *Storia della teoria dei quanti* (Torino, 1980).

the second of which gives for any rotator the average mechanical energy $U^{m}(\beta) = 1/2\beta$. The natural generalization of Nernst's hypothesis on the existence of an energy threshold $\varepsilon(\nu)$ for the linear oscillator is now the existence of a critical action, or action threshold, A. Thus in analogy with ref. (2,3) we can define n_0, n_1, U_0 and U_1 by

$$(4)\qquad \begin{cases} n_0 = \int\limits_0^A \varrho(p)\,\mathrm{d}p\,, & n_1 = \int\limits_A^\infty \varrho(p)\,\mathrm{d}p\,, \\ U_0 = \int\limits_0^A \frac{p^2}{2}\,\varrho(p)\,\mathrm{d}p\,, & U_1 = \int\limits_A^\infty \frac{p^2}{2}\,\varrho(p)\,\mathrm{d}p\,, \end{cases}$$

with

$$(5)\qquad n_0 + n_1 = 1\,, \qquad n_0 U_0 + n_1 U_1 = \frac{1}{2\beta}\,.$$

The thermodynamic energy U^{th} is then defined by

$$(6)\qquad U^{th} = U^{m} - U_0\,,$$

which is Nernst's prescription, or equivalently by

$$(7)\qquad U^{th} = n_1(U_1 - U_0)\,,$$

which is the prescription of ref. (3), the equivalence just following by (5). It turns out that these relevant quantities can all be expressed through the standard error function

$$(8)\qquad \operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\int\limits_0^x \exp\,[-t^2]\,\mathrm{d}t$$

TABLE I.

β	U	U^{th}	δ
0.1	4.4627	4.9121	$9.15\cdot 10^{-2}$
0.2	2.1000	2.3124	$9.19\cdot 10^{-2}$
0.5	0.7795	0.8443	$7.67\cdot 10^{-2}$
0.6	0.6363	0.6437	$1.15\cdot 10^{-2}$
0.8	0.4540	0.4768	$1.09\cdot 10^{-1}$
0.9	0.4026	0.4083	$1.40\cdot 10^{-2}$
1	0.3600	0.3550	$1.41\cdot 10^{-2}$
1.1	0.3208	0.3113	$3.05\cdot 10^{-2}$
1.2	0.2898	0.2761	$4.96\cdot 10^{-2}$
1.4	0.2425	0.2205	$9.98\cdot 10^{-2}$
1.6	0.2075	0.1790	$1.59\cdot 10^{-1}$
1.8	0.1807	0.1472	$2.28\cdot 10^{-1}$
2	0.1594	0.1231	$2.95\cdot 10^{-1}$
3	0.0950	0.0561	$6.93\cdot 10^{-1}$
4	0.0600	0.0283	1.12
5	0.0380	0.0150	1.53

by

$$(9)\quad \begin{cases} n_0 = \operatorname{erf}\left(A\sqrt{\dfrac{\beta}{2}}\right), & n_1 = 1 - \operatorname{erf}\left(A\sqrt{\dfrac{\beta}{2}}\right), \\[2ex] U_0 = \dfrac{1}{2\beta} - \dfrac{A}{\sqrt{2\beta\pi}}\, \dfrac{\exp[-\beta A^2/2]}{\operatorname{erf}(A\sqrt{\beta/2})}, & U_1 = \dfrac{1}{2\beta} + \dfrac{A}{\sqrt{2\beta\pi}}\, \dfrac{\exp[-\beta A^2/2]}{1-\operatorname{erf}(A\sqrt{\beta/2})}, \end{cases}$$

so that one finds

$$(10)\qquad U^{\text{th}} = \frac{A}{\sqrt{2\beta\pi}}\, \frac{\exp[-\beta A^2/2]}{\operatorname{erf}(A\sqrt{\beta/2})}.$$

