# Extended canonical Monte Carlo methods: Improving accuracy of microcanonical calculations using a reweighting technique

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Velazquez and Curilef [J. Stat. Mech. (2010) P02002; (2010) P04026] have proposed a methodology to extend Monte Carlo algorithms that are based on canonical ensemble. According to our previous study, their proposal allows us to overcome slow sampling problems in systems that undergo any type of temperature-driven phase transition. After a comprehensive review about ideas and connections of this framework, we discuss the application of a reweighting technique to improve the accuracy of microcanonical calculations, specifically, the well-known multihistograms method of Ferrenberg and Swendsen [Phys. Rev. Lett. **63**, 1195 (1989)]. As an example of application, we reconsider the study of the four-state Potts model on the square lattice $L \times L$ with periodic boundary conditions. This analysis allows us to detect the existence of a very small latent heat per site $q_L$ during the occurrence of temperature-driven phase transition of this model, whose size dependence seems to follow a power law $q_L(L) \propto (1/L)^z$ with exponent $z \simeq 0.26 \pm 0.02$. Discussed is the compatibility of these results with the continuous character of temperature-driven phase transition when $L \to +\infty$.

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## I. INTRODUCTION

Recently [1,2], Velazquez and Curilef proposed a methodology that overcomes slow sampling problems due to the presence temperature-driven discontinuous phase transitions (PT). Essentially, their proposal allows us to improve any Monte Carlo (MC) algorithms based on canonical ensemble by introducing some suitable modifications. These extended canonical MC algorithms reduce exponential dependence of decorrelation time $\tau(N) \propto \exp(\gamma N)$ on the system size $N$ by a very weak power-law behavior $\tau(N) \propto N^w$. According to early estimations considering two-dimensional (2D) $q$-state Potts models [3–5], critical exponents $w$ of these algorithms are lower than the ones achieved using the multicanonical method and its variants [6–8]. Recently, we have shown that the extended canonical MC algorithms also exhibit a great performance near critical point of a temperature-driven continuous PT [9]. Surprisingly, we have verified that an extended version of the Metropolis importance sample [10,11] exhibits an efficiency slightly greater than the canonical cluster algorithms of Swendsen-Wang and Wolff [3–5].

The main goal of this work is to combine extended canonical MC algorithms with a reweighting technique to improve the accuracy of microcanonical calculations. Information collected from different MC simulations can be combined to estimate properties at new different conditions [12]. Specifically, we will consider the *multihistograms method* of Ferrenberg and Swendsen [13]. We shall reconsider the study of the four-state Potts model on the square lattice $L \times L$ with periodic boundary conditions to improve microcanonical calculations performed in our previous work [9]. This new analysis allows us to detect the existence of a very small, but definitely nonvanishing, latent heat $q_L$ and states with negative heat capacities $C < 0$ for lattice size range of $L = 22$–$90$, which are typical behaviors of a *finite system* that undergoes a temperature-driven discontinuous PT [14–19]. All associated thermodynamical behaviors, such as the entropy defect $\Delta s$ due to the region of convexity, are very small (see Fig. 8). Even using the present improvements, they are only revealed with a careful analysis of microcanonical dependencies.

At first glance, these results seem to be in contradiction with Baxter's exact results [20], which emphasize the continuous character of PT of this model *in the thermodynamic limit* $L \to +\infty$. Anticipating our discussions on this question, we think that there is no contradiction here. Baxter's exact results do not forbid the existence of negative heat capacities outside the thermodynamic limit. In fact, the Potts model on the square lattice $L \times L$ with $q = 4$ is *a marginal case* for this family of models [20–22], and therefore there is nothing strange if ambiguities in some thermodynamical behaviors are detected for finite lattice sizes $L$. Besides, the size dependence of our MC estimates of latent heat per site $q_L$ seems to follow a power law $q_L(L) \propto (1/L)^z$ with exponent $z \simeq 0.26$, which is fully compatible with an eventual vanishing of this quantity when $L \to +\infty$.

The paper is organized into sections as follows. Section II is devoted to discuss some important antecedents of this study. For the sake of self-consistency of the paper, we start reviewing some generalized fluctuation relations derived by Velazquez and Curilef and their relevance in MC simulations [23–28]. Afterwards, we discuss the main ideas associated with extension of canonical MC methods [1,2,9] as well as connections with other MC methods that perform microcanonical calculations [12]. Section III is devoted to discuss the application of the multihistograms method to improve these type of microcanonical MC calculations. As an example of application, we discuss the improvement of microcanonical estimations of the four-state Potts model on

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the square lattice $L \times L$ with periodic boundary conditions. Final remarks and open questions are discussed in the Sec. IV.

## II. ANTECEDENTS

### A. Generalized fluctuation relations and their application to MC simulations

Since early demonstration of the generalized fluctuation relation

$$C = \beta^2 \langle \delta U^2 \rangle + C \langle \delta\beta_\omega \delta U \rangle \tag{1}$$

by Velazquez and Curilef, it was clearly evidenced that its associated background conditions of derivation can be employed to extend any MC algorithm based on the canonical ensemble

$$\omega_c(U|\beta) = \frac{1}{Z(\beta)} \exp(-\beta U) \tag{2}$$

(see Sec. 3.1 in Ref. [23]). As shown earlier by Boltzmann and Gibbs [29], the canonical ensemble (2) describes a system of interest that is put in thermal contact with an environment of constant temperature or, equivalently, a thermal bath of infinite heat capacity. In full analogy with the known relation [30]

$$C = \beta^2 \langle \delta U^2 \rangle \tag{3}$$

of classical fluctuation theory is employed in any MC study based on canonical ensemble (2) to obtain the heat capacity $C$ from the energy fluctuations, the more general fluctuation relation (1) can be employed with the same purpose in any MC study where the environmental inverse temperature $\beta_\omega$ experiences thermal fluctuations that are coupled with thermal fluctuations of the system energy $U$ [23–25].

