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SPECIFIC HEAT OF A FREE PARTICLE IN A GENERALIZED BOLTZMANN-GIBBS STATISTICS

by

Abstract

We discuss some relevant properties within the framework of a recently proposed generalized Boltzmann-Gibbs statistics. We then apply this formalism to calculate the thermal dependence of the specific heat associated with a free particle ($\varepsilon_n = \lambda n^2 + B$; $\lambda > 0$). In addition to that, we calculate the classical limit for a larger family of systems ($\varepsilon_n = \lambda n^2 + B$; λ , r > 0).

<u>Key-words:</u> generalized statistical mechanics; free particle; specific heat; generalized thermodynamics.

I INTRODUCTION AND GENERAL CONSIDERATIONS.

In a recent paper 11, one of us proposed a possible generalization of the Boltzmann-Gibbs statistics. This extension was based on the following expression for the entropy:

$$S_{q} = k \frac{1 - \sum_{n} p_{n}^{q}}{q - 1}$$
 (1)

where n runs over all possible microstates of the system, $\{p_n\}$ are the associated probabilities and q is any real number which labels different statistics; the q+1 limit yields the standard Shannon entropy $S_1 = -k\sum_n p_n \ln(p_n)$. The entropy given by Eq.(1) is related with the Renyi entropy [2] given by

$$S_q^R = k \frac{\ln(\sum p_n^q)}{q-1}$$
 (2)

as follows:

$$S_{q}^{R} / k = \frac{\ln[1 + (1-q)S_{q}/k]}{1-q}$$
(3)

Like S_q , S_q^R recovers the Shannon entropy in the q+1 limit. We immediately verify^[3] that S_q^R is a monotonic function of S_q for all values of q. Nevertheless, their concavities might be different (this is illustrated in Fig.1 for a binary variable, i.e, total number of microstates equal 2). As it will become transparent later on, the concavity under discussion is relevant for the sign of the specific heat, for <u>arbitrary</u> values of q.

In order to obtain the <u>equilibrium</u> distribution, the standard variational procedure has been adopted in Ref.[1] by using S_q and by assuming the (generalized) internal energy $\sum_{n} p_n \epsilon_n$, where $\{\epsilon_n\}$

is the "spectrum" of the system. Consequently, the canonical distribution at temperature $T=1/k\beta$ is given by $p_n = \alpha - (1-\beta(q-1)\epsilon_n)^{1/(q-1)}$. If we assume instead that the generalized internal energy is given by

$$U_{\mathbf{q}} = \sum_{\mathbf{n}} \mathbf{p}_{\mathbf{n}}^{\mathbf{q}} \mathbf{\varepsilon}_{\mathbf{n}} \tag{4}$$

the canonical distribution will be given by

$$p_{n} = \frac{[1-\beta(1-q)\epsilon_{n}]^{1/(1-q)}}{Z_{q}}$$
 (5)

with

$$Z_{q} = \sum_{n} \left[1-\beta(1-q)\epsilon_{n}\right]^{1/(1-q)}.$$
 (6)

This distribution is represented in Fig.2 for typical values of q. We verify that distribution given by Eq.(5) coincides, through transformation 1-q+q-1, with that associated with the internal energy $\sum p_i \epsilon_i$.

Furthermore Curado and Tsallis [3] have shown that the entire mathematical structure of the connection between standard statistical mechanics and thermodynamics is preserved through the present generalization. To be more specific, they prove that

$$\partial S_{a}/\partial U_{a}=1/T,$$
 (7)

that

$$U_{q} = -(\delta/\delta\beta) [(Z_{q}^{1-q}-1)/(1-q)]$$
 (8)

and that

$$\mathbf{F}_{\mathbf{q}} = \mathbf{U}_{\mathbf{q}} - \mathbf{T} \mathbf{S}_{\mathbf{q}} \tag{9}$$

$$=-kT(Z^{1-q}-1)/(1-q)$$
 (10)

Let us now define as follows the generalized specific heat

$$C_{q} = T \partial S_{q} / \partial T$$
 (11)

Since T is not a natural variable of U_q and S_q , Eq.(9) implies $\partial F_q/\partial T = -S_q$. Deriving once more yields $\partial^2 F_q/\partial T^2 = -\partial S_q/\partial T$, hence, by using definition given by Eq.(11),

$$C_{q} = -T \partial^{2} F_{q} / \partial T^{2}. \tag{12}$$

It is also straightforward to establish that

$$C_q = \partial U_q / \partial T$$
. (13)

By using Eqs.(4), (5) and (6) we obtain

$$c_{q}/k = \frac{q}{(kT)^{2}} \left\{ \sum_{n} \left[p_{n}^{q} \frac{\varepsilon_{n}^{2}}{1 - \beta (1 - q) \varepsilon_{n}} \right] - \left[\sum_{n} p_{n}^{q} \varepsilon_{n} \right] \left[\sum_{n} p_{n} \frac{\varepsilon_{n}}{1 - \beta (1 - q) \varepsilon_{n}} \right] \right\}. \quad (14)$$

It straightforwardly follows that

$$C_q/k = qZ^{1-q} < (E_n - < E_n >)^2 > /(kT)^2$$
 (15)

with

$$E_{n} * \varepsilon_{n} / [1 - \beta (1 - q) \varepsilon_{n}]$$
 (16)

and where $\langle f(\epsilon_n) \rangle$ stands for $\Sigma_n p_n f(\epsilon_n)$, f being an arbitrary function. We notice that the <u>fluctuation form</u> of the specific heat is preserved through the present generalization. Furthermore, we remark that C_q has the sign of q (i.e., $C_q \ge 0$ for q > 0 and $C_q \le 0$ for q < 0).

Since the q=1 case corresponds to the well known Boltzmann-Gibbs Statistics, we shall analyse the cases q*1. Let us illustrate the typical situation by discussing the two (degenerate) level system (if the number of levels N>2 the situation is slightly more complex, but follows essentially along the same lines). We denote by ε_0 (ε_1) and g_0 (g_1), the fundamental (excited) energy level and its associated degeneracy.