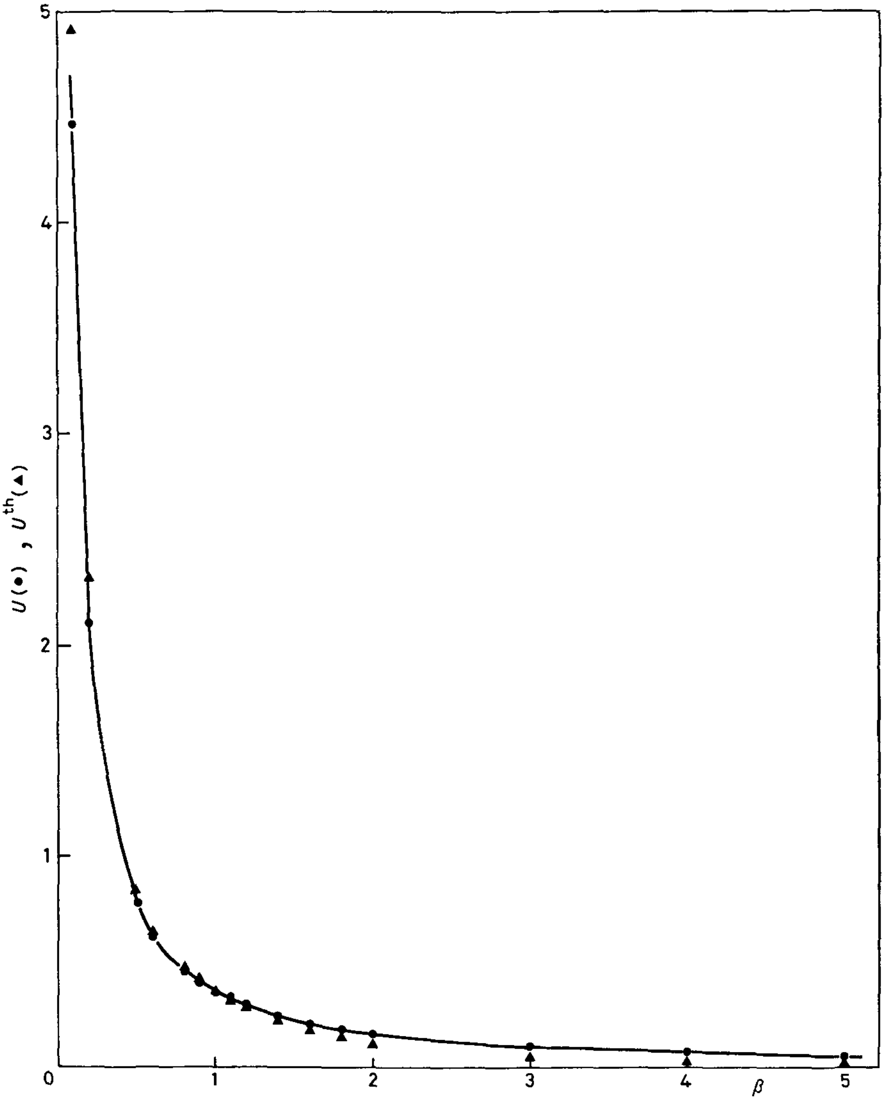

Fig. 1. – The quantum internal energy U (•) and the internal energy *à la* Nernst U^{th} (▲) *vs.* the inverse temperature β.

In order to have a comparison of the function $U^{th}(\beta)$ with the corresponding quantum function $U(\beta)$ defined by (1), one has obviously to put $A = \hbar$. Evidently, in the present case, at variance with the case of the linear oscillator, one has that the two formulae are analytically different; however, the limits as $\beta \to 0$ and $\beta \to \infty$ are clearly the same. Moreover, the actual values do not differ much. This is shown for example by the values reported in table I, together with the values for relative difference $\delta = |U^{th} - U|/U^{th}$, in correspondence to 16 values of β in the interval (0.1, 5). As one sees, δ takes even values of the order of 1, but only for values of U so large or so small that the curves for $U^{th}(\beta)$ and $U(\beta)$ are essentially undistinguishible, as shown in fig. 1.

Nothing will be said here of the completely open problem of justifying, on the basis of classical dynamics, the existence of an action threshold characterizing frozen motions. For a comparison with the results that are obtained when the plane rotator is quantized according to the method of the so-called stochastic electrodynamics, see ref. [9].

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[9] T. H. BOYER: *Phys. Rev. D*, **1**, 2257 (1970). We thank S. BERGIA for bringing this paper to our attention.