PHYSICAL REVIEW E **80**, 015702(R) (2009)

Calculating thermodynamics properties of quantum systems by a non-Markovian Monte Carlo procedure

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(Received 7 April 2009; published 21 July 2009)

We present a history-dependent Monte Carlo scheme for the efficient calculation of the free energy of quantum systems inspired by Wang-Landau and metadynamics. In the two-dimensional quantum Ising model, chosen here for illustration, the accuracy of free energy, critical temperature, and specific heat is demonstrated as a function of simulation time and successfully compared with the best available approaches. The approach is based on a path integral formulation of the quantum problem and can be applied without modifications to quantum Hamiltonians of any level of complexity. The combination of high accuracy and performance with a much broader applicability is a major advance with respect to other available methods.

DOI: 10.1103/PhysRevE.80.015702 PACS number(s): 05.10.Ln, 02.70.Ns, 02.70.Ss, 05.30.−d

Calculating certain thermodynamical quantities, such as the free energy (FE) or the entropy, by Monte Carlo (MC) simulation is a notoriously difficult problem. The difficulty arises because standard MC [1] is devised so as to generate configurations X distributed according to their Boltzmann weight $P_X=e^{-\beta E_X}/Z$, where E_X is the energy of the configuration X and $Z=\Sigma_X e^{-\beta E_X}$ is the partition function. This is efficient if we are interested in calculating quantities such as the average energy $\langle E\rangle=\Sigma_X E_X P_X$ since the configurations generated by MC are just those that contribute significantly to the average. Calculating, however, the free energy $F=-\beta^{-1}\log(Z)$ requires a knowledge of the partition function Z which is not accurately given by the simulation.

A major step forward, in this respect, came with the Wang-Landau (WL) idea [2]. In a nutshell, since

$$Z=\sum_X e^{-\beta E_X}=\int dE g(E)e^{-\beta E}, \tag{1}$$

where $g(E)=\Sigma_X\delta(E-E_X)$ is the density of states with energy E, if we devise a MC that generates configurations distributed according to $1/g(E_X)$, then we will effectively reconstruct the full *histogram* for $g(E)$ in a single simulation. This allows computing the partition function Z and hence all thermodynamical quantities at any temperature $T=1/k_B\beta$, where k_B is the Boltzmann constant. This is particularly useful if the system can undergo a first-order phase transition. Indeed, using the WL approach, the system can diffuse over barriers between different local minima following pathways that would represent, in normal finite-T MC, "rare events."

This discussion applies to classical systems; how should one proceed for a *quantum* system [3]? Consider, to fix ideas, the transverse-field quantum Ising model (QIM),

$$\hat{H}_{\mathrm{QIM}}=-J\sum_{\langle ij\rangle}^{N}\hat{\sigma}_i^z\hat{\sigma}_j^z-h\sum_i^N\hat{\sigma}_i^z-\Gamma\sum_i^N\hat{\sigma}_i^x, \tag{2}$$

where $\hat{\sigma}_i^z$ and $\hat{\sigma}_i^x$ are the Pauli matrices, $J>0$ is an exchange constant, h and Γ are the longitudinal and transverse magnetic fields, respectively, and $\langle ij\rangle$ denotes nearest neighbors on a lattice of N sites. The partition sum $Z_{\mathrm{QIM}}=\Sigma_X\langle X|e^{-\beta\hat{H}}|X\rangle$, where $X=\{\sigma_{i=1,\ldots,N}\}$ is a configuration of all N spins, involves now a matrix element of $e^{-\beta\hat{H}}$. The first step toward rewriting it in a form similar to Eq. (1) consists in performing a Suzuki-Trotter decomposition [4] leading to a path-integral expression $Z_{\mathrm{QIM}}\approx\Sigma_{\bar{X}}e^{-\beta\mathcal{A}(\bar{X})}$. Effectively, we have a classical system with an extra time dimension, whose configurations $\bar{X}$, over which we sum, are given by $\bar{X}=\{\sigma_{i=1,\ldots,N;p=1,\ldots,P}\}$. The extra index p labels the P *Trotter slices* in the time direction [5]. In the QIM case, the action $\mathcal{A}$ reads as

