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A Partition Function Approximation Using Elementary Symmetric Functions

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Abstract

In statistical mechanics, the canonical partition function Z can be used to compute equilibrium properties of a physical system. Calculating Z however, is in general computationally intractable, since the computation scales exponentially with the number of particles N in the system. A commonly used method for approximating equilibrium properties, is the Monte Carlo (MC) method. For some problems the MC method converges slowly, requiring a very large number of MC steps. For such problems the computational cost of the Monte Carlo method can be prohibitive. Presented here is a deterministic algorithm – the direct interaction algorithm (DIA) – for approximating the canonical partition function Z in $\sim N^2$ operations. The DIA approximates the partition function as a combinatorial sum of products known as elementary symmetric functions (ESFs), which can be computed in $\sim N^2$ operations. The DIA was used to compute equilibrium properties for the isotropic 2D Ising model, and the accuracy of the DIA was compared to that of the basic Metropolis Monte Carlo method. Our results show that the DIA may be a practical alternative for some problems where the Monte Carlo method converge slowly, and computational speed is a critical constraint, such as for very large systems or web-based applications.

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Introduction

In statistical mechanics, the partition function Z, for a canonical ensemble of particles is given by

$$Z = \sum_X e^{-E_X/k_B T} \quad (1)$$

where k_B is the Boltzmann constant, T is the temperature, E_X is the energy of microstate X, and the sum is over all accessible microstates [1]. The partition function can be used to calculate macroscopic thermodynamic properties of systems in equilibrium [2]. For applications where energy is a function of non-uniform interactions between particles, [3–7] such as the 3D Ising model for magnetic phase transition, the calculation of the partition function Z in Eq. (1), has been shown to be computationally intractable, i.e. NP complete [8–11]. One of the most commonly used methods for approximating equilibrium properties, is the Monte Carlo (MC) method, which scales as $\sim sN$, where s is the number of Monte Carlo steps and N is the number of particles in the system. However, for problems involving systems with long-range correlation the MC method converges slowly [12,13], and therefore may be impractical for some applications.

Presented here is a deterministic approximation – direct interaction algorithm (DIA) – for computing the partition function Z in Eq. (1). The DIA scales as $\sim N^2$ in the number of particles. For a selected particle, the DIA defines direct interactions as pairwise interactions involving the selected particle, and indirect interactions as pairwise interactions that do not involve the selected particle, as illustrated in Fig. 1. The DIA computes the exact contribution of direct interactions to the partition function, while using an average value for indirect interactions. In the hypothetical case where all the indirect interactions are equal, the partition function calculated by the DIA is exact to within numerical precision.

The DIA was applied to the computation of thermal average magnetization, internal energy and heat capacity for the isotropic 2D Ising model with no external field, for system size ranging from $N = 4 \times 4$ to 128×128, and the dimensionless temperature range of $k_B T/J = 0.1$ to 10, where J is the interaction potential between neighboring sites in the 2D Ising model. The accuracy of the DIA was compared to that of the commonly used basic (single-flip without biased sampling) Metropolis Monte Carlo (MC) method. Accuracy was measured as the root mean square (RMS) error relative to the exact computation.

Many other methods have been developed for approximating thermodynamic properties using the principles of statistical mechanics, though none are as widely used as the MC method, for practical problems. Most likely, this is due to the higher computational costs required for these other methods to achieve comparable levels of accuracy. For example, for systems involving non-uniform long range interaction, preliminary results (not included here) indicate that two such methods, the Wang Landau [14,15] and the cluster Monte Carlo [16,17] methods, can take two or more orders of magnitude longer to converge to accuracy levels comparable to that of the Monte Carlo method.

The accuracy of the MC method depends on the number of MC iterations used in the computation. In general, if the MC

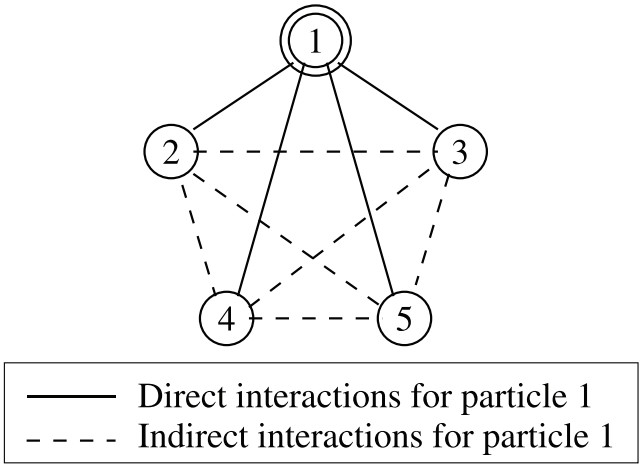

Figure 1. Direct and indirect interactions. For the five particle system shown here, with particle 1 as the selected particle, the direct interactions are shown as solid lines, and indirect interactions as dotted lines.
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method is run for a sufficiently large number of iterations, it will converge to the correct solution within some desired level of accuracy. However, for very large problems and/or web-based applications computation time can be a critical constraint, such as for the computation of protonation states in biomolecules [18,19]. To determine if the DIA may be a practical alternative to the MC method for such applications, we chose the number of MC iterations to be such that its computation time is at least 10 times longer than that of the DIA. For the 2D Ising systems considered here, the MC method converges slowly for temperature around and below the critical temperature of $k_BT/J \approx 2.2$. For MC runs with computation times that are 10 times longer than for the DIA, thermal average magnetization and heat capacity computed by the DIA are on average more accurate than those computed by the MC, while internal energy is more accurate for the MC method. Thus, for some problems where the MC method converges slowly and computation time is a critical constraint, the DIA may be a practical alternative.

