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EXTENDED VARIATIONAL METHOD IN STATISTICAL MECHANICS

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ABSTRACT

Through cumulant expansions of the free energy and the susceptibility, a new variational procedure is proposed with the purpose of improving the standard Variational Method in Equilibrium Statistical Mechanics. The procedure is tested for two types of classical anharmonic single oscillators, namely those whose elastic potential is proportional to x^{2n} $(n = 1,2,...)$ and those of the type $ax^2 + bx^4$, whose exact free energy, specific heat and susceptibility are herein established. Although convergence problems (similar to those appearing in the asymptotic series) exist (at least for the free energy) in the limit of high perturbative orders, great improvement (typically of the order of 40 with respect to the standard Variational Method) is obtained in all the physically meaningfull situations and quite satisfactory description is provided (with a "single shot") for both limits $T \to 0$ and $T \to \infty$ simultaneously. Incidentally a new recursive relation among cumulants is established.

I - INTRODUCTION

The Variational Method (VM) in Equilibrium Statistical Mechanics (for general purposes see Refs. [1-8]) enables the approximative calculation of the thermal behaviour of various quantities (free and internal energies, specific heat, susceptibility, equations of states among others) for a great variety of systems. For example problems like superconductivity [9-11], isolated [6,8,12] or coupled [13] anharmonic oscillators (eventually within the context of structural phase transitions [14-19], pure [1-3,5,7,20,21] and random [22] magnetism as well as nuclear reactions [23] have been treated within this framework.

The VM has the advantage of leading, for *all* temperatures, to results which are qualitatively correct (some notorious counterexamples do exist however; for example the use of a non interacting spins trial Hamiltonian, i.e. the Mean Field Approximation (MFA), to treat the one-dimensional Ising ferromagnet leads to a non vanishing critical temperature, which is definitively wrong), but has the disadvantage of being a "single shot" procedure, in the sense that the improvement of its results requires, for a given problem, a new choice for the trial Hamiltonian (noted $\mathcal{H}_0$), i.e. the complete reformulation of the treatment. Other "single shot" procedures (usually better than the MFA, in what magnetism concerns) do exist in the literature, for example Onsager's Reaction Field Approximation (RFA) [24-28] which, contrarily to the MFA, satisfies the fluctuation-dissipation theorem but does not minimize a certain free

energy. The RFA unfortunately is, like the VM, not exempted from some notorious wrong results (it leads, for example, to a vanishing critical temperature for the two-dimensional Ising ferromagnet).

Contrarily to the VM, the formulation of the perturbation techniques (for instance the low- and high- temperature series) usually allow for successive approximations to the exact result, but present the disadvantage of describing only one region of the domain of variation of the external parameters of the problems (in the example we have just quoted, $T \to 0$ or $T \to \infty$ but not both as well as intermediate temperatures). The idea of formulating procedures which ally the advantage of the VM (full description) with that of the perturbative techniques (possibility of successive approximations) is no doubt a quite tempting one. The Zubarev's Green function techniques constitute of course a successful attempt in this sense, but we are presently interested in those whose formal structure is close to the VM, within this line an interesting self-consistent procedure has been introduced [29,30] a few years ago to treat random magnetism. In the present work we introduce, through cumulant expansions (see for example Refs. [31,32]) and in principle for all kinds of systems (whose Hamiltonian will be noted $\mathcal{H}$), another type of self-consistent procedure which extends the VM and which will therefore be referred hereafter as to the Extended Variational Method (EVM). In order to verify its performances, we test it for classical anharmonic single oscillators (which are exactly solved herein): although the procedure is, as we shall see, not exempted from defects

(coming essentially from the possible inexistence, in general, of a condition playing for the EVM a role similar to the one played by the Bogolyubov (or Bogolyubov-Peierls) inequality for the VM), it provides algorithms which very sensibly improve (typically 40 times better) those associated to the VM.

II - EXTENDED VARIATIONAL METHOD

II.1 Free energy

Let us here assume for simplicity that the real and trial Hamiltonians $\mathcal{H}$ and $\mathcal{H}_0$ commute (i.e. either classical systems or quantum systems with $[\mathcal{H}, \mathcal{H}_0] = 0$). The free energy associated to Hamiltonian $\mathcal{H}$ is given by

$$F = -\frac{1}{\beta} \ln \mathrm{Tr}\, e^{-\beta \mathcal{H}} \tag{1}$$

or *identically* by

$$F = F_0 - \frac{1}{\beta} \ln \langle e^{-\beta(\mathcal{H} - \mathcal{H}_0)} \rangle_0 \tag{2}$$

with

$$F_0 \equiv -\frac{1}{\beta} \ln \mathrm{Tr}\, e^{-\beta \mathcal{H}_0} \tag{2'}$$

where $\beta \equiv 1/k_B T$ and $\langle \cdots \rangle_0$ denotes the canonical thermal mean value associated to the distribution law $\rho_0 \propto \exp(-\beta \mathcal{H}_0)$.
Through formal expansion F can be rewritten as follows:

$$F = F_0 + \sum_{j=1}^{\infty} \frac{(-\beta)^{j-1}}{j!} \kappa_j \tag{3}$$

where κ_j is the j-th order cumulant associated to $(\mathcal{H} - \mathcal{H}_0)$.
In order to illustrate this point let us first introduce the moments $\{\mu_j\}$ through

$$\mu_j \equiv \langle (\mathcal{H} - \mathcal{H}_0)^j \rangle_0 \qquad (j = 1, 2 \ldots) \tag{4}$$

and the centered moments $\{\mu'_j\}$ through

$$\mu'_j \equiv \langle \left[(\mathcal{H} - \mathcal{H}_0) - \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 \right]^j \rangle_0 \quad (j=1,2,\ldots) \qquad (5)$$

The first four cumulants are given by

$$\kappa_1 = \mu_1$$

$$\kappa_2 = \mu_2 - \mu_1^2 = \mu'_2$$

$$\kappa_3 = \mu_3 - 3\mu_2\mu_1 + 2\mu_1^3 = \mu'_3$$

$$\kappa_4 = \mu_4 - 4\mu_3\mu_1 + 12\mu_2\mu_1^2 - 6\mu_1^4 - 3\mu_2^2 \neq \mu'_4$$

and in general [33]

$$\kappa_j = j! \sum_{\{n_i\}} \left\{ (-1)^{\bar{n}-1} (\bar{n}-1)! \prod_{i=1}^{j} \left[\frac{(\mu_i/i!)^{n_i}}{n_i!} \right] \right\} \qquad (6)$$

where $\bar{n} \equiv \sum_{i=1}^{j} n_i$ and $\{n_i\}$ refers to all sets of integers that satisfy $\sum_{i=1}^{j} i\, n_i = j$. Remark that for $j \geq 4$ it will in general be $\kappa_j \neq \mu'_j$. A recursive relation can be established among the cumulants, namely

$$\kappa_j = \mu_j - \frac{1}{j} \sum_{i=1}^{j-1} i \binom{j}{i} \mu_{j-i}\, \kappa_i \qquad (7)$$

This relation (never registered in the literature as far as we know) is very convenient for operational purposes as it straigh forwardly provides the expansion indicated in Eq.(6) for the j-th order cumulant once the preceding ones are known (we have used it in Section III to obtain the results associated to values of j up to 28).

