All-Temperature Partition Function from Variationally Optimized Canonical Density Matrix

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For the canonical density matrix $C(\boldsymbol{r}, \boldsymbol{r}_0, \beta)$ a variational ansatz $\bar{C}_{\mathrm{f}} = (1-\bar{f})\, C_{\mathrm{cl}} + \bar{f} C_{\mathrm{gr}}$ is made where C_{cl} and C_{gr} are the classical and the ground state expressions which are exact in the high-temperature ($\beta \to 0$) and in the low-temperature limits ($\beta \to +\infty$), respectively, and $\bar{f}$ is a trial function subject to the restriction that $\bar{f} \to 0$ for $\beta \to 0$ and $\bar{f} \to 1$ for $\beta \to \infty$. With the approximation that $\bar{f}$ be dependent only upon β, not upon spatial variables, the mean square error arising when $\bar{C}_{\mathrm{f}}$ is inserted into the Bloch equation is made a minimum. The Euler equation for this variational problem is an ordinary second order differential equation for $\bar{f} = f(\beta)$ to be solved numerically. The method is tested for the exactly solvable case of the one-dimensional harmonic oscillator.

1. Introduction

The partition function Z of a quantal system of N particles can be determined either by direct summation of Boltzmann factors

$$Z(\beta) = \sum_j g_j \cdot \exp(-\beta E_j) \tag{1}$$

or by performing the trace

$$Z(\beta) = \mathrm{Tr}\,(\hat{\varrho}(\beta)) \tag{2}$$

of the density operator

$$\hat{\varrho}(\beta) = \exp(-\beta \hat{H}) \tag{3}$$

in a representation where the Hamiltonian $\hat{H}$ is not diagonal, see e.g. [1]. E_j is the j-th eigenvalue of $\hat{H}$ with degeneracy g_j, $\beta = \ k_B T)^{-1}$, k_B Boltzmann constant and T absolute temperature.

For low temperatures ($\beta \to \infty$) the exponential terms in equation (1) decrease so rapidly relative to the ground state term $\exp(-\beta E_0)$ that it is sufficient to determine only a few of the lowest levels E_j. When the temperature is raised, however, the contribution of the higher energy levels become more and more important so that, in the limit $\beta \to 0$, it is quite impractical to use expression (1). For only a few Hamiltonians can (1) be evaluated exactly for all temperatures, the best-known example being the harmonic oscillator.

Therefore, numerous authors have dealt with the approximate evaluation of expression (2). The various approaches may be classified as follows

a) *Thermodynamic perturbation theory*

A lot of references can be found in the textbook by Münster [1] or in a recent article by Bohmann and Witschel [2]. In the formulation of Siegert [3] the zeroth and first order terms of the perturbation series read

$$\hat{\varrho}(\beta) = \hat{\varrho}_0(\beta) - \int_0^\beta \mathrm{d}\beta'\, \hat{\varrho}_0(\beta')\,(\hat{H} - \hat{H}_0) \cdot \hat{\varrho}_0(\beta - \beta') + \dots \tag{4}$$

with some unperturbed density operator $\hat{\varrho}_0(\beta) = \exp(-\beta \hat{H}_0)$ which is chosen such that the trace of the right-hand side can be performed, e.g. by techniques of operator algebra.

b) *Functional integral approach*

Feynman's representation of the canonical density matrix as path integral [4], [5] is approximated by multidimensional integrals in position space which then are evaluated e.g. by Monte Carlo methods [6], [7]. It turns out that these procedures work quite well in the high temperature regime ($\beta \to 0$) but that errors are increasing for $T \to 0$. Since the last two decades much work on analytical approximations, refinements and modifications of the path integral approach has been published. For the

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calculation of partition functions see e.g. references [8]–[17].

c) Bounds on thermodynamic potentials

Besides other thermodynamic quantities, the Helmholtz free energy F and thus the partition function can be confined by upper and lower bounds valid for all T. Since they often can be evaluated exactly, they are important tools to estimate the true partition function, see the reviews of Girardeau and Mazo [18] and of Huber [19]. Further work based on the path integral representation of Z is given by references [20], [21], [22]. A combination of thermodynamic perturbation theory (a) with variation of bounds depending on free parameters has been applied very successfully to anharmonic oscillators by Witschel [23].

d) Classical and semiclassical solutions of the Bloch equation

By use of the canonical density matrix

$$C(\boldsymbol{r}, \boldsymbol{r}_0, \beta) = \langle \boldsymbol{r} | \hat{\varrho}(\beta) | \boldsymbol{r}_0 \rangle = \sum_i \Psi_i^*(\boldsymbol{r}_0)\, \Psi_i(\boldsymbol{r})\, e^{-\beta E_i}, \tag{5}$$

where the sum runs over all eigenstates Ψ_i of $\hat{H}$ the partition function (2) reads

$$Z(\beta) = \int \mathrm{d}^{3N} r\, C(\boldsymbol{r}, \boldsymbol{r}, \beta)\,. \tag{2a}$$

C satisfies the Bloch equation

$$\left(\hat{H}_r + \frac{\partial}{\partial \beta}\right) C(\boldsymbol{r}, \boldsymbol{r}_0, \beta) \equiv \left(-\frac{\hbar^2}{2m} \sum_{n=1}^{N} \Delta_{\boldsymbol{r}_n} + V(\boldsymbol{r}) + \frac{\partial}{\partial \beta}\right) \cdot C(\boldsymbol{r}, \boldsymbol{r}_0, \beta) = 0 \tag{6}$$

with initial condition

$$C(\boldsymbol{r}, \boldsymbol{r}_0, 0) = \quad (\boldsymbol{r} - \boldsymbol{r}_0) \tag{7}$$

if the system is supposed to obey Boltzmann statistics [1].