The remainder of this paper is organized as follows. The *Methods* section provides a detailed derivation of the DIA. The accuracy of the DIA for the 2D Ising model are discussed in the *Results and Discussion* section. Finally, the method and results are summarized in the *Conclusions*.

Methods

The direct interaction algorithm (DIA) assumes that there are only two possible states for each particle. This is true for many problems. For example, in the electrostatics of biomolecules, each ionizable amino acid can have absolute charge of 0 (neutral) or 1 (charged), and in the 3D Ising model, each particle can have a spin of $\pm 1/2$. Moreover, systems with more than two states can be mapped to a two state system by replacing each particle with a set of two state "pseudo" particles [20]. Without loss of generality we also assume that the values of the two possible states are 0 and 1, because any two state problem can be mapped to an equivalent problem with states $\{0,1\}$ [21].

For a selected site k, the DIA defines direct interactions as pairwise interactions w_{ij} that involve the selected site, i.e. i or $j=k$. Indirect interactions are defined as pairwise interactions w_{ij} that do not involve the selected site, i.e. i and $j \neq k$. See Fig. 1. A previous study [21] suggested that, for some problems, direct interactions may be more important than indirect interactions for the computation of the partition function. Based on this finding, the DIA computes the contribution of direct interactions exactly, while using an average value for indirect interactions. By design the partition function calculated by the DIA is exact when all indirect interactions are equal. The algorithms and computations used by the DIA are derived below.

The derivation of the DIA consists of three steps. (1) The partition function Z in Eq. (1) is reformulated to partition all possible microstates into subsets with the same number of indirect interactions. (2) The indirect interactions are approximated by an average value. (3) The contribution of direct interaction to the partition function is represented as a combinatorial sum of products known as elementary symmetric functions, which are computed in $\sim N^2$ operations using the binary split-merge algorithm described below.

Step 1: Partition Microstates into Subsets with the Same Number of Indirect Interactions

The partition function in Eq. (1) involves the summation over all 2^N possible microstates $X=[x_1 x_2 \ldots x_N]$, where $x_i=\{0,1\}$ is the state of particle i. This summation can be subdivided into the sum over two subsets of microstates. One subset in which the state of the selected particle k, $x_k=0$, and another subset in which $x_k=1$, as illustrated in Fig. 2, i.e.

$$Z=\sum_{X:x_k=0} e^{-E_X/k_BT}+\sum_{X:x_k=1} e^{-E_X/k_BT} \qquad (2)$$

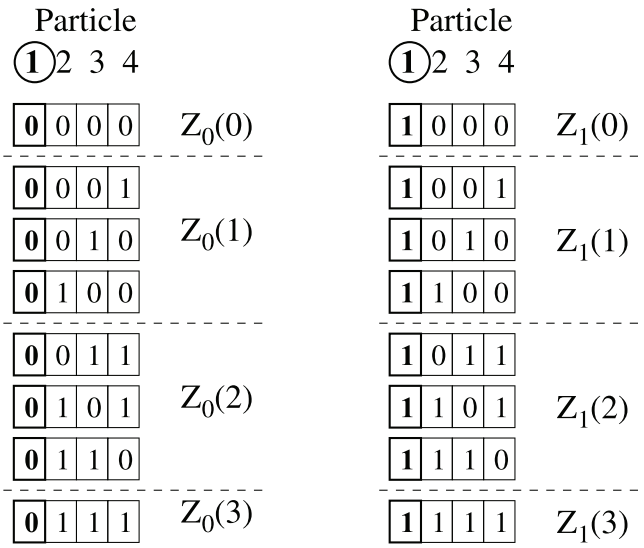

Figure 2. Partitioning of microstates. For a 4 particle system, the set of all possible 2^4 microstates are partitioned into subsets of states as follows. With particle 1 as the selected particles, the microstates are first partitioned into two subsets, one with particle 1 in state $x_1=0$ and another with $x_1=1$, with contributions to the partition function corresponding to Z_0 and Z_1 respectively (Eq. (3)). Each of these subsets are further partitioned into subsets with the same number of particles, m, in state $x_i=1, i\neq 1$, with contributions to the partition function corresponding to $Z_0(m)$ and $Z_1(m)$ in Eq. (10) and (11) respectively.
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$$= Z_0 + Z_1 \tag{3}$$

where Z_0 and Z_1 are the contributions to the partition function due to microstates with $x_k = 0$ and $x_k = 1$ respectively.

Each of these subsets of microstates can be further subdivided into N subsets each, such that each subset has the same number of particles in state $x_i = 1, i \neq k$, as illustrated in Fig. 2, i.e.

$$Z_0 = \sum_{m=0}^{N-1} Z_0(m) \tag{4}$$

$$Z_1 = \sum_{m=0}^{N-1} Z_1(m) \tag{5}$$

where $Z_0(m)$ and $Z_1(m)$ represent the contribution to the partition function due to microstates with m particles in state $x_i = 1, i \neq k$, and with the particle k being in state $x_k = 0$ and $x_k = 1$ respectively.

