Extended variational method in statistical mechanics

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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 meaningful'situations, and a quite satisfactory description is provided (with a "single shot") for both limits $T \rightarrow 0$ and $T \rightarrow \infty$ simultaneously.

I. INTRODUCTION

The variational method (VM) in equilibrium statistical mechanics (for general purposes see Refs. 1-8) enables the approximative calculation of the thermal behavior 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 coupled¹³ anharmonic oscillators (eventually within the context of structural phase transitions),¹⁴⁻¹⁹ pure^{1-3,5,7,20,21} and random²² 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 noninteracting spins trial Hamiltonian, i.e., the mean-field approximation (MFA), to treat the one-dimensional Ising ferromagnet leads to a nonvanishing 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 \mathscr{H}_0) i.e., the complete reformulation of the treatment. Other "single-shot" procedures (usually better than the MFA, in, let us say, magnetism) 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 exempt from notoriously wrong results (it leads, for example, to a vanishing critical temperature for the two-dimensional Ising ferromagnet).

Contrary to the VM, the formulation of the perturbation techniques (for instance, the low- and high-temperature series) usually allows for successive approximations to the exact result, but presents 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, $T \rightarrow 0$ or $T \rightarrow \infty$ 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 was 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 and 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 exempt 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 with the VM.

II. EXTENDED VARIATIONAL METHOD

A. 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 with Hamiltonian \mathcal{H} is given by

$$F = -\frac{1}{\beta} \ln \operatorname{Tr} e^{-\beta \mathscr{F}}$$
(1)

or identically by

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

with

$$\kappa_{j} = j! \sum_{\{n_{i}\}} \left[(-1)^{\overline{n}-1} (\overline{n}-1)! \prod_{i=1}^{j} \left[\frac{(\mu_{i}/i!)^{n_{i}}}{n_{i}!} \right] \right],$$

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

$$\kappa_{j} = \mu_{j} - \sum_{i=1}^{j-1} {j-1 \choose i=1} \mu_{j-i} \kappa_{i} .$$
(7)

This relation (which can, in fact, be recovered as a particular case, namely, $g(z) = z^{j-1}$, of the relation appearing in the footnote of page 409 of Ref. 34] is very convenient for operational purposes as it straightforwardly provides the expansion indicated in Eq. (6) for the *j*th order cumulant once the preceding ones are known (we have used it in Sec. III to obtain the results associated with values of *j* up to 28).

Let us now introduce, by truncating expansion

$$F_0 \equiv -\frac{1}{\beta} \ln \operatorname{Tr} e^{-\beta \mathscr{K}_0}, \qquad (2')$$

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

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

where κ_j is the *j*th-order cumulant associated with $\mathscr{H} - \mathscr{H}_0$. In order to illustrate this point let us first introduce the moments $\{\mu_i\}$ through

$$\mu_j \equiv \langle (\mathscr{H} - \mathscr{H}_0)^j \rangle_0, \quad j = 1, 2...$$
(4)

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

$$\mu'_{j} \equiv \langle [(\mathscr{H} - \mathscr{H}_{0}) - \langle \mathscr{H} - \mathscr{H}_{0} \rangle_{0}]^{j} \rangle_{0} , \qquad (5)$$

$$j = 1, 2, \dots$$

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 general³³

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(3), the *l*th-order free energy

$$F^{(l)} \equiv F_0 + \sum_{j=1}^{l} \frac{(-\beta)^{j-1}}{j!} \kappa_j , \quad l = 1, 2, \dots$$
 (8)

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

$$\lim_{l \to \infty} F^{(l)}(\mathscr{H}_0; T) = F(T)$$
(9)

no matter the choice of 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 dependent on the parameters $\{B\}$, there is no general reason for relation (9) to be 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

$$\frac{\partial F^{(l)}(\{B\};T)}{\partial B} = 0, \quad l = 1, 2, \dots$$
(10)

thus extending the standard VM minimization equation. If we call $\{B^{(l)}\}$ the parameters satisfying Eq. (10), then $F^{(l)}(\{B^{(l)}(T)\};T)$ 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

$$\lim_{l \to \infty} \frac{d^{(i)} F^{(l)}(\{B^{(l)}(T)\};T)}{dT^{i}} = \frac{d^{(i)} F(T)}{dT^{i}},$$

$$i = 1, 2, \dots (11)$$

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 Sec. III).