For general potentials $V(\boldsymbol{r})$, (6) can be solved analytically only in the limit $\beta \to 0$ yielding the classical density matrix [24]

$$C_{\mathrm{cl}}(\boldsymbol{r}, \boldsymbol{r}_0, \beta) = \left(\frac{m}{2\pi \hbar^2 \beta}\right)^{3N/2} \cdot \exp\left[-\frac{m\,|\boldsymbol{r} - \boldsymbol{r}_0|^2}{2\beta \hbar^2} - \beta\, W(\boldsymbol{r}, \boldsymbol{r}_0)\right], \tag{8}$$

where

$$W(\boldsymbol{r}, \boldsymbol{r}_0) \equiv \int_0^1 V[\boldsymbol{r}_0 + \lambda (\boldsymbol{r} - \boldsymbol{r}_0)]\, \mathrm{d}\lambda\,. \tag{9}$$

Quantum corrections are accounted for by multiplying C_{cl} by a power series expansion in $\hbar^2$ the coefficients of which depend on β and on spatial derivatives of V [24]. The diagonal elements of the semiclassical (= quantum corrected) density matrix

$$C_{\mathrm{sc}}(\boldsymbol{r}, \boldsymbol{r}, \beta) = C_{\mathrm{cl}}(\boldsymbol{r}, \boldsymbol{r}, \beta) \cdot \left\{1 - \frac{\hbar^2 \beta^2}{12 m} \sum_{k=1}^{N} \left[\Delta_{\boldsymbol{r}_k} V(\boldsymbol{r}) - \frac{\beta}{2} (\nabla_{\boldsymbol{r}_k} V(\boldsymbol{r}))^2\right] + O(\hbar^4)\right\} \tag{10}$$

have been already derived by Wigner [25] and Kirkwood [26]. When C_{sc} is used instead of C_{cl} to calculate Z, the improvement is substantial in the limit $\beta \to 0$ (provided that the spatial derivatives of the potential exist), for low temperatures ($\beta \to \infty$) the semiclassical formula fails badly in that the partition function in this approximation can take on even negative values, see below.

In the present work the partition function is calculated starting from the Bloch equation an approximate solution of which is constructed such as to combine automatically the features of the high-temperature classical expression, Eq. (8), with those of the low-temperature, i.e. ground-state expression emerging from (5)

$$C_{\mathrm{gr}}(\boldsymbol{r}, \boldsymbol{r}_0, \beta) \equiv \Psi_0^*(\boldsymbol{r}_0)\, \Psi_0(\boldsymbol{r})\, e^{-\beta E_0} \tag{11}$$

after all higher terms have been neglected for $\beta \to \infty$. Of course, the latter approximation is valid only if at least E_0 is separated from the higher levels by a finite gap. Furthermore, the ground state is supposed to be nondegenerate, for simplicity. Since C_{gr} can be approximated relatively easily, e.g. by the Ritz variational principle, the approximate all-temperature solution will be represented as a linear combination of C_{cl} and C_{gr} the coefficients of which are determined by a variational procedure rather different from the method of varying bounds (see paragraph c) on the partition function.

The variational principle used for the trial density matrix is set up in Section 2. Section 3 describes the general way of solving the Euler equation associated with this variational principle. In the 4. Section the method is applied for test to an exactly solvable case, namely the linear harmonic oscillator. The partition function, the Helmholtz free energy, the internal energy, the entropy, and the specific heat are calculated and compared with the exact values. Results are summarized and discussed in the last section.

2. A variational principle for the canonical density matrix

When the operator $\hat{H}_{\boldsymbol{r}} + \partial/\partial\beta$ is applied to an arbitrary, sufficiently differentiable real function $\bar{C}(\boldsymbol{r}, \boldsymbol{r}_0, \beta)$ which satisfies condition (7), the result is, of course, a real function $w(\boldsymbol{r}, \boldsymbol{r}_0, \beta)$ which is different from zero, in general.

$$w(\boldsymbol{r}, \boldsymbol{r}_0, \beta) \equiv \left(\hat{H}_{\boldsymbol{r}} + \frac{\partial}{\partial\beta}\right) \bar{C}(\boldsymbol{r}, \boldsymbol{r}_0, \beta) . \qquad (12)$$

Let us define the functional

$$J[\bar{C}] \equiv \int_0^\infty \mathrm{d}\beta \int \mathrm{d}^{3N} r \int \mathrm{d}^{3N} r_0\, w^2(\boldsymbol{r}, \boldsymbol{r}_0, \beta) , \qquad (13)$$

where the spatial integrations are to be extended all over the space in which the system is enclosed.

Especially, when $\bar{C}$ is chosen to be the exact density matrix C, we have evidently that

$$w(\boldsymbol{r}, \boldsymbol{r}_0, \beta) \equiv 0 \quad \text{for all} \quad \boldsymbol{r}, \boldsymbol{r}_0, \beta ,$$

whence

$$J[C] = 0 . \qquad (14)$$

On the other hand, if $\bar{C} \neq C$ then w cannot vanish identically for all $\boldsymbol{r}$, $\boldsymbol{r}_0$, and β thus leading to

$$J[\bar{C}] > 0 . \qquad (15)$$

In other words, the functional (13) vanishes if and only if $\bar{C} = C$. $J[\bar{C}]$ can be used as a measure of deviation of $\bar{C}$ from C in the sense that a certain trial function $\bar{C}_1$ is to be regarded as a better approximation to C than another function $\bar{C}_2$ if

$$0 \leqq J[\bar{C}_1] < J[\bar{C}_2] . \qquad (16)$$

In choosing the trial density matrix $\bar{C}$ we shall try, of course, to incorporate information about the exact matrix C. According to the general ideas sketched in the introduction, let us use a trial matrix which (i) satisfies (7), (ii) becomes identical with the correct expressions (8) and (11) in the limits $\beta \to 0$ and $\beta \to \infty$, respectively. This can be achieved simply by the ansatz

$$\bar{C} = (1 - \bar{f})\, C_{\mathrm{cl}} + \bar{f} C_{\mathrm{gr}} , \qquad (17)$$

where

$$\lim_{\beta \to 0_+} \bar{f} = 0 \qquad (18\mathrm{a})$$

and

$$\lim_{\beta \to \infty} \bar{f} = 1 . \qquad (18\mathrm{b})$$

When the function $\bar{f}$ is allowed to depend also on $\boldsymbol{r}$ and $\boldsymbol{r}_0$, (17) contains no approximation at all, since, in principle, $\bar{f}$ can be adjusted so that the left-hand side of (17) is just the exact C. However, the determination of $\bar{f}$ would then be at least as difficult as for C.