Let us now introduce, by truncating expansion (3), the ℓ-th order free energy

$$F^{(\ell)} \equiv F_0 + \sum_{j=1}^{\ell} \frac{(-\beta)^{j-1}}{j!} \kappa_j \qquad (\ell=1,2,\ldots) \qquad (8)$$

We remark that $F^{(1)} \equiv F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$ is precisely the standard VM free energy which satisfies $F^{(1)} \geq F$ (Bogolyubov inequality). It is clear that one should like that

$$\lim_{\ell\to\infty} F^{(\ell)}(\mathcal{H}_0; T) = F(T) \qquad (9)$$

no matter the choice for the functional form of $\mathcal{H}_0$, but there is no reason for being so in general. Furthermore for a given trial Hamiltonian $\mathcal{H}_0$ depending on the parameters $\{B\}$, there is no general reason for relation (9) being true *no matter the choice* of the parameters $\{B\}$. However if we take into account that F does not depend on $\{B\}$, a natural choice for $\{B\}$ is to look for those values which satisfy

$$\frac{\partial F^{(\ell)}(\{B\}; T)}{\partial B} = 0 \qquad (\ell=1,2,\ldots) \qquad (10)$$

thus extending the standard VM minimization equation. If we call $\{B^{(\ell)}\}$ the parameters satisfying Eq.(10), then $F^{(\ell)}(\{B^{(\ell)}(T)\};T)$ will be the present ℓ-th order approximation for the free energy F(T). Let us anticipate that severe problems will appear concerning Eq.(9); let us however stress that the violation of Eq. (9) does not necessarily imply the violation of

$$\lim_{\ell\to\infty} \frac{d^{(i)}F^{(\ell)}(\{B^{(\ell)}(T)\}; T)}{d\,T^i} = \frac{d^{(i)}F(T)}{d\,T^i} \qquad (i=1,2,\ldots) \qquad (11)$$

and we can therefore have an unsatisfactory convergence for the free energy simultaneously with a satisfactory convergence for

let us say the specific heat (see Section III).

II.2 General static mean values

We shall now restrict the discussion to classical systems. Let ϕ ({x} , {p}) be a function of the dynamical variables of the system ({x} and {p} respectively denote the generalized coordinates and momenta). We are interested in the mean value associated to $\mathcal{H}$ namely

$$\langle \phi \rangle \equiv \frac{\mathrm{Tr}\ \phi\ e^{-\beta \mathcal{H}}}{\mathrm{Tr}\ e^{-\beta \mathcal{H}}} \tag{12}$$

Let us consider the Hamiltonian

$$\mathcal{H}' = \mathcal{H} + \lambda\ \phi \tag{13}$$

and its partition function

$$Z' = \mathrm{Tr}\ e^{-\beta\ \mathcal{H}'} \tag{14}$$

It is straightforward to prove (in analogy to the fluctuation-dissipation theorem) that

$$\langle \phi \rangle = -\frac{1}{\beta} \lim_{\lambda \to 0} \frac{\partial\ \ell n\ Z'}{\partial \lambda} \tag{15}$$

If we now expand $(-\beta^{-1} \ell n\ Z')$ following Eq.(3) and then truncate, we obtain possible successive approximations, noted $\langle \phi \rangle^{(\ell)}$, of the mean value $\langle \phi \rangle$. In analogy with Eq.(9) and by introducing the solutions of Eq.(10), one should like that

$$\lim_{\ell \to \infty} \langle \phi \rangle^{(\ell)} \left(\{ B^{(\ell)}(T) \}\ ;\ T \right) = \langle \phi \rangle\ (T) \tag{16}$$

The procedure we have just outlined provides, for the first three orders of approximation, the following expressions

$$\langle \phi \rangle^{(1)} = \langle \phi \rangle_0 \qquad (17\text{-a})$$

$$\langle \phi \rangle^{(2)} = \langle \phi \rangle_0 - \beta \left[\langle \phi \, (\mathcal{H} - \mathcal{H}_0) \rangle_0 - \langle \phi \rangle_0 \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 \right] \qquad (17\text{-b})$$

$$\langle \phi \rangle^{(3)} = \langle \phi \rangle_0 - \beta \left[\langle \phi \, (\mathcal{H} - \mathcal{H}_0) \rangle_0 - \langle \phi \rangle_0 \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 \right]$$

$$+ \frac{\beta^2}{2} \left[\langle \phi \, (\mathcal{H} - \mathcal{H}_0)^2 \rangle_0 - \langle \phi \rangle_0 \langle (\mathcal{H} - \mathcal{H}_0)^2 \rangle_0 + \right.$$

$$\left. + 2 \langle \phi \rangle_0 \langle \mathcal{H}_0 - \mathcal{H}_0 \rangle_0^2 - 2 \langle \phi (\mathcal{H} - \mathcal{H}_0) \rangle_0 \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 \right] \qquad (17\text{-c})$$

We shall use these expressions in Sections III and IV to calculate the isothermal susceptibility ($\propto \langle x^2 \rangle$). The approximation $\langle \phi \rangle^{(1)}$ corresponds to the standard VM. We shall next test the EVM on classical anharmonic single oscillators associated to pure (Section III) or mixed (Section IV) elastic potentials.

III - FIRST APPLICATION: PURE ELASTIC POTENTIAL

III.1 Free energy

Let us consider the following Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + b x^{2n} \qquad (b > 0;\ n=1,2,\ldots) \qquad (18)$$

where for simplicity odd powers have been avoided in order to eliminate thermal slipping of the center of oscillation (as a matter of fact no particular difficulty appears if a potential $b|x|^{\sigma}$ with positive real σ is considered). The semi-classical partition function is given by

$$Z = \frac{1}{h} \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx \; e^{-\beta \mathcal{H}}$$

$$= \frac{\sqrt{8\pi m k_B T}}{h} \Gamma \left(\frac{2n+1}{2n} \right) \left(\frac{k_B T}{b} \right)^{1/2n} \qquad (19)$$

where h is Planck's constant and the standard Gamma function has been introduced. The associated free energy is given by

$$F = -k_B T \ \ell n \ Z \tag{20}$$

Let us now introduce the following trial Hamiltonian:

$$\mathcal{H}_o = \frac{p^2}{2m} + B\, x^{2s} \qquad (B > 0; s = 1, 2, \ldots) \tag{21}$$

The associated free energy is given by

$$F_o = - k_B T \ \ell n \ Z_o \tag{22}$$

where

$$Z_o = \frac{\sqrt{8\pi\, m k_B T}}{h} \ \Gamma\left(\frac{2s+1}{2s}\right) \left(\frac{k_B T}{B}\right)^{1/2s}$$