A simple realization of this effect arises when the system of interest is put in thermal contact with a bath with finite heat capacity $C_\omega$. The inverse temperature $\beta_\omega$ of the bath will no longer be a constant parameter as the case of canonical ensemble (2). On the contrary, it turns a *dynamical variable* that evolves as a consequence of the underlying thermodynamic interaction, which is described in Eq. (1) by the existence of a nonvanishing correlation function $\langle \delta\beta_\omega \delta U \rangle$. For any MC study based on the consideration of a bath with finite heat capacity, its corresponding inverse temperature $\beta_\omega$ is a dynamical variable that evolves during the course of simulation. It is noteworthy that these same arguments were employed in the past by Gerling and Hüller to proposed the so-called dynamic ensemble method [31]. The Velazquez and Curilef methodology to extend canonical MC algorithms could be regarded as an improvement of the Gerling and Hüller proposal [9]. This methodology now includes modifications that enhance potentialities of this type of formalism, which also share several connections with some ideas proposed in the past by Challa and Hetherington [32–34].

An advantage of this perspective is that it involves *a stronger control on the system fluctuating behavior and its stability* than the one considered by canonical ensemble (2). Equation (1) is compatible with the existence of negative heat capacities $C < 0$ that appear during the occurrence of a temperature-driven discontinuous PT [14–19]. This fact is easy to see by rephrasing Eq. (1) as follows:

$$C[1 - \langle \delta\beta_\omega \delta U \rangle] = \beta^2 \langle \delta U^2 \rangle, \tag{4}$$

where the prerequisite of negative heat capacity $C < 0$ implies the inequality $\langle \delta\beta_\omega \delta U \rangle > 1$. Clearly, the study of systems with this behavior is not possible for MC simulations based on canonical ensemble (2), where thermal fluctuations of bath inverse temperature $\delta\beta_\omega \equiv 0$. In fact, its associated fluctuation relation (3) is compatible with positive heat capacities only. The presence of states with negative heat capacity can be manifested by the *multimodal character* of energy distribution function within the canonical ensemble [1]. This mathematical behavior of canonical energy distributions is shown in Fig. 1 for the case of the 10-state Potts model on the square lattice. It is noteworthy that states with negative heat capacity associated with the S bend of microcanonical caloric curve $\beta(u)$ are poorly populated within the canonical ensemble. Such anomalous states can be studied in a MC simulation that implements the existence of a thermal contact with a bath of finite heat capacity, which is shown in Fig. 2 for the same model system [23].

Recently [9], we have emphasized that the present arguments can be useful in MC studies of systems that undergo a temperature-driven continuous PT. As discussed elsewhere [30], heat capacity $C$ can be very large, or even diverge, when a system approaches the critical point of a temperature-driven

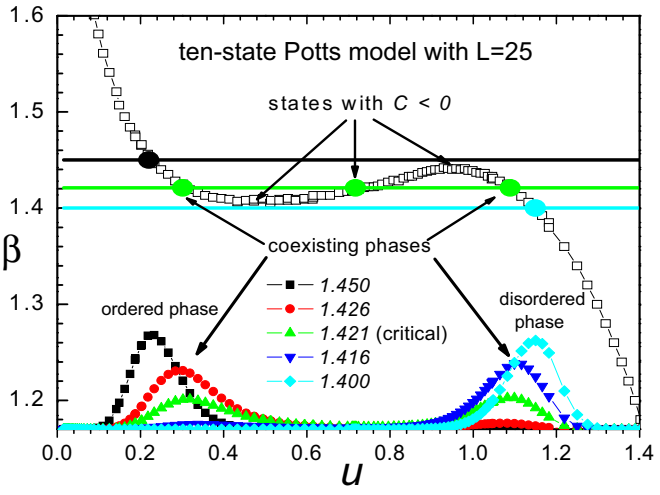


FIG. 1. (Color online) Behavior of energy distributions within canonical ensemble (2) along the occurrence of phase coexistence phenomenon of the 10-state Potts model on the square lattice $25 \times 25$ with periodic boundary conditions ($u = U/N$ is the energy per site) (after [23]). This study clearly illustrates the bimodal character of energy distribution functions when the inverse temperature parameter $\beta$ of the canonical ensemble takes values around the critical value $\beta_c \simeq 1.421$ of temperature-driven discontinuous PT. Notice that the branch of *microcanonical caloric curve* $\beta(u) = \partial s(u)/\partial u$ (open squares) with states with negative heat capacities $C < 0$ is poorly populated by using a bath with constant temperature since these states are canonically unstable. The values of bath inverse temperature $\beta$ are represented here by horizontal lines. Intersection points of these horizontal lines with microcanonical inverse temperature correspond to the energies where the energy distribution function exhibits its local maxima and minima.