If q<1, three different basic situations can be distinguished,

<u>.</u>

namely:

(i) If $\varepsilon_1 > \varepsilon_0 > 0$ it follows that: for $T \in [0, (1-q)\varepsilon_0/k]$ we have a thermally forbidden (physically unaccessible) region because at least one level must be populated (we recall that $\Sigma_n p_n = 1$); for $T \in$ $((1-q)\epsilon_0/k,(1-q)\epsilon_1/k]$ we have a thermally frozen region since $p_0=1/q_0$ and $p_1=0$; for T> $(1-q)\epsilon_1/k$ we have a thermally active region; finally for all negative values of the temperature, the system is thermally active. In fact it is thermally active even for T=0 if we are approximating from negative temperatures and at this point, the population of the fundamental state and the excited state are respectively $p_0 = g_0 \varepsilon_0^{1/(1-q)} / (g_0 \varepsilon_0^{1/(1-q)} + g_1 \varepsilon_1^{1/(1-q)})$ and $p_1 = g_1 \varepsilon_1^{1/(1-q)} / (g_0 \varepsilon_0^{1/(1-q)} + g_1 \varepsilon_1^{1/(1-q)});$

(ii) If $\varepsilon_1 > 0 > \varepsilon_0$ it follows that: for $T \in [0, (1-q)\varepsilon_1/k]$ we have a thermally frozen region since $p_0 = 1/g_0$ and $p_1 = 0$; for $T > (1-q)\varepsilon_1/k$ we have a thermally active region; for $T \in [(1-q)\varepsilon_0/k, 0]$ we have another thermally frozen region (now with $p_1 = 1/g_1$ and $p_0 = 0$), and for $T < (1-q)\varepsilon_0/k$ we have another thermally active region;

(iii) If $\varepsilon_0 < \varepsilon_1 < 0$ it follows that: the system is thermally active for all positive values of the temperature. In fact it is thermally active even for T=0 if we are approximating from positive temperatures and, at this point, the populations of the fundamental and the excited states are respectively $p_0 = g_0 |\varepsilon_0|^{1/(1-q)} / (g_0 |\varepsilon_0|^{1/(1-q)} + g_1 |\varepsilon_1|^{1/(1-q)})$ and

thermally active region.

If q>1, again we have three different basic situations, namely: (i) If $\varepsilon_1 > \varepsilon_0 > 0$ it follows that: the system is thermally active for all positive values of the temperature. In fact it is thermally active even for T=0 if we are approaching from positive temperatures and at this point, the populations of the fundamental and the excited states are respectively $p_0 = g_0 \varepsilon_0^{1/(1-q)} / (g_0 \varepsilon_0^{1/(1-q)} + g_1 \varepsilon_1^{1/(1-q)}) \quad \text{and} \quad p_1 = g_1 \varepsilon_1^{1/(1-q)} / (g_0 \varepsilon_0^{1/(1-q)} + g_1 \varepsilon_1^{1/(1-q)}).$

For $T \in [(1-q)\varepsilon_0/k,0]$ we have a <u>thermally forbidden</u> region, for $T \in [(1-q)\varepsilon_1/k,(1-q)\varepsilon_0/k)$ we have a <u>thermally frozen</u> region, and for $T < (1-q)\varepsilon_1/k$ we have another <u>thermally active</u> region;

(ii) If $\varepsilon_1>0>\varepsilon_0$ it follows that: for $T\in [(1-q)\varepsilon_0/k,0]$ we have a thermally frozen region since $p_0=1/g_0$ and $p_1=0$, for $T>(1-q)\varepsilon_0/k$ the system is thermally active. For $T\in [(1-q)\varepsilon_1/k,0]$ we have another thermally frozen region with $p_1=1/g_1$ and $p_0=0$, and for $T<(1-q)\varepsilon_1/k$ the system is once again thermally active;

(iii) If $\varepsilon_0 < \varepsilon_1 < 0$ it follows that: for $T \in [0, (1-q)\varepsilon_1/k]$ we have a thermally forbidden region, for $T \in ((1-q)\varepsilon_1/k, (1-q)\varepsilon_0/k]$ we have a thermally frozen region since $p_0 = 1/g_0$ and $p_1 = 0$, for $T > (1-q)\varepsilon_0/k$ the system is thermally active, and for all negative values of the temperature the system is, once again, thermally active. In fact it is thermally active even for T = 0 if we are approaching from negative temperatures and, at this point, the populations of the fundamental and the excited states are respectively $p_0 = g_0 |\varepsilon_0|^{1/(1-q)} / (g_0 |\varepsilon_0|^{1/(1-q)} + g_1 |\varepsilon_1|^{1/(1-q)})$ and $p_1 = g_1 |\varepsilon_1|^{1/(1-q)} / (g_0 |\varepsilon_0|^{1/(1-q)} + g_1 |\varepsilon_1|^{1/(1-q)})$.

If q*1, the absolute value of ϵ_0 is physically relevant, consequently an additive constant in the spectrum will produce physical effects (contrarily to what happens for q=1, in which case additive constants in the spectra are completely inocuous).