Through use of relation (8) we obtain the following ℓ-th order approximative free energy

$$F^{(\ell)} = F_o + k_B T \sum_{i=0}^{\ell} \frac{a_i^{(\ell)}}{u^i} \tag{23}$$

where

$$u \equiv \frac{k_B T}{b} \left(\frac{B}{k_B T} \right)^{n/s} \tag{24}$$

and, for $\ell = 1, 2, \ldots,$

$$a_o^{(\ell)} = - \frac{1}{2s} \sum_{i=1}^{\ell} \frac{1}{i} \tag{25.a}$$

$$a_i^{(\ell)} = \left[\frac{ni}{s(\ell - i)} + 1 \right] a_i^{(\ell-1)} \qquad (0 < i < \ell) \tag{25.b}$$

$$a_{\ell}^{(\ell)} = \frac{(-1)^{\ell-1}}{\ell!} \kappa_{\ell}\left[bx^{2n}\right] b^{-\ell} \left(\frac{B}{k_B T}\right)^{n\ell/s} \qquad (25.c)$$

where $\kappa_{\ell}\left[bx^{2n}\right]$ is the ℓ-th order cumulant associated to bx^{2n} (instead of ~~$\mathcal{H}$~~ - ~~$\mathcal{H}_0$~~). To be more explicit $\kappa_{\ell}\left[bx^{2n}\right]$ is given by Eq.(6) where

$$\mu_i\left[bx^{2n}\right] = \langle b^i x^{2ni} \rangle_0 = b^i \frac{\Gamma\left(\frac{2ni+1}{2s}\right)}{\Gamma\left(\frac{1}{2s}\right)} \left(\frac{k_B T}{B}\right)^{ni/s} \qquad (26)$$

For example

$$a_1^{(1)} = \frac{\Gamma\left(\frac{2n+1}{2s}\right)}{\Gamma\left(\frac{1}{2s}\right)} \qquad (27.a)$$

$$a_2^{(2)} = \frac{1}{2!}\left\{\left[\frac{\Gamma\left(\frac{2n+1}{2s}\right)}{\Gamma\left(\frac{1}{2s}\right)}\right]^2 - \frac{\Gamma\left(\frac{4n+1}{2s}\right)}{\Gamma\left(\frac{1}{2s}\right)}\right\} \qquad (27.b)$$

and

$$a_3^{(3)} = \frac{1}{3!}\left\{\frac{\Gamma\left(\frac{6n+1}{2s}\right)}{\Gamma\left(\frac{1}{2s}\right)} - 3\frac{\Gamma\left(\frac{4n+1}{2s}\right)}{\Gamma\left(\frac{1}{2s}\right)}\frac{\Gamma\left(\frac{2n+1}{2s}\right)}{\Gamma\left(\frac{1}{2s}\right)} + 2\left[\frac{\Gamma\left(\frac{2n+1}{2s}\right)}{\Gamma\left(\frac{1}{2s}\right)}\right]^3\right\} \qquad (27.c)$$

Let us now introduce an adimensional free energy $f^{(\ell)}$ through

$$f^{(\ell)} \equiv \frac{F^{(\ell)} - F}{k_B T} \qquad (28)$$

The use of Eqs.(19), (20) and (23) immediately leads to

$$f^{(\ell)}(n,s;u) = \ell n \left| \frac{\Gamma\left(\frac{2n+1}{2n}\right)}{\Gamma\left(\frac{2s+1}{2s}\right)} \right| + \frac{\ell n\, u}{2n} + \sum_{i=0}^{\ell} \frac{a_i^{(\ell)}}{u^i} \qquad (29)$$

$$\sim \frac{\ell n\, u}{2n} \qquad \text{if } u \to \infty \qquad (29')$$

$$\sim a_\ell^{(\ell)}/u^\ell \qquad \text{if } u \to 0 \qquad (29'')$$

Through these reduced variables, the whole discussion of the thermal behaviour of $F^{(\ell)}$ consists now in verifying how close to zero is $f^{(\ell)}$ for the *single* chosen value of u. In the limit $u \to \infty$, $f^{(\ell)}(u)$ is a monotonically increasing function of u (see Eq.(29')) whereas in the limit $u \to 0$ it depends on the sign of $a_\ell^{(\ell)}$ (see Eq.29'')) hence on (n,s,ℓ): if $n > s$ then $a_\ell^{(\ell)} > 0$ ($\ell=1,2,\ldots$), therefore $f^{(\ell)}$ monotonically decreases (increases) for increasing u and odd (even) values of ℓ; for $n < s$ the behaviour is less regular. If we extremize $f^{(\ell)}$ we obtain

$$\frac{u^\ell}{2n} - \sum_{i=1}^{\ell} a_i^{(\ell)}\, i\, u^{\ell-i} = 0 \qquad (\ell=1,2,\ldots) \qquad (30)$$

whose roots will be noted $u^{(\ell)}$ (only real positive roots are physically acceptable). For n=s and all values of ℓ, the Eq.(30) admits the solution $u^{(\ell)} = 1$ which leads, through Eq.(29), to $f^{(\ell)}(u^{(\ell)}) = 0$ as expected.

In order to study the possible convergence properties we have computationally discussed the cases n=1,2,..., 50, s==1,2,...,50 and j=1,2,...,28 (after this limit some computational complexities appear, and in any case 28 is large enough to have a good idea of the general behaviours). For

$n > s$ ($n < s$) the roots $u^{(\ell)}$ (whenever there are) present a tendency to grow (decrease) with increasing ℓ. For all the cases we have studied we observed that: (a) $\ell=1,3$ lead to an unique root of Eq. (30) which corresponds to a minimum of $f^{(\ell)}(u)$; (b) $\ell=2$ provides no roots for Eq.(30); (c) $\ell=4$ provides roots for Eq.(30) in a very small number of cases; (d) $\ell=5$ provides a solution of Eq.(30) which corresponds to a minimum of $f^{(\ell)}(u)$ (if $s \simeq n > 2$ other two real positive roots exist which practically collapse with that of the minimum); (e) for $\ell \geq 6$ a more and more complex structure appears for $f^{(\ell)}(u)$. The whole study exhibits that, for arbitrary pairs (n,s), $f^{(\ell)}(u^{(\ell)})$ unfortunately does not converge, for increasing ℓ, towards the exact solution (namely zero): it is first approached and then abandoned (thus presenting a certain similarity with asymptotic series). As an illustration we present in Fig.1 and Table 1, for $n = 2s = 2$, the evolution, in the plane $f^{(\ell)}(u^{(\ell)})$ - $u^{(\ell)}$, of the minimum of $f^{(\ell)}(u)$ (the minimum corresponding to the highest root of Eq.(30) if there are more than one). In order to see the influence of (n,s) we have introduced an *improvement factor* (for the free energy) through the definition

$$\mu_f^{(1,3)} \equiv f^{(1)}\left(u^{(1)}\right) / f^{(3)}\left(u^{(3)}\right) \tag{31}$$

The results are presented in Table 2 (similar results have been obtained by comparing let us say $f^{(3)}(u^{(3)})$ and $f^{(5)}(u^{(5)})$). We remark that unless we consider completely unphysical regions ($n \simeq 50$ and $s \simeq 1$) the result provided by $f^{(3)}$ is better than that provided by $f^{(1)}$; typically for $n=2$ and $s=1$ we obtain $\mu_f^{(1,3)} \simeq 41$.

III.2 Specific heat

Let us now discuss the specific heat $C \equiv -T(d^2F/dT^2)$ associated to the Hamiltonian (18). From Eqs.(19) and (20) we obtain[12]

$$C = \frac{k_B}{2}\left(1 + \frac{1}{n}\right) \qquad (n=1,2,\ldots) \qquad (32)$$

This expression generalizes the classical equipartition principle ($n = 1$ and $n \to \infty$ respectively correspond to a harmonic oscillator and a particle in a box). If we take into account that $f^{(\ell)}(u)$ is a pure number then Eq.(28) immediately leads to $d^2F^{(\ell)}/dT^2 = d^2F/dT^2$ hence

$$C^{(\ell)} = C \qquad (\ell = 1,2,\ldots) \qquad (33)$$

To all orders and through any trial Hamiltonian of the type (21) the present formalism provides the *exact* answer for the specific heat.

