By concrete examples it is shown that a variational approximation to the partition function (VPF) may have singularities of the phase transition types. Sufficient conditions for the existence of such singularities are given. One of these conditions is the presence of a continuous part in the spectrum of the underlying Hamiltonian.

1. Introduction

It was shown [1] that a generalized version of the Lippmann—Schwinger variational principle can be used to calculate (approximately) the partition function of statistical mechanics:

\[ \mathcal{Z}(P) = Tr \{ e^{-\beta (H + PK)} \}, \quad \beta = (k_B T)^{-1}. \]  

(1)

\( H \) and \( K \) are the unperturbed and the perturbed parts of a Hamiltonian of a proper physical system, respectively, and \( P \) is a variable scalar parameter. \( k_B \) and \( T \) are, as usual, Boltzmann's constant and the absolute temperature. 

In this paper we discuss the singularities of the variational approximation to the partition function (called variational partition function, VPF). In order to do this we choose special model Hamiltonians \( H \) and \( K \) which are assumed to be given in the spectral representation. Furthermore, it is assumed that these Hamiltonians possess a discrete and a continuous spectrum. The presence of the continuous spectrum (typically for the Hamiltonian of a large system) is the essential supposition of this paper. We show then that there is, under some other conditions, a way to derive a VPF which itself is finite and well behaved but which possesses discontinuous derivatives with respect to \( P \) of a certain order (at fixed \( T \)). This order depends on the properties of the given physical system (e.g. the density of states per energy interval).

First the general theory is reviewed. Then, after a little specialization which makes the procedure tractable, we present the examples.
2. The general theory

Defining the average

$$\langle \ldots \rangle_0 = \frac{1}{\mathcal{Z}(0)} \text{Tr} \{ \ldots e^{-\beta H} \},$$  \hspace{1cm} (2)

one can calculate the partition function in the form [2]

$$\mathcal{Z}(P) = \mathcal{Z}(0) \langle U(\beta, 0) \rangle_0,$$  \hspace{1cm} (3)

where

$$U(\tau, \tau_1) = 1 - P \int_{\tau_1}^{\tau} d\tau' K(\tau') U(\tau', \tau_1)$$  \hspace{1cm} (4)

and write down the operator valued Lippmann–Schwinger functional [4]

$$F(V^*, V; \tau_2, \tau_1) = 1 - P \int_{\tau_1}^{\tau_2} d\tau [V^*(\tau, \tau_2)_K(\tau) + K(\tau)V(\tau, \tau_1)] +$$

$$+ P \int_{\tau_1}^{\tau} d\tau V^*(\tau, \tau_2)_K(\tau) V(\tau, \tau_1) + P^2 \int_{\tau_1}^{\tau} d\tau' \int_{\tau_1}^{\tau} d\tau'' V^*(\tau, \tau_2)_K(\tau).$$  \hspace{1cm} (7)

As shown in [1, 4] the following basic theorem is valid:

**Theorem:** The values of the operators $V$ and $V^*$ for which the functional is stationary, with respect to variations $\delta V$ and $\delta V^*$, are the evolution operators of the Hamiltonian $PK$. Furthermore, the stationary value of the functional itself reduces to the evolution operator for the interval $\tau_1$ to $\tau_2$.

With the help of the integral equation (4) one can generate the operators

$$U_{n+1}(\tau, \tau_1) = - P \int_{\tau_1}^{\tau} d\tau' K(\tau') U_n(\tau', \tau_1), \quad n \geq 0$$  \hspace{1cm} (9a)

$$U^*_{n+1}(\tau, \tau_2) = P \int_{\tau}^{\tau_2} d\tau' U^*_n(\tau', \tau_2) K(\tau') \quad n \geq 0,$$  \hspace{1cm} (9b)

with

$$U_0(\tau, \tau_1) = 1.$$  \hspace{1cm} (9c)