B. General static mean values

We shall now restrict the discussion to classical systems. Let $\phi(\{x\}, \{p\})$ 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,

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

Let us consider the Hamiltonian

$$\mathscr{H} = \mathscr{H} + \lambda \phi \tag{13}$$

and its partition function

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

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

$$\langle \phi \rangle = -\frac{1}{\beta} \lim_{\lambda \to 0} \frac{\partial \ln Z'}{\partial \lambda}$$
 (15)

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

$$\lim_{l \to \infty} \langle \phi \rangle^{(l)} \{ B^{(l)}(T) \}; T \} = \langle \phi \rangle(T) .$$
(16)

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

$$\langle \phi \rangle^{(1)} = \langle \phi \rangle_0 ,$$

$$\langle \phi \rangle^{(2)} = \langle \phi \rangle_0 - \beta [\langle \phi(\mathscr{H} - \mathscr{H}_0) \rangle_0 - \langle \phi \rangle_0 \langle \mathscr{H} - \mathscr{H}_0 \rangle_0] ,$$

$$(17a)$$

$$(17b)$$

$$\begin{split} \langle \phi \rangle^{(3)} &= \langle \phi \rangle_0 - \beta [\langle \phi(\mathscr{H} - \mathscr{H}_0) \rangle_0 - \langle \phi \rangle_0 \langle \mathscr{H} - \mathscr{H}_0 \rangle_0] \\ &+ \frac{\beta^2}{2} [\langle \phi(\mathscr{H} - \mathscr{H}_0)^2 \rangle_0 - \langle \phi \rangle_0 \langle (\mathscr{H} - \mathscr{H}_0)^2 \rangle_0 + 2 \langle \phi \rangle_0 \langle \mathscr{H}_0 - \mathscr{H}_0 \rangle_0^2 - 2 \langle \phi(\mathscr{H} - \mathscr{H}_0) \rangle_0 \langle \mathscr{H} - \mathscr{H}_0 \rangle_0] \,. \end{split}$$

We shall use these expressions in Secs. 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 with pure (Sec. III) or mixed (Sec. IV) elastic potentials.

III. FIRST APPLICATION: PURE ELASTIC POTENTIAL

A. Free energy

Let us consider the following Hamiltonian

$$\mathscr{H} = \frac{p^2}{2m} + bx^{2n}, \quad b > 0; \quad n = 1, 2, \dots$$
 (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 semiclassical partition function is given by

$$Z = \frac{1}{h} \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx \ e^{-B \varkappa}$$
$$= \frac{\sqrt{8\pi m k_B T}}{h} \Gamma \left(\frac{2n+1}{2n}\right) \left(\frac{k_B T}{b}\right)^{1/2n}, \qquad (19)$$

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

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7a)

(17c)

 $F = -k_B T \ln Z \ . \tag{20}$

Let us now introduce the following trial Hamiltonian:

$$\mathscr{H}_0 = \frac{p^2}{2m} + Bx^{2s}, \quad B > 0; \ s = 1, 2, \dots$$
 (21)

The associated free energy is given by

$$F_0 = -k_B T \ln Z_0 , \qquad (22)$$

where

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$$Z_0 = \frac{\sqrt{8\pi m k_B T}}{h} \Gamma \left[\frac{2s+1}{2s} \right] \left[\frac{k_B T}{B} \right]^{1/2s}.$$

Through use of relation (8) we obtain the following lth order approximative free energy:

$$F^{(l)} = F_0 + k_B T \sum_{i=0}^{l} \frac{a_i^{(l)}}{u^i} , \qquad (23)$$

where

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

and, for l = 1, 2, ...,

$$a_{2}^{(2)} = \frac{1}{2!} \left[\left(\frac{\Gamma\left(\frac{2n+1}{2s}\right)}{\Gamma(1/2s)} \right)^{2} - \frac{\Gamma\left(\frac{4n+1}{2s}\right)}{\Gamma(1/2s)} \right]$$

and

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

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

$$f^{(l)} \equiv \frac{F^{(l)} - F}{k_B T} \ . \tag{28}$$

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

$$f^{(l)}(n,s;u) = \ln\left[\Gamma\left(\frac{2n+1}{2n}\right) \middle/ \Gamma\left(\frac{2s+1}{2s}\right)\right] + \frac{\ln u}{2n} + \sum_{i=0}^{l} \frac{a_i^{(l)}}{u^i}, \qquad (29)$$

$$\sim \left\{ \frac{\ln u}{2n} \quad \text{if } u \to \infty \right.$$

$$\left[a_{l}^{(l)}/u^{l} \text{ if } u \rightarrow 0 \right] . \tag{29''}$$

$$a_0^{(l)} = -\frac{1}{2s} \sum_{i=1}^{l} \frac{1}{i}$$
, (25a)

$$a_i^{(l)} = \left[\frac{ni}{s(l-i)} + 1\right] a_i^{(l-1)}, \quad 0 < i < l$$
 (25b)