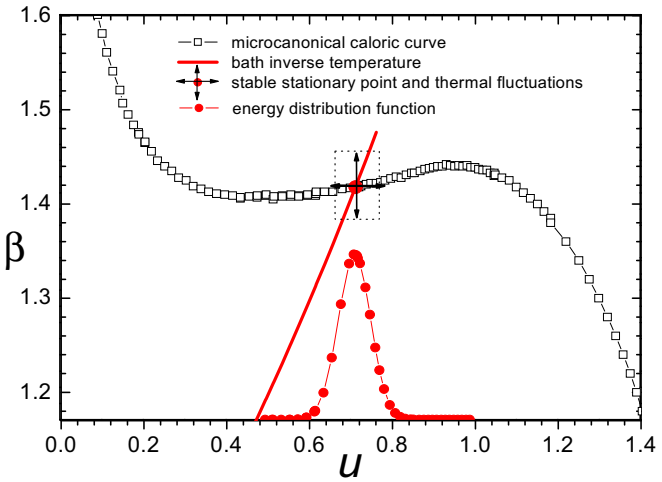


FIG. 2. (Color online) The use of a bath with a finite heat capacity $C_\omega$ enables a direct study of the branch of microcanonical caloric curve (open squares) with negative heat capacities, which is shown for the same model system of Fig. 1 (after [23]). Here, energy distribution exhibits a single Gaussian peak that is located inside the region where microcanonical caloric curve exhibits negative heat capacities $C < 0$. Both the bath inverse temperature $\beta_\omega$ (thick red line) and the system energy $U$ exhibit thermal fluctuations around their equilibrium values (coordinates of the red circle that mark the interception point between microcanonical caloric curve and the bath inverse temperature curve). In the past [31], Gerling and Hüller proposed this type of arguments to obtain microcanonical caloric curve considering the expectation values $\langle\beta_\omega\rangle$ and $\langle U\rangle$. The analysis of their thermal fluctuations $\langle\delta U^2\rangle$ and $\langle\delta\beta_\omega\delta U\rangle$ enables a direct derivation of a negative value of microcanonical heat capacity $C$ at the equilibrium energy considering fluctuation relation (1).

continuous PT. According to canonical fluctuation relation (3), a divergence of the heat capacity $C$ implies a divergence of energy fluctuations $\langle\delta U^2\rangle$. In MC simulations, large fluctuations imply large configurational changes that are also accompanied by slow sampling problems [12]. Commonly, the strategy to overcome these difficulties is the implementation of nonlocal MC moves, namely, the use of *cluster MC algorithms* [3–5]. By itself, fluctuation relation (1) suggests an alternative way to face these problems: the use of a bath with positive finite heat capacity $C_\omega$.

For a simple illustration of the above idea, let us consider the first-order approximation for thermal fluctuations of bath inverse temperature $\delta\beta_\omega = -\beta_\omega^2\delta U_\omega/C_\omega \equiv \beta^2\delta U/C_\omega$, which enables us to rephrase the fluctuation relation (1) as follows:

$$\frac{CC_\omega}{C+C_\omega} = \beta^2\langle\delta U^2\rangle. \tag{5}$$

Accordingly, the system energy fluctuations are fully determined by the bath heat capacity $C_\omega$ when the system heat capacity $C \to +\infty$:

$$C_\omega = \beta^2\langle\delta U^2\rangle \equiv \beta^2\left\langle\delta U_\omega^2\right\rangle. \tag{6}$$

It is easy to realize that this last result is fully equivalent to canonical relation (3) when one permutes the roles of the bath and the system of interest. The positivity of the right-hand side of Eq. (5) also implies that the study of a system with negative heat capacity $C < 0$ demands the fulfillment of the following inequality:

$$C_\omega < |C|\,, \tag{7}$$

which was derived by Thirring in Ref. [14]. These reasonings show that heat capacity $C_\omega$ of the bath should not be finite only, but also it must satisfy the above constraint. In addition, the value of heat capacity $C_\omega$ can be optimized to reduce as low as possible the statistical uncertainties associated with determination of the microcanonical caloric curve of the system of interest [see Eq. (28)]. Fluctuation relation (5) was also derived by Challa and Hetherington in Ref. [34] using different arguments.

Energy-temperature fluctuation relation (1) is just a particular case of more general fluctuation theorems [26,27]. As an example, the following fluctuation relation [30]

$$\chi_T = \beta\langle\delta M^2\rangle \tag{8}$$

is also widely employed in MC simulations to obtain isothermal magnetic susceptibility $\chi_T$ from thermal fluctuations of the total magnetization $M$ of a certain magnetic system [12]. This relation can be generalized as follows:

$$\begin{aligned}\chi_T = {}& \beta\langle\delta M^2\rangle - \beta\chi_T\langle\delta H_\omega\delta M\rangle \\ & + [T(\partial M/\partial T)_T - M]\langle\delta\beta_\omega\delta M\rangle,\end{aligned} \tag{9}$$

while the corresponding fluctuation relation for the heat capacity at constant magnetic field $C_H$ is given by

$$\begin{aligned}C_H = {}& \beta^2\langle\delta Q^2\rangle + C_H\langle\delta\beta_\omega\delta Q\rangle \\ & - [T(\partial M/\partial T)_T - M]\beta^2\langle\delta H_\omega\delta Q\rangle.\end{aligned} \tag{10}$$

Here, $\beta_\omega$ and $H_\omega$ represent the environmental inverse temperature and the intensity of the external magnetic field that is applied over a magnetic system of interest. Moreover, $\delta Q = \delta U - H\delta M$ is the amount of heat absorbed or transferred by the system at the equilibrium, where $\langle\delta Q\rangle = 0$. Under general thermodynamical conditions, all these macroscopic quantities and thermodynamical parameters undergo thermal fluctuations that are coupled among them.

Correlated thermal fluctuations as those commented in Fig. 3 are systematically omitted by conventional ensembles of statistical mechanics, such as canonical ensemble (2) and its generalization, the so-called Boltzmann-Gibbs distributions [30]. Consequently, its associated fluctuation relations as (3) and (8) are incompatible with the existence of response functions with anomalous values, such as negative heat capacities $C_H < 0$ or negative isothermal susceptibilities $\chi_T < 0$ in a ferromagnetic system. Some direct consequences as the inequality (7) also imply a violation of zeroth law of thermodynamics [9,35,36]. In the framework of MC simulations, all these general fluctuation relations are relevant because the occurrence of phase transitions is mostly accompanied with the existence of anomalous values in response functions [17]. This connection is also shown in Fig. 4 for the case of the Ising model on the square lattice $L \times L$ with periodic boundary conditions, where fluctuation relation (9) was employed to study anomalous values of isothermal magnetic susceptibility $\chi_T$ that are found below the critical temperature of ferromagnetic-paramagnetic PT of this paradigmatic model system [26]. All that is discussed

