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A variational approach for the free energy

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Abstract. To calculate thermodynamic functions in statistical mechanics we propose a new variational approach which has as particular cases the approaches of Bogoliubov, Oguchi and Tsallis–da Silva, but introduces some improvements, mainly in the short-range order effects above the critical temperature. It requires a choice of a trial Hamiltonian that defines an approximate ensemble through which the thermodynamic functions may be calculated. To check the efficiency of our approach we apply it to the ferromagnetic Ising model by using the simplest possible trial Hamiltonian.

1. Introduction

Several variational approaches for the free energy have been proposed as attempts to improve results obtained through the well established Bogoliubov principle. This principle requires the use of a trial Hamiltonian depending on one or more variational parameters. The only way to improve the Bogoliubov principle by itself is to choose a more complete trial Hamiltonian, closing it to the exact one, but in almost all cases the possibilities are soon exhausted. The usual mean field approximation may be obtained using the above principle utilising a sum of single spins in an effective field (the variational parameter) as the trial Hamiltonian. Choices like a sum of linear chains and a sum of double linear chains have been made (Plascak and Silva 1982). Some authors have preferred to present alternative variational methods. Oguchi (1976) presented a bounded function whose minimum is considered as an approximate free energy. Oguchi's procedure has already been investigated (Faleiro Ferreira and Silva 1983b). Oguchi (1984) then amplified his ideas but Stolze (1985) has contested some of the results. Ferreira *et al* have (1977) employed the Bogoliubov principle, combining cluster division and series approximation. Tsallis and da Silva (1982) proposed what they called an extended variational method, obtained from a cumulant expansion, and studied two types of classical anharmonic single oscillators. This has already been used to calculate critical temperatures of the Ising ferromagnet (Faleiro Ferreira and Silva 1982).

We intend to propose a variational approach, more general than those above, and show how they can be seen as particular cases of a general approximate free energy. Also we show that such a variational approach presents thermodynamic consistency not present in other methods, except in the Bogoliubov treatment (Argyres *et al* 1974). Unlike the other methods (except for that of Bogoliubov) we can present an adequate

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ensemble to calculate thermal averages. One main failure of some variational approaches is that they modify the Bogoliubov free energy but still go on using the Bogoliubov ensemble to make calculations. In addition some improvements over results obtained through the Bogoliubov principle are presented. For example, none of them, including Bogoliubov, can show short-range order effects above the critical temperature when a sum of isolated spins is used as the trial Hamiltonian. However, our approximation can preserve such effects with the same trial Hamiltonian.

2. An upper bound to the exact free energy

Let A and B be positive, self-adjoint, trace class operators with a spectrum in the domain of definition of the convex function g; then by using Klein's inequality (Ruelle 1969) we have:

$$\mathrm{Tr}[g(A)-g(B)-(A-B)g'(B)]\geqslant 0. \tag{1}$$

The choice of $g(t)=t\ln t$ leads to

$$\mathrm{Tr}(A\ln A)-\mathrm{Tr}(A\ln B)\geqslant \mathrm{Tr}(A-B). \tag{2}$$

By setting $\mathrm{Tr}\, A=1$ and $B=\rho=\mathrm{e}^{-\beta H}/\mathrm{Tr}\,\mathrm{e}^{-\beta H}$, where $\beta=1/kT$, equation (2) becomes

$$F_A=\mathrm{Tr}\, A[H+kT\ln A]\geqslant \mathrm{Tr}\,\rho[H+kT\ln\rho]=F_{\mathrm{exact}}. \tag{3}$$

The RHS of inequality (3) is the exact free energy associated with H, the 'exact' Hamiltonian whose thermodynamic properties are looked for. A plays the role of a density matrix with the function F_A leading to an upper bound to the exact free energy; the equality holds for $A=\rho$. If one puts $A=f(\lambda)$, λ being one or more variational parameters to be determined, the minimum of F_A with respect to λ is to be considered as a good approximate free energy. A simple choice such as

$$A=\mathrm{e}^{-\beta H_0(\lambda)}\mathrm{Tr}\,\mathrm{e}^{-\beta H_0(\lambda)}=\rho_0$$

leads to the well known Bogoliubov inequality:

$$F_{\mathrm{Bog}}=\min[-kT\ln\mathrm{Tr}\,\mathrm{e}^{-\beta H_0}+\langle H-H_0\rangle\geqslant F_{\mathrm{exact}} \tag{4}$$

where $\langle\ldots\rangle=\mathrm{Tr}\,\rho_0\ldots$ and here H_0 is a trial Hamiltonian.