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

where $k_l(bx^{2n})$ is the *l*th-order cumulant associated with bx^{2n} (instead of $\mathscr{H} - \mathscr{H}_0$). To be more explicit, $\kappa_l(bx^{2n})$ is given by Eq. (6), where

$$\mu_{i}(bx^{2n}) = \langle b^{i}x^{2ni} \rangle_{0}$$
$$= b^{i} \frac{\Gamma\left(\frac{2ni+1}{2s}\right)}{\Gamma(1/2s)} \left(\frac{k_{B}T}{B}\right)^{ni/s}.$$
 (26)

For example

$$a_{1}^{(1)} = \frac{\Gamma\left[\frac{2n+1}{2s}\right]}{\Gamma(1/2s)}$$
, (27a)

(27b)

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

$$\frac{u^{l}}{2n} - \sum_{i=1}^{l} a_{i}^{(l)} i u^{l-i} = 0 , \quad l = 1, 2, \dots$$
 (30)

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

In order to study the possible convergence properties, we have computationally discussed the cases $n = 1, 2, \dots, 50, s = 1, 2, \dots, 50, and j = 1, 2, \dots, 28$ (after this limit some computational complexities appear, and, in any case, 28 is large enough to have a good idea of the general behavior). For n > s (n < s) the roots $u^{(l)}$ (whenever they exist) present a tendency to grow (decrease) with increasing *l*. For all the cases we have studied we observed that: (a) l = 1,3 lead to an unique root of Eq. (30) which corresponds to a minimum of $f^{(\bar{l})}(u)$; (b) l=2 provides no roots for Eq. (30); (c) l = 4 provides roots for Eq. (30) in a very small number of cases; (d) l = 5 provides a solution of Eq. (30) which corresponds to a minimum of $f^{(l)}(u)$ (if $s \simeq n > 2$ other two real positive roots exist which practically collapse with that of the minimum); (e) for l > 6 a more and more complex structure appears for $f^{(l)}(u)$. The whole study exhibits that, for arbitrary pairs (n,s), $f^{(l)}(u^{(l)})$ 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 I, for n = 2s = 2, the evolution, in the plane $f^{(1)}(u^{(1)})$; $u^{(1)}$, of the minimum of $f^{(1)}(u)$ (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

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



FIG. 1. The pure potential case n = 2s = 2: locus of the minima of the *l*th-order adimensional free energy $f^{(l)}(u)$ 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.

The results are presented in Table II [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 $(n \ge 50$ and $s \ge 1$) the result provided by $f^{(3)}$ is better than that provided by $f^{(1)}$; typically for n = 2 and s = 1 we obtain $\mu_f^{(1,3)} \ge 41$.

B. 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 obtain¹²

$$C = \frac{k_B}{2} \left[1 + \frac{1}{n} \right], \quad n = 1, 2, \dots$$
 (32)

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

$$C^{(l)} = C$$
, $l = 1, 2, \dots$ (33)

l = 2,4 provide no minimum).				
I	u ⁽¹⁾	$\frac{f^{(l)}(u^{(l)})}{\times 1000}$		
1	3	47.2		
2				
3	6.719	1.15		
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 I. See caption of Fig. 1 (we recall that

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

C. Susceptibility

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

$$\chi_T = \frac{q^2}{k_B T} \langle x^2 \rangle \tag{34}$$

which, for the Hamiltonian (18), leads to¹²

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

$$n = 1, 2, \dots .$$
(35)

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

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

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

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

hence [through Eq. (24)]

$$B^{(1)} = \left(\frac{2n\Gamma\left(\frac{2n+1}{2s}\right)b}{\Gamma(1/2s)k_BT}\right)^{s/n} k_BT.$$

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

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

thus obtaining the exact thermal dependence but a wrong numerical factor [except the cases (n = 1; $\forall s$) and, of course, n = s where the full exact answer is obtained]. Equations (35) and (37) enable the calculation (see Table III) of the factor

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

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

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

TABLE II. 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 firstand 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* $\mu_f^{(1,3)} \equiv f^{(1)}(u^{(1)})/f^{(3)}(u^{(3)})$ (notice that in almost all the present cases $|\mu_f^{(1,3)}| > 1$; (---) means that the computer indications were not clear enough.