II FREE PARTICLE: QUANTUM CASE

In the framework where the generalized internal energy is assumed to be $\Sigma_n p_n \epsilon_n$, specific heat calculations are available for the two-level system^[1,4], the harmonic oscillator^[4] and the one-dimensional Ising model^[5]. In the present paper we focus, along the lines of Ref.[3] (i.e., by assuming Eq.(4)), the specific heat of a one-dimensional free particle characterized by

$$\varepsilon_{n} = An^{2} + B$$
 $(n=0,\pm 1,\pm 2,...)$ (17)

where A>0 and B any real number. The replacement of this spectrum into Eq.(14) enables in principle the calculation of the specific heat C_q/k as a function of (kT/A,B/A,q). We have not succeeded in analytically calculating this function for the general case. However, in all cases, the numerical treatment is possible. Moreover, the analytical calculation is mathematically tractable (though not trivial) for some special cases, such as q=(m+1)/m (m=1,2,3,...) and arbitrary B. Let us illustrate this fact by presenting the (q,B)=(2,0) case:

$$C_2/k = \frac{1}{4} \left[\tanh^2 x + \frac{1+2x^2}{x} \tanh x - 2x \tanh^3 x - 1 \right]$$
 (18)

with $x=\pi\sqrt{kT/A}$.

We present, in Fig.3 the thermal evolution of C_{σ}/k for B=0

and typical values of q. We remark:

- (i) For $q\ge 1$, C_q is positive everywhere excepting at T=0 where it vanishes; both $C_q(T)$ and dC_q/dT are continuous for all finite temperatures;
- (ii) For 1/2 < q < 1, C_q is positive for all temperatures above (1-q)A/k, and vanishes in the interval $T \in [0,(1-q)A/k]$; $C_q(T)$ is continuous everywhere, but not dC_q/dT , which presents discontinuities at $T_{\nu} = (1-q)A\nu^2/k$, $(\nu=1,2,3,...)$;
- (iii) For $0 \le q \le 1/2$, C_q is positive for almost all temperatures above (1-q)A/k, and vanishes in the interval $T \in [0,(1-q)A/k]$; $C_q(T)$ itself presents now discontinuities at $T_{\nu} = (1-q)A\nu^2/k$, $(\nu=1,2,3,...)$ $(C_q(T)$ vanishes also for $T + T_{\nu} = 0$)
- (iv) For $q \leftrightarrow 0$, $C_q(T)$ vanishes everywhere excepting at $T_{\nu} = \hbar \nu^2 / k$ ($\nu = 1, 2, 3, ...$) where it takes positive values which monotonically increase with ν ;
- (v) For $q \leftarrow 0$, $C_q(T)$ vanishes everywhere excepting at $T_{\nu} = \lambda \nu^2/k$ ($\nu = 1, 2, 3, ...$) where it takes large negative values which become larger as ν increases;
- (vi)For q<0, C_q is negative for almost all temperatures above (1-q)A/k, and vanishes in the interval $T \in [0,(1-q)A/k]$; $C_q(T)$ itself presents discontinuities at $T_{\nu}=(1-q)A\nu^2/k$, $(\nu=1,2,3,...)$ $(C_q(T)$ vanishes also for $T+T_{\nu}=0$).

Let us now exhibit the influence of B (which, we recall, is irrelevant only for q=1). We present in Fig.(4) an example for q>1, and in Fig.(5) an example for q<1. We remark in Fig.(4) (which illustrates the case q>1) that for $B\geq 0$, $C_q(T)$ is continuous everywhere, positive for all finite temperatures and vanishes at T=0, whereas, for B<0, $C_q(T)/k$ vanishes in the interval $T\in T=0$

[0,(q-1)|B|/k], presents a discontinuity at T=(q-1)|B|/k where it achieves (for T+(q-1)|B|/k+0) the value $(2\pi^2/3)(q-1)k|B|/A$, and varies continuously thereafter.

Concerning Fig.(5) (which illustrates the case 0 < q < 1) we can distinguish three situations, namely:

(i) For B>0, the region T \in [0,(1-q)B/k] is thermally forbidden, the region T \in ((1-q)B/k,(1-q)(A+B)/k] is thermally frozen, and finally, for T>(1-q)(A+B)/k, C_q is positive everywhere and presents discontinuities at T_{\nu}=(1-q)(A\nu^2+B)/k (\nu=2,3,4,...);

(ii) For B<0 and A+B>0, the system is frozen in the interval T \in [0,(1-q)(A-|B|)/k], C_q is positive for higher temperatures and presents discontinuities at T_{ν}=(1-q)(A ν ²-|B|)/k (ν =1,2,3,...);

(iii) For B<0 and A+B<0, the system is frozen only at T=0, active at all finite temperatures and C_q is positive and presents discontinuities at $T_{\nu}=(1-q)\,(\lambda\nu^2-|B|)/k$ at all integer values of ν above a value ν^* which increases with increasing |B|.

The influence of B*0 for the q<0 cases mainly relies on the fact that the discontinuities of C_q (which everywhere satisfies $C_q^{\leq 0}$) occur at temperatures which depend on B, more precisely at temperatures $T_{\nu}=(1-q)\;(\lambda\nu^2+B)/k$.

III FREE PARTICLE: CLASSICAL CASE

The classical behavior of the specific heat (noted C_q^{class}) is obtained, for q=1, by replacing, in Eq.(14), the sums by integrals. We shall follow along these lines for generic q.

For 1<q<3, we obtain

$$\frac{C_q}{k} = \frac{(3-q)(q-1)^{(q-1)/2}}{4} \left\{ \sqrt{\pi} \frac{\Gamma[(3-q)/(2q-2)]}{\Gamma[1/(q-1)]} \right\}^{1-q}$$

$$\frac{kT/A}{kT/A+(q-1)B/A} (19)$$

For q+1 we recover, for all finite values of T, the well known result $C_1/k=1/2$. Although some of integrals (replacing sums in Eq.(14)) diverge, the specific heat seems to vanish for all finite values of T for $q\ge 3$.

For 1/2≤q<1, we obtain

$$\frac{C_q}{k} = \frac{(3-q)(1-q)^{(q-1)/2}}{4} \left\{ \sqrt{\pi} \frac{\Gamma[(2-q)/(1-q)]}{\Gamma[(5-3q)/(2-2q)]} \right\}^{1-q}.$$

$$kT/A \qquad (20)$$

$$kT/A + (q-1)B/A$$

Also here, for q+1, we recover for all finite temperatures, the result $C_1/k=1/2$.

