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Local-states method for the calculation of free energies in Monte Carlo simulations of lattice models

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We present and demonstrate an accurate, reliable, and computationally cheap method for the calculation of free energies in Monte Carlo simulations of lattice models. Even in the critical region it yields good results with comparatively short simulation runs. The method combines upper and lower bounds on the thermodynamic limit entropy density to yield not only an accurate estimate of the free energy but a bound on the possible error as well. The method is demonstrated on the two- and three-dimensional Ising models and the three-dimensional, three-states Potts model.

Monte Carlo (MC) simulations have been used for many years in the investigation of the thermodynamic properties of lattice models. The commonly used importance sampling methods readily yield information on quantities that are thermal averages of observables that can be measured at each step of the simulation run, but they do not yield an estimate for the partition function Z. Thus, whereas order parameters, internal energy U, and the like, are easily calculated, neither the free energy $F=-k_BT\ln Z$ nor the entropy $S=(U-F)/T$ are obtained directly.

Because of the importance of the free energy in the construction of phase diagrams, considerable effort has been devoted to devising methods for its calculation with MC methods. We refer the reader to the review article by Binder.[1]

We present a method for the calculation of the free energies in importance sampling MC simulations of lattice models that combines two conceptually different, but computationally similar, techniques for entropy estimation in one algorithm. The entropy estimates are based on a cumulant expansion taken from the cluster-variation method[2] (CVM) and on a recently proven global Markov property.[3]

The method is easy to implement and is computationally cheap. The free energy under a specified set of conditions is obtained from data of one simulation under those conditions, in contrast to the multiple simulations that are required for other methods (thermodynamic integration,[4] multistage sampling,[5] and related methods[6]). It can be implemented as an integral part of a standard Metropolis MC algorithm, and it can even be used to monitor the free energy during the course of the simulation. In this respect our method differs completely from techniques based on evaluation of transfer matrix eigenvalues, which can be very accurate, but require a completely separate and time-consuming calculation.[7] The method can be used on large lattices and it yields accurate results with comparatively short simulation runs, even in the critical region. It is applicable to lattice models with a finite number N of discrete degrees of freedom and translation-invariant interactions.

It can be shown rigorously that the Markovian entropy estimates, i.e., the ones based on the Markov property mentioned above, correspond to a converging net of upper bounds on the thermodynamic limit entropy density (i.e., entropy per lattice point).[3] The entropy formulas that were derived in the CVM are either proven or conjectured to be lower bounds.[8] By combining such upper and lower bounds in one algorithm we obtain not only a very accurate estimate of the free energy but a reliable indication of the possible error as well.

We classify our method as a local states method, since it uses measurements of local observables to estimate a global quantity (the thermodynamic entropy density), and to acknowledge its kinship to the approach of Meirovitch,[9] who has previously considered our Markovian estimates but based them on more heuristic arguments.

We demonstrate the reliability and accuracy of our method by comparison with exact results for the two-dimensional Ising model. In this case we use a CVM expression for the entropy density that is a proven lower bound. For the three-dimensional Ising model the CVM entropy formula is only conjectured to be a lower bound; we present numerical results that lend support to this conjecture. To illustrate that the usefulness of the method is not limited to simple Ising models we also present some results on the free-energy density of the three-dimensional, three-states Potts model.

Applications to the anisotropic next-nearest-neighbor Ising model and to Widom's microemulsion model[10] are currently in progress.

The method starts from the statistical definition of the entropy S_L of a lattice L,

$$S_L=-k_B\sum_{\omega_L}p(\omega_L)\ln p(\omega_L)\,, \tag{1}$$

where $p(\omega_L)$ denotes the probability of finding the configuration ω_L on the lattice L. The quantity of thermodynamic interest is the thermodynamic limit s of

$|L|^{-1}S_L$, where $|L|$ denotes the number of lattice sites of L. The problem in simulation practice is that Eq. (1) can be used only to find S_L if each configuration ω_L is encountered sufficiently often to determine $p(\omega_L)$ accurately. This will be the case only if the total number of configurations $N^{|L|}$ (N being the number of degrees of freedom per lattice site) is fairly small, hence if the lattice L is small. But for a small lattice, $|L|^{-1}S_L$ is not a good estimate of the thermodynamic entropy density s.

To overcome this problem, we calculate entropy values S_X for a few small sublattices X (henceforth called clusters) embedded in the large lattice L on which the simulation is performed, and we estimate s from these cluster entropies by means of an extrapolation to the limit.

The extrapolation technique is an adaptation of the cluster variation method,[2] which is an analytical method for studying lattice models; it is based on the following result for s.[11] If the thermodynamic system is invariant under some group H of translations, then

$$s=\frac{1}{p}\sum_X^{*}(-1)^{|X|}\sum_{Y\subset X}(-1)^{|Y|}S_Y . \tag{2}$$

Here $\sum^{*}$ denotes a summation over all nonequivalent clusters, equivalence being defined with respect to H; i.e., two clusters are equivalent if a translation of H maps one onto the other; p is the number of nonequivalent lattice sites.