It is very useful to put $A=\rho_0 D$, where D is an arbitrary positive operator satisfying $[H_0, D]=0$ and $\langle D\rangle=1$. Returning to equation (3) we may rewrite it as

$$F_A=-kT\ln\mathrm{Tr}\,\mathrm{e}^{-\beta H_0}+\langle D(H-H_0)\rangle+kT\langle D\ln D\rangle. \tag{5}$$

To verify the thermodynamic consistency between statistical and thermodynamic calculation we may think of an operator X, i.e.

$$X=-(\partial H/\partial x) \tag{6}$$

from the statistical mechanics point of view. For instance, having in mind the Ising model, if x is the external field we may obtain the magnetisation as

$$m=-(\partial F_A/\partial h)_\beta \tag{7}$$

from the thermodynamic point of view and obtain it through

$$m'=\mathrm{Tr}\, A\sigma \qquad \text{with} \qquad \sigma=-(\partial H/\partial h) \tag{8}$$

from the statistical mechanics one. In the exact treatment $m = m'$, of course. However, if we use an effective temperature-dependent trial Hamiltonian, the equality is not trivial. Similarly, if x is an exchange constant, the correlation between nearest neighbours ε may be calculated as

$$\varepsilon = \operatorname{Tr} A\sigma\sigma'$$

where

$$\sigma\sigma' = -(\partial H/\partial J)$$

or

$$\varepsilon = -(\partial F_A/\partial J)_\beta.$$

Firstly we recall that the stationarity condition of the LHS of equation (3):

$$(\partial F_A/\partial\lambda)_\beta = \operatorname{Tr}\{(\partial A/\partial\lambda)_\beta H + kT[\partial(A\ln A)/\partial\lambda]_\beta\} = 0 \tag{9}$$

leads to a solution $\lambda = \lambda(f(\lambda, x), \lambda)$ that may be an explicit and/or implicit function of x. From (3) we can write

$$(\partial F_A/\partial x)_\beta = \operatorname{Tr} A(\partial H/\partial x)_\beta + \operatorname{Tr}\{(\partial A/\partial\lambda)_\beta H + kT[\partial(A\ln A)/\partial\lambda]_\beta\}(\partial\lambda/\partial x)_\beta$$

which together with equation (9) shows the desired consistency.

Therefore the $\min(F_A)$ may be considered a good approximate free energy that preserves the thermodynamic consistency and is related to an ensemble that allows the appropriate calculations of the thermodynamic functions. They are to be evaluated as modified averages in a simpler ensemble:

$$\langle\ldots\rangle_A = \operatorname{Tr} A\ldots = \operatorname{Tr}\rho_0 D\ldots = \langle D\ldots\rangle. \tag{10}$$

Now in order to make a particular approximation we have to make a choice for D. If we choose $D=1$ in equation (5) we get the Bogoliubov inequality and with a choice as

$$D = e^{-\beta(H-H_0)}/\langle e^{-\beta(H-H_0)}\rangle \tag{11}$$

considering $[H, H_0] = 0$, we have

$$F_A = -kT\ln\operatorname{Tr} e^{-\beta H} \equiv F_{\text{exact}}.$$

Therefore, we have to find a choice which is better than $D=1$ but which is easily treatable.

3. Oguchi's procedure

If we consider $V = H - H_0$ as a sum of m divisions, each containing n sites, we may write $V = \Sigma V_i$ and we choose D as a product of D_i, where

$$D_i = e^{-\beta V_i}/\langle e^{-\beta V_i}\rangle. \tag{12}$$

If we make the following approximation:

$$\langle D_i D_{i'}\rangle \simeq \langle D_i\rangle\langle D_{i'}\rangle \qquad \text{for} \qquad i \neq i'$$

we can satisfy $\langle D\rangle = 1$.

Bringing (12) into (5) we have:

$$F_A = -kT\ln\operatorname{Tr} e^{-\beta H_0} - kT\sum_i \ln\langle e^{-\beta V_i}\rangle \tag{13}$$

which is the expression proposed by Oguchi (1976). But now, for example, the correct approximate magnetisation must be calculated as

$$m = \mathrm{Tr}\, A\sigma = \mathrm{Tr}\, A\rho_0 D\sigma = \langle D\sigma \rangle \tag{14}$$

and not simply as $m = \langle \sigma \rangle$. A similar correction should be done on the correlation

$$\varepsilon = \mathrm{Tr}\, A\sigma\sigma' = \langle \sigma\sigma' \rangle_A = \langle D\sigma\sigma' \rangle. \tag{15}$$

To make it clear, we make an application to a two-dimensional Ising model defined by

$$H = -J_1 \sum \sigma_{ij}\sigma_{i+1j} - J_2 \sum \sigma_{ij}\sigma_{ij+1} \tag{16}$$

where $\sigma = \pm 1$ is the spin variable on the ij site and J_1, J_2 are the exchange constants between nearest neighbours along the two lattice directions.

We use a trial Hamiltonian as a sum of isolated spins in an effective field h_0 that is the variational parameter:

$$H_0 = -h_0 \sum \sigma_{ij}. \tag{17}$$

Several divisions of V have already been made (Oguchi 1976, Faleiro Ferreira and Silva 1983a). The main novelty is the calculation of the correlation between nearest neighbours in accordance with (15) above the critical temperature T_c:

$$\langle \sigma_1 \sigma_1' \rangle_A = \frac{\frac{1}{2} \sinh 2\beta J_1 \cosh 2\beta J_2}{\cosh^2 \beta J_1 \cosh^2 \beta J_2 + \sinh^2 \beta J_1 \sinh^2 \beta J_2} \qquad \text{for } T \geqslant T_c \tag{18}$$

and similarly, for the correlation $\langle \sigma_2 \sigma_2' \rangle_A$ along the J_2 direction, we should exchange J_1 and J_2.