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

$$\chi_{T}^{(3)} = \begin{cases} \frac{2s^{2} + 3s + 1}{2s^{2}} \frac{\Gamma(3/2s)}{\Gamma(1/2s)} \frac{1}{(u^{(3)})^{1/n}} \\ + \frac{n + s + 1}{s} \left[\frac{\Gamma(3/2s)}{\Gamma(1/2s)} \frac{\Gamma\left[\frac{2n + 1}{2s}\right]}{\Gamma(1/2s)} - \frac{\Gamma\left[\frac{2n + 3}{2s}\right]}{\Gamma(1/2s)} \right] \frac{1}{(u^{(3)})^{(n+1)/n}} \\ + \left[\frac{\Gamma(3/2s)}{\Gamma(1/2s)} \left[\frac{\Gamma\left[\frac{2n + 1}{2s}\right]}{\Gamma(1/2s)} \right]^{2} - \frac{\Gamma\left[\frac{2n + 1}{2s}\right]}{\Gamma(1/2s)} \frac{\Gamma\left[\frac{2n + 3}{2s}\right]}{\Gamma(1/2s)} \\ + \frac{\Gamma\left[\frac{4n + 3}{2s}\right]}{2\Gamma(1/2s)} - \frac{\Gamma(3/2s)}{2\Gamma(1/2s)} \frac{\Gamma\left[\frac{4n + 1}{2s}\right]}{\Gamma(1/2s)} \\ \end{bmatrix} \frac{1}{(u^{(3)})^{(2n + 1)/n}} \\ \end{cases} \frac{q^{2}}{b^{1/n}} \left[k_{B}T \right]^{(1/n) - 1}, \tag{39}$$

where $u^{(3)}$ is the (physically meaningful) root of Eq. (30) with l=3; we obtain once more the *exact* thermal dependence but a (slightly) *wrong* numerical factor [except the cases $(n = 1; \forall s)$ and, of course, n = s where

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TABLE III. Selected results obtained for the pure potential classical single oscillator (x^{2n}) treated with x^{2} . 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* $\mu_{\chi}^{(1,3)} \equiv (1-q_{\chi}^{(1)})/(1-q_{\chi}^{(3)})$ (notice that in all the present cases $|\mu_{\chi}^{(1,3)}| > 1$); (---) means that the computer indications were not clear enough.

				and the second sec		
s n	1	2	5	10	20	50
1	1	0.854	0.510	0.305		
	1	0.996	0.728	0.390		_
	$-\infty$	38.940	1.800	1.139		
2	1	1	0.798	0.625	0.473	
	1	1	0.972	0.799	0.570	
	$-\infty$		7.151	1.865	1.226	
	1	1.078	1	0.910	0.818	0.701
5	1	0.998	1	0.992	0.927	0.773
5	- ∞	-51.747	~	11.857	2.489	1.314
10	1	1.095	1.055	1	0.947	0.879
	1	0.997	1.001	1	0.995	0.938
	— ∞	-33.773	37.247	œ	10.880	1.960
20	1	1.101	1.073	1.034	1	0.962
	1	0.997	1.005	1.001	1	0.993
	— ∞	- 32.872	15.484	27.811	œ	5.646
50	1	1.102	1.079	1.046	1.021	1
	1	0.997	1.007	1.004	1.001	1
	$-\infty$	- 30.484	11.249	10.531	16.953	8

the full exact answer is obtained]. Equations (35) and (39) enable the calculation (see Table III) of the factor

$$q_{\chi}^{(3)} \equiv \chi_T^{(3)} / \chi_T .$$
⁽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 Table III 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 notice 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

A. Free energy

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

$$\mathscr{H} = \frac{p^2}{2m} + bx^2 + cx^4 , \quad b, c > 0 .$$
(42)

Its associated free energy is given by

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

$$\sim \begin{cases} F(c=0) + \frac{3}{4}c \left(\frac{k_B T}{b}\right)^2 & \text{if } T \to 0, \\ F(b=0) + \frac{\Gamma(\frac{3}{4})}{b} \left[\frac{k_B T}{b}\right]^{1/2} & \text{if } T \end{cases}$$
(43')

$$\left[F(b=0) + \frac{\Gamma(\frac{1}{4})}{\Gamma(\frac{1}{4})} b\left(\frac{ngT}{c}\right) \quad \text{if } T \to \infty , \qquad (43'')$$