The contribution to the partition function due to each of these subsets of microstates can now be represented as the product of contributions due to direct interactions and indirect interaction, i.e.

$$E_X = E_X^{dir} + E_X^{indir} \tag{6}$$

$$Z_X = e^{-E_X/k_BT} \tag{7}$$

$$= e^{-E_X^{dir}/k_BT} e^{-E_X^{indir}/k_BT} \tag{8}$$

$$= Z_X^{dir} Z_X^{indir} \tag{9}$$

$$Z_0(m) = Z_0^{dir}(m) Z_0^{indir}(m) \qquad m = 0 \ldots N-1 \tag{10}$$

$$Z_1(m) = Z_1^{dir}(m) Z_1^{indir}(m) \qquad m = 0 \ldots N-1 \tag{11}$$

where Z_X is the contribution to the partition function due to state X, and the superscript "*dir*" and "*indir*" represent the contributions due to direct and indirect interactions respectively.

Step 2: Approximate the Contribution Due to Indirect Interactions

The contribution to the partition function due to indirect interactions in Eq. (10) and (11) can be approximated as follows

$$E_X^{indir} = \sum_{i \neq k} \sum_{j > i; j \neq k} w_{i,j} x_i x_j \tag{12}$$

$$\hat{w} = \sum_{i \neq k} \sum_{j > i; j \neq k} \frac{2 w_{i,j}}{(N-1)(N-2)} \tag{13}$$

$$Z_0^{indir}(m) \approx Z_1^{indir}(m) \approx \exp\left(\frac{-\hat{w} m(m-1)}{2 k_B T}\right) \quad m = 0 \ldots N-1 \tag{14}$$

where $w_{i,j}$ is the interaction between particles i and j, and $\hat{w}$ is the average indirect interaction. The factor $(N-1)(N-2)/2$ in Eq. (13) is the total number of indirect interactions, and the factor $m(m-1)/2$ in Eq. (14) is the number of indirect interactions when m particles are in state $x_i = 1, i \neq k$.

Step 3: Calculate the Exact Contribution Due to Direct Interactions

The contribution to the partition function due to direct interactions $Z_0^{dir}(m)$ and $Z_1^{dir}(m)$ can be represented by the combinatorial sum of products known as elementary symmetric functions $f_0(m)$ and $f_1(m)$, as follows

$$Z_0^{dir}(0) = f_0(0) = 1 \tag{15}$$

$$\begin{aligned} Z_0^{dir}(m) &= f_0(m) \\ &= \sum_{i_1} \ldots \sum_{i_m} \exp\left(\frac{-w_{i_1,i_1}}{k_BT}\right) \ldots \exp\left(\frac{-w_{i_m,i_m}}{k_BT}\right) \end{aligned} \tag{16}$$

$$\text{where } \; m = 1 \ldots N-1; i_{j-1} < i_j; i_j \neq k; j = 1 \ldots m$$

$$f_1(0) = 1 \tag{17}$$

$$Z_1^{dir}(0) = f_1(0) \exp\left(\frac{-w_{k,k}}{k_BT}\right) \tag{18}$$

$$\begin{aligned} f_1(m) = \sum_{i_1} \ldots \sum_{i_m} &\exp\left(\frac{-(w_{i_1,i_1} + w_{i_1,k})}{k_BT}\right) \ldots \\ &\exp\left(\frac{-(w_{i_m,i_m} + w_{i_m,k})}{k_BT}\right) \end{aligned} \tag{19}$$

$$Z_1^{dir}(m) = f_1(m) \exp\left(\frac{-w_{k,k}}{k_BT}\right) \tag{20}$$

$$\text{where } \; m = 1 \ldots N-1; i_{j-1} < i_j; i_j \neq k; j = 1 \ldots m$$

In Eq. (15) and (16) the selected particle k is in state $x_k = 0$, and in Eq. (17)–(20) $x_k = 1$. When $x_k = 0$, there is no direct interaction between k and any of the other particles ($w_{k,i} = 0$), and the contribution to Z_0^{dir} only consists of the self interaction terms $w_{i,i}$. When $x_k = 1$ the contribution to Z_1^{dir} consists of the self interaction terms $w_{k,k}$ and $w_{i,i}$, and the direct interaction term $w_{i,k}$.

Although the summations in Eq. (16) and (19) consist of 2^N terms, where each term represents the contribution due to one of the 2^N microstates of the system, the elementary symmetric functions themselves can be computed recursively in $\sim N^2$

operations using the Newton's identity generating function [22,23]. However, the Newton's identity generating function can suffer from large numerical errors due to catastrophic cancellations, the loss of precision in computations involving small differences between very large number. For example, for a 16×16 2D Ising model, as described below, the partition function Z calculated using Newton's identity is 2.25, whereas the correct value, without the numerical error is 2.40. The above computations were carried out with 64-bit double precision arithmetic.

Presented here is an alternate algorithm – the binary split-merge algorithm – that avoids the catastrophic cancellations inherent in the Newton's identity calculations. The binary split-merge algorithm is based on the following theorem [24].