III.3 Susceptibility

If the oscillator carries an electric charge q, its isothermal susceptibility for vanishing external field is given, through the fluctuation-dissipation theorem, by

$$\chi_T = \frac{q^2}{k_B T} < x^2 > \qquad (34)$$

which, for the Hamiltonian (18), leads to[12]

$$\chi_T = \frac{\Gamma(3/2n)}{\Gamma(1/2n)} \frac{q^2}{b^{1/n}} (k_B T)^{\frac{1}{n} - 1} \qquad (n=1,2,\ldots) \qquad (35)$$

The first order approximation associated to the trial Hamiltonian (21) is, through use of $\phi = x^2$ into Eq.(17.a), given by

$$\chi_T^{(1)} = \frac{q^2}{k_B T} \frac{\Gamma(3/2s)}{\Gamma(1/2s)} \left[\frac{k_B T}{B(1)}\right]^{1/s} \tag{36}$$

If we now use Eqs.(27.a) and (30) for $\ell=1$ we obtain

$$u^{(1)} = 2n \frac{\Gamma\left(\frac{2n+1}{2s}\right)}{\Gamma\left(\frac{1}{2s}\right)}$$

hence (through Eq.(24))

$$B^{(1)} = \left[\frac{2n\ \Gamma\left(\frac{2n+1}{2s}\right)\ b}{\Gamma\left(\frac{1}{2s}\right)\ k_B T}\right]^{s/n} k_B T$$

Substituting this expression into Eq.(36) we obtain finally

$$\chi_T^{(1)} = \left\{\frac{\Gamma(1/2s)}{2n\ \Gamma\left(\frac{2n+1}{2s}\right)}\right\}^{1/n} \frac{\Gamma(3/2s)}{\Gamma(1/2s)} \frac{q^2}{b^{1/n}} (k_B T)^{\frac{1}{n}-1} \qquad (n,s=1,2,\ldots) \tag{37}$$

thus obtaining the *exact* thermal dependence but a *wrong* numerical factor (excepting the cases ($n = 1$; $\forall$ s) and of course $n = s$ where the full exact answer is obtained). Eqs. (35) and (37) enable the calculation (see Table 3) of the factor

$$q_\chi^{(1)} \equiv \chi_T^{(1)}/\chi_T \tag{38}$$

We verify that $q_{\chi}^{(1)} \gtrless 1$ (< 1) if $s \gtrless n (s < n)$.

We recall that no second order approximation exists as Eq.(30) admits no positive real roots for $\ell=2$. By following, for $\ell=3$, the same procedure we have just outlined for $\ell = 1$, we obtain

$$\chi_T^{(3)} = \left\{ \frac{2s^2+3s+1}{2s^2} \frac{\Gamma\left(\frac{3}{2s}\right)}{\Gamma\left(\frac{1}{2s}\right)} \frac{1}{\left[u^{(3)}\right]^{1/n}} \right.$$

$$+ \frac{n+s+1}{s} \left[\frac{\Gamma\left(\frac{3}{2s}\right)}{\Gamma(1/2s)} \frac{\Gamma\left(\frac{2n+1}{2s}\right)}{\Gamma(1/2s)} - \frac{\Gamma\left(\frac{2n+3}{2s}\right)}{\Gamma(1/2s)} \right] \frac{1}{\left[u^{(3)}\right]^{\frac{n+1}{n}}}$$

$$+ \left[\frac{\Gamma\left(\frac{3}{2s}\right)}{\Gamma(1/2s)} \left(\frac{\Gamma\left(\frac{2n+1}{2s}\right)}{\Gamma(1/2s)} \right)^2 - \frac{\Gamma\left(\frac{2n+1}{2s}\right)}{\Gamma(1/2s)} \frac{\Gamma\left(\frac{2n+3}{2s}\right)}{\Gamma(1/2s)} + \frac{\Gamma\left(\frac{4n+3}{2s}\right)}{2\Gamma(1/2s)} \right.$$

$$\left. \left. - \frac{\Gamma\left(\frac{3}{2s}\right)}{2\Gamma(1/2s)} \frac{\Gamma\left(\frac{4n+1}{2s}\right)}{\Gamma(1/2s)} \right] \frac{1}{\left[u^{(3)}\right]^{\frac{2n+1}{n}}} \right\} \frac{q^2}{b^{1/n}} \left(k_B T\right)^{\frac{1}{n}-1} \tag{39}$$

where $u^{(3)}$ is the (physically meaningful) root of Eq.(30) with $\ell = 3$; we obtain once more the *exact* thermal dependence but a (slightly) *wrong* numerical factor (excepting the cases ($n = 1$; $\forall$ s) and of course $n = s$ where the full exact answer is obtained). Eqs. (35) and (39) enable the calculation (see Table 3) of

the factor

$$q_\chi^{(3)} \equiv \chi_T^{(3)}/\chi_T \tag{40}$$

We verify that $q_\chi^{(3)} \leq 1$ if $s \leq n$. In order to measure how many times $\chi_T^{(3)}$ is better than $\chi_T^{(1)}$ we have also indicated in the Table 3 the *improvement factor*

$$\mu_\chi^{(1,3)} \equiv \frac{\chi_T - \chi_T^{(1)}}{\chi_T - \chi_T^{(3)}} = \frac{1 - q_\chi^{(1)}}{1 - q_\chi^{(3)}} \tag{41}$$

We remark that in all the cases the third order approximation is better than the first order one; typically for $n = 2$ and $s = 1$ we obtain $\mu_\chi^{(1,3)} \simeq 39$.

IV - SECOND APPLICATION: MIXED ELASTIC POTENTIAL

IV.1 Free energy

As a second test of the EVM let us consider the Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + bx^2 + cx^4 \qquad (b,c > 0) \tag{42}$$

Its associated free energy is given by

$$F = - k_B T \ln \left[\left(\frac{\pi b m k_B T}{2 c h^2} \right)^{1/2} e^{b^2/8c k_B T} K_{1/4}(b^2/8c k_B T) \right] \tag{43}$$

$$\sim F(c=0) + \frac{3}{4} c \left(\frac{k_B T}{b} \right)^2 \qquad \text{if} \quad T \to 0 \tag{43'}$$

$$\sim F(b=0) + \frac{\Gamma(3/4)}{\Gamma(1/4)} b \sqrt{\frac{k_B T}{c}} \qquad \text{if} \quad T \to \infty \tag{43''}$$

where $K_\nu(Z)$ is the standard Bessel function and where

$$F(c=0) = - k_B T \ \ell n \left[\left(\frac{2\pi^2 m}{b\ h^2} \right)^{1/2} k_B T \right]$$

and

$$F(b=0) = - k_B T \ \ell n \left[\frac{1}{2} \Gamma \left(\frac{1}{4} \right) \left(\frac{2\pi m\ k_B T}{h^2} \right)^{1/2} \left(\frac{k_B T}{c} \right)^{1/4} \right]$$

$$\simeq - k_B T \ \ell n \left[1.8128 \left(\frac{2\pi m\ k_B T}{h^2} \right)^{1/2} \left(\frac{k_B T}{c} \right)^{1/4} \right]$$