The fact that the limits (18a, b) are independent of $\boldsymbol{r}$, $\boldsymbol{r}_0$ suggests an approximation where $\bar{f}$ is independent of the spatial coordinates for all temperatures, i.e. we put

$$\nabla_{\boldsymbol{r}_i} \bar{f} = \nabla_{\boldsymbol{r}_{i,0}} \bar{f} = 0 . \qquad (19)$$

When the ansatz (17) is inserted into (12), it follows after some algebra

$$w(\boldsymbol{r}, \boldsymbol{r}_0, \beta) = [1 - \bar{f}(\beta)]\, A(\boldsymbol{r}, \boldsymbol{r}_0, \beta) + (\mathrm{d}\bar{f}(\beta)/\mathrm{d}\beta)\, B(\boldsymbol{r}, \boldsymbol{r}_0, \beta) , \qquad (20)$$

where

$$A(\boldsymbol{r}, \boldsymbol{r}_0, \beta) \equiv (\hbar^2 \beta/2m)\, \{\Delta_{\boldsymbol{r}} W(\boldsymbol{r}, \boldsymbol{r}_0) - \beta [\nabla_{\boldsymbol{r}} W]^2\} \cdot C_{\mathrm{cl}}(\boldsymbol{r}, \boldsymbol{r}_0, \beta) , \qquad (21)$$

$$B(\boldsymbol{r}, \boldsymbol{r}_0, \beta) \equiv C_{\mathrm{gr}}(\boldsymbol{r}, \boldsymbol{r}_0, \beta) - C_{\mathrm{cl}}(\boldsymbol{r}, \boldsymbol{r}_0, \beta) . \qquad (22)$$

In deriving (20) it has been used that C_{gr} is an exact solution of (6) which, however, does not satisfy condition (7).

With the definitions

$$L_1(\beta) \equiv \int A^2\, \mathrm{d}\tau_N , \qquad (23)$$

$$L_2(\beta) \equiv \int AB\, \mathrm{d}\tau_N , \qquad (24)$$

$$L_3(\beta) \equiv \int B^2\, \mathrm{d}\tau_N \qquad (25)$$

($\mathrm{d}\tau_N \equiv \mathrm{d}^{3N} r\, \mathrm{d}^{3N} r_0$) we can write the functional (13)

$$J[\bar{C}] = \int_0^\infty \mathrm{d}\beta\, [L_1 (1 - \bar{f})^2 + 2 L_2 (1 - \bar{f}) \bar{f}' + L_3 \bar{f}'^2] \equiv \Phi[\bar{f}] , \qquad (26)$$

where $\bar{f}' \equiv \mathrm{d}\bar{f}/\mathrm{d}\beta$ and Φ is a new functional of $\bar{f}$. Since the variability of $\bar{C}$ has been restricted due to the approximation (19), it is not possible, in general, to find $\bar{f}(\beta)$ so that $\Phi[\bar{f}] = 0$. However, we may look for a function $\bar{f}=f(\beta)$ which makes Φ at least a minimum. In the next chapter the Euler equation of this minimization will be established and treated.

Once the minimizing f has been found, we obtain the approximate partition function from (17)

$$Z_f(\beta)=\int \mathrm{d}^{3N}r\, C_f(\boldsymbol{r},\boldsymbol{r},\beta)\,, \tag{27}$$

where

$$C_f(\boldsymbol{r},\boldsymbol{r}_0,\beta)=[1-f(\beta)]\, C_{\mathrm{cl}}(\boldsymbol{r},\boldsymbol{r}_0,\beta) + f(\beta)\, C_{\mathrm{gr}}(\boldsymbol{r},\boldsymbol{r}_0,\beta)\,. \tag{28}$$

It follows from (8), (9), and from (11) that

$$Z_f(\beta)=\left[\frac{m}{2\pi\hbar^2\beta}\right]^{3N/2}[1-f(\beta)] \cdot \int \mathrm{d}^{3N}r\, e^{-\beta V(\boldsymbol{r})}+f(\beta)\, e^{-\beta E_0}. \tag{29}$$

From this expression basic thermodynamic functions may be calculated using the well-known relations of statistical mechanics, e.g. for the Helmholtz (free) energy F_f, internal energy E_f, entropy S_f, and specific heat c_f

$$F_f=-\frac{1}{\beta}\ln Z_f, \tag{30}$$

$$E_f=-\frac{\mathrm{d}\ln Z_f}{\mathrm{d}\beta}, \tag{31}$$

$$S_f=k_{\mathrm{B}}\beta(E_f-F_f)\,, \tag{32}$$

$$c_f=\frac{\mathrm{d}E_f}{\mathrm{d}T}=k_{\mathrm{B}}\beta^2\frac{\mathrm{d}^2\ln Z_f}{\mathrm{d}\beta^2}. \tag{33}$$

3. Minimization of the functional Φ

When the minimum of the functional

$$\Phi[\bar{f}]=\int_0^\infty K(\beta,\bar{f},\bar{f}')\,\mathrm{d}\beta \tag{34}$$

with respect to variations of the trial function $\bar{f}(\beta)$ is to be determined, the minimizing function $f(\beta)$ necessarily satisfies the Euler equation (see e.g. Courant and Hilbert [27])

$$\frac{\partial K}{\partial f}-\frac{\mathrm{d}}{\mathrm{d}\beta}\left(\frac{\partial K}{\partial f'}\right)=0. \tag{35}$$

From (26) we have that

$$K(\beta,f,f')=L_1(1-f)^2+2L_2(1-f)f'+L_3f'^2 \tag{36}$$

so (35) reads

$$-2L_1(1-f)-2L_2f'-[2L_2(1-f)+2L_3f']'=0$$

or

$$L_3f''+L_3'f'+(L_1+L_2')(1-f)=0\,. \tag{37}$$

In general, numerical methods have to be applied to solve (37) subject to boundary conditions (18a, b). Nevertheless, this differential equation being an ordinary one represents a problem which can be handled very much easier than the partial differential equation (6) for C.