For q<1/2 some mathematical subtleties are encountered related to the fact that, at $T=T_{\nu}^{E}(1-q)(A\nu^{2}+B)/k$, discontinuities exist in the specific heat. More precisely, at $T=T_{\nu}$ three different values can be calculated for the specific heat, namely

Eqs.(19) and (20) yield, for B=0, $C_q \propto T^{(1-q)/2}$, consequently: (i) in the T+0 limit, C_q^{class} diverges (vanishes) for q>1 (1/2 \leq q<1); (ii) in the T+ ∞ limit, C_q^{class} diverges (vanishes) for 1/2 \leq q<1 (q>1). These facts are exhibited in Fig.(6). In Fig.(7) we plot, for finite typical values of B the temperature evolution of C_q . We can remark some points: i) The T+ ∞ dominant behaviour still satisfies $C_q \propto T^{(1-q)/2}$ for all finite values of B; (ii) In the low temperature region, C_q vanishes when T+0 (diverges like $[T-|(q-1)B|]^{-(q+1)/2}$ when T+|(q-1)B|+0 and vanishes when T<|(q-1)B|) for $1/2\leq$ q<1 and B>0 as well as for q>1 and B>0 (for $1/2\leq$ q<1 and B>0 as well as for q>1 and B>0).

In the $T^{+\infty}$ limit, the replacement (in Eq.(14)) of the sums by integrals becomes inocuous, hence we expect $C_q(T) \sim C_q^{\text{class}}(T)$. This fact is exhibited for q>1 (Fig.(8)), $1/2 \leq q < 1$ (Fig.(9)) and q=1 (Fig.(10)).

Fig. (10) deserves a comment. Indeed, any Statistical Mechanics textbook contains the <u>classical</u> result $C_1/k=1/2$, but—surprisingly enough!—we found nowhere the <u>quantum</u> result (this curious absence is probably due to the fact that, for all typical physical systems, the quantum region of a free particle specific heat only appears at tremendously low temperatures). It is now worth stressing that the quantum free particle specific heat presents, as a function of T, a maximum, similarly to that of

the standard rigid rotator and in variance with that of the harmonic oscillator (for which C, monotonically increases with T).

Finally, we have calculated C_q^{class} corresponding to the spectrum $\epsilon_n = An^r + B$ n=0,1,2,...) for A>0, r>0 and B any real number. We obtain, for 1<q<r+1

$$C_q/k=r^{q-1}(r+1-q)(q-1)^{(q-1)/r}\left[\frac{\Gamma(1/r)\Gamma(1/(q-1)-1/r)}{\Gamma(1/(q-1))}\right]^{1-q}$$

$$\frac{kT/A}{\left[kT/A+(q-1)B/A\right]^{(r+q-1)/2}}$$
 (21)

and for q<1

$$C_{q}/k=r^{q-3}(r+1-q)(1-q)^{(q-1)/r}\left[\frac{\Gamma(1/r)\Gamma[(2-q)/(1-q)]}{\Gamma[(r+(r+1)(1-q))/(r(1-q))]}\right]^{1-q}$$

$$\frac{kT/A}{kT/A+(q-1)B/A}^{(r+q-1)/2}$$
 (22)

Eqs. (21) and (22) yield, in the $q\rightarrow 1$ limit, $C_1/k=1/r$ for all finite temperatures, thus extending the result obtained in Refs.[6]. It is also worth mentioning that Eqs. (21) and (22) do not reproduce, for r=2, the classical specific heat given by Eqs. (19) and (20) (but rather 2^{q-1} times it); the reason is of course transparent,

namely related to the fact that in this last part we have used n=0,1,2,3,..., instead of $n=0,\pm1,\pm2,...$

- IV CONCLUSION

We studied here a possible generalization of Boltzmann-Gibbs statistics. It has been observed some uncommon results for the specific heat of a 1-dimensional free particle. For instance, the thermodynamical third principle is violated; the same happens, at T + \infty, for the classical equipartition of energy. However, in the present generalization, both the quantum and classical calculations assymptotically coincide at high temperatures. Another interesting fact is that the result found for q=1 can be faced as a non-uniform convergence of those found for q≠1. Last but not least, we exhibit here (surprisingly enough, for the first time as far as we could check) the quantum Boltzmann-Gibbs specific heat of a free particle.

Let us conclude by stressing here that until now it has not been established the experimental limits for the Boltzmann-Gibbs statistics, i.e, the precision within which q=1. Also, it may be that for some process, for instance biological ones (see for example Ref.[7]) the entropy formula needed is other than the Shannon one.

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CAPTION FOR FIGURES

<u>Fig.1</u> p-dependence of S_q (a) and S_q^R (b) for number of microstates equal 2 and typical values of q (let us mention here an Erratum of Ref.[3], namely that property 3 holds as stated for S_q but not always for S_q^R)

Fig.2 $\beta \epsilon_n$ -dependence of Z_{q}^p for typical values of q (this figure has been adapted from the corresponding one in Ref.[1]); the vertical dashed line represents the q=2 asymptote.

Fig.3 Thermal evolution of C_q/k for B=0 and typical values of q: (a) $q \ge 1/2$; (b) 0 < q < 1/2; (c) q < 0.

Fig.4 Thermal evolution of C_q/k for q=2 and typical values of B: (a) $B/A \ge -0.08$; (b) $B/A \le -0.08$

Fig. 5 Thermal evolution of C_q/k for q=1/2 and typical values of B.

<u>Fig.6</u> Thermal evolution of C_q^{class}/k for B=0 and typical values of q.