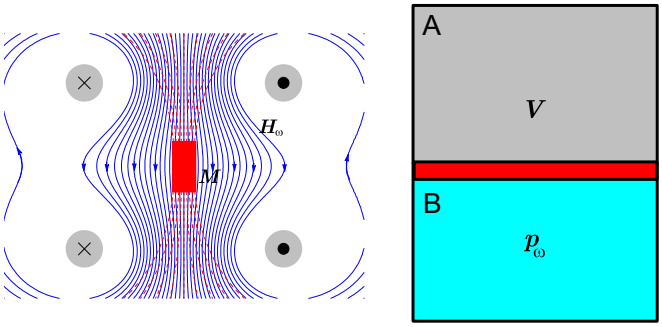


FIG. 3. (Color online) Correlated thermal fluctuations analogous to the one described by fluctuation relation (1) can also be observed among other pairs of conjugated thermodynamical variables. Left: Thermal fluctuations of the total magnetization $M$ of a magnetic sample (red rectangle) induce thermal fluctuations in its associated total magnetic flux (red dash lines) through the Helmholtz coils (whose cross sections are represented here by four gray circles). As consequence of electromagnetic induction, the total magnetic field $H_\omega$ of these Helmholtz coils (blue lines) experiences correlated thermal fluctuations $\langle \delta H_\omega \delta M \rangle$ with the total magnetization $M$ of the sample. Right: Schematic representation of two finite fluid systems **A** and **B** that are separated by a moving wall or piston (red rectangle). The total volume $V$ of fluid system **A** experiences correlated thermal fluctuations $\langle \delta p_\omega \delta V \rangle$ with the external pressure $p_\omega$ of fluid system **B**.

in this work concerning the MC study of microcanonical energy-temperature dependence and its associated response function, the microcanonical heat capacity, can directly be extended to other situations with several control parameters introducing appropriate modifications. This perspective was employed in Ref. [26] to obtain microcanonical magnetization *versus* magnetic field dependence shown in Fig. 4.

### B. Extended canonical MC algorithms

As already commented, the use of a bath with finite heat capacity in MC simulations was first proposed by Gerling and Hüller [31]. These authors considered that the system of interest is put in thermal contact with a *bath with constant heat capacity* $C_\omega$ (e.g., the system acting as a bath can be an ideal gas). Let us denote by $U_T$ the total energy of the system and the bath, which remains fixed when they are put in thermal contact. It can be shown that the inverse temperature of the bath under the above conditions depends on the system energy $U$ as follows:

$$\beta_\omega(U) = \frac{C_\omega}{U_T - U}. \tag{11}$$

As naturally expected, this situation is just a particular case among all possible equilibrium situations considered by generalized fluctuation relation (1). If the system size $N$ is sufficiently large, the thermodynamic influence of every bath with finite heat capacity $C_\omega > 0$ turns asymptotically equivalent as a consequence of applicability of Gaussian approximation for energy fluctuations. However, significant differences in system fluctuating behavior arise when the system size is not so large. In fact, the bath proposed by Gerling and Hüller is not the most convenient one.

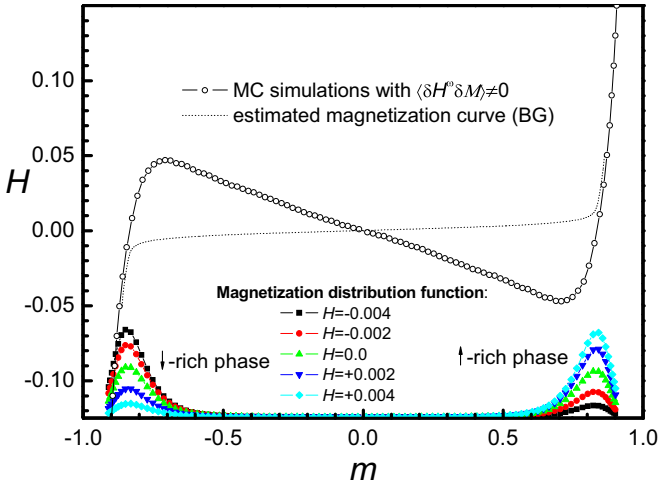


FIG. 4. (Color online) Behavior of distributions of magnetization per site $m = M/N$ of the Ising model on the square lattice with periodic boundary conditions for different constant values of the external magnetic field $H$ at constant temperature $T < T_c$, where $T_c$ is the temperature critical value of ferromagnetic-paramagnetic continuous PT of this model (after [26]). Open circles are a MC estimation of microcanonical dependence of magnetization vs the external magnetic field (analogous to microcanonical caloric curve). Dotted line represents dependence of average magnetization $\langle m \rangle$ when the intensity of the external magnetic field $H$ is smoothly varying from negative to positive values at constant temperature. Clearly, this canonical dependence (constant values of control parameters $T$ and $H$) fails to describe the S bend of its microcanonical counterpart. Moreover, the region with negative values of isothermal magnetic susceptibility $\chi_T < 0$ is poorly populated by magnetization distributions for constant values of the external magnetic field $H$ and temperature $T$. In full analogy as the energy-temperature fluctuation relation (1) enables the study of systems with negative heat capacities $C < 0$, fluctuation relation (9) was employed in this MC study to obtain anomalous values of isothermal magnetic susceptibility $\chi_T$.