It is convenient to introduce a new variable τ by

$$1-f(\beta)\equiv\exp(-\tau(\beta))\,. \tag{38}$$

Equation (37) then leads to the differential equation

$$L_3\tau''+L_3'\tau'-L_3\tau'^2+L_1+L_2'=0 \tag{39}$$

which is of first order in τ'. Furthermore, when

$$R(\beta)\equiv L_3(\beta)\,\tau'(\beta) \tag{40}$$

is substituted in (39), the first order equation

$$L_3R'-R^2+L_3(L_1+L_2')=0 \tag{41}$$

is obtained.

Evidently, the boundary conditions (18a, b) on f are transformed to

$$\lim_{\beta\to 0_+}\tau(\beta)=0 \tag{42a}$$

and

$$\lim_{\beta\to\infty}\tau(\beta)=+\infty\,. \tag{42b}$$

Noting (42a) we obtain from (40)

$$\tau(\beta)=\int_0^\beta\frac{R(u)}{L_3(u)}\,\mathrm{d}u \tag{43}$$

and therefore from (38)

$$f(\beta)=1-\exp\left[-\int_0^\beta\frac{R(u)}{L_3(u)}\,\mathrm{d}u\right]. \tag{44}$$

Thus we have to solve (41) under the condition that (43) is integrable for any finite upper limit β, however, that

$$\int_0^\infty\frac{R(u)}{L_3(u)}\,\mathrm{d}u=+\infty \tag{45}$$

in accordance with (42b).

In practice, it is advantageous to find the asymptotic behaviour of $L_1(\beta)$, $L_3(\beta)$, and $L_2'(\beta)$ for $\beta\to\infty$ and hence the asymptotic form of $R(\beta)$, say $R_\infty(\beta)$. When

$$G(\beta)\equiv R(\beta)/R_\infty(\beta) \tag{46}$$

is substituted in (41), a differential equation is obtained for $G(\beta)$ to be solved under the condition

$$\lim_{\beta\to\infty} G(\beta) = 1\,. \tag{47}$$

Starting then a numerical integration procedure (e.g. a Runge-Kutta method [28], [29]) beginning at a large value $\beta=\beta_\infty$ with $G(\beta_\infty)=1$, the integration may be performed down to $\beta=0$ with excellent numerical stability, as will be seen in the next section.

4. Demonstration by an exactly solvable potential: Harmonic oscillator in one dimension

4.1. Setting up the differential equation for f

The foregoing general procedure will be exemplified for the harmonic oscillator in one dimension with Hamiltonian

$$\hat{H}_x = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{m\,\omega^2}{2}\,x^2\,. \tag{48}$$

The exact canonical density matrix $C(x, x_0, \beta)$ is given by (Husimi [30])

$$C(x, x_0, \beta) = \left(\frac{m\,\omega}{2\pi\,\hbar\sinh(2\mu)}\right)^{1/2} \cdot \exp\left\{-\frac{(\xi-\xi_0)^2}{4}\coth\mu - \frac{(\xi+\xi_0)^2}{4}\tanh\mu\right\} \tag{49}$$

with dimensionless variables

$$\xi \equiv x\sqrt{m\,\omega/\hbar}\,, \tag{50a}$$

$$\xi_0 \equiv x_0\sqrt{m\,\omega/\hbar}\,, \tag{50b}$$

$$\mu \equiv \tfrac{1}{2}\,\hbar\,\omega\,\beta\,. \tag{50c}$$

From (49) the exact partition function

$$Z(\beta) = \int_{-\infty}^{+\infty} C(x, x, \beta)\,\mathrm{d}x = 1/2\sinh\mu \tag{51}$$

is obtained, and hence the exact Helmholtz (free) energy F, internal energy E, entropy S, and specific heat c are given by

$$F = \hbar\,\omega\ln(2\sinh\mu)/(2\mu)\,, \tag{52}$$

$$E = \tfrac{1}{2}\,\hbar\,\omega\coth\mu\,, \tag{53}$$

$$S = k_\mathrm{B}[\mu\coth\mu - \ln(2\sinh\mu)]\,, \tag{54}$$

$$c = k_\mathrm{B}\left(\frac{\mu}{\sinh\mu}\right)^2. \tag{55}$$

Let us now write down the ansatz (17) for the harmonic oscillator. From (9) we find

$$W(x, x_0) = \int_0^1 \mathrm{d}\lambda\,\frac{m\,\omega^2}{2}\,[x_0 + \lambda(x-x_0)]^2 = \frac{m\,\omega^2}{6}\,(x^2 + x\,x_0 + x_0^2) \tag{56}$$

and so

$$C_\mathrm{cl}(x, x_0, \beta) = \frac{1}{2}\left(\frac{m\,\omega}{\pi\,\hbar\,\mu}\right)^{1/2} \cdot \exp\left\{-\frac{(\xi-\xi_0)^2}{4\mu} - \frac{\mu}{3}(\xi^2 + \xi\,\xi_0 + \xi_0^2)\right\}. \tag{57}$$

At first sight it might seem that, in the limit $\mu\to 0$, this expression agrees with the exact one, equation (49), only for $\xi_0=\xi$, when $\coth\mu\approx\mu^{-1}$ and $\tanh\mu\approx\sinh\mu\approx\mu$ are inserted. However, one has to go to the next order in the expansion of $\coth\mu$,

$$\coth\mu \approx \frac{1}{\mu} + \frac{\mu}{3}$$

in order to compare the exponents of (49) and (57) consistently which are then seen to agree for arbitrary ξ, ξ_0 as $\mu\to 0$.