Theorem 1. *If a system is partitioned into two subsystems A and B, then the elementary symmetric function $f(m)$ for the combined system can be calculated from the elementary symmetric functions $f_A(i)$ and $f_B(j)$, for A and B respectively, as follows.*

$$f(m)=\sum_{k=0}^{m} f_A(k)f_B(m-k) \tag{21}$$

Proof

1. Let $-a(i),i=1\ldots N-1$ be the roots of a polynomial $P=\Pi_{i=1}^{N-1}(x+a(i))$, where $a(i)=\exp(-w_{i,i}/k_BT)$ which are the individual terms in the ESF $f_0(m)$ (Eq. (16)).
2. Then each elementary symmetric function $f_0(m)$ in Eq. (16) is the coefficient of x^{N-1-m} in the polynomial P.
3. Let the subsystem A consist of particles $1\ldots q$, and the subsystem B of particles $q+1\ldots N-1$.
4. Then $-a(i),i=1\ldots q$ are the roots of the polynomial $P_A=\Pi_{i=1}^{q}(x+a(i))$ with the ESF for A, with $f_A(k)$ being the coefficients of x^{q-k} in the polynomial P_A. And $-a(i),i=q+1\ldots N-1$ are the roots of the polynomial $P_B=\Pi_{i=q+1}^{N-1}(x+a(i))$ with the ESF for B, with $f_B(k)$ being the coefficients of $x^{N-1-q-k}$ in the polynomial P_B.
5. Also, $P=P_AP_B$ since $-a(i),i=1\ldots N-1$ are the roots of the polynomials P and P_AP_B.
6. Therefore, $f_0(m)$ the coefficients of x^{N-1-m} in $P=P_AP_B$ are

$$f_0(m)=\sum_{k=0}^{m} f_A(k)f_B(m-k) \tag{22}$$

The above proof is for the ESF $f_0(m)$. The same proof applies to the ESF $f_1(m)$ in Eq. (19) with $a(i)=\exp(-(w_{i,i}+w_{i,k})/k_BT)$.

The binary split-merge algorithm consists of two stages, as illustrated in Fig. 3. First, in the split stage, the particles are recursively split into a binary tree where each node with n particles has two branches with $\lfloor n/2 \rfloor$ and $n-\lfloor n/2 \rfloor$;particles in each. The elementary symmetric function values, for the leaf nodes with only one particle i, are $f_0(0)=f_1(0)=1$, $f_0(1)=\exp(-w_{i,i}/k_BT)$, and $f_1(1)=\exp(-(w_{i,i}+w_{i,k})/k_BT)$. Then, in the merge stage, the elementary symmetric function from the two branches of a node are recursively combined, starting from the bottom, using Eq. (21).

An additional benefit of the binary split-merge algorithm is that it can be used to reduce the error in the indirect interaction approximation in Eq. (14). Instead of using the same average value $\hat{w}$ for all indirect interactions, one can include in the partition function approximations (Eq. (10) and (11)) an average indirect interaction value in each merge step that is based only on the indirect interactions between the subset of particles being merged, as follows. Let $Z_A(r)$ be the contribution to the partition function, including direct and indirect interaction, for the subset A (Eq. (21)) with r particles in state $x_i=1,i\in A$. And let $Z_B(s)$ be the contribution to the partition function, for the subset B with s particles in state $x_i=1,i\in B$. Then, applying the same principle used in Eq. (21), the contribution to the partition function for the combined system $Z_{AB}(r+s)$ can be approximated as:

$$\hat{w}_{AB}=\sum_{i\in A}\sum_{j\in B} w_{ij}/q(n-q) \tag{23}$$

$$Z_{AB}(r+s)\approx Z_A(r)Z_B(s)\exp\left(\frac{-\hat{w}_{AB}rs}{k_BT}\right) \tag{24}$$

where $\hat{w}_{AB}$ is the average indirect interaction between the subsets A and B with q and $n-q$ particles respectively, and $q(n-q)$ are the number of indirect interactions across the two subsets. If the indirect interactions between A and B are all equal, then Eq. (24) is exact.

It may be possible to increase the accuracy of the DIA by selecting multiple particles, for determining direct and indirect interactions. Any interactions involving any of the selected particles would be treated exactly (direct interactions), while an average value would be used for interactions not involving any of the selected particles (indirect interactions). Since fewer interactions are approximated, this modification should improve accuracy. However, the modification would require reformulation of the equations developed above, and would increase computational cost. Such a modification to the DIA has not been explored in this study.

2D Ising Model

The 2D Ising model of ferromagnetism was selected to test the accuracy of the DIA. It is one of the most thoroughly investigated system in statistical mechanics [25,26]. Despite its simplicity the 2D Ising model exhibits many of the thermodynamic properties, such as spontaneous magnetization, of real, and much more complex, systems. Thus one can gain insights into these more complex systems through the study of the simpler 2D Ising model. Moreover, there exists an exact solution for the isotropic 2D ising model with periodic boundary condition and no external field. The exact solution by Onsager [27], was generalized by Kaufman [28], and implemented by Beale [29,30]. This open source implementation computes exact values for thermal average magnetization $<M>$, internal energy U, and heat capacity C_v, for a given system size and temperature range.

The exact values for $<M>$, U, and C_v, for the 2D Ising model described below, provided the baseline for evaluating the accuracy of the DIA. The accuracy of the DIA was also compared to that of the basic (single-flip without biased sampling) Metropolis Monte Carlo (MC) method. The MC method includes a thermalization phase, prior to sampling data for estimating the above thermodynamic properties. The same number of steps were used for the thermalization phase as for the sampling phase.