For an arbitrary bath with probability weight $\omega(U)$, its corresponding inverse temperature $\beta_\omega(U)$ can be expressed as follows[1] [23]:

$$\beta_\omega(U) = -\frac{\partial}{\partial U} \ln \omega(U). \tag{12}$$

Notice that this definition contains temperature parameter $\beta$ of canonical ensemble as a particular case (2). The energy dependence of inverse temperature $\beta_\omega(U)$ can be developed in power series around a certain reference energy $U_s$ as follows:

$$\beta_\omega(U) = \beta_s + \sum_{n=1}^{+\infty} a_n (U - U_s)^n . \tag{13}$$

If thermal fluctuations of the system energy are sufficiently small, in particular, when the size $N$ of the system under study is sufficiently large, high-order terms in power expansion (13)

[1]This definition follows from combining Einstein postulate $dp(U|U_T) = A \exp[S_T(U|U_T)]\, dU$ of classical fluctuation theory and the additivity of entropy $S_T(U|U_T) = S(U) + S_\omega(U_T - U)$.

can be disregarded, except the term corresponding to linear approximation

$$\beta_\omega(U) = \beta_s + \lambda_s (U - U_s)/N. \tag{14}$$

For the sake of convenience, we have identified here $a_1 \equiv \lambda_s/N$. Moreover, additional parameters $U_s$ and $\beta_s$ can be regarded as roughly estimates of the expectation values $\langle U\rangle$ and $\langle\beta_\omega\rangle$. Expression (14) is the simplest mathematical dependence for the bath inverse temperature $\beta_\omega$ that captures the existence of correlated fluctuations $\langle\delta\beta_\omega\delta U\rangle$ described by fluctuation relation (1). Hereinafter, we shall assume this dependence is *exact*, that is, let us assume a bath that fulfills this expression.

According to definition (12), linear dependence (14) corresponds to the *Gaussian ensemble*

$$\omega_G(U|\theta) = \exp[f(\theta) - \phi(U|\theta)] \tag{15}$$

introduced by Challa and Hetherington [32–34], where $\theta \equiv (U_s,\beta_s,\lambda_s)$ with parameter $\lambda_s \geqslant 0$, and $\phi(U|\theta)$ is the second-order polynomial function

$$\phi(U|\theta) = \beta_s (U - U_s) + \frac{1}{2N}\lambda_s (U - U_s)^2. \tag{16}$$

Formally speaking, Gaussian ensemble (15) corresponds to a bath that is composed of a *hypothetical substance* whose heat capacity $C$ depends on its temperature $T$ as $C \propto 1/T^2$. This type of dependence is indeed observed in the high-temperature limit of a paramagnetic system [30]. However, Gaussian ensemble (15) can also be regarded as a *nonphysical ensemble* for the purpose of MC simulations. Certainly, there is nothing wrong with this interpretation. Nonphysical statistical ensembles are usually considered in MC studies with different purposes, as the case of the so-called multicanonical ensemble [12]. The use of this generalized statistical ensemble here is fully justified by practical purposes. Gaussian ensemble (15) contains canonical ensemble (2) in the limit $\lambda_s \to 0^+$, as well as microcanonical ensemble

$$\omega(U|U_s) = \frac{1}{\Omega(U_s)}\delta[U - U_s] \tag{17}$$

in the limit $\lambda_s \to +\infty$. This ensemble is easy to combine with any MC algorithm based on canonical ensemble (2) regardless whether its character is local or nonlocal [9]. The rough idea is to replace constant temperature parameter $\beta$ of canonical ensemble (2) by the *transition inverse temperature* $\beta_{ij}^t = [\beta_\omega(U_i) + \beta_\omega(U_j)]$ of the initial and final configurations with energies $U_i$ and $U_j$, respectively. For the case of the Metropolis importance sample [10,11], its acceptance probability is modified as follows:

$$W(U_i \to U_j) = \min\left[1, \exp\left(-\beta_{ij}^t \Delta U_{ij}\right)\right], \tag{18}$$

where $\Delta U_{ij} = U_j - U_i$. Implementation of this statistical ensemble for canonical cluster MC algorithms was extensively discussed in Sec. II C of our previous paper [9]. The simple mathematical form of this ensemble makes all analytical developments of the present methodology easier, such as the analysis of detailed balance and the analysis about the incidence of finite size effects [9].

As naturally expected, statistical expectation values of physical quantities are *ensemble dependent*. To avoid this difficulty, the primary goal of extended canonical MC methods is the calculation of *microcanonical quantities* derived from the first derivatives of the system microcanonical entropy $S(U)$, such as the microcanonical caloric curve $\beta(U)$ (energy dependence of the system inverse temperature) and the curvature curve $\kappa(U)$:

$$\beta(U) = \frac{\partial S(U)}{\partial U} \quad \text{and} \quad \kappa(U) = -N\frac{\partial^2 S(U)}{\partial U^2}. \tag{19}$$

This second quantity is directly related to the microcanonical heat capacity $C$ as $\kappa = \beta^2 N/C$. In full analogy with the dynamic ensemble MC method [31], calculation of the microcanonical caloric curve can be achieved in the framework of Gaussian approximation of energy distribution function using the expectation values of the bath inverse temperature and the system energy

$$\beta_e \simeq \langle\beta_\omega\rangle \text{ and } U_e \simeq \langle U\rangle, \tag{20}$$

where $U_e$ represents the most likely value of the system energy. The value of microcanonical curvature $\kappa_e = \kappa(U_e)$ at the energy $U_e$ can be estimated from generalized fluctuation relation (1) as follows:

$$\kappa_e \simeq \frac{1 - \lambda_s\langle\delta U^2\rangle/N}{\langle\delta U^2\rangle/N}. \tag{21}$$

Although the above estimations of microcanonical dependencies (19) are only exact in the thermodynamic limit $N \to \infty$, the incidence of finite size effects is considerably reduced using the following formulas [1]:

$$\begin{aligned} U_e &= \langle U\rangle - \frac{1-\psi_1}{2\langle\delta U^2\rangle}\langle\delta U^3\rangle + O\left(\frac{1}{N^3}\right), \\ \beta_e &= \langle\beta_\omega\rangle - \lambda_s\frac{1-\psi_1}{2N\langle\delta U^2\rangle}\langle\delta U^3\rangle + O\left(\frac{1}{N^3}\right), \\ \kappa_e &= \frac{1 - \psi_1 - \lambda_s\langle\delta U^2\rangle/N}{\langle\delta U^2\rangle/N} + O\left(\frac{1}{N^2}\right). \end{aligned} \tag{22}$$