$$\mathcal{A}(\bar{X})=N\left[JU_{\bar{X}}+J^{\perp}K_{\bar{X}}-hM_{\bar{X}}-\frac{P}{\beta}\ln C\right], \tag{3}$$

where $U_{\bar{X}}=-(NP)^{-1}\Sigma_p\Sigma_{\langle ij\rangle}\sigma_{i,p}\sigma_{j,p}$ is the classical interaction energy per spin, $K_{\bar{X}}=-(NP)^{-1}\Sigma_{i,p}\sigma_{i,p}\sigma_{i,p+1}$ is the quantum "kinetic energy" per spin, $M_{\bar{X}}=(NP)^{-1}\Sigma_{i,p}\sigma_{i,p}$ is the magnetization per spin, $J^{\perp}=-(P/2\beta)\ln[\tanh(\beta\Gamma/P)]>0$ is the ferromagnetic coupling between adjacent spins in the time-direction, and $C^2=(1/2)\sinh(2\beta\Gamma/P)$. By introducing a multidimensional density of states $g(U,K,M)=\Sigma_{\bar{X}}\delta(U-U_{\bar{X}})\delta(K-K_{\bar{X}})\delta_{(M-M_{\bar{X}})}$ we can easily rewrite the following:

$$\begin{aligned}Z_{\mathrm{QIM}}&\approx\int dUdKdMg(U,K,M)e^{-\beta A(U,K,M)}\\&=\int dUdKdMe^{-\beta F(U,K,M)},\end{aligned} \tag{4}$$

where $A(U,K,M)=N[JU+J^{\perp}K-hM-(P/\beta)\ln C]$ and $F(U,K,M)$ defines the FE as a function of (U,K,M). For $h=0$ the relevant coordinates are two, U and K. Using the WL idea to reconstruct Z_{QIM} for all values of β and Γ requires now sampling a *two-dimensional* density of states histogram $g(U,K)$ in terms of which $Z_{\mathrm{QIM}}\propto\int dUdKg(U,K)e^{-\beta N(JU+J^{\perp}K)}$. This approach is, however, not very efficient (see below).

A much more convenient ("state-of-the-art") route is

based on the so-called *stochastic series expansion* (SSE) [6,7] and involves using a WL approach to reconstruct the coefficients $g(n)=\mathrm{Tr}(-\hat{H})^n$ of a high-temperature expansion of the partition function $Z=\Sigma_n(\beta^n/n!)g(n)$ [8]. The SSE approach is particularly suited to treat quantum spin systems and other lattice quantum problems but is in general not straightforward, for instance, for quantum problems on the continuum.

We propose here a method to effectively calculate the FE of a quantum system. Our approach is based only on a path-integral formulation. Thus, it can be easily applied to complicated off-lattice quantum problems. This is a major advantage with respect to SSE. The crucial ingredients were borrowed from the WL method and the *metadynamics* approach, a method which proved useful for exploring the FE landscape of complex classical systems [9] as a function of many collective variables (CVs) $\mathbf{S}=(S_1,\ldots,S_d)$.

In metadynamics, sampling is enhanced by introducing a history-dependent potential $V_G(\mathbf{S},t)$, defined as a sum of Gaussians centered along the "walk" in CV-space that in time "flattens" the FE histogram as a function of the CVs: $V_G(\mathbf{S},t\to\infty)\sim -F(\mathbf{S})$ [10]. This approach has been mainly used within molecular dynamics. During the simulation the system is guided by the action of two forces: the thermodynamic one, which move it toward the local FE minimum, and that due to the history-dependent potential, which pushes it away from local minima.

We show here how to integrate metadynamics in a MC procedure, in particular in a path-integral MC (PIMC), to sample the FE landscape of quantum systems as a function of physically relevant CVs. Again, we illustrate this approach in the quantum Ising model where we reconstruct the FE as a function of three CVs, the magnetization M, the potential energy U, and the kinetic energy K. As we will show, a calculation performed at a single point (β,Γ,h) in parameter space is sufficient to obtain the FE in a whole neighborhood of that point. The method is tested by comparing its efficiency against the state-of-the-art WL-SSE method [8] or a WL over a standard PIMC [3]: we show that our approach is at least as good as the WL-SSE on a lattice quantum problem, as well as being physically transparent and easily generalizable to different models.