The Ising model used for testing the DIA is an isotropic 2D model with nearest neighbor interaction potential J, on an $L\times L$ lattice, with periodic boundary conditions and no external field. Each vertex of the lattice can have a spin of $s_i=\{+1,-1\}$. The energy E_X of this system in state $X=[s_1\ldots s_N]$ is given by

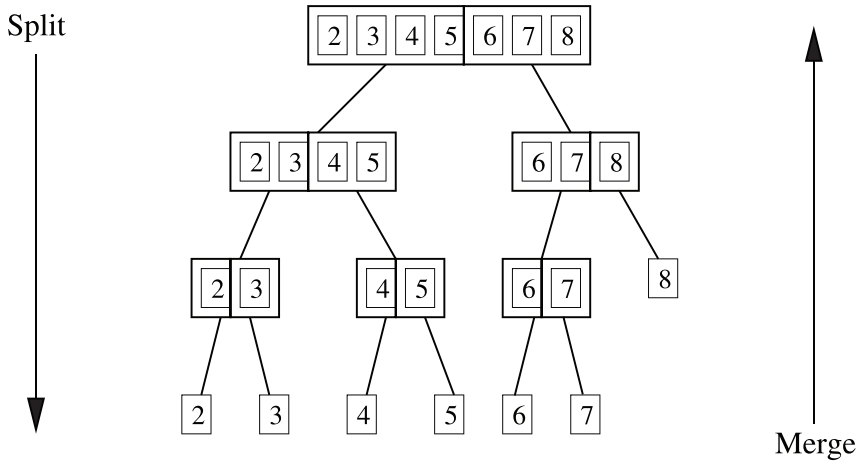

Figure 3. Split-merge algorithm. Consider an 8-particle system, with particle 1 being the selected particle. First, the split-merge algorithm recursively separates the particles, other than the selected particle, into a hierarchical binary tree. Next, the elementary symmetric function (ESF) for the leaf nodes, which consist of a single particle, are calculated. The ESF for all the other nodes, are then computed by recursively, starting from the bottom, merging the ESF from the two branches for each node using Eq. (21).
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$$E_X = -J \sum_{nn} s_i s_j \tag{25}$$

where the number of lattice sites $N = L^2$ and the sum is over pairs of nearest neighbors (nn) only. For the purpose of this analysis, a value of $J = 1$ is used. The thermal average magnetization $< M >$, internal energy U, and heat capacity C_v are defined as follows:

$$< M > = \frac{\sum_X M_X e^{-E_X/k_B T}}{Z} \tag{26}$$

$$M_X = \sum_{i=1}^{N} s_i \tag{27}$$

$$U = < E > = \frac{\sum_X E_X e^{-E_X/k_B T}}{Z} \tag{28}$$

$$C_v = \partial < E > / \partial T \tag{29}$$

$$= \left(< E^2 > - < E >^2 \right) / (k_B T)^2 \tag{30}$$

$$< E^2 > = \frac{\sum_X E_X^2 e^{-E_X/k_B T}}{Z} \tag{31}$$

where E_X is the energy of state X, k_B is the Boltzmann constant, T is the temperature, and M_X is the total magnetization (spin) of state X.

The spin states $s_i = \{+1, -1\}$ in the 2D Ising model can be mapped to $x_i = \{0,1\}$ in the DIA as follows:

$$x_i = (s_i + 1)/2 \tag{32}$$

$$E_X = -4J \sum_{nn} x_i x_j + 8J \sum_{i=1}^{N} x_i - 2NJ \tag{33}$$

$$M_X = \sum_{i=1}^{N} s_i = 2 \sum_{i=1}^{N} x_i - 1 \tag{34}$$

For the DIA, $< M >$, U, and C_v, with the mapping from x_i back to s_i, are computed as follows:

$$< M > = 2 \frac{\Sigma_{m=0}^{N-1} m (Z_0(m) + Z_1(m-1))}{Z} - 1 \tag{35}$$

$$U = < E > = k_B T^2 \Delta \ln Z / \Delta T \tag{36}$$

$$C_v = \Delta < E > / \Delta T \tag{37}$$

where $Z_0(m)$ and $Z_1(m)$ are as defined earlier by Eq. (10) and (11). $\Delta T k_B / J = 0.1$ is used to numerically compute the derivatives in Eq. (36) and (37).

The 2D Ising model described above, was chosen here for assessing the accuracy of the DIA because an exact solution is available for this system. However, many practical problems do not have a tractable exact solution. To evaluate the effectiveness of the DIA for such problems, it may be possible to use the Monte Carlo method to define a baseline for comparison. If the MC method is run for a sufficiently large number of MC steps, the results should converge to the correct value. Therefore, for some problems the results from a MC run with a very large number of MC steps may serve as a baseline for comparison.

Results and Discussion

To make the quantities in the following analysis dimensionless, temperature T is divided by J/k_B, internal energy U is divided by J, and heat capacity C_v is divided by k_B, where J is the nearest neighbor interaction potential and k_B is the Boltzmann constant.

The DIA was used to compute thermodynamic properties for $4\times4, 8\times8, 16\times16, 32\times32, 64\times64$ and 128×128 2D Ising systems described above. Accuracy of the DIA was compared to that of the basic Metropolis Monte Carlo (MC) method. Accuracy was measured as the RMS error relative to the exact computation for the dimensionless temperature range $k_BT/J=0.1$ to 10.0 in increments of 0.01. Computation time was measured by CPU time (all testing was performed on a workstation with a dual core Intel pentium 4, 3.2 GHz processor).

A goal of the following analysis is to determine if and when the DIA may be a practical alternative to the MC method, specifically for applications with computation time constraints, such as web services for computing protonation states in biomolecules [18,19]. Therefore, for the results shown below the number of Monte Carlo steps for the MC method is chosen such that MC computation time is at least 10 times longer than that of the DIA. See Table 1. Note that for these computation times, the MC method may not have sufficiently converged. Therefore, the following comparisons are only meaningful in the context of applications where computation time is a critical consideration. Where computation time is not a critical constraint, in general the MC method can be run long enough to achieve a desired level of accuracy.