Here, $\psi_1 = \frac{6}{5}\epsilon_2 + \frac{11}{30}\epsilon_1$ is a second-order correction term defined from the cumulants $\epsilon_1$ and $\epsilon_2$:

$$\epsilon_1 = \frac{\langle\delta U^3\rangle^2}{\langle\delta U^2\rangle^3}, \quad \epsilon_2 = 1 - \frac{\langle\delta U^4\rangle}{3\langle\delta U^2\rangle^2}. \tag{23}$$

These same calculations enable us to obtain rough estimations for the third- and the fourth-order derivatives of the entropy:

$$\begin{aligned} \zeta_e^3 &= N^2\frac{\partial^3 S(U_e)}{\partial U^3} = N^2\frac{\langle\delta U^3\rangle}{\langle\delta U^2\rangle^3}(1 - 3\psi_1) + O\left(\frac{1}{N^2}\right), \\ \zeta_e^4 &= N^3\frac{\partial^4 S(U_e)}{\partial U^4} = -\psi_2\frac{N^3}{\langle\delta U^2\rangle^3} + O\left(\frac{1}{N}\right), \end{aligned} \tag{24}$$

where $\psi_2 = \frac{12}{5}\epsilon_2 + \frac{41}{15}\epsilon_1$. Ideas behind derivation of this procedure are discussed in the Appendix, Sec. A 1. Applicability of these formulas is subject to applicability of *Gaussian approximation* for describing system fluctuating behavior within the Gaussian ensemble (15). This means that its control parameters $(U_s,\beta_s,\lambda_s)$ must be carefully chosen to guarantee applicability of the Gaussian approximation.

Roughly speaking, the MC estimation procedure (20) to obtain microcanonical caloric curve $\beta(U)$ of a given system resembles practical measurements of this dependence. The statistical ensemble that is employed in this type of MC simulation mimics thermodynamical influence of a measuring instrument, e.g., a thermometer. This procedure is always subjected to statistical uncertainties that could be reduced but never eliminated at all [28]. According to approximation (21), statistical uncertainties for a simultaneous determination energy and its inverse temperature can be estimated in terms of microcanonical curvature $\kappa_e$ as follows:

$$\langle \delta U^2 \rangle \simeq \frac{N}{\kappa_e + \lambda_s} \text{ and } \left\langle \delta \beta_\omega^2 \right\rangle \simeq \frac{1}{N} \frac{\lambda_s^2}{\kappa_e + \lambda_s}. \tag{25}$$

Accordingly, statistical uncertainty of the energy can be reduced by increasing the value of parameter $\lambda_s$. However, this procedure also implies an increasing of statistical uncertainty of its inverse temperature. Therefore, it is absolutely necessary to establish a compromise between these statistical uncertainties, for example, to minimize the *total dispersion* $\Delta_T^2$:

$$\Delta_T^2 = \left\langle \frac{1}{N} \delta U^2 + N \delta \beta_\omega^2 \right\rangle \simeq \frac{1 + \lambda_s^2}{\kappa_e + \lambda_s}. \tag{26}$$

This criterion leads to the following optimal value of the control parameter $\lambda_s$:

$$\lambda_s = \lambda_\Delta(\kappa_e) = \sqrt{1 + \kappa_e^2} - \kappa_e \quad \text{and} \quad \min\left(\Delta_T^2\right) = 2\lambda_\Delta. \tag{27}$$

According to first-order approximation $\delta\beta_\omega = \beta^2 \delta U / C_\omega$ employed in derivation of fluctuation relation (5), the parameter $\lambda_s$ of Gaussian ensemble (15) corresponds to the heat capacity $C_\omega$ of the bath as $\lambda_s \leftrightarrow N\beta^2/C_\omega$. This way, one obtains the optimal value for the heat capacity $C_\omega^{\text{opt}}$ of the bath (or the thermometer):

$$C_\omega^{\text{opt}} = N\beta^2 \left[ \sqrt{1 + \left( \frac{N\beta^2}{C} \right)^2} + \frac{N\beta^2}{C} \right] \tag{28}$$

that reduces as low as possible the statistical uncertainties during a determination of the microcanonical caloric curve of a given system. It is noteworthy that this last result concerns both its practical determination [24] as well as its theoretical MC estimation. The fulfillment of this optimization criterion is the best way to force applicability of the Gaussian approximation for energy distributions, which is a requirement for the application of point statistical estimation formulas (22)–(24). This criterion also leads to a considerable reduction of finite size effects. This fact is shown in Fig. 2 for a model system of relative small size. As clearly evidenced, the Gaussian shape of energy distribution is a very good approximation regardless that its maximum is located inside the region with negative heat capacities.

The number $M$ of MC steps that is necessary to reach a convergence of microcanonical caloric curve $\beta(U)$ and the curvature $\kappa(U)$ with an accuracy $N\langle \delta\beta^2 \rangle + \langle \delta U^2 \rangle / N \leqslant a^2$ and $\langle \delta \kappa^2 \rangle < a^2$ can be estimated as follows:

$$M \simeq \eta / N a^2 \text{ and } M \simeq 2\left(1 + \kappa_e^2\right) \tau / a^2, \tag{29}$$

TABLE I. Dynamic critical exponents $w_\tau$ and $w_\eta$ associated with the size dependencies of decorrelation time $\tau(N) \propto N^{w_\tau}$ and efficiency factor $\eta(N) \propto N^{w_\eta}$ at temperature of PT of the four-state Potts model on the square lattice $L \times L$ with periodic boundary conditions, with $N = L^2$ (after [9]).