Let us now introduce the following trial Hamiltonian

$$\mathcal{H}_o = \frac{p^2}{2m} + B\ x^2 \qquad (B > 0) \qquad (44)$$

whose associated free energy is given by

$$F_o = - k_B T \ \ell n \left[\left(\frac{2\pi^2 m}{B\ h^2} \right)^{1/2} k_B T \right] \qquad (45)$$

The use of Eq.(8) for $\ell = 1$ leads to

$$F^{(1)} = F_o + \left(\frac{b-B}{2B} \right) k_B T + \frac{3}{4} c \left(\frac{k_B T}{B} \right)^2 \qquad (46)$$

whose minimum is located at

$$B^{(1)} = \frac{1}{2} \left(b + \sqrt{b^2 + 12c\ k_B T} \right) \qquad (47)$$

The substitution of this equation into Eq.(46) leads, in the limit $T \to 0$, to the *exact* answer (Eq.(43') and, in the limit $T \to \infty$, to

$$F^{(1)} \sim - k_B T \ln \left[\frac{e^{1/4}\, \pi^{1/2}}{3^{1/4}} \left(\frac{2\pi m\, k_B T}{h^2} \right)^{1/2} \left(\frac{k_B T}{c} \right)^{1/4} \right] + \frac{b}{2\sqrt{3}} \sqrt{\frac{k_B T}{c}}$$

$$\simeq - k_B T \ln \left[1.7293 \left(\frac{2\pi m\, k_B T}{h^2} \right)^{1/2} \left(\frac{k_B T}{c} \right)^{1/4} \right] + \frac{b}{2\sqrt{3}} \sqrt{\frac{k_B T}{c}} \qquad (48)$$

The thermal dependences are the *exact* ones; the pure number inside the logarithm is 4.6% *wrong*; the pure number in front of the term $\sqrt{T}$ is 14.6% *wrong* ($\Gamma(3/4)/\Gamma(1/4) \simeq 0.3380$ and $1/2\sqrt{3} \simeq 0.2887$).

Let us now consider the third order approximation. The use of Eq.(8) for $\ell=3$ leads to

$$F^{(3)} = F_o + \frac{b-B}{B} \left[\frac{k_B T}{2} - \frac{3}{2} c \left(\frac{k_B T}{B} \right)^2 + \frac{12 c^2 (k_B T)^3}{B^4} \right]$$

$$+ 3c \left(\frac{k_B T}{B} \right)^2 \left(\frac{1}{4} - \frac{c\, k_B T}{B^2} \right)$$

$$+ \left(\frac{b-B}{B} \right)^2 \left[\frac{9}{4} c \left(\frac{k_B T}{B} \right)^2 - \frac{k_B T}{4} \right]$$

$$+ \frac{1}{6} \left(\frac{b-B}{B} \right)^3 k_B T + \frac{99}{4} c^3 \frac{(k_B T)^4}{B^6} \qquad (49)$$

whose minimum is located at $B = B^{(3)}$ where

$$\left(B^{(3)}\right)^6 - 3b \left(B^{(3)}\right)^5 + (3b^2 - 18c\, k_B T) \left(B^{(3)}\right)^4$$
$$+ (36bc\, k_B T - b^3) \left(B^{(3)}\right)^3 + \left(120 c^2\, k_B{}^2 T^2 - 18 b^2 c\, k_B T\right) \left(B^{(3)}\right)^2$$
$$- 120 c^2 b\, k_B{}^2 T^2\, B^{(3)} - 297 c^3\, k_B{}^3 T^3 = 0 \qquad (50)$$

This equation leads, for $T \to 0$, to

$$B^{(3)} \sim b + \alpha \frac{c\ k_B T}{b} \tag{51}$$

where α satisfies

$$\alpha^3 - 18\alpha^2 + 120\alpha - 297 = 0 \tag{52}$$

$$\text{hence} \quad \alpha = 6 + \left(\frac{\sqrt{337}+9}{2}\right)^{1/3} - \left(\frac{\sqrt{337}-9}{2}\right)^{1/3} \simeq 6.71902 \tag{52'}$$

Eq.(51) substituted into Eq.(49) leads to the *exact* answer (Eq. (43')). In the limit $T \to \infty$, Eq.(50) provides

$$B \sim \sqrt{\alpha\ c\ k_B T} \tag{53}$$

which, substituted into Eq.(49), leads to

$$F^{(3)} \sim - k_B T\ \ell n \left[1.8107 \left(\frac{2\pi\ m\ k_B T}{h^2}\right)^{1/2} \left(\frac{k_B T}{c}\right)^{1/4}\right]$$

$$+ 0.3367\ b \sqrt{\frac{k_B T}{c}} \tag{54}$$

which once more contains the *exact* thermal dependences but (slightly) *wrong* numerical factors: the pure number inside the logarithm is 0.1% wrong and the one in front of $\sqrt{T}$ is 0.4% wrong; we see that the third order perturbation is about 40 times better than the first order one.

IV.2 Specific heat

By derivating twice Eq.(43) we obtain the specific heat $C = - T\ d^2F/dT^2$ associated to Hamiltonian (42):

ℓ	$u^{(\ell)}$	$f^{(\ell)}\left(u^{(\ell)}\right)$ x 1000
1	3	47.2
2	~~4~~	~~4~~
3	6.719	1.15
4	~~4~~	~~4~~
5	13.74	- 1.35
6	19.52	- 1.61
7	26.22	- 1.78
8	33.85	- 1.90
9	42.43	- 1.98
10	51.95	- 2.045
11	62.41	- 2.092
12	73.82	- 2.129
13	86.18	- 2.158
14	99.48	- 2.183
15	113.8	- 2.197
16	128.9	- 2.216
17	145.1	- 2.226
18	162.2	- 2.241
19	180.2	- 2.249
20	199.2	- 2.256
21	219.2	- 2.265
22	240.1	- 2.271
23	262.0	- 2.273
24	284.8	- 2.278
25	308.5	- 2.283
26	333.2	- 2.287
27	358.9	- 2.291
28	385.4	- 2.293

TABLE 1

s \ n	1	2	5	10	20	50
1	0 0 $-\infty$	0.047 0.001 40.917	0.239 0.133 1.799	0.462 0.438 1.054	-	-
2	0.031 -0.003 -9.504	0 0 ∞	0.047 0.008 6.004	0.135 0.088 1.537	0.253 0.249 1.017	-
5	0.097 -0.041 -2.376	0.028 0.0006 46.867	0 0 ∞	0.012 0.001 8.819	0.044 0.024 1.821	0.1080 0.1083 0.997
10	0.132 -0.055 -2.392	0.055 0.004 15.292	0.008 0.0004 22.864	0 0 ∞	0.006 0.0008 7.852	0.030 0.022 1.372
20	0.152 -0.044 -3.443	0.073 0.008 8.850	0.020 0.002 8.338	0.004 0.0002 18.539	0 0 ∞	0.005 0.001 3.963
50	0.166 -0.029 -5.671	0.087 0.014 6.405	0.031 0.006 4.981	0.012 0.002 6.021	0.003 0.0003 11.185	0 0 ∞