Table 2 summarizes the overall accuracy (RMS error) for the DIA and the MC method, and Figure 4 shows the accuracy for the two methods as a function of system size. The MC method, after computation times that are 10 times longer than that of the DIA, has not sufficiently converged. As a result thermal average magnetization $<M>$ and heat capacity C_v calculated by the MC method are less accurate on average than for the DIA. Internal energy U calculated by the MC method is however more accurate than the DIA for these computation times.

To better understand why the DIA may be more accurate in some cases, consider the values of these three thermodynamic properties, for the DIA and MC methods compared to the exact computation, as a function of temperature (Figure 5).

As expected, the MC method is less accurate around and below the critical temperature of $k_BT/J\sim2.2$, where long range correlation becomes important and where the MC method converges slowly. At higher temperatures, where there is little long range correlation, the MC method converges more rapidly. Note that techniques have been developed, such as clustering and umbrella sampling, that can improve the accuracy of the Monte Carlo method in the critical and low temperature regions for some problems.

Table 1. Number of Monte Carlo (MC) steps.

Size	4×4	8×8	16×16	32×32	64×64	128×128
DIA CPU sec.	0.0012	0.0019	0.0120	0.1618	2.4834	39.0148
MC CPU sec.	0.0144	0.0196	0.1460	1.6276	27.3846	417.5865
MC steps	1.5×10^4	1.0×10^4	2.0×10^4	2.0×10^4	6.0×10^4	2.0×10^5

The number of MC steps is chosen such that the computation time (CPU time) for the MC method is at least 10 times the computation time for the direct interaction algorithm (DIA).
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Table 2. Accuracy comparison.

	RMS error	
	DIA	MC
Average Magnetization ($<M>/N$)	0.0066	0.1270
Internal Energy (U/NJ)	0.2031	0.0829
Heat Capacity (C_v/NK_B)	0.2952	1.1098

Accuracy for the direct interaction algorithm (DIA) and the Metropolis Monte Carlo (MC) method. Accuracy is calculated as the RMS error relative to the exact value. The number of steps is chosen such that the computation time for the MC method is at least 10 times the computation time for the DIA (Table 1).
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As seen in Figure 5, accuracy of the DIA depends on the temperature and the thermodynamic property of interest. Let us take a look at accuracy of the DIA for each thermodynamic property – thermal average magnetization $<M>$, internal energy U, and heat capacity C_v – in each of the three temperature regions: the low temperature region where $k_BT/J<1$, the high temperature region where $k_BT/J>4$, and the critical temperature region where $1\le k_BT/J\le4$. In the low temperature region the partition function Z is dominated by the two low energy states where the spins are aligned, all $+1$ or all -1. For these states, the energy E_X calculated using the average indirect interaction potential $\hat{w}$, Eq. (13), is the same as the exact value. Therefore the DIA is quite accurate in the low temperature region for all three thermodynamic properties. In the high temperature region, the value of $<M>$ in Eq. (26) is dominated by the multiplicity for different spin states. Since the DIA uses the exact value for the multiplicity of spin states in its computations, $<M>$ is quite accurate in the high temperature region. U on the other hand also depends on energy E_X, Eq. (28). In the high temperature region U is dominated by the partition function Z in Eq. (28). E_X calculated using the average indirect interaction potential $\hat{w}$ may be over or under estimated in this region, but since $-E_X$ is in the exponent of Z, the underestimated terms in Z (which is in the denominator in Eq. (28) for U) are dominant, and thus U is overestimated, as seen in Figure 5(b). Heat capacity C_v calculated by the DIA is however quite accurate in the high temperature region, Figure 5(c). The DIA uses the derivative of U to compute C_v, Eq. (37). Although DIA overstates U, the value of U converges to the exact value as $T\to\infty$, at close to the same rate as the exact computation. As a result the DIA closely approximates the correct value for C_v in the high temperature region. The DIA, in some sense being a mean-field like approximation, is not very accurate around the critical temperature, for all three thermodynamic properties. In this region, the accuracy of both energy E_X and the partition function Z become important, and therefore the accuracy of the DIA is highly sensitive to any difference between the correct value for the indirect interaction potential w_{ij} and the average value $\hat{w}$ used by the DIA.

The above results suggest that for some problems where the MC method converges slowly, and where computation time is a critical constraint, the DIA may be a practical alternative.

Conclusions

In statistical mechanics, the partition function Z can be used to compute equilibrium thermodynamic properties of a system. However, the computation of the partition function scales