In standard textbooks on quantum mechanics the ground state wave function of the harmonic oscillator is calculated to be

$$\psi_0(x) = \left(\frac{m\,\omega}{\hbar\,\pi}\right)^{1/4}\exp\left(-\frac{m\,\omega\,x^2}{2\hbar}\right) \tag{58}$$

belonging to $E_0=\hbar\,\omega/2$. Thus it follows from (11), (50a–c), and (58) that

$$C_\mathrm{gr}(x, x_0, \beta) = \frac{1}{\pi}\left(\frac{m\,\omega}{\hbar}\right)^{1/2} \cdot \exp\left[-\tfrac{1}{2}(\xi^2+\xi_0^2) - \mu\right]. \tag{59}$$

Using (56), (57), and (59), we can determine A, B, see (21), (22), and hence the integrals L_1, L_2, and L_3, see (23), (24), (25). Since all integrands are sums of terms of the form

$$u^\nu\exp(-\gamma\,u^2 + \delta u)\,,\quad u=\xi \quad\text{or}\quad \xi_0\,,$$

with $\nu=0$, 1, 2, 3, 4 and $\gamma>0$ all the double integrations over ξ and ξ_0 can be performed analytically. The somewhat lengthy, but elementary calculations yields

$$L_1 = \left(\frac{\hbar\,\omega}{2}\right)^2 l_1(\mu)\,, \tag{60a}$$

$$L_2 = \left(\frac{\hbar\,\omega}{2}\right) l_2(\mu)\,, \tag{60b}$$

$$L_3 = l_3(\mu)\,, \tag{60c}$$

where

$$l_1(\mu) = \frac{\mu}{9p}\sqrt{\frac{3}{q}}\left(3 + \frac{\Omega}{p}\right), \tag{61a}$$

$$l_2(\mu) = \frac{1}{\sqrt{3}}\left\{\frac{6\mu\,e^{-\mu}}{s\sqrt{t}}\left[2\mu + 1 - \frac{\mu\,(2\mu+3)^2}{4t}\right] - Y\right\}, \tag{61b}$$

$$l_3(\mu) = \frac{1}{\mu}\left[\mu\,e^{-2\mu} - 2\mu\,e^{-\mu}\sqrt{\frac{3}{t}} + \frac{1}{4}\sqrt{\frac{3}{q}}\right] \tag{61c}$$

with abbreviations

$$p = 4\mu^2 + 3\,, \tag{62}$$

$$q = \mu^2 + 3\,, \tag{63}$$

$$\Omega = 12\mu^4 + \frac{27}{4q}(2\mu^2 - 3) + \frac{2187}{64q^2}\,, \tag{64}$$

$$s = 4\mu^2 + 6\mu + 3\,, \tag{65}$$

$$t = (\mu + 1)(\mu^2 + 3\mu + 3)\,, \tag{66}$$

$$Y = \frac{1}{2p\sqrt{q}}\left(2\mu^2 + 3 - \frac{27}{8q}\right). \tag{67}$$

The differential equation (37) for f then reads

$$l_3\ddot{f} + \dot{l}_3\dot{f} + (l_1 + \dot{l}_2)(1 - f) = 0\,, \tag{68}$$

where e.g.

$$\dot{f} \equiv \frac{\mathrm{d}f}{\mathrm{d}\mu} = \frac{2}{\hbar\,\omega}\frac{\mathrm{d}f}{\mathrm{d}\beta} = \frac{2}{\hbar\,\omega}f'.$$

When the dimensionless function

$$r(\mu) \equiv \frac{2}{\hbar\,\omega}R(\beta) \tag{69}$$

is introduced in (41) we obtain

$$l_3\dot{r} - r^2 + l_3(l_1 + \dot{l}_2) = 0 \tag{70}$$

and, after this equation has been solved, from (43) by

$$u = (2/\hbar\,\omega)\,\lambda\,, \tag{71}$$

$$\tau = \int_0^{\mu}\frac{r(\lambda)}{l_3(\lambda)}\,\mathrm{d}\lambda\,. \tag{72}$$

4.2. Asymptotic behaviour of the function $r(\mu)$

For $\mu \to \infty$ the coefficients l_1, $\dot{l}_2$, l_3 occurring in (70) are obtained from (61a)–(67)

$$l_1(\mu) \sim \sqrt{3}/12\,, \tag{73a}$$

$$\dot{l}_2(\mu) \sim 1/4\sqrt{3}\,\mu^2\,, \tag{73b}$$

$$l_3(\mu) \sim \sqrt{3}/4\mu^2\,, \tag{73c}$$

so (70) takes on the form

$$\dot{r} = \frac{r^2}{l_3} - l_1 - \dot{l}_2 \sim \frac{4}{\sqrt{3}}\mu^2 r^2 - \frac{\sqrt{3}}{12}\,. \tag{74}$$

We obtain the correct solution of this asymptotic differential equation by consideration of the following possible suppositions:

a) $\mu r \to \infty$

Then in (74) the constant $\sqrt{3}/12$ may be neglected and (74) can be solved by separation of variables

$$\frac{\dot{r}}{r^2} \sim \frac{4}{\sqrt{3}}\mu^2$$

the solution being

$$r \sim -1/(a + (4/3\sqrt{3})\,\mu^3)\,, \tag{75}$$

where a is a constant of integration. However, for this solution we infer $\mu r \to 0$ contrary to the supposition.

b) $\mu r \to 0$

Equation (74) now yields

$$\dot{r} \sim -\sqrt{3}/12$$

or

$$r \sim -(\sqrt{3}/12)\,\mu \tag{76}$$

not in agreement with the supposition.

c) $\mu r \to M \neq 0$

(74) reads

$$\dot{r} \sim \frac{4}{\sqrt{3}}M^2 - \frac{\sqrt{3}}{12}$$

or

$$r \sim \left(\frac{4}{\sqrt{3}}M^2 - \frac{\sqrt{3}}{12}\right)\mu\,. \tag{77}$$