TABLE 2

s \ n	1	2	5	10	20	50
1	1 1 - ∞	0.854 0.996 38.940	0.510 0.728 1.800	0.305 0.390 1.139	-	-
2	1 1 - ∞	1 1 -	0.798 0.972 7.151	0.625 0.799 1.865	0.473 0.570 1.226	-
5	1 1 - ∞	1.078 0.998 -51.747	1 1 ∞	0.910 0.992 11.857	0.818 0.927 2.489	0.701 0.773 1.314
10	1 1 - ∞	1.095 0.997 -33.773	1.055 1.001 37.247	1 1 ∞	0.947 0.995 10.880	0.879 0.938 1.960
20	1 1 - ∞	1.101 0.997 -32.872	1.073 1.005 15.484	1.034 1.001 27.811	1 1 ∞	0.962 0.993 5.646
50	1 1 - ∞	1.102 0.997 -30.484	1.079 1.007 11.249	1.046 1.004 10.531	1.021 1.001 16.953	1 1 ∞

TABLE 3

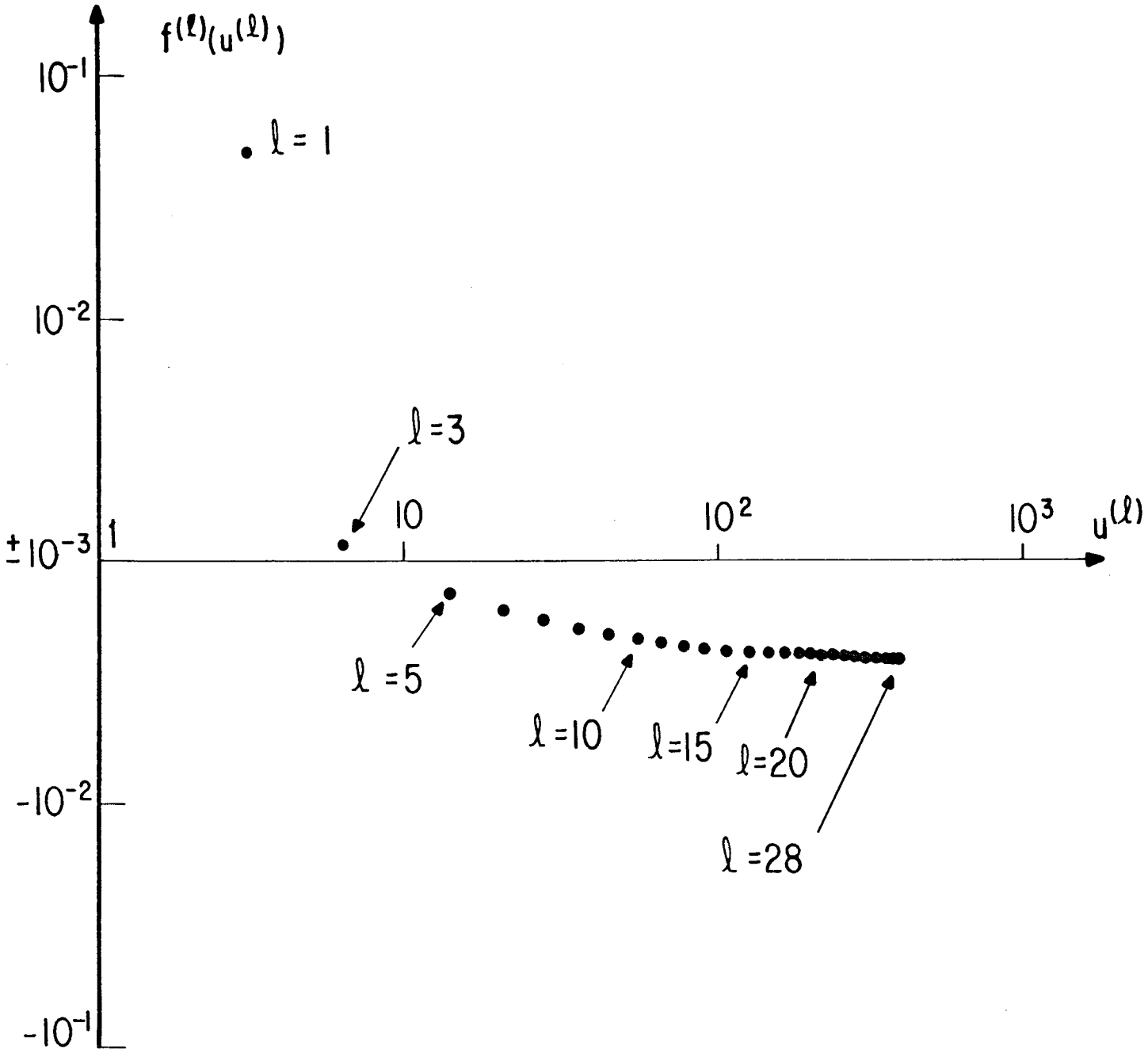
$f^{(\ell)}(u^{(\ell)})$
10^{-1}
$\ell = 1$
10^{-2}
$\ell = 3$
$\pm 10^{-3}$
1
10
10^2
10^3
$u^{(\ell)}$
$\ell = 5$
$\ell = 10$
$\ell = 15$
$\ell = 20$
$\ell = 28$
-10^{-2}
-10^{-1}