| MC method | $w_\tau$ | $w_\eta$ |
|---|---|---|
| Metropolis | $1.06 \pm 0.01$ | $1.42 \pm 0.01$ |
| Extended Metropolis | $0.777 \pm 0.006$ | $0.790 \pm 0.008$ |
| Swendsen-Wang | $0.432 \pm 0.007$ | $0.792 \pm 0.008$ |
| Extended Swendsen-Wang | $0.098 \pm 0.004$ | $0.117 \pm 0.004$ |
| Wolff | $0.474 \pm 0.005$ | $0.833 \pm 0.007$ |
| Extended Wolff | $0.094 \pm 0.006$ | $0.103 \pm 0.006$ |

where $\tau$ is the decorrelation time and $\eta$ the so-called efficiency factor [9]:

$$\eta = \tau \Delta_T^2. \tag{30}$$

Decorrelation time $\tau$ is the minimum number of MC steps needed to generate effectively independent, identically distributed samples in the Markov chain [12]. This quantity crucially depends on the concrete MC algorithm employed in simulations and it is widely regarded as a measure of its efficiency. However, the estimation of microcanonical caloric curve using the present MC methodology is better characterized by the efficiency factor (30), which also includes the incidence of the system fluctuating behavior. The simplest way to improve the convergence of a given extended canonical MC algorithm is to minimize the total dispersion $\Delta_T^2$. As clearly evidenced in Table I, this criterion also involves a sensible improvement of behavior of decorrelation time $\tau$ [9]. Since the efficiency factor $\eta$ for a given extended canonical MC method crucially depends on control parameters $\theta = (U_s, \beta_s, \lambda_s)$ of Gaussian ensemble (15) and the energy value of interest, it is recommended to employ a variable number $M$ of MC moves for calculating each point estimation of microcanonical dependencies (19).

### C. Multicanonical MC methods

Microcanonical entropy $S(U)$ of a system of interest can be estimated from reweighting MC methods that implement multicanonical ensemble [6], as the case of the Wang-Landau method [7]. Roughly speaking, the essential idea of these MC methods is to carry out a progressive reconstruction of a certain probabilistic weight $\omega_M(U)$ that guarantees the existence of *flat energy histograms*:

$$\omega_M(U) W(U) = \text{const}, \tag{31}$$

which allows a direct estimation $\hat{W}(U)$ of density of states $W(U)$. Once an estimation for microcanonical entropy $\hat{S}(U) = \ln \hat{W}(U)$ is obtained, this information can be employed to calculate any statistical expectation value in any desirable statistical ensemble with probability weight $\omega(U)$ as follows:

$$\langle a \rangle = \sum_U a(U) \omega(U) \exp[\hat{S}(U)]. \tag{32}$$

The many advantages of this type of methodology have been extensively reviewed by Landau and Binder in their book

[12]: its capacity to enhance *rare events* and obtain a complete information about density states in a single simulation run [7]; its feasibility to describe systems with complex energy landscapes [37,38] as well as quantum systems [39,40]. A comparison between the present MC methodology and the above reweighting techniques is possible. However, we find it more useful to discuss how their different *working principles* could be combined to enhance their respective potentialities. The application of a reweighting technique to improve the accuracy of microcanonical calculations will be discussed in the next section. Therefore, let us restrict here to discuss how arguments employed in the present MC methodology could be employed to improve some aspects of reweighting MC methods.

The point statistical estimates of microcanonical dependencies (19) can be easily employed to provide a *piecewise estimation* for microcanonical entropy $S(U)$ using numerical integration and interpolation methods. This idea was already employed by Viana Lopes and co-workers to develop a progressive piecewise reconstruction of the probabilistic weight of multicanonical ensemble [41]

$$\omega_M^{(n)}(U) = A\exp[-S^{(n)}(U)]. \tag{33}$$

Here, $S^{(n)}(U)$ is a *polynomial interpolation* of microcanonical entropy inside a previous explored region $U_{n+1} < U < U_0$:

$$S_{VL}^{(n)}(U) = \begin{cases} \beta_0 U, & U > U_0 \\ b_0 + \beta_0 \Delta U_0 - \Delta U_0^2/2\sigma_0^2, & U_1 < U < U_0 \\ \vdots & \vdots \\ b_n + \beta_n \Delta U_n - \Delta U_n^2/2\sigma_n^2, & U_{n+1} < U < U_n \\ b_{n+1} + \beta_{n+1}\Delta U_{n+1}, & U < U_{n+1} \end{cases} \tag{34}$$

plus a *linear extrapolation* outside this region. Here, $\Delta U_i \equiv U - U_i$, the parameters $(b_j,\beta_j,U_j)$ are obtained as follows:

$$\begin{aligned} U_{j+1} &= U_j - \alpha\sigma_j, \quad \beta_{j+1} = \beta_j + \alpha/\sigma_j, \\ b_{j+1} &= \beta_j U_{j+1} - \alpha^2/2, \end{aligned} \tag{35}$$

where the step parameter $\alpha \simeq 2$–$4$. The parameters $\beta_i$ and $\sigma_i$ are point estimates of microcanonical inverse temperature and the energy statistical dispersion within canonical ensemble at the energy $U_i$:

$$\frac{dS(U_i)}{dU} = \beta_i \quad \text{and} \quad -\frac{d^2S(U_i)}{dU^2} \simeq \frac{1}{\sigma_i^2}. \tag{36}$$

External linear extrapolation in (34) enables the exploration of unknown energy region $U < U_{n+1}$ at constant inverse temperature, which is employed to estimate statistical dispersion $\sigma_{n+1}^2$ using the rule

$$\sigma_{n+1}^2 = \langle (U - U_{n+1})^2 \Theta(U_{n+1} - U)\rangle, \tag{37}$$

with $\Theta(x)$ being the Heaviside step function. According to these authors, piecewise estimations (33) and (34) reduce *tunneling times* of multicanonical MC dynamics [41].