This result can be used to generate estimates of s as linear combinations of cluster entropies, by judiciously truncating the sum $\sum^{*}$ over X.

As an explicit illustration, consider the ferromagnetic Ising model on the square lattice. There is invariance under all lattice translations, hence $p=1$. If we keep in Eq. (2) only terms corresponding to clusters X that are a subset of a $n\times m$ rectangular set $R(n,m)$ of lattice points, then s is estimated according to

$$s=S_{R(n,m)}-S_{R(n,m-1)}-S_{R(n-1,m)}+S_{R(n-1,m-1)} . \tag{3}$$

This procedure for generating extrapolation formulas can be considered as the basis of the analytic techniques of the CVM, including the mean-field and quasichemical methods (although this is not the traditional point of view).[12] This means that for most situations a judicious choice (see above) of extrapolation formulas can be made simply by consulting the extensive CVM literature.

To establish the degree of reliability of the result obtained by the procedure described above, our method supplements the CVM estimate with a Markovian estimate. This is easily done within a single algorithm, since the Markovian estimates, though based on an altogether different reasoning, are also linear combinations of cluster entropies. Specifically, s is estimated as a conditional entropy, namely a difference of two cluster entropies $S_Z-S_{Z'}$, with Z having one lattice site more than Z'. The cluster Z is chosen as part of an infinite, stepped, $(d-1)$-dimensional dividing surface in the d-dimensional lattice (see Figs. 1 and 2 for examples). This choice may be understood intuitively by considering the lattice with spiraling boundary conditions: The sites of Z are chosen from the ones that contribute to the corresponding winding-to-site transfer matrix.

Combining the two independent estimates for s, we obtain more than just a check on the result, since, as we mentioned earlier, the Markovian estimate corresponds to an upper bound on s, whereas the formulas that are used in the CVM are typically lower bounds. We use the average of the two values as the best estimate; half their difference bounds the intrinsic error.

The free-energy density f is calculated from the energy per lattice site u and the estimated entropy density s, $f=u-Ts$. The variational principle, which states that the difference $u-Ts$ is a minimum for a situation of thermodynamic equilibrium, makes its value insensitive to statistical fluctuations. We observe that the entropy bounds fluctuate in tandem and that the above-mentioned insensitivity also holds for our free-energy estimate. As a consequence, good results for f are obtained from relatively short simulation runs, even in the critical region.

This also means that it is possible to monitor the free energy in the course of a long simulation, by applying the technique to successive subsets of, e.g., 1000 lattice configurations. This enables one to study the equilibration process or fluctuations between metastable and stable states.

A more extensive discussion of the theoretical aspects of the method, focusing on application to two-dimensional models, is given elsewhere.[13] To demonstrate the method, we applied it in MC simulations of the two- and three-dimensional Ising models and the three-dimensional, three-states Potts model.

For the two-dimensional Ising model we used the CVM formula Eq. (3) with $n=4$, $m=2$ in combination with the Markovian estimate[3,4,13] $s=S_H-S_{H'}$, with the clusters H and H' as depicted in Fig. 1. Simulations were performed on a 64×64 lattice, at various reduced temperatures, using the standard Metropolis algorithm. The cluster entropies were calculated from an analysis of 10000 lattice configurations by counting the occurrences of the various

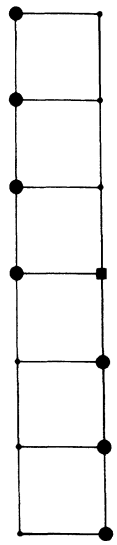

FIG. 1. The clusters H and H'. ● and ■: sites of the cluster H; ●: sites of the cluster H'.

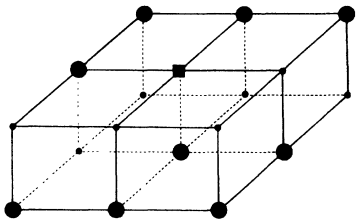

FIG. 2. The clusters D and D'. ● and ■: sites of the cluster D; ●: sites of the cluster D'.

cluster configurations ω to arrive at an estimate of the cluster configuration probabilities $p(\omega)$.

Table I compares the resulting estimates of the free-energy density with the results from Onsager's analytical expression. The agreement is seen to be excellent. The exact value for $-f/k_BT$ occasionally exceeds the sum of the estimated value and the estimated error bound; this is a consequence of the finite size of the simulation lattice and the finite duration of the simulation.

For the three-dimensional models the analog of the CVM formula Eq. (3) is

$$s = S(n,m,k) - S(n,m,k-1) - S(n,m-1,k) + S(n,m-1,k-1) - S(n-1,m,k) + S(n-1,m,k-1) + S(n-1,m-1,k) - S(n-1,m-1,k-1) . \quad (4)$$

Here $S(n,m,k)$ stands for the entropy of an $n \times m \times k$ block of lattice sites. For the Ising model Eq. (4) was used with $n=4$, $m=2$, $k=2$ and for the Potts model with $n=3$, $m=2$, $k=2$. For both models is was combined with the Markovian estimate $s = S_D - S_{D'}$, with clusters D and D' as depicted in Fig. 2. The simulations were performed on an $30 \times 30 \times 30$ lattice and in each run at least 10000 configurations were analyzed for the determination of the cluster entropies.

