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On the Zero Fluctuation of the "Microscopic Free Energy" and Its Potential Use

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The fluctuations of the "microscopic free energy" calculated with the ensemble probability are shown to be zero. We suggest that this result be used for estimating approximate free energies calculated on the basis of the minimum free energy principle. As an example the estimation is performed with respect to a certain computer simulation of the square Ising lattice. The zero fluctuations also can be used to obtain relations among fluctuations with the accurate ensemble probability distribution.

KEY WORDS: Minimum free energy principle; fluctuations; computer simulation; Ising lattice.

We consider a system in equilibrium which can be described by the canonical distribution, e.g., the probability P_i of the ith configuration is given by

$$P_i = Z^{-1} \exp(-E_i/kT) \tag{1}$$

where E_i is its microscopic energy, Z is the partition function, k is the Boltzmann constant, and T is the absolute temperature.

The Helmholtz free energy F is

$$F = \sum_{\substack{i \\ \text{all configurations}}} P_i(E_i + kT \log P_i) \tag{2}$$

Here F is expressed as the statistical average of the "microscopic free energy" F_i:

$$F_i = E_i + kT \log P_i \tag{3}$$

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By substituting Eq. (1) into (3) we obtain for all i

$$F_i = E_i + kT[-(E_i/kT) - \log Z] = -kT\log Z \tag{4}$$

Therefore F_i is a constant function defined on phase space,

$$F_i = F \tag{5}$$

which means that *F has zero fluctuations:*

$$\langle \Delta F^2 \rangle = 0 \tag{6}$$

where $\langle \Delta F^2 \rangle$ stands for the variance of F. By a similar treatment the same result is obtained for the corresponding free energies in the other ensembles and for the entropy in the microcanonical ensemble. This property of zero fluctuations appears to be ignored by most textbooks of statistical mechanics.[(1,2),2] We point it out here not only in view of its theoretical interest but also because certain applications can be derived from it, as described in what follows. In this context let us recall the well-known minimum free energy principle,[(2,3)] which states that the free energy functional $F(\mathbf{P}')$,

$$F(\mathbf{P}') = \sum_i P_i'(E_i + kT\log P_i') \tag{7}$$

is never smaller than the true F, defined with the Boltzmann distribution [Eq. (1)]. In Eq. (7), $\mathbf{P}'$ is any probability distribution (PD) defined on phase space. For such $\mathbf{P}'$, $\langle \Delta F^2(\mathbf{P}') \rangle$ and $\langle \Delta E^2(\mathbf{P}') \rangle$ denote the free energy and energy fluctuations, respectively. Many approximate methods in statistical mechanics are based on the minimum value principle, trying to minimize $F(\mathbf{P}')$, with respect to $\mathbf{P}'$, under restrictions imposed by the approximations. The various thermodynamic quantities can be calculated in such a manner, but their accuracy cannot be estimated. For that purpose we suggest to use the property of zero fluctuation in F. First, however, we have to stress that the equation $\langle \Delta F^2(\mathbf{P}') \rangle = 0$ provides a sufficient condition for determining the exact equilibrium distribution, i.e., Boltzmann's distribution, but only for $\mathbf{P}'$ that do not exclude part of phase space. [Any PD that excludes part of phase space and preserves the condition $P_i' \sim \exp(-E_i/kT)$ for the rest of the space will likewise give $\langle \Delta F^2(\mathbf{P}') \rangle = 0$.] For that reason one can envisage PDs that effectively exclude part of phase space while giving almost constant probability to the rest of it, with the result that $\langle \Delta F^2(\mathbf{P}') \rangle$ is very small, although $F(\mathbf{P}')$ is far from true! In that case, however, $\langle \Delta E^2(\mathbf{P}') \rangle$ will also be small. The above indicates that caution is needed in the use of $\langle \Delta F^2(\mathbf{P}') \rangle = 0$. For our purposes, we need a quantity having strong positive correlation with $F(\mathbf{P}')$. Therefore, a reasonable choice seems to be the ratio

$$\Delta = \langle \Delta^2 F(\mathbf{P}') \rangle / \langle \Delta^2 E(\mathbf{P}') \rangle \tag{8}$$

[2] In Ref. 1, Tolman calculates the free energy fluctuations with the Gaussian approximation and obtains $\langle \Delta F^2 \rangle = (kT/2)^2$, which practically means it is zero. In Ref. 2, Gibbs derives Eq. (4), but without relating it to fluctuations.

rather than $\langle \Delta^2 F(\mathbf{P}') \rangle$ alone. Using Eq. (8), we shall estimate the accuracy of a value of the free energy calculated with the help or a particular method. In principle, such an estimation can be extended to other approximate methods as well.