This expression is consistent with the supposition $r \sim M/\mu$ only if

$$\frac{4}{\sqrt{3}} M^2 - \frac{\sqrt{3}}{12} = 0$$

or

$$M = \pm \tfrac{1}{4} . \tag{78}$$

From (45) it is clear that only the positive sign is reasonable, so we obtain for the asymptotic behaviour of $r(\mu)$

$$r(\mu) \sim 1/4\mu \equiv r_\infty(\mu) . \tag{79}$$

When a function

$$g(\mu) \equiv r(\mu)/r_\infty(\mu) = 4\mu\, r(\mu) \tag{46a}$$

is introduced, according to (46), into (70) we obtain

$$\dot g = \frac{g}{\mu}\left[1 + \frac{g}{4 l_3}\right] - 4\mu\,(l_1 + \dot l_2) \tag{80}$$

which has to be solved under the condition

$$\lim_{\mu \to \infty} g(\mu) \equiv g(\infty) = 1 . \tag{47a}$$

4.3. *Results*

The differential equation (80) has been solved numerically by means of a fourth-order Runga-Kutta-procedure. The initial condition (47a) was approximated by the condition that $g = 1$ at a certain value $\mu = \mu_\infty$ which is chosen sufficiently large. It turns out that $\mu_\infty \gtrsim 7$ is a convenient choice. The integration was performed from $\mu = \mu_\infty$ down to $\mu = 0$. The solution $g(\mu)$ proved to be very stable with respect to variations in the choice of $g(\mu_\infty)$.

The function $f(\mu)$ which is obtained from equations (46a), (72), and (38) is shown in Figure 1. (For simplicity we use the same function symbol f whether the independent variable is β or μ).

When $\beta V(x) = \mu \xi^2$ and $\beta E_0 = \mu$ are inserted in expression (29), we find the partition function

$$Z_f = (1-f)\, Z_{\mathrm{cl}} + f Z_{\mathrm{gr}} , \tag{81}$$

where, from (57) and (59),

$$Z_{\mathrm{cl}} = 1/2\mu \tag{82}$$

and

$$Z_{\mathrm{gr}} = e^{-\mu} \tag{83}$$

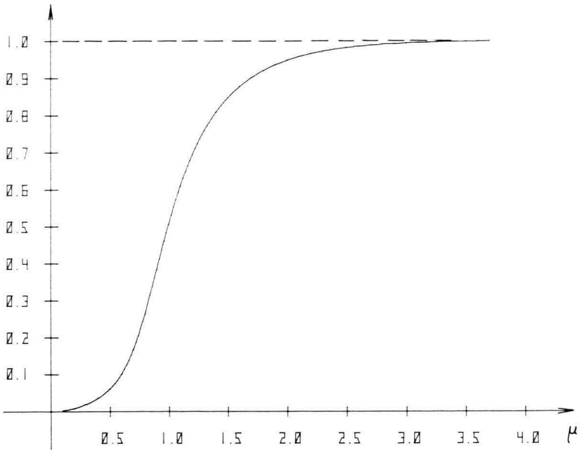

Fig. 1. Solution $f(\mu)$ of the Euler equation (68) for the linear harmonic oscillator ($\mu = \hbar\,\omega\,\beta/2$).

are the partition functions in the classical and in the ground state limits, respectively. The exact partition function Z is obtained from (49)

$$Z = \frac{1}{2\sinh\mu} . \tag{84}$$

Furthermore, the semiclassical partition function Z_{sc}, has been calculated from the diagonal element of expression (10) which now reads

$$\begin{aligned} C_{\mathrm{sc}}(x, x, \beta) &= \left(\frac{m}{2\pi\hbar^2\beta}\right)^{1/2} e^{-\beta V(x)} \\ &\quad \cdot \left\{1 + \frac{\beta^2\hbar^2}{12m}\left[\frac{\beta}{2}\left(\frac{\mathrm{d}V}{\mathrm{d}x}\right)^2 - \frac{\mathrm{d}^2 V}{\mathrm{d}x^2}\right]\right\} \\ &= \left(\frac{m\,\omega}{\hbar}\right)^{1/2} \frac{e^{-\mu\xi^2}}{\sqrt{4\pi\mu}} \left\{1 + \frac{\mu^3}{3}\xi^2 - \frac{\mu^2}{3}\right\} . \end{aligned} \tag{10a}$$

We find that

$$Z_{\mathrm{sc}} = \frac{1}{2\mu}\left(1 - \frac{\mu^2}{6}\right) . \tag{85}$$

Some values of these expressions for the partition function are tabulated in Table 1, together with the variational function $f(\mu)$.

For small values $\mu \ll 1$ the agreement between Z and Z_{sc} is excellent, as must be expected; however, for $\mu > \sqrt{6} \approx 2,46$, Z_{sc} becomes even negative. The logarithms of the expressions (81), (82), (84), and (85) are shown in Figure 2. It is seen that the variational partition function Z_f agrees very well with the exact Z for all temperatures.

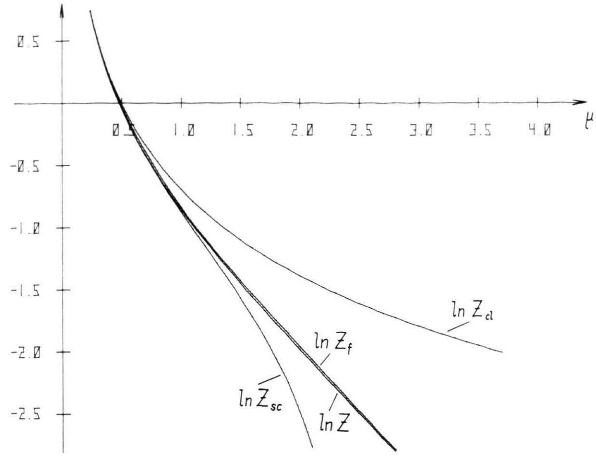

Fig. 2. Logarithms of the exact and of various approximate partition functions for the linear harmonic oscillator versus $\mu = \hbar\omega\beta/2$. Z, Z_{cl}, Z_{sc}, and Z_f are the exact, classical, semiclassical, and the present approximations, respectively, see equations (84), (82), (85), and (81).