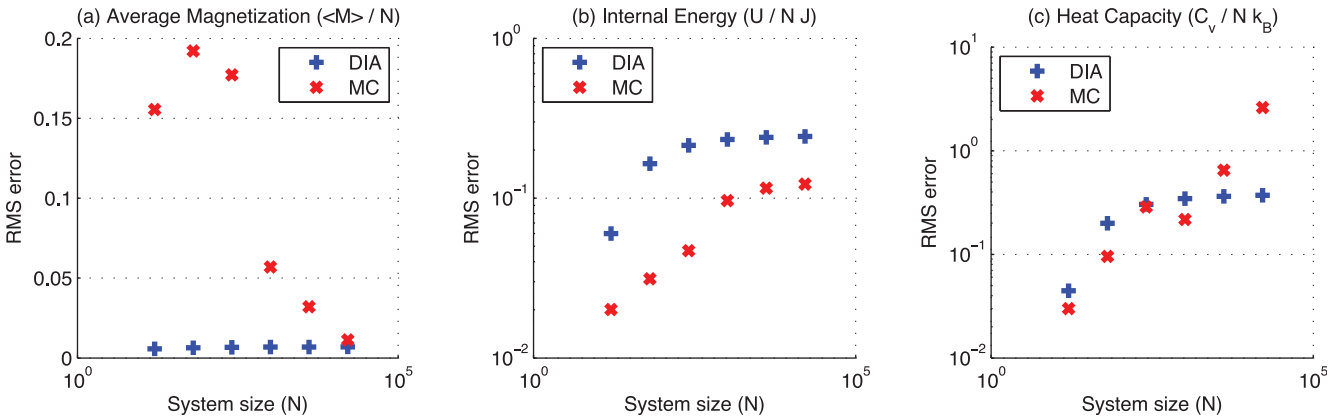

Figure 4. Accuracy as a function of system size. Accuracy for the direct interaction algorithm (DIA) and the Metropolis Monte Carlo (MC) method as a function of system size N (log-log scale). Accuracy is calculated as the RMS error relative to the exact value. The number of steps is chosen such that the computation time for the MC method is at least 10 times the computation time for the DIA (Table 1).
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exponentially in the number of particles N, and is therefore in general intractable for systems with $N \gtrsim 50$. Therefore, most practical problems, the Monte Carlo (MC) method is commonly used to approximate the values of equilibrium thermodynamic properties. However for some problems, such as those with long range order, the MC method converges slowly and may be impractical for applications where computation time is a critical constraint, such as for large systems and/or web-based applications.

The direct interaction algorithm (DIA) presented here, approximates the partition function in $\sim N^2$ operations. For a selected particle, the DIA computes the contribution to the partition function due to direct interactions (interactions involving the selected particle) exactly, while using an average value for indirect interactions (interactions not involving the selected particle). Even with this approximation, the exact computation of the contribution due to direct interaction involves the calculation of the so called elementary symmetric functions, where the number of terms grow exponentially with N. The Newton's identity generating function can be used to recursively calculate these elementary symmetric functions in $\sim N^2$ operations. However, the Newton's identity generating function can result in large numerical errors due to catastrophic cancellations. A binary split-merge algorithm was developed to compute the elementary symmetric function without these numerical errors. This algorithm first partitions the system into a hierarchical binary tree where the root node contains the entire system and each leaf node contains a single particle. Then, starting with the leaf node, the algorithm recursively merges the elementary symmetric function for the two child nodes to compute the elementary symmetric function for the parent node. The software implementation of the DIA can be downloaded from http://sourceforge.net/projects/isingdia/files/.

The direct interaction algorithm (DIA) was used to calculate thermal average magnetization $< M >$, internal energy U, and heat capacity C_v for the isotropic 2D Ising model with periodic boundary condition, no external field, and systems ranging in size from $N = 4 \times 4$ to 128×128. Accuracy of the DIA was compared to that of the basic Metropolis Monte Carlo (MC) method, where accuracy was measured as RMS error relative to the exact computation.

Where computation time is not a critical constraint, in general the MC method can be run long enough to achieve a desired level of accuracy. There are however many applications where computation time is a critical constraint, such as for very large

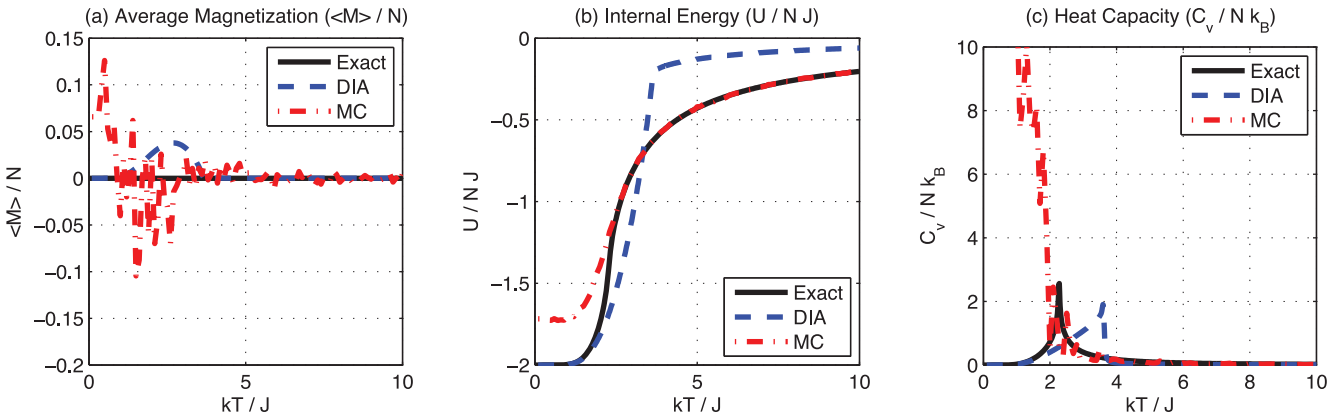

Figure 5. Calculated values for the 128×128 2D Ising system. (a) Thermal average magnetization $< M >$, (b) internal energy U and (c) heat capacity C_v, as a function of dimensionless temperature $k_B T/J$ for the 128×128 2D Ising system, as calculated by the direct interaction algorithm (DIA), the Metropolis Monte Carlo (MC) method, and the exact solution. The number of steps for the MC method was chosen such that the MC computation time is at least 10 times the computation time for the DIA. Connecting lines are shown to guide the eye.
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systems or web-based applications. To determine the potential usefulness of the DIA for such applications, we compared the DIA to the MC method with the number of MC steps chosen such that the computation times for the MC were at least 10 times longer than that of the DIA. The MC method may not converge sufficiently for these computation times, and therefore this comparison is only meaningful for applications where computation time is a critical consideration. Our results show that, for these computation times and the systems considered here, the DIA can be on average more accurate than the MC method, for the computation of thermal average magnetization $< M >$ and heat capacity C_v. Thus the DIA may be a practical alternative for some problems.