FIG. 1

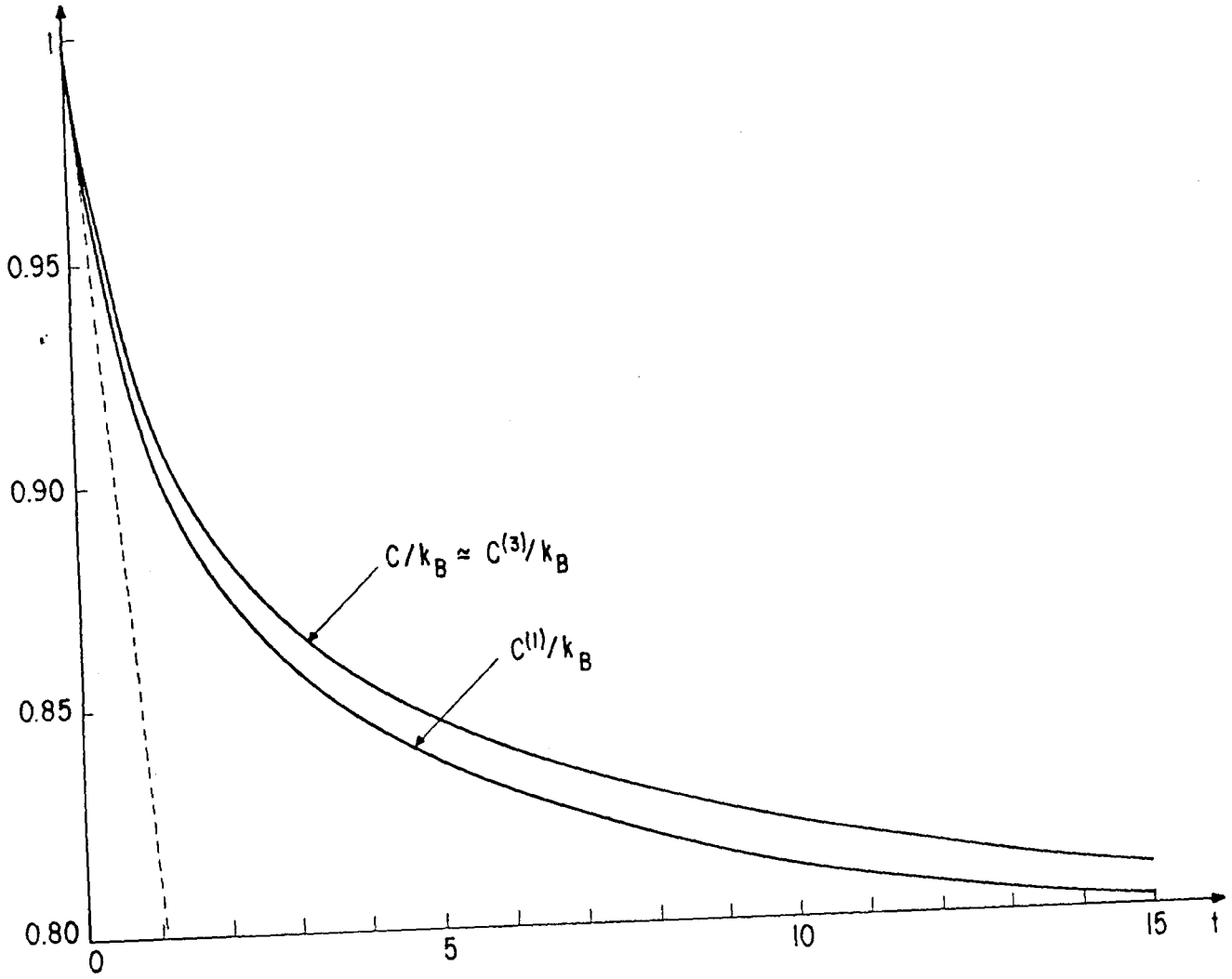

FIG.2

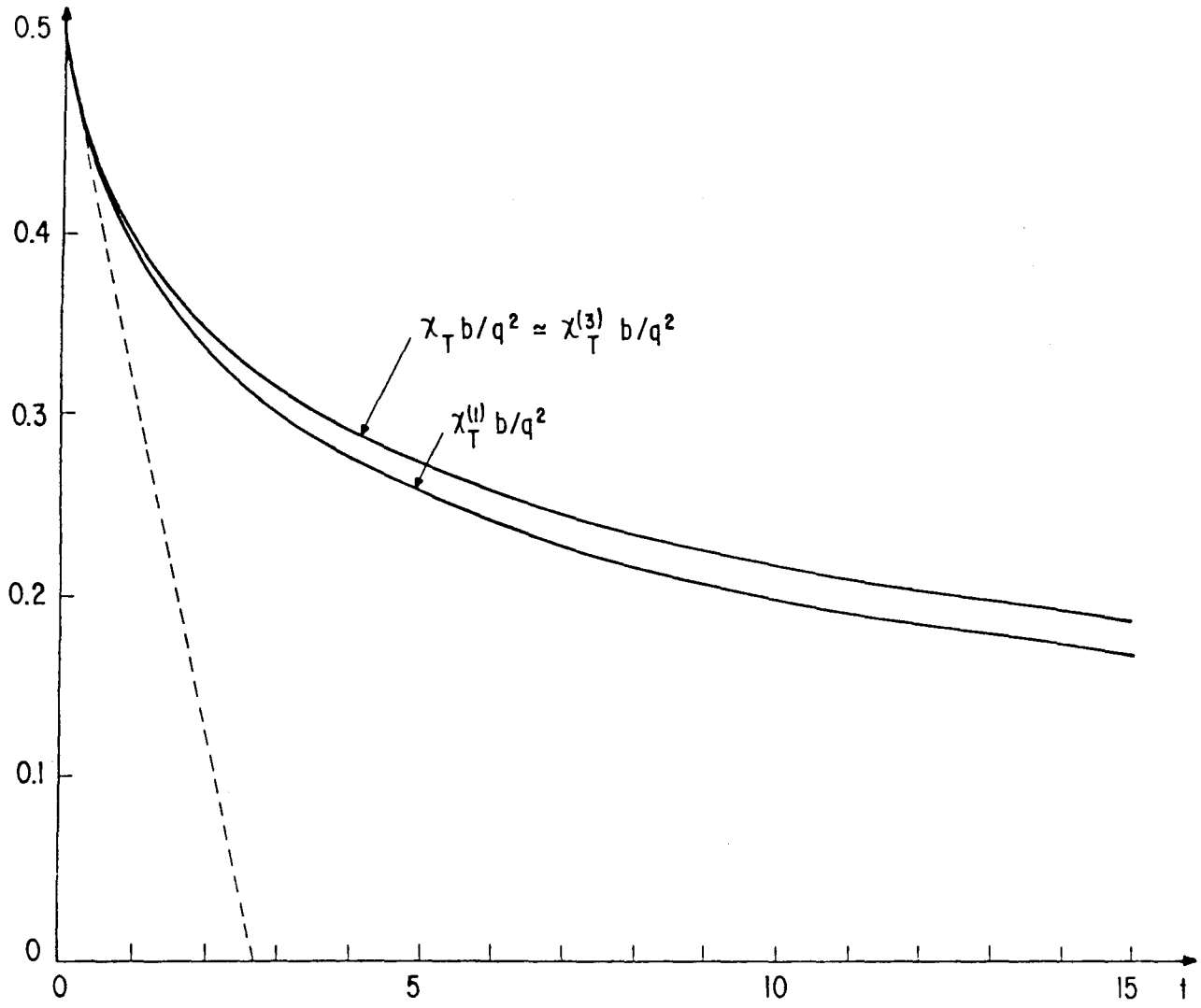

FIG.3

TABLE 3 Selected results obtained for the pure potential classical single oscillator (X^{2n} treated with (X^{2s}). The top and intermediate numbers respectively are the reduced vanishing field isothermal susceptibilities $q_\chi^{(1)}$ and $q_\chi^{(3)}$ defined through Eqs.(38) and (40) (the exact result is $q_\chi = 1$); the bottom number is the *improvement factor* $\mu_\chi^{(1,3)} \equiv \left[1 - q_\chi^{(1)}\right] \Big/ \left[1 - q_\chi^{(3)}\right]$ (remark that in all the present cases $\left|\mu_\chi^{(1,3)}\right| > 1$); (—) means that the computer indications were not clear enough.

CAPTION FOR FIGURES AND TABLES

Fig. 1 The pure potential case $n = 2s = 2$: locus of the minima of the ℓ-th order adimensional free energy $f^{(\ell)}(u)$ as a function of the adimensional variational parameter u (when more than one minimum exists we have considered the one associated to the higher value of u) ; the exact answer is $f = 0$.

Fig. 2 Thermal dependences of the exact, first- and third-order specific heats of the mixed potential (bx^2+cx^4) classical single oscillator; they all converge to $\frac{3}{4}\,k_B$ in the limit $t \to \infty$; $t \equiv 8\,ck_BT/b^2$.

Fig. 3 Thermal dependences of the exact, first- and third-order vanishing field isothermal electric susceptibilities of the mixed potential (bx^2+cx^4) classical single oscillator with charge q; they all vanish in the limit $t \to \infty$; $t \equiv 8\,ck_BT/b^2$.