The result in (18) is non-vanishing, unlike the one Oguchi's procedure would lead to. Some numerical results are presented in § 6.

4. Extended variational method

If we choose

$$D = 1 - \beta(V - \langle V \rangle) \tag{19}$$

with $V = H - H_0$, we satisfy $\langle D \rangle = 1$. However that particular approximation is not suitable for low temperatures which may violate the positive-definite and normed condition. With equations (5) and (19) we may write:

$$F_A = -kT \ln \mathrm{Tr}\, e^{-\beta H_0} + \langle V \rangle - \beta(\langle V^2 \rangle - \langle V \rangle^2) + kT \langle D \ln D \rangle.$$

If we replace the last term by a second-order term approximation (the first one vanishes)

$$\langle D \ln D \rangle \simeq \tfrac{1}{2}\beta^2(\langle V^2 \rangle - \langle V \rangle^2)$$

we obtain

$$F_A = -kT \ln \mathrm{Tr}\, e^{-\beta H_0} + \langle V \rangle - \tfrac{1}{2}\beta(\langle V^2 \rangle - \langle V \rangle^2). \tag{20}$$

That is the expression proposed by Tsallis and da Silva (1982) but they did not modify the H_0 ensemble. We have already used the above expression in a previous paper (Faleiro Ferreira and Silva 1982). Using those calculations with the same choice of equations (13) and (14), we may write for $T \geqslant T_c$:

$$\langle \sigma_1 \sigma_1' \rangle_A = J_1 / kT \tag{21a}$$

along the J_1 direction and

$$\langle \sigma_2 \sigma_2' \rangle_A = J_2/kT \tag{21b}$$

along the J_2 direction. Again we show the numerical results in § 6 in order to make comparisons.

5. Two other approximations

5.1.

In a previous paper (Faleiro Ferreira and Silva 1983a) we have made the following approximation in the last term of equation (20):

$$\langle D \ln D \rangle \simeq 0. \tag{22}$$

Without repeating all of the calculation we may write, for $T \geq T_c$:

$$\langle \sigma_1 \sigma_1' \rangle_A = J_1/kT \tag{23a}$$

and

$$\langle \sigma_2 \sigma_2' \rangle_A = J_2/kT. \tag{23b}$$

5.2.

We now show another choice for D, taken from several possibilities, that D corresponds to (11), at least in first order:

$$D = (kT - V)/(kT - \langle V \rangle) \qquad V = H - H_0 \tag{24}$$

and, with the same approximation made in (22), we have from (20)

$$F_A = -kT \ln \operatorname{Tr} e^{-\beta H_0} + \langle V \rangle - (\langle V^2 \rangle - \langle V \rangle^2)/(kT - \langle V \rangle). \tag{25}$$

Again, with the same Hamiltonians (16) and (17), we may partially use previous calculations (Faleiro Ferreira and Silva 1983a) and find a stationarity condition $(\partial F_A/\partial h_0)_\beta = 0$ which is a self-consistent equation in h_0. In the limit $h_0 \to 0$ we have an equation for the critical temperature kT_c:

$$(kT_c)^3 - 6c(kT_c)^2 + (2a + 16b)kT_c + 2ac = 0 \tag{26}$$

where

$$a = J_1^2 + J_2^2 \qquad b = J_1 J_2 \qquad c = J_1 + J_2.$$

The correlation between nearest neighbours along a direction of the lattice above kT_c is given by:

$$\langle \sigma_1 \sigma_1' \rangle_A = J_1/kT \qquad \text{for } T \geq T_c \tag{27a}$$

and

$$\langle \sigma_2 \sigma_2' \rangle_A = J_2/kT \qquad \text{for } T \geq T_c. \tag{27b}$$

Numerical results are presented in table 1.

Table 1. Some numerical results for a two-dimensional isotropic ($J_1 = J_2$) Ising lattice.

Method	Critical temperature kT_c	Critical correlation
Bogoliubov	4.00	0.00
Oguchi (1976)	2.77	0.00
Faleiro Ferreira and Silva (1982)	3.00	0.00
§ 3	2.77	0.38
§ 4	3.00	0.33
§ 5.1	2.54	0.39
§ 5.2	2.43	0.41
Exact	2.269	0.707

6. Results and conclusions

We have presented a set of approximations that may not only consistently improve results obtained from the Bogoliubov inequality but also add an important correction to the current variational approaches. In addition, a large range of new approximations may be made with varied choices of D. We show in table 1 some numerical results for a two-dimensional isotropic ($J_1 = J_2$) Ising lattice which point out the improvements brought out by the present work. A more complete trial Hamiltonian is under investigation and will be published soon.

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