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

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

and

$$F(b=0) = -k_B T \ln\left[\frac{1}{2}\Gamma\left(\frac{1}{4}\right)\left(\frac{2\pi mk_B T}{h^2}\right)^{1/2}\left(\frac{k_B T}{c}\right)^{1/4}\right]$$
$$\simeq -k_B T \ln\left[1.8128\left(\frac{2\pi mk_B T}{h^2}\right)^{1/2}\left(\frac{k_B T}{c}\right)^{1/4}\right].$$

Let us now introduce the following trial Hamiltonian

$$\mathscr{H}_0 = \frac{p^2}{2m} + Bx^2 , \ B > 0 \tag{44}$$

whose associated free energy is given by

$$F_0 = -k_B T \ln \left[\left(\frac{2\pi^2 m}{Bh^2} \right)^{1/2} k_B T \right].$$
(45)

The use of Eq. (8) for l = 1 leads to

$$F^{(1)} = F_0 + \left[\frac{b-B}{2B}\right] k_B T + \frac{3}{4} c \left[\frac{k_B T}{B}\right]^2, \qquad (46)$$

whose minimum is located at

$$B^{(1)} = \frac{1}{2} \left[b + (b^2 + 12ck_B T)^{1/2} \right].$$
(47)

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

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

(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 $[\Gamma(\frac{3}{4})/\Gamma(\frac{1}{4})\simeq 0.3380$ and $1/(2\sqrt{3}\simeq 0.2887]$.

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

$$F^{(3)} = F_0 + \frac{b-B}{B} \left[\frac{k_B T}{2} - \frac{3}{2} c \left[\frac{k_B T}{B} \right]^2 + \frac{12c^2(k_B T)^3}{B^4} \right] + 3c \left[\frac{k_B T}{B} \right]^2 \left[\frac{1}{4} - \frac{ck_B T}{B^2} \right] + \left[\frac{b-B}{B} \right]^2 \left[\frac{9}{4} c \left[\frac{k_B T}{B} \right]^2 - \frac{k_B T}{4} \right] + \frac{1}{6} \left[\frac{b-B}{B} \right]^3 k_B T + \frac{99}{4} c^3 \frac{(k_B T)^4}{B^6} , \qquad (49)$$

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

$$(B^{(3)})^{6} - 3b(B^{(3)})^{5} + (3b^{2} - 18ck_{B}T)(B^{(3)})^{4} + (36bck_{B}T - b^{3})(B^{(3)})^{3} + (120c^{2}k_{B}^{2}T^{2} - 18b^{2}ck_{B}T)(B^{(3)})^{2} - 120c^{2}bk_{B}^{2}T^{2}B^{(3)} - 297c^{3}k_{B}^{3}T^{3} = 0.$$
 (50)

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

$$B^{(3)} \sim b + \alpha \frac{ck_B T}{b} , \qquad (51)$$

where α satisfies

$$\alpha^3 - 18\alpha^2 + 120\alpha - 297 = 0 , \qquad (52)$$

hence

$$\alpha = 6 + \left[\frac{\sqrt{337} + 9}{2}\right]^{1/3} - \left[\frac{\sqrt{337} - 9}{2}\right]^{1/3}$$

~6.71902. (52')

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

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

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

$$F^{(3)} \sim -k_B T \ln \left[1.8107 \left[\frac{2\pi m k_B T}{h^2} \right]^{1/2} \left[\frac{k_B T}{c} \right]^{1/4} \right] + 0.3367 b \left[\frac{k_B T}{c} \right]^{1/2}, \qquad (54)$$

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.

B. Specific heat

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

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

where

$$t \equiv \frac{8ck_BT}{b^2} \tag{56}$$

and where standard recursive relations³⁵ for the Bessel functions have been used. As far as we know expression (55) has never been registered in the literature. It leads to

$$C \sim k_B (1 - \frac{3}{16}t)$$
 if $t \to 0$ (55')

and to

$$C \sim k_B \left[\frac{3}{4} + \frac{\Gamma(3/4)}{\sqrt{2}\Gamma(1/4)} \frac{1}{\sqrt{t}} \right]$$
$$\simeq k_B \left[\frac{3}{4} + 0.2390 \frac{1}{\sqrt{t}} \right] \text{ if } t \to \infty . \tag{55''}$$