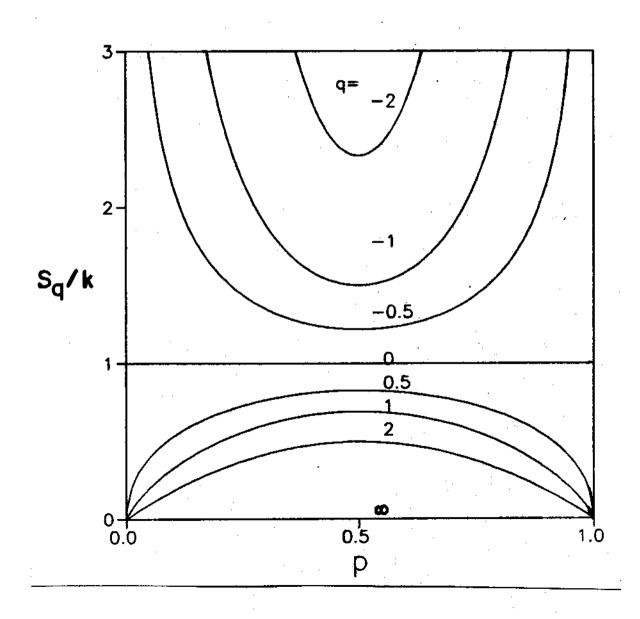
<u>Fig.7</u> Thermal evolution of C_q^{class}/k for typical values of q and B

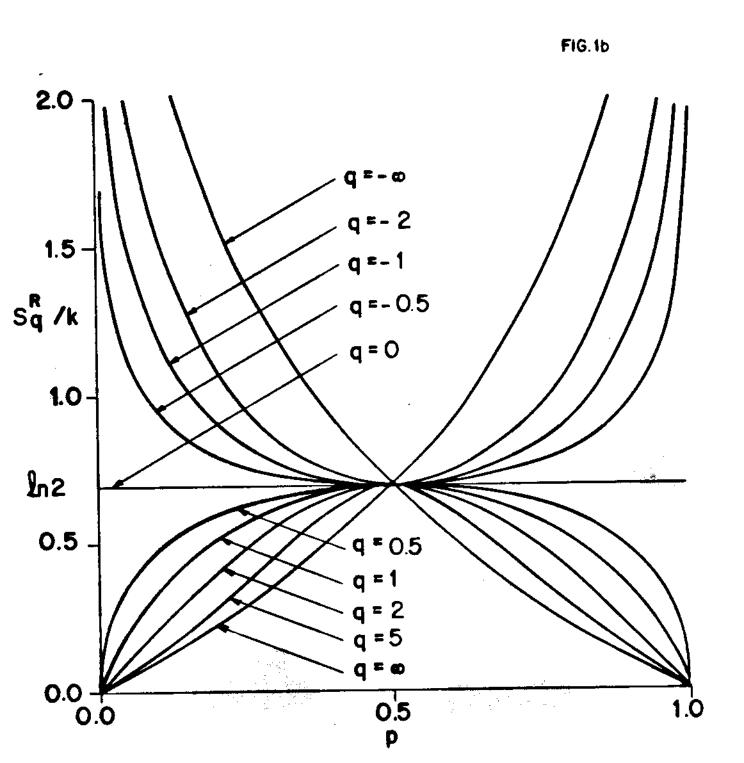
Fig.8 Comparison, for typical values of q>1 and B=0, of the classical and quantum specific heats.

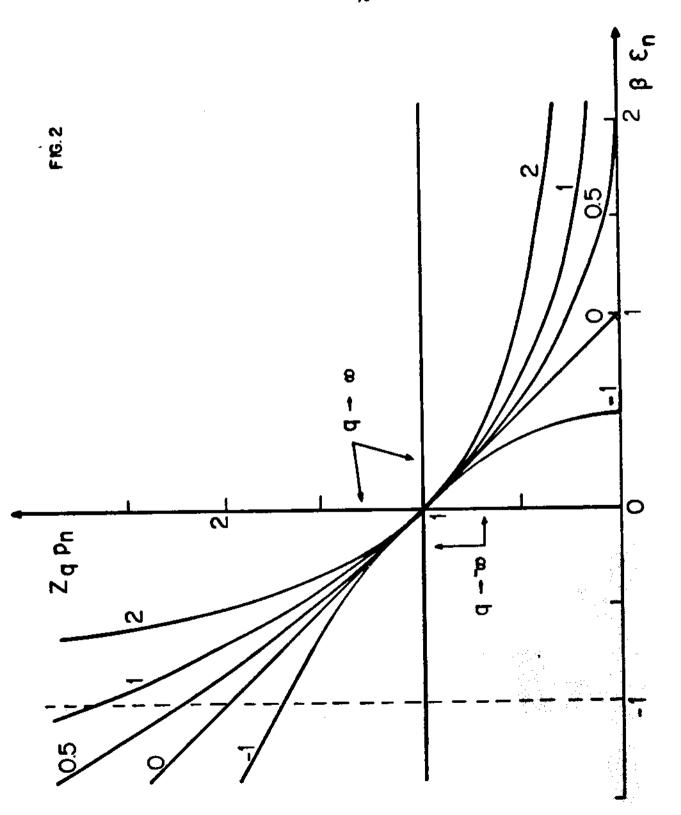
<u>Fig.9</u> Comparison, for B=0, of the classical and quantum specific heat: (a) standard temperature scale and typical values of q<1; (b) very large temperature scale and q=1/2.