The results for the Ising model are given in Table II and compared with other results, compiled by Meirovitch and believed to be of high accuracy.[14] At and above T_c these data clearly support the conjecture that the CVM estimate is a lower bound on s. Below T_c the situation is unresolved, especially since in this temperature regime the results we use for comparison are known to overestimate the free-energy density f. In any case the CVM estimate is very accurate. The accuracy of our Markovian estimate is in line with the related results reported by Meirovitch.[14] The results for the three-states Potts model are given in Table III.

The simulations were done on Cray 1S-2300 and Cray X-MP EA/164 computers. In practice, the accuracy that can be achieved with our method is more likely to be

TABLE I. Free-energy density f of the two-dimensional Ising model. T_c is the critical temperature of the infinite lattice. The exact value f_{exact} is also for the infinite lattice. f_{lsm} is the result of our local states method from simulations on a 64×64 lattice. The statistical error in the last decimal is given in parentheses. Δf_{lsm} is the estimated bound on the intrinsic (systematic) error of our result.

Temperature T/T_c	Free energy $-f_{\text{exact}}/k_BT$	Free energy $-f_{lsm}/k_BT$	Error bound $\Delta f_{lsm}/k_BT$
0.50	1.763668	1.763668(1)	0.000001
0.60	1.472101	1.472100(1)	0.000001
0.70	1.266895	1.266894(1)	0.000001
0.80	1.117583	1.117581(1)	0.000001
0.90	1.007893	1.007894(1)	0.000010
1.00	0.929695	0.9295(1)	0.0014
1.10	0.880055	0.88013(1)	0.00030
1.50	0.786246	0.786247(1)	0.000005
2.00	0.743755	0.743753(1)	0.000001
3.00	0.715121	0.715118(1)	0.000001
4.00	0.705409	0.705406(1)	0.000001

TABLE II. Free-energy density f of the three-dimensional Ising model. T_c is given by $J/k_BT_c = 0.22169$ with J the coupling constant. f_{SM} and f_{ser} have been taken from Ref. 12. f_{SM} was obtained with the stochastic model simulation method (see Ref. 15), f_{ser} was obtained by a thermodynamic integration over C/T where C is a series expansion estimate of the specific heat. The lower of the two (i.e., higher value for $-f/k_BT$) is believed to be the more accurate. Our result is denoted f_{lsm} and is obtained from simulations on a $30 \times 30 \times 30$ lattice. The statistical error in the last decimal is given in parentheses. Δf_{lsm} is the estimated bound on the intrinsic (systematic) error of our result.

Temperature T/T_c	Free energy $-f_{\text{SM}}/k_BT$	Free energy $-f_{\text{ser}}/k_BT$	Free energy $-f_{lsm}/k_BT$	Error bound $-\Delta f_{lsm}/k_BT$
0.94336	0.79522	0.79520	0.79537(1)	0.00012
0.96387	0.78788	0.78782	0.78808(2)	0.00020
0.98093	0.78261	0.78248	0.78295(2)	0.00032
1.00000	0.77777	0.77787	0.77855(7)	0.00140
1.02161	0.77334	0.77349	0.77388(2)	0.00063
1.04080	0.76982	0.76994	0.77024(2)	0.00047
1.05567	0.76728	0.76739	0.76762(2)	0.00041

TABLE III. Free-energy density f of the three-dimensional three-states ferromagnetic Potts model. J is the coupling constant. f_{lsm} is the result of our method and is obtained from simulations on a $30\times30\times30$ lattice. The statistical error of the last decimal is given in parentheses. Δf_{lsm} is the estimated bound on the intrinsic (systematic) error of our result.

Temperature J/k_BT	Free energy $-f_{lsm}/k_BT$	Error bound $-\Delta f_{lsm}/k_BT$
0.558	1.7836(2)	0.0011
0.556	1.7797(2)	0.0012
0.554	1.7759(2)	0.0013
0.552	1.7724(2)	0.0017
0.550	1.7692(2)	0.0023
0.548	1.7660(2)	0.0020
0.542	1.7565(2)	0.0017
0.536	1.7472(2)	0.0015
0.530	1.7381(2)	0.0014

determined by the available memory than by computing speed. In theory the accuracy of our method can be improved without limit, but to do so one must use larger clusters, which means keeping track of more cluster configurations. It proves, however, that surprisingly small clusters already give very good results, which indicates that the extrapolation techniques for estimating the entropy density are sufficiently powerful.

In summary, we have presented and demonstrated a new method for the determination of free energies in Monte Carlo simulations of lattice models with translational invariance. The method uses data from only one run, is easily implemented into any standard Monte Carlo computer code and yields surprisingly accurate results with comparatively little computational effort in all test cases. Its most important feature, however, is that it combines two different and complementary approaches to entropy estimation in one algorithm, and so enables an assessment of the reliability of the result.

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