Given the classical-like path-integral expression for the partition function of our quantum model, $Z\approx\Sigma_{\bar{X}}e^{-\beta\mathcal{A}(\bar{X})}$, we first define a small number d of CVs $S_l(\bar{X})$, $l=1,\ldots,d$, which appear in the action $\mathcal{A}(\bar{X})=A[\mathbf{S}(\bar{X})]$: in the QIM case there are $d=3$ physically meaningful CVs, the potential energy $S_1=U$, the kinetic energy $S_2=K$, and the magnetization $S_3=M$, in terms of which the action is $A(\mathbf{S})=N[JU+J^{\perp}K-hM-(P/\beta)\ln C]$. Next, we perform a Metropolis walk in configuration space $\{\bar{X}\}$ in which the transition probability from $\bar{X}$ to $\bar{X}'$ is modified adding to the action a history-dependent potential $V_G[\mathbf{S}(\bar{X}),t]$:

$$\mathcal{P}(\bar{X}\to\bar{X}',t)\equiv\min\{1,e^{-\beta[\delta A+\delta V_G(t)]}\},\tag{5}$$

where $\delta A=\mathcal{A}(\bar{X}')-\mathcal{A}(\bar{X})$ is the change in action and $\delta V_G(t)=V_G[\mathbf{S}(\bar{X}'),t]-V_G[\mathbf{S}(\bar{X}),t]$. Whether or not a move is accepted, we update V_G by adding to it a small localized repulsive potential (a Gaussian in normal metadynamics [9]). Technically, this is best done by grid-discretizing the CV-space and keeping track of $V_G(\mathbf{S}^{(k)},t)$ only at grid points $\mathbf{S}^{(k)}$; the value of V_G at a generic point $\mathbf{S}(\bar{X})$ is then calculated by a linear interpolation $\mathcal{L}$ from the neighboring grid values: $V_G[\mathbf{S}(\bar{X}),t]=\mathcal{L}[V_G(\mathbf{S}^{(k)},t)]$, where $\mathcal{L}(\cdots)$ is the linear interpolation function, and $\mathbf{S}^{(k)}$, $k=1,\ldots,2d$, are the points of the grid nearest-neighbors of $\mathbf{S}(\bar{X})$. In this scheme, the potential V_G is updated on the neighboring grid points $\mathbf{S}^{(k)}$ as

$$V_G(\mathbf{S}^{(k)},t+1)=V_G(\mathbf{S}^{(k)},t)+w\prod_{l=1}^{d}\left(\frac{S_l^{(k)}-S_l(\bar{X})}{\Delta S_l}\pm 1\right),\tag{6}$$

where the (+) sign is used if $S_l^{(k)}\le S_l(\bar{X})$ and the (−) sign otherwise, ΔS_l is the spacing of the grid in the S_l direction and w is a parameter that determines the speed of the FE reconstruction. Therefore, similarly to in WL, the acceptance changes every time a move is accepted or rejected, and the walk in configuration space is intrinsically non-Markovian (it depends on the history). At the beginning of the simulation the potential $V_G(\mathbf{S}^{(k)},t=0)$, stored on the grid, is set to zero. Then, as the system moves in configuration space, V_G is updated at each move as in Eq. (6). After a sufficient time, V_G will approximately compensate the underlying FE profile [10]. A further improvement can be obtained by taking as estimator of the FE not just a single profile V_G, but the arithmetic average of all the profiles between a "filling" time t_F and the total simulation time t_{tot}:

$$F(\mathbf{S})\approx-\frac{1}{t_{tot}-t_F}\int_{t_F}^{t_{tot}}dtV_G(\mathbf{S},t).\tag{7}$$

This reduces the error of the method, which drops fast to zero for large $t_{tot}-t_F$ [9]. Convergence problems can occur if an important CV is not included in the bias [9].