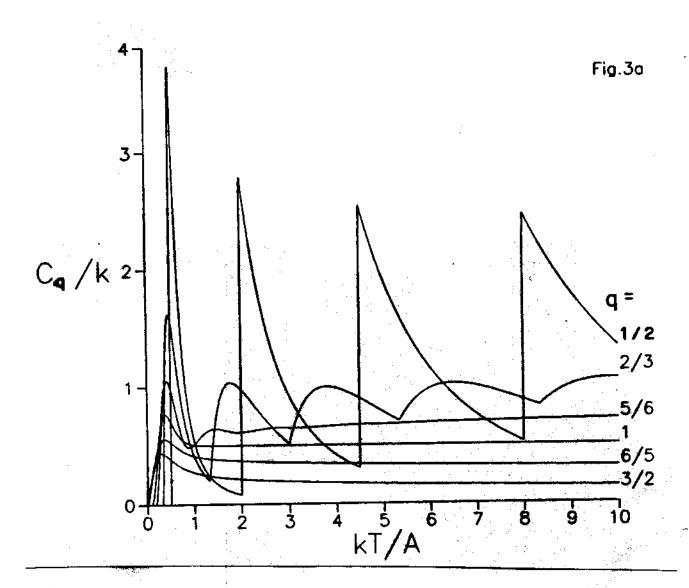
<u>Fig.10</u> Comparison, for q=1 (Boltzmann-Gibbs statistics) and arbitrary B, of the classical and quantum specific heats.