The particular approximate method has been described previously[4] and here it will be applied to the square Ising lattice consisting of $L \times L$ spins. The method strives to sample the equilibrium lattice configurations for a given temperature T. Sampling of the lattice configurations is carried out by a stochastic construction procedure: One begins with an empty lattice (only the first row has spins). The spins' orientation is fixed step by step by a Monte Carlo lottery, according to a set of parametrized transition probabilities that depend on the orientation of the last L spins. After performing this construction, one knows the microscopic energy of the configuration E_i and its probability P_i, which is the product of L^2 transition probabilities of the construction. Thus the procedure defines a probability distribution $\mathbf{P}(\mathbf{x})$ of all configurations for a particular choice of a set of parameters $\mathbf{x}$. We sample many configurations with $\mathbf{P}(\mathbf{x})$ computing the average value of the corresponding free energy functional $F(\mathbf{x})$ [see Eq. (7)]:

$$F(\mathbf{x}) = \sum P_i(\mathbf{x})[E_i + kT \log P_i(\mathbf{x})] \tag{9}$$

We seek the optimal set of parameters ($\mathbf{x}^*$) giving the minimum value for the related free energy $F(\mathbf{x}^*)$; for these "best" values we compute the average energy and other average lattice quantities of interest.

To estimate the accuracy in $F(\mathbf{x}^*)$, we choose sets of parameters $\mathbf{x}$ different from the optimal $\mathbf{x}^*$ and calculate the related averages and fluctuations; these are plotted as $F(\mathbf{x})$ vs. Δ in Fig. 1. Each type of symbol in the figure represents the variation of one parameter, e.g., a short-range or a long-range parameter (for details see elsewhere[5]) while the rest of the set $\mathbf{x}^*$ is kept constant. The plots show a strong correlation between $F(\mathbf{x})$ and Δ, which can be represented by a smooth line describing the variation of the various parameters. We are interested, of course, in the intersection of the line with the F axis, which should give the accurate F. In order to estimate this point, we have to assume that the behavior of the curve remains unchanged as $\Delta \to 0$, i.e., it describes a monotonic decreasing concave function. With these assumptions, one can plot the tangent to the curve at its lowest point; the accurate free energy can be only larger than or equal to the intersection of this tangent with the F axis.

In Fig. 1 the quantities have been calculated for the Ising reciprocal temperature $J/kT = 0.45$. The tangent intersects the free energy axis at the value 0.9437. The best value $F(\mathbf{x}^*)$ for this temperature is 0.94325. The conclusion is that the first three digits in $F(\mathbf{x}^*)$ are certainly accurate. For comparison, the accurate free energy is 0.94336.[6]

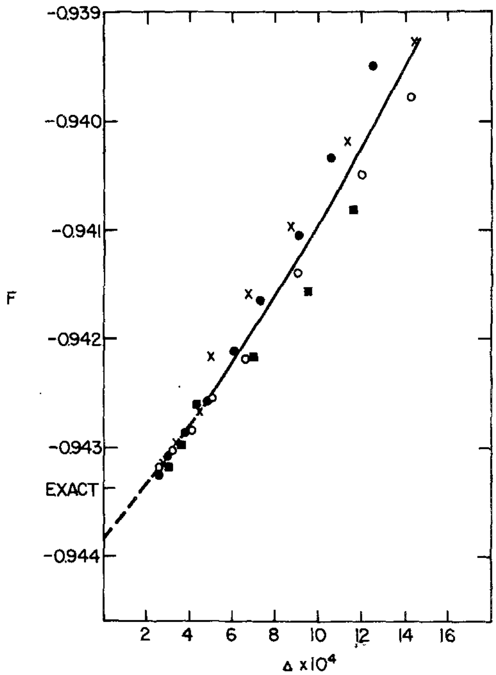

Fig. 1. A plot of $\Delta = \langle \Delta F^2 \rangle / \langle \Delta E^2 \rangle$ vs. F/NkT for reciprocal Ising temperature $K = 0.45$. (●) The short-range parameter is decreased from its optimal value. (×) The same parameter is increased from its optimal value. (■) The long-range order parameter is decreased. (○) All parameters are decreased from their optimal values. The dashed line is the tangent at the lowest point of the best fit curve.

Another aspect worth mentioning is the following: Relations between fluctuations in the various thermodynamic quantities can be obtained with the Gaussian approximation[1,7] and in an accurate way,[8] using the Boltzmann distribution, which is often tedious. The property of zero fluctuations in F enables one to derive easily such relations in an accurate way. As an example, we shall calculate the fluctuations $\langle \Delta S^2 \rangle$ in entropy.

$$\langle \Delta F^2 \rangle = \langle [E - TS - (\langle E \rangle - T\langle S \rangle)]^2 \rangle = \langle \Delta E^2 \rangle + T^2 \langle \Delta S^2 \rangle - 2T(\langle ES \rangle - \langle E \rangle \langle S \rangle) \quad (10)$$

The averages in the last term of (10) can be computed directly with the help of Eq. (1) for P_i, where entropy is $-k\langle \log P \rangle$; this gives

$$\langle \Delta F^2 \rangle = T^2 \langle \Delta S^2 \rangle - \langle \Delta E^2 \rangle \quad (11)$$

Since $\langle \Delta F^2 \rangle = 0$ we obtain

$$T^2 \langle \Delta S^2 \rangle = \langle \Delta E^2 \rangle \quad (12)$$

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