When $F(U,K,M)$ for a given value of the external parameters (β,Γ,h) is known, one can readily recalculate the new FE profile for a whole neighborhood in parameter space. The equations for this extrapolation can be written as

$$F(U,K,M)_{\beta'}=\frac{\beta}{\beta'}[F(U,K,M)_{\beta}-N(JU+J_{\beta}^{\perp}K-hM)]+N(JU+J_{\beta'}^{\perp}K-hM)+\frac{NP}{\beta'}\ln\left[\frac{C(\beta)}{C(\beta')}\right],\tag{8}$$

$$F(U,K,M)_{\Gamma'}=F(U,K,M)_{\Gamma}+N(J_{\Gamma'}^{\perp}-J_{\Gamma}^{\perp})K+\frac{NP}{\beta}\ln\left[\frac{C(\Gamma)}{C(\Gamma')}\right],\tag{9}$$

$$F(U,K,M)_{h'}=F(U,K,M)_{h}-N(h'-h)M.\tag{10}$$

By logarithmic integration of $F(U,K,M)$ with respect to one or more variables we immediately get the free energy as a function of a reduced number of CVs. For instance,

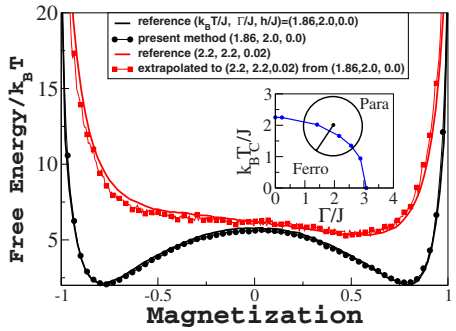

FIG. 1. (Color online) Free-energy profile for the 8×8 QIM as a function of the magnetization for two different parameter values. The results at $(k_BT=1.86,\ \Gamma=2.0,\ h=0)$ (in units of J) are obtained by first calculating $F(U,K,M)$ and then performing a logarithmic integration [Eq. (11)] to calculate $F(M)$. The results at $(k_BT=2.2,\ \Gamma=2.2,\ h=0.02)$ are instead obtained by extrapolating the previous $F(U,K,M)$ using Eqs. (8)–(10) and then integrating to obtain $F(M)$. As a reference for the comparison we use the results of an accurate umbrella sampling calculation [11] (solid line). The inset shows the phase diagram of the model and the circle suggests the size of the extrapolation region.

$$F(M) = -\frac{1}{\beta}\ln\left[\int dUdKe^{-\beta F(M,U,K)}\right]. \tag{11}$$

Figure 1 shows $F(M)$ for the QIM on a 8×8 lattice ($N=64$ spins), with $P=30$ Trotter slices at two different points in parameter space. The agreement between the reference $F(M)$ and that calculated from $F(U,K,M)$ is good even if we extrapolate the $F(U,K,M)$ from the ordered to the disordered side (or vice versa) of the phase transition line. Thus, with a single calculation of $F(U,K,M)$ at a point (T,Γ,h) in parameter space, we can get reliable information for $F(U,K,M)$ in a whole neighborhood of that point (see inset). An appropriate reference (T,Γ,h) can be easily chosen by a preliminary estimate on a smaller system or by an approximate calculation.

In order to test the efficiency of the proposed method we compare it with a SSE-WL simulation [7,8], as well as with a direct application of WL to PIMC in which the two-dimensional $g(U,K)$ is calculated. For the same system of Fig. 1 we estimate T_c (conventionally defined as the temperature at which the specific heat reaches its maximum value) as a function of the MC time with the three methods. The results are shown in Fig. 2. As a reference, we also computed T_c by a very long PIMC calculation (red line with error bars in the figure). In the SSE+WL calculation the histogram is considered flat when for all the values of n the histogram is larger than 95% of its average [12] (the limit of 80% suggested in Ref. [2] leads, for this specific system, to systematic errors, data not shown). Instead, for PIMC-WL the 80% limit is sufficient to reach convergence. The specific heat for our method was calculated computing a $F(U,K)$ at $k_BT/J=1.8$ and $\Gamma/J=2.0$, $h/J=0.0$ and extrapolating in temperature according to Eq. (8). The grid spacing in the U and K directions was of 10 and 1 energy levels, respectively. However we needed a finer grid spacing of 1 also for U for states

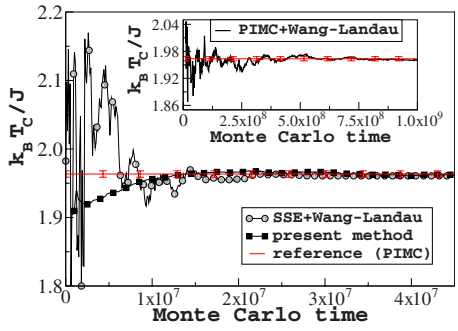

FIG. 2. (Color online) Critical temperature for a 8×8 QIM, as a function of the MC time, calculated using three different methods: SSE-WL (solid circles), our method (solid squared), and the PIMC-WL algorithm (inset). The reference (red line with error bars) is obtained by a long PIMC simulation.

too close to the parameter boundary values $-2<U<2$, where systematic errors may otherwise arise.