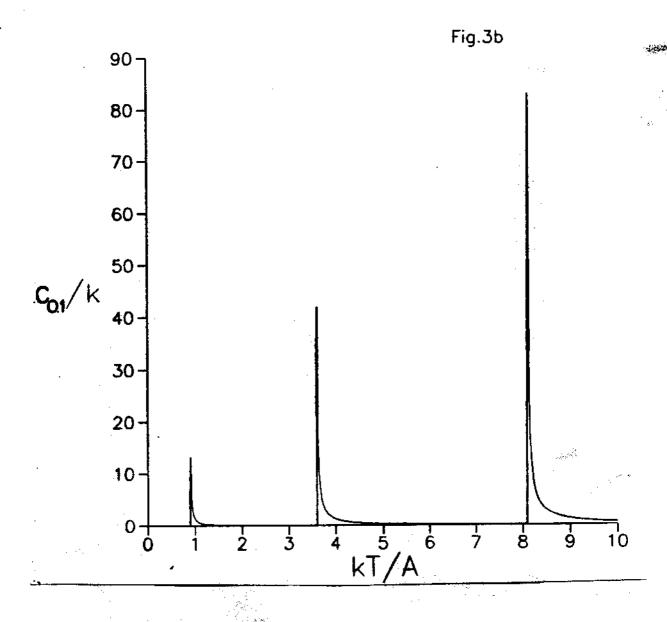
FIG. 1a

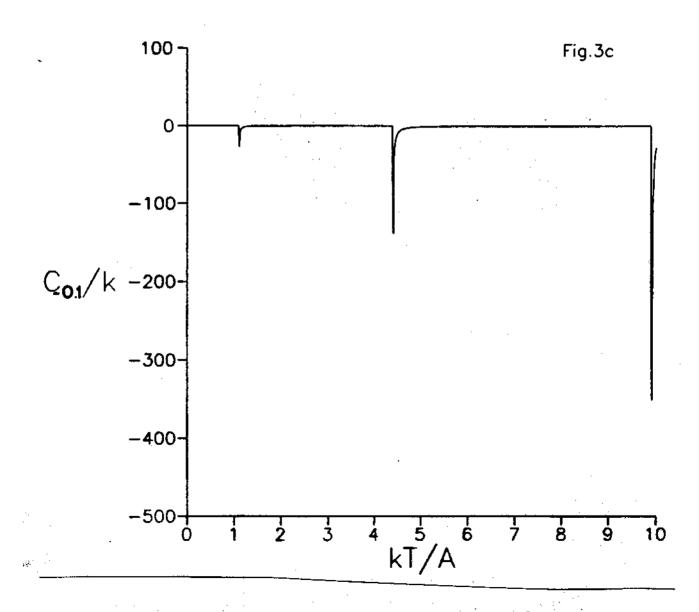


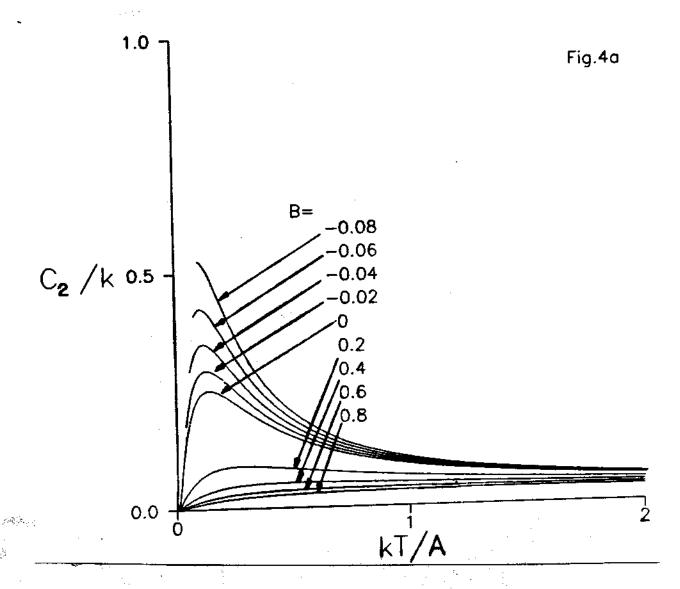




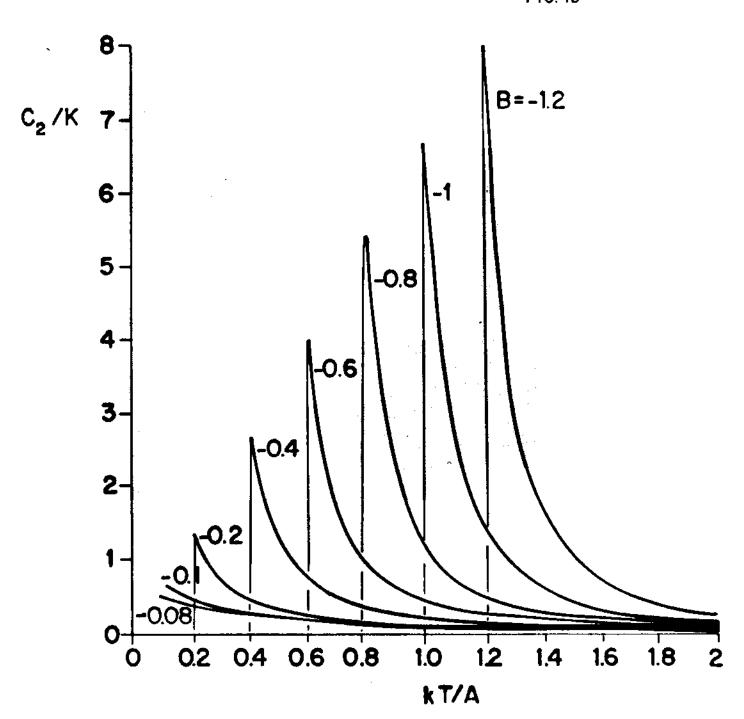


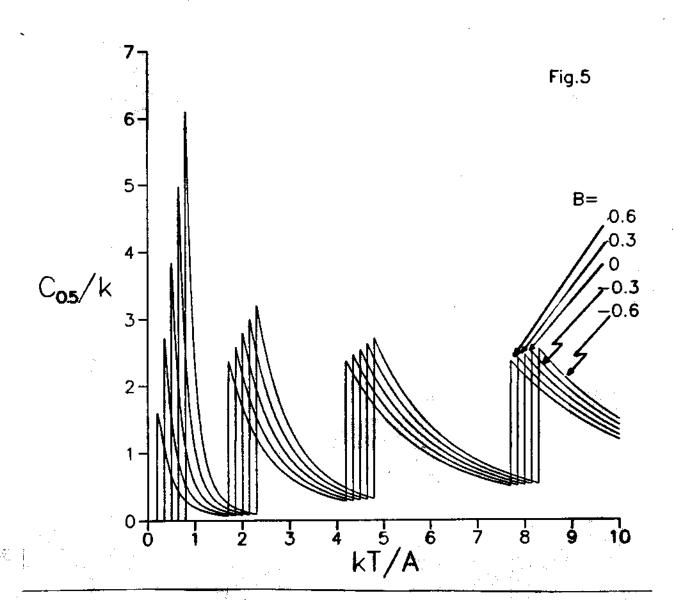


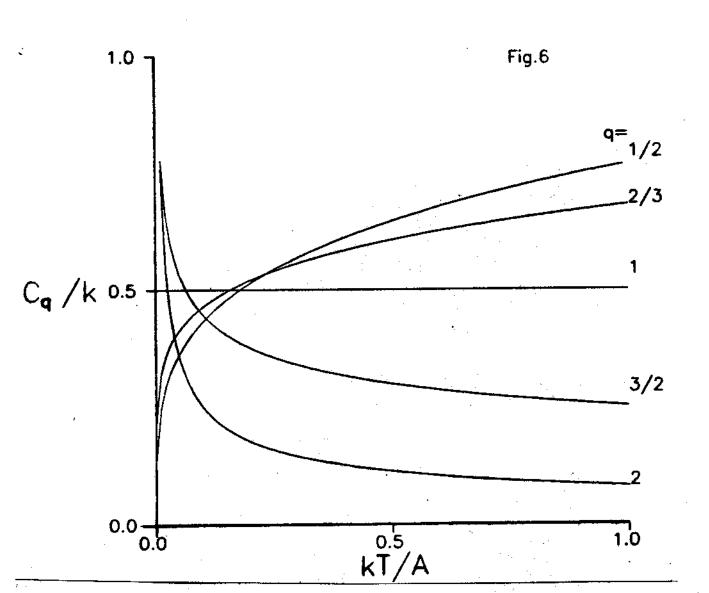