The *l*th-order approximative specific heat is given by

$$C^{(l)} = -T \frac{d^2 F^{(l)}(T, B^{(l)}(T))}{dT^2} .$$
(57)

Straightforward calculations lead, in the limit $T \rightarrow 0$, to the *exact* asymptotic behavior [Eq. (55')] for both $C^{(1)}$ and $C^{(3)}$ and, in the limit $T \rightarrow \infty$, to

the following results:

$$C^{(1)} \sim k_B \left[\frac{3}{4} + \frac{1}{2\sqrt{6}} \frac{1}{\sqrt{t}} \right]$$

$$\simeq k_B \left[\frac{3}{4} + 0.2041 \frac{1}{\sqrt{t}} \right]$$
(58)

and

$$C^{(3)} \sim k_B \left[\frac{3}{4} + 0.2381 \frac{1}{\sqrt{t}} \right].$$
 (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.

C. Susceptibility

Through calculation of $\langle x^2 \rangle$ we obtain the thermal dependence of the electric susceptibility, namely,

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

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

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

and

$$\chi_T \sim \frac{2\sqrt{2}\Gamma(3/4)}{\Gamma(1/4)} \frac{q^2}{b\sqrt{t}}$$

$$\simeq 0.9560 \frac{q^2}{b\sqrt{t}} \quad \text{if } t \to \infty \ . \tag{60''}$$

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

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

and

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

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



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 $t \to \infty$; $t \equiv 8ck_BT/b^2$; the dashed line indicates the initial slope.



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 $t \to \infty$; $t \equiv 8ck_BT/b^2$; the dashed line indicates the initial slope.

V. CONCLUSION

For classical systems associated to Hamiltonians ${\mathscr H}$ (as well as for quantum systems such that ${\mathscr H}$ commutes with a trial Hamiltonian \mathscr{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. Within the present context a sequence of *l*th-order approximative free energies appears which exhibits convergence problems in the limit $l \rightarrow \infty$ (similarly to what happens in asymptotic series); these problems do not necessarily persist for other quantities (like the specific heat or the susceptibility).

The whole proceudre 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 meaningful situations the exact thermal dependences are recovered for all approximation orders and simultaneously for both limits $T \rightarrow 0$ and $T \rightarrow \infty$. Furthermore great improvement 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

$$F_{0} + \langle \mathscr{H} - \mathscr{H}_{0} \rangle_{0} - \frac{\beta}{2} \left[\langle (\mathscr{H} - \mathscr{H}_{0})^{2} \rangle_{0} - \langle \mathscr{H} - \mathscr{H}_{0} \rangle_{0}^{2} \right] \\ + \frac{\beta^{2}}{6} \left[\langle (\mathscr{H} - \mathscr{H}_{0})^{3} \rangle_{0} - 3 \langle (\mathscr{H} - \mathscr{H}_{0})^{2} \rangle_{0} \langle \mathscr{H} - \mathscr{H}_{0} \rangle_{0} + 2 \langle \mathscr{H} - \mathscr{H}_{0} \rangle_{0}^{3} \right]$$

(third-order approximation),

instead of

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

(first-order approximation).

As an illustration let us recall our results for the pure-type elastic potential associated with n=2 treated with the trial potential associated with s=1; we have obtained, for all temperatures, the exact specific heat in both first- and third-order approximations and a third approximation to the susceptibility which is 39 times better than the first-order one. In the case of the mixed-type elastic potential we have obtained (still using s=1) a third-order approximation for both specific heat and susceptibility which is 39 times better than the first-order one (the relevant comparison refers to the limit $T \rightarrow \infty$ where the discrepancy achieves its maximum value).

On general grounds we must keep in mind that only the first-order approximation [standard variational method (VM)] is *a priori* justified (through the Bogolyubov inequality); higher-order approximations [extended variational method (EVM)] can eventually violate the positive definiteness of the underlying probability space.^{36,37} It seems nevertheless clear that for physically important oscillating systems (like *d*-dimensional crystals,¹³ for example) the EVM (in its third-order approximation) can be numerically quite performant. 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.

Note added in proof: A recursion relation quite similar to our Eq. (7) appears in H. E. Stanley and T. A. Kaplan [Phys. Rev. Lett. <u>16</u>, 981 (1966)]. Several points of interest concerning the VM are discussed by T. A. Kaplan and P. N. Argyres [Ann. Phys. (N.Y.) <u>92</u>, 1 (1975)].

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