Table 1. Some values of $f(\mu)$ and the partition function $Z_f(\mu)$ derived thereof. For comparison, also the exact (Z), classical (Z_{cl}), and semiclassical (Z_{sc}) partition functions are quoted.

μ	$f(\mu)$	Z_f	Z	Z_{cl}	Z_{sc}	Z_{gr}
0.1	0.0024	4.990	4.992	5	4.992	0.9048
0.2	0.0092	2.485	2.483	2.5	2.483	0.8187
0.3	0.0202	1.648	1.642	1.667	1.642	0.7408
0.5	0.0620	0.9756	0.9595	1	0.9583	0.6065
1.0	0.5083	0.4328	0.4255	0.5	0.4167	0.3679
2.0	0.9478	0.1413	0.1379	0.25	0.0833	0.1353
4.0	0.9994	0.01838	0.01832	0.125	−0.2083	0.01832

From (30)−(33) the thermodynamic quantities F_f, E_f, S_f, and c_f are derived and represented in Figures 3−6. In these diagrams also the corresponding quantities are shown which are derived from the exact, from the classical, and from the semiclassical expressions for the partition function. In the case of the semiclassical approximations the values are given only up to $\mu = \sqrt{6}$ where $\ln Z_{\text{sc}}$ becomes singular. The exact quantities F, E, S, and c have already been quoted by (52)−(55). When Z_f in (30)−(33) is replaced by Z_{cl}, (82), and by Z_{sc}, (85), we obtain in classical and in semiclassical approximation

$$F_{\text{cl}} = \frac{\hbar\omega}{2}\,\frac{\ln(2\mu)}{\mu}\,, \tag{86}$$

$$E_{\text{cl}} = \frac{\hbar\omega}{2}\,\frac{1}{\mu}\,, \tag{87}$$

$$S_{\text{cl}} = k_{\text{B}}[1 - \ln(2\mu)]\,, \tag{88}$$

$$c_{\text{cl}} = k_{\text{B}}\,, \tag{89}$$

and

$$F_{\text{sc}} = \frac{\hbar\omega}{2}\,\frac{1}{\mu}\left[\ln(2\mu) - \ln\left(1 - \frac{\mu^2}{6}\right)\right], \tag{90}$$

$$E_{\text{sc}} = \frac{\hbar\omega}{2}\,\frac{1}{\mu}\,\frac{1 + \mu^2/6}{1 - \mu^2/6}\,, \tag{91}$$

$$S_{\text{sc}} = k_{\text{B}}\left[\frac{1 + \mu^2/6}{1 - \mu^2/6} - \ln(2\mu) + \ln\left(1 - \frac{\mu^2}{6}\right)\right], \tag{92}$$

$$c_{\text{sc}} = k_{\text{B}}\,\frac{1 - \frac{2}{3}\mu^2 - \frac{1}{36}\mu^4}{(1 - \mu^2/6)^2}\,. \tag{93}$$

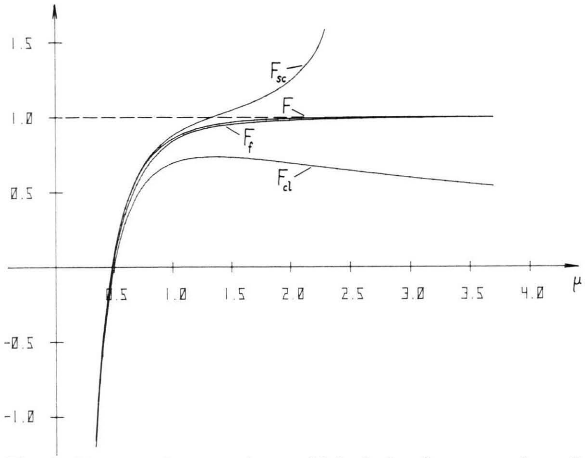

Fig. 3. Exact and approximate Helmholtz free energies of the linear harmonic oscillator in units of $\hbar\omega/2$ as functions of $\mu = \hbar\omega\beta/2$. F, F_{cl}, F_{sc}, and F_f are exact and in classical, semiclassical, and in the present approximations, respectively, see equations (52), (86), (90), and (30), (81).

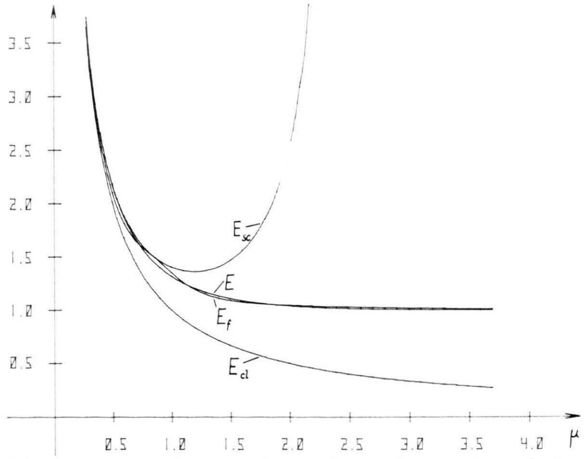

Fig. 4. Exact and approximate internal energies of the linear harmonic oscillator in units of $\hbar\omega/2$ as functions of $\mu = \hbar\omega\beta/2$. E, E_{cl}, E_{sc}, and E_f are exact and in classical, semiclassical, and in the present approximations, respectively, see equations (53), (87), (91), and (31), (81).