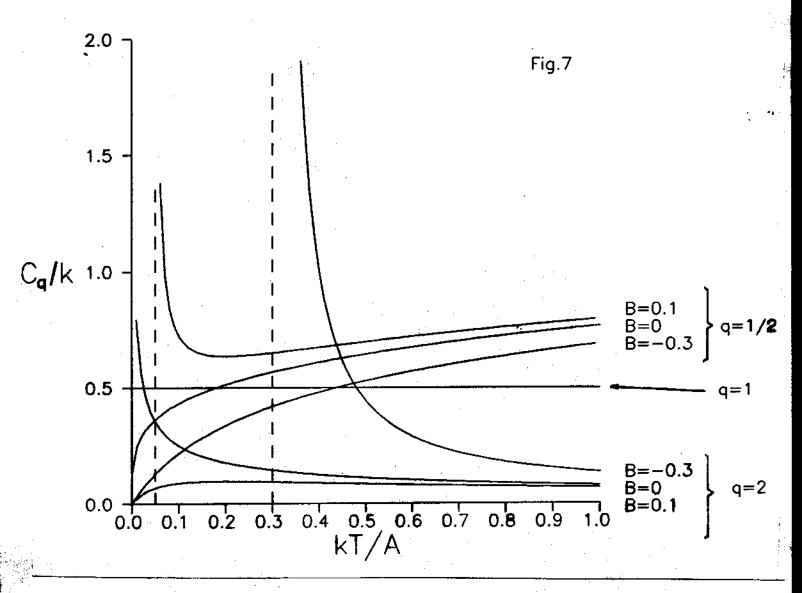


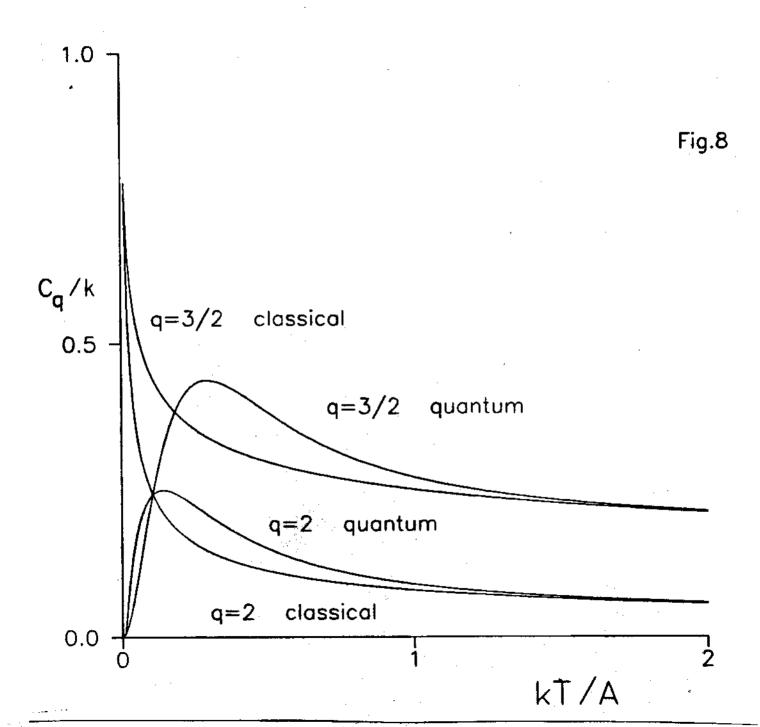


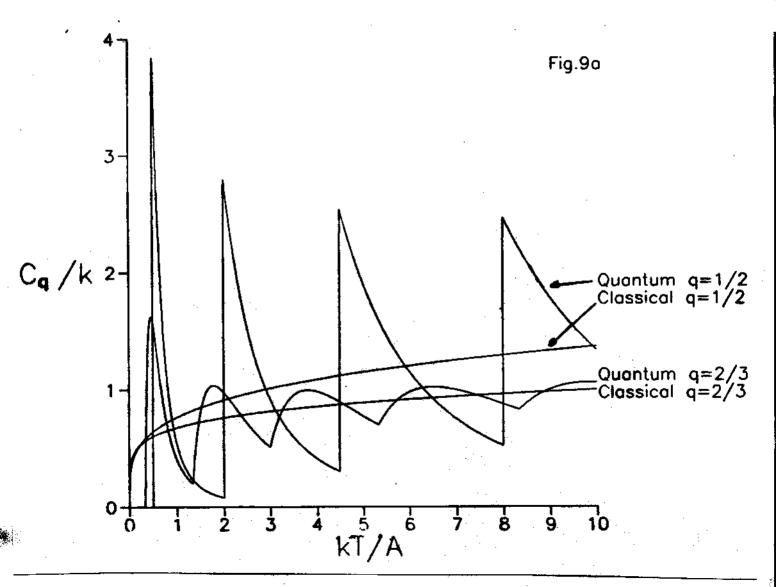




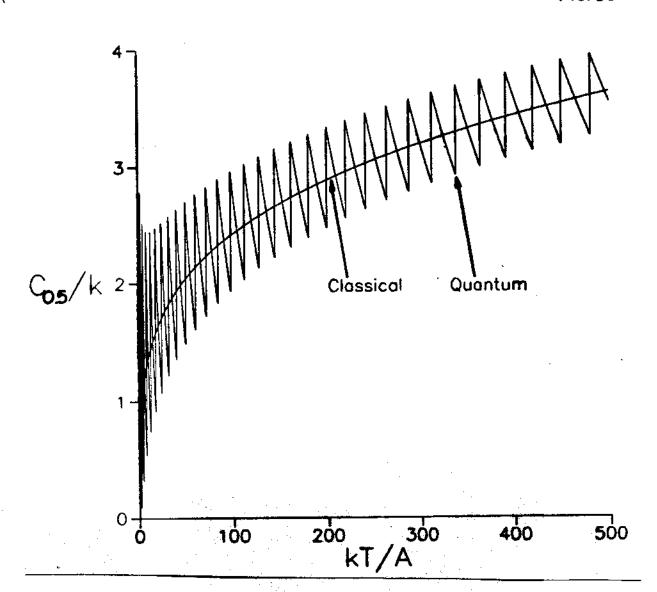


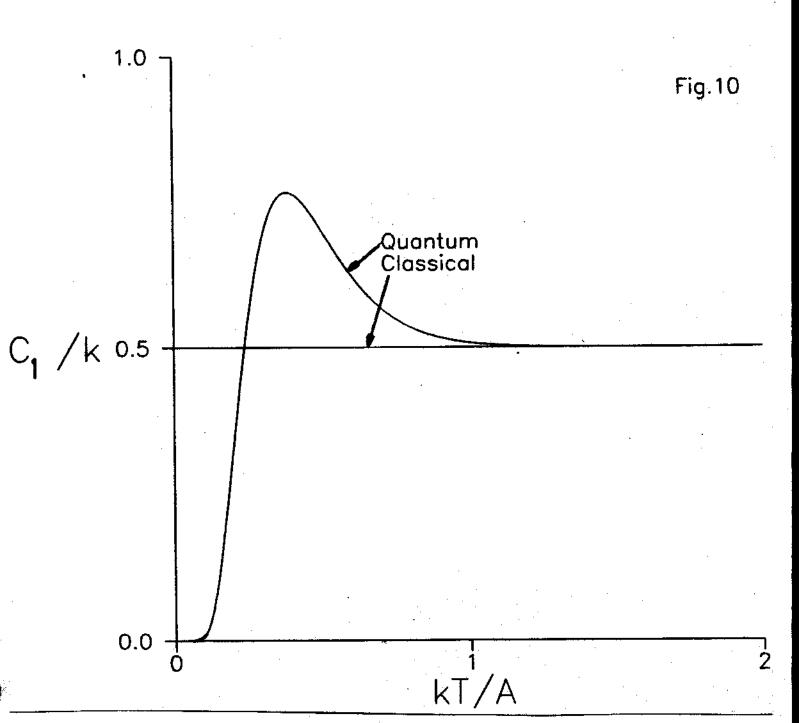












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