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Author Contributions

Conceived and designed the experiments: RA. Performed the experiments: RA. Analyzed the data: RA. Contributed reagents/materials/analysis tools: RA. Wrote the paper: RA.

References

1. Glazer M, Wark J (2001) Statistical Mechanics. A survival guide. Oxford University Press.
2. Kittel C, Kroemer H (1980) Thermal Physics, W.H. Freeman and Company, chapter 3. 2nd edition.
3. Garliauskas A (2006) Nonlinearities in artificial neural systems interpreted as an application of Ising physics. Nonlinear Analysis: Modelling and Control 11: 367–383.
4. Nayfonov A, Däppen W (1998) The signature of the internal partition function in thermodynamical quantities. Astrophys J 499: 489–495.
5. Bakk A, Høye J (2003) One-dimensional Ising model applied to protein folding. Phys A: Stat Mech App 323: 504–518.
6. Bryngelson JD, Wolynes PG (1987) Spin glasses and the statistical mechanics of protein folding. Proceedings of the National Academy of Sciences 84: 7524–7528.
7. Bashford D, Karplus M (1990) pKa's of ionizable groups in proteins: Atomic detail from a continuum electrostatic model. Biochemistry 29: 10219–10225.
8. Barahona F (1982) On the computational complexity of Ising spin glass models. J Phys A: Math Gen 15: 3241–3253.
9. Cipra B (2000) The Ising model is NP-complete. SIAM News 33: 1–3.
10. Goldberg L, Jerrum M, Paterson M (2003) The computational complexity of two-state spin systems. Random Structures and Algorithms 23: 133–154.
11. Istrail S (2001) Statistical mechanics, three-dimensionality and NP-completeness: I. Universality of intractability of the partition functions of the Ising model across non-planar lattices. Proceedings of the 32nd ACM Symposium on the Theory of Computing (STOC00) : 87–96.
12. Krauth W (2006) Statistical Mechanics: Algorithms and Computations, Oxford University Press, chapter 5.
13. Binder K, Heermann D (1997) Monte Carlo Simulations in Satistical Physics, Springer, chapter 2. 3rd edition.
14. Wang F, Landau DP (2001) Efficient, Multiple-Range Random Walk Algorithm to Calculate the Density of States. Physical Review Letters 86: 2050–2053.
15. Landau DP, Tsai SH, Exler M (2004) A new approach to Monte Carlo simulations in statistical physics: Wang-Landau sampling. American Journal of Physics 72: 1294–1302.
16. Wolff U (1989) Collective Monte Carlo Updating for Spin Systems. Physical Review Letters 62: 361–364.
17. Blöte HWJ, Heringa JR, Luijten E (2002) Cluster Monte Carlo: Extending the range. Computer Physics Communications 147: 58–63.
18. Anandakrishnan R, Aguilar B, Onufriev AV (2012) H++3.0: automating pK prediction and the preparation of biomolecular structures for atomistic molecular modeling and simulations. Nucleic Acids Research 40: W537–W541.
19. Kilambi KP, Gray JJ (2012) Rapid Calculation of Protein pKa Values Using Rosetta. Biophysical Journal 103: 587–595.
20. Bashford D, Case DA, Dalvit C, Tennant L, Wright PE (1993) Electrostatic calculations of side-chain pKa values in myoglobin and comparison with NMR data for histidines. Biochemistry 32: 8045–8056.
21. Anandakrishnan R, Onufriev A (2008) Analysis of basic clustering algorithms for numerical estimation of statistical averages in biomolecules. Journal of Computational Biology 15: 165–184.
22. Mead DG (1992) Newton's identities. The American Mathematical Monthly 99: 749–751.
23. Robinson DW (1961) A matrix application of Newton's identities. The American Mathematical Monthly 68: 367–369.
24. Baker FB, Harwell MR (1996) Computing elementary symmetric functions and their derivatives: A didactic. Applied Psychological Measurement 20: 169–192.
25. Baxter RJ (2010) Some comments on developments in exact solutions in statistical mechanics since 1944. Journal of Statistical Mechanics: Theory and Experiment 2010: P11037+.
26. McCoy B, Wu T (1973) The Two Dimensional Ising Model. Harvard University Press.
27. Onsager L (1944) Crystal statistics. I. A two-dimensional model with an order-disorder transition. Physical Review Online Archive (Prola) 65: 117–149.
28. Kaufman B (1949) Crystal statistics. II. Partition function evaluated by spinor analysis. Physical Review Online Archive (Prola) 76: 1232–1243.
29. Pathria R, Beale P (2011) Statistical Mechanics, Academic Press, chapter 13. 3rd edition.
30. Beale PD (1996) Exact Distribution of Energies in the Two-Dimensional Ising Model. Physical Review Letters 76: 78–81.