In order to extrapolate the FE in a meaningful temperature interval $\Delta T\sim\pm J/k_B$ including the peak of the specific heat, it is necessary to obtain quickly a large maximum value of $V_G\sim80k_BT/J$ for the system considered here. This is accomplished by starting the simulation with $w=8\times10^{-3}$ decreasing it up to 10^{-4} in 2×10^6 MC steps [t_F in Eq. (7)], then w is not changed anymore, and the free energy is estimated using Eq. (7). It is clear from the previous discussion that the optimal filling protocol is system dependent.

As shown in Fig. 2, using our approach we can obtain T_c within the PIMC error bar, with an efficiency similar to the SSE+WL algorithm. The PIMC+WL method is by comparison an order of magnitude slower (Fig. 2, inset). Of course, the efficiency of the approach presented here is strongly influenced by the temperature where the reconstruction is performed, which should not be too far from T_c ($\sim10\%$ smaller in the example considered here). However, T_c can always be estimated approximately, e.g., by performing a preliminary calculation on a system of smaller size.

Figure 3 shows the specific heat as a function of T for a larger system, $N=32\times32$, with $P=100$ Trotter slices, calcu-

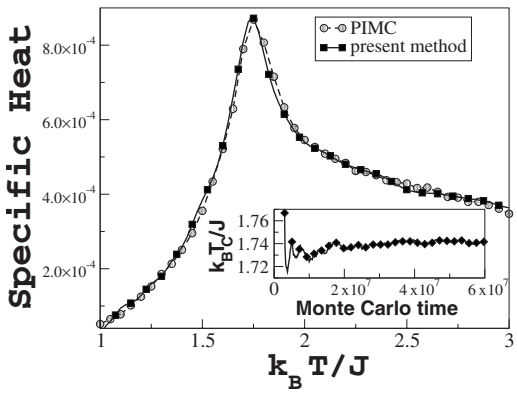

FIG. 3. Specific heat as a function of the temperature for the 32×32 QIM using two different methods, the PIMC technique (solid circles), and the proposed method (solid squares). The inset shows how the estimate of T_c evolves as a function of the MC time using the present scheme.

lated with PIMC and with the present method. Also in this case we computed $F(U,K)$ and extrapolated in temperature according to Eq. (8), with a grid spacing of 150 and 10 energy levels in U and K directions, respectively (no need to reduce the grid spacing near the parameter boundaries since the free energy is very high there). In this case w was decreased from 10^{-1} to 5×10^{-3} in 1.1×10^{6} MC steps. After this time the free energy is estimated using Eq. (7). As shown in Fig. 3, our approach reproduces the specific heat accurately between 1 and $3k_BT/J$. In the inset we show how T_c converges as a function of the MC time. Even for this much larger 32×32 system the convergence of T_c needs roughly the same order of magnitude of MC steps of those needed for the small 8×8 system: thus, the computational cost grows only linearly with the system size.

In conclusion, we have introduced an efficient history-dependent Monte Carlo scheme that allows the accurate calculation of the free-energy landscape of quantum systems. The proposed approach was tested on a two-dimensional quantum Ising model, where we reconstruct the free energy as a function of two and three collective variables. This allows reproducing the thermodynamic properties in a whole neighborhood of the point in parameter space at which the calculation is performed. The number of MC steps that are necessary to estimate T_c in a relatively large system ($32\times32\times100$) is of the same order as that required in a small system ($8\times8\times30$). The efficiency in estimating T_c is similar to that of SSE+WL, the state-of-the-art approach. Based on path-integral MC, our method can however be directly applied to continuous off-lattice quantum problems, where SSE would be harder to implement. The combination of optimal performance and a broader applicability is a major advance with respect to other available methods.

This research was partially supported by a MIUR/PRIN contract and benefited from the environment provided by the CNR/ESF/EUROCORES/FANAS/AFRI project.

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