TABLE 1 See caption of Fig. 1 (we recall that $\ell = 2,4$ provide no minimum).

TABLE 2 Selected results obtained for the pure potential classical single oscillator (X^{2n} treated with X^{2s}) . The top and intermediate numbers respectively are the minimized first- and third-order adimensional free energies $f^{(1)}(u^{(1)})$ and $f^{(3)}(u^{(3)})$ (the exact result is $f = 0$); the bottom number is the corresponding *improvement factor* $\mu_f^{(1,3)} \equiv f^{(1)}(u^{(1)})/f^{(3)}(u^{(3)})$ (remark that in almost all the present cases $|\mu_f^{(1,3)}| > 1$; (—) means that the computer indications were not clear enough.

$$C = k_B \left[\frac{3}{4} + \frac{1}{t^2} + \frac{K_{3/4}(1/t)\, t}{2\, K_{1/4}(1/t)} - \frac{K^2_{3/4}(1/t)}{t^2\, K^2_{1/4}(1/t)} \right] \tag{55}$$

where

$$t \equiv \frac{8c\ k_B T}{b^2} \tag{56}$$

and where standard recursive relations[34] for the Bessel functions have been used. As far as we know expression (55) has never been registered in the literature. It leads to

$$C \sim k_B \left(1 - \frac{3}{16}\, t \right) \qquad \text{if} \quad t \to 0 \tag{55'}$$

and to

$$C \sim k_B \left[\frac{3}{4} + \frac{\Gamma(3/4)}{\sqrt{2}\ \Gamma(1/4)}\ \frac{1}{\sqrt{t}} \right]$$

$$\simeq k_B \left(\frac{3}{4} + 0.2390\, \frac{1}{\sqrt{t}} \right) \qquad \text{if} \quad t \to \infty \tag{55''}$$

The ℓ-th order approximative specific heat is given by

$$C^{(\ell)} = - T\, \frac{d^2 F^{(\ell)}(T, B^{(\ell)}(T))}{d\, T^2} \tag{57}$$

Straightforward calculations lead, in the limit $T \to 0$ to the *exact* asymptotic behaviour (Eq.(55')) for both $C^{(1)}$ and $C^{(3)}$ and, in the limit $T \to \infty$, to the following results:

$$C^{(1)} \sim k_B \left(\frac{3}{4} + \frac{1}{2\sqrt{6}}\ \frac{1}{\sqrt{t}} \right) \simeq k_B \left(\frac{3}{4} + 0.2041\, \frac{1}{\sqrt{t}} \right) \tag{58}$$

and

$$C^{(3)} \sim k_B \left(\frac{3}{4} + 0.2381 \quad \frac{1}{\sqrt{t}} \right) \tag{59}$$

The pure factors in front of $t^{-1/2}$ are respectively 14.6% and 0.4% wrong (see Eq.(55")) . The complete thermal dependences of C, $C^{(1)}$ and $C^{(3)}$ are represented in Fig. 2.

IV.3 Susceptibility

Through calculation of $< x^2 >$ we obtain the thermal dependence of the electric susceptibility, namely

$$\chi_T = \frac{q^2}{b} \frac{2}{t} \left[\frac{K_{3/4}(1/t)}{K_{1/4}(1/t)} - 1 \right] \tag{60}$$

This expression (never registered in the literature as far as we know) leads to

$$\chi_T \sim \frac{q^2}{2b} \left(1 - \frac{3}{8} t \right) \qquad \text{if } t \to 0 \tag{60'}$$

and

$$\chi_T \sim \frac{2\sqrt{2}\,\Gamma(3/4)}{\Gamma(1/4)} \frac{q^2}{b\sqrt{t}} \simeq 0.9560 \frac{q^2}{b\sqrt{t}} \qquad \text{if } t \to \infty \tag{60"}$$

Within the present EVM the use of Eqs. (17.a) and (17.c) (with $\phi = x^2$) enables the calculation of the thermal dependences of the first- and third- order approximative susceptibility. In particular, in the limit $T \to 0$, the exact asymptotic behaviour (Eq.(60')) is recovered for both $\chi_T^{(1)}$ and $\chi_T^{(3)}$. In the other limit ($T \to \infty$) the following results have been obtained:

$$\chi_T^{(1)} \sim \sqrt{\frac{2}{3}} \frac{q^2}{b\sqrt{t}} \simeq 0.8165 \frac{q^2}{b\sqrt{t}} \tag{61}$$

and

$$\chi_T^{(3)} \sim \frac{q^2}{b} \frac{0.9524}{\sqrt{t}} \tag{62}$$

Once more the thermal dependences are the *exact* one and the pure numbers are respectively 14.6% and 0.4% *wrong*. The full thermal dependences of χ_T, $\chi_T^{(1)}$ and $\chi_T^{(3)}$ have been represented in Fig.3.

V - CONCLUSION

For classical systems associated to Hamiltonians $\mathcal{H}$ (as well as for quantum systems such that $\mathcal{H}$ commutes with a trial Hamiltonian $\mathcal{H}_0$) we have performed a cumulant expansion of the associated free energy (and, for classical systems, of the susceptibility as well) and have outlined a new procedure (referred to as the Extended Variational Method) whose purpose is to improve the results obtained within the framework of the standard Variational Method in Equilibrium Statistical Mechanics. A sequence of ℓ-th order approximative free energies appears within the present context which exhibits convergence problems in the limit $\ell \to \infty$ (similarly to what happens in asymptotic series); these problems do not necessarily persist for other quantities (like the specific heat or the susceptibility). Incidentally a new recursive relation (Eq.(7)) among cumulants is established.

The whole procedure has been tested for two different types of classical anharmonic single oscillators, namely

those whose elastic potential is proportional to x^{2n} with n=1,2,... (pure type) and those whose potential is of the type $bx^2 + cx^4$ (mixed type). For both types the exact free energy, specific heat and susceptibility are established (in the mixed case for the first time as far as we know) and then compared with successive approximations (obtained by using trial elastic potentials proportional to x^{2s} (s=1,2,...) for the pure type and to x^2 for the mixed one). In *all* the physically meaningfull situations the exact thermal dependences are recovered for all approximation orders and *simultaneously* for both limits $T \to 0$ and $T \to \infty$. Furthermore great improvement (typically of the order of 40) is obtained for the eventually wrong numerical coefficients (which are nevertheless frequently quite close to the exact ones and sometimes coincide with them) by minimizing

$$F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 - \frac{\beta}{2} \left[\langle (\mathcal{H} - \mathcal{H}_0)^2 \rangle_0 - \langle \mathcal{H} - \mathcal{H}_0 \rangle_0^2 \right]$$

$$+ \frac{\beta^2}{6} \left[\langle (\mathcal{H} - \mathcal{H}_0)^3 \rangle_0 - 3 \langle (\mathcal{H} - \mathcal{H}_0)^2 \rangle_0 \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 \right.$$

$$\left. + 2 \langle \mathcal{H} - \mathcal{H}_0 \rangle_0^3 \right]$$

instead of

$$F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$$

in spite of the fact that only the latter is justified through the Bogolyubov inequality. No doubt that the application of the present procedure to other systems (like simple magnetic systems) and/or its extension to general quantum ones should clarify its possibilities and limitations.

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