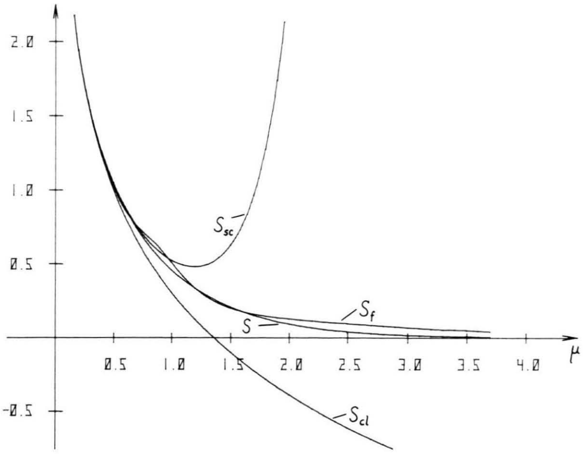

Fig. 5. Exact and approximate entropies of the linear harmonic oscillator in units of the Boltzmann constant k_B as functions of $\mu = \hbar\,\omega\,\beta/2$. S, S_{cl}, S_{sc}, and S_f are exact and in classical, semiclassical, and in the present approximations, respectively, see equations (54), (88), (92), and (30)–(32), (81).

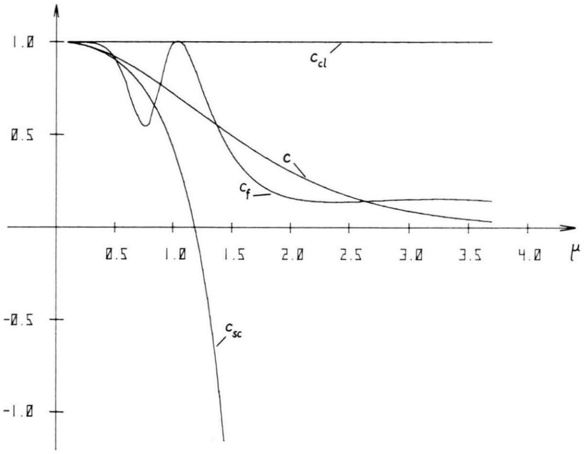

Fig. 6. Exact and approximate specific heats of the linear harmonic oscillator in units of k_B as functions of $\mu = \hbar\,\omega\,\beta/2$. c, c_{cl}, c_{sc}, and c_f are exact and in classical, semiclassical and in the present approximations, respectively, see (55), (89), (93), and (33), (81).

5. Summary and Discussion

The canonical density matrix $C(\boldsymbol{r}, \boldsymbol{r}_0, \beta)$ has been approximated by expression (17) where f is a variational function depending only on β, but not on $\boldsymbol{r}$, $\boldsymbol{r}_0$. Expression (17) becomes exact in the limits $\beta \to 0$ and $\beta \to \infty$ if (18a, b) are satisfied. The classical and the ground state density matrix are supposed to be known. The trial function f is chosen such that C_f satisfies the Bloch equation (6) as well as possible in the sense that the mean square error functional $J[\bar{C}]$, Eq. (13), which vanishes for the exact density matrix C, becomes a minimum. The Euler equation (37) associated with this variational problem has to be solved for the solution $f = f(\beta)$ subject to conditions (18a, b). From the resulting optimized density matrix C_f the partition function Z_f, see (27), (28), can be determined and hence thermodynamic quantities of interest, Eqs. (30)–(33), can be calculated.

In order to test the method, it has been applied to the very simple case of a one-dimensional particle moving in the harmonic oscillator potential so that the results of the present approach can be compared to the well-known, exact values. Figure 2 shows very good agreement between $\ln Z_f$ and the exact $\ln Z$ for all temperatures. The same is true for the free energy, see Figure 3.

Determination of the internal energy and of entropy requires the derivative $d \ln Z_f/\mathrm{d}\mu$, i.e. $\mathrm{d}f/\mathrm{d}\mu$, too. Since the derivatives of variational functions are more sensitive with respect to the choice of the ansatz, we find deviations from the exact values slightly larger as was the case for the free energy (Figures 4, 5). Finally, the specific heat shows considerable errors (Figure 6) since also $\mathrm{d}^2 f/\mathrm{d}\mu^2$ is involved. The integrand of the functional $\Phi(\bar{f})$, equation (26), depends on $\bar{f}$ and $\mathrm{d}\bar{f}/\mathrm{d}\beta$, but not on $\mathrm{d}^2\bar{f}/\mathrm{d}\beta^2$. So, Φ is directly sensitive to changes of $\bar{f}$ and its first derivative. Changes of the second derivative effect Φ only indirectly, in as much as they cause changes of $\bar{f}$ and $\mathrm{d}\bar{f}/\mathrm{d}\beta$ which may be relatively small, however. Thus it is expected that the second derivative of the minimizing f, and hence the specific heat will not yield satisfying results unless a modified variation principle is developed which includes $\mathrm{d}^2\bar{f}/\mathrm{d}\beta^2$, too.

Improvements should also be possible by more precise limiting density matrices and by an ansatz with greater flexibility. For instance, C_{cl} in the ansatz (17) could be replaced by some modified semiclassical density matrix which coincides with C_{sc}, Eq. (10), for high temperatures, but does not lead to negative values of its diagonal elements when the temperature decreases. As concerns the flexibility of the ansatz, it is tempting e.g. to use two independent variational functions f and g to be associated with the high- and with the low-temperature density matrices, respectively.

It is the advantage of the present approach that application to systems having more degrees of freedom will increase only the complexity of the integral $J[\bar{C}] = \int_0^\infty \mathrm{d}\beta \int w^2 \mathrm{d}\tau$, but does not lead to partial differential equations. Nevertheless, since J cannot be evaluated analytically, in general, numerical treatment is necessary which becomes more and more awkward with increasing number of dimensions of integration. Numerical work will be reduced, however, if a variational method can be set up which is based not on the whole density matrix, but only on its diagonal elements, since only these are needed for calculating the partition function. While the present approach demonstrated its basic validity, future work is intended to develop further improvements and refinements along these lines.

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