A clear limitation of the above procedure is that the microcanonical entropy $S(U)$ is assumed to be *a concave function everywhere*. This means that this method cannot be applied to systems with negative heat capacities. A simple way to overcome this limitation is to employ the following piecewise formula:

$$S_G^{(n)}(U) = \begin{cases} \beta_0 U, & U > U_0 \\ b_0 + \beta_0 \Delta U_0 - \kappa_0 \frac{\Delta U_0^2}{2N}, & U_1 < U < U_0 \\ \vdots & \vdots \\ b_n + \beta_n \Delta U_n - \kappa_n \frac{\Delta U_n^2}{2N}, & U_{n+1} < U < U_n \\ b_{n+1} + \phi(U|\theta_{n+1}), & U < U_{n+1} \end{cases} \tag{38}$$

where the use of statistical dispersions $\sigma_i^2$ was replaced by the microcanonical curvature $\kappa_i$. Moreover, the linear branch of Eq. (34) for energies $U < U_{n+1}$ is now replaced by the function $\phi(U|\theta_{n+1})$ of Gaussian ensemble (15) with control parameters $\theta_{n+1} = (U_{n+1},\beta_{n+1},\lambda_s)$. The optimal value of parameter $\lambda_s$ can be estimated from expression (27) using the previous value of microcanonical curvature $\kappa_e \simeq \kappa_n$. The values of the energy $U_{n+1}$ and its corresponding microcanonical inverse temperature $\beta_{n+1}$ can be estimated as follows:

$$U_{n+1} = U_n - \alpha\sigma_n, \quad \beta_{n+1} = \beta_n + \alpha\kappa_n\sigma_n/N, \tag{39}$$

while the value of constant parameters $b_{j+1}$ is obtained by the continuity condition

$$b_{j+1} = b_j + \beta_j\Delta_j - \kappa_j\Delta_j^2/2N, \tag{40}$$

where $\Delta_j = -\alpha\sigma_j$ and $b_0 = \beta_0 U_0$. Statistical dispersion $\sigma_{n+1}^2$ is also obtained from the rule (37), which can be employed to estimate microcanonical curvature $\kappa_{n+1}$ using the Gaussian approximation

$$\kappa_{n+1} \simeq N/\sigma_{n+1}^2 - \lambda_s. \tag{41}$$

As expected, polynomial interpolation (38) is now able to describe convex regions of microcanonical entropy. The use of Gaussian ensemble in the unexplored energy region $U < U_{n+1}$ enables the access to regions with negative values of microcanonical curvature curve $\kappa(U)$.

Procedures of numerical integration or interpolation, such as (32) and (38), do not produce a significant enhancement of statistical uncertainties of any MC estimation of the entropy using reweighting techniques or the point statistical estimation of microcanonical dependencies (19). However, statistical uncertainties turn significant when one is interested in the calculation of entropy derivatives using MC estimation $\hat{S}(U)$. Although they are small, statistical errors introduce considerable affectation during a direct numerical differentiation of entropy estimation $\hat{S}(U)$. A particular demonstration of this problem is shown in Fig. 5, where entropy estimation $\hat{S}(U)$ of the four-state Potts model on the square lattice $32 \times 32$ obtained from the Wang-Landau MC method was employed to estimate microcanonical caloric curve $\hat{\beta}(U)$ by direct numerical differentiation [9].

One can employ different criteria to reduce *roughness* of numerical derivatives, such as adjacent averaging or Savitzky-Golay filter [42]. To our knowledge, the previous methods do not follow specific statistical criteria to deal with data obtained from MC simulations. We think that a more suitable criterion to obtain smoothly derivatives for MC estimates of entropy $\hat{S}(U)$ is the use of point statistical estimation formulas (22)–(24). Statistical expectation values of this procedure can be obtained

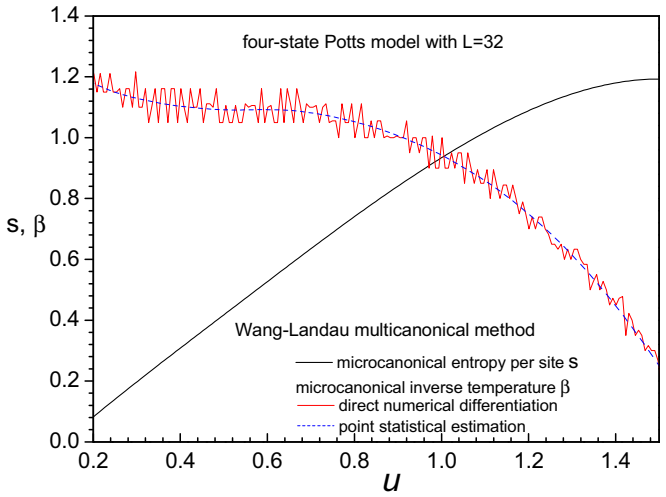


FIG. 5. (Color online) Entropy per site $s(u)$ and microcanonical inverse temperature $\beta(u)$ of 2D four-state Potts model estimated from the Wang-Landau multicanonical algorithm. Here, the variable $u$ denotes the energy per site $u = U/N$, with $N = L^2$.

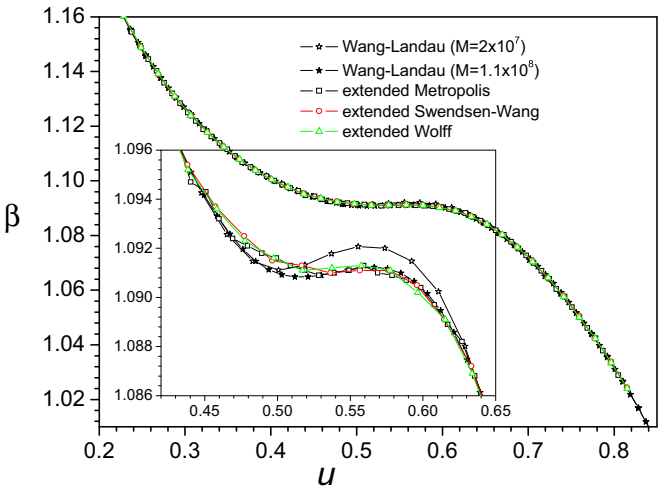


FIG. 6. (Color online) Microcanonical caloric curve of the four-state Potts model system on the square lattice $32 \times 32$ with periodic boundary conditions, which was estimated from two different realizations of the Wang-Landau method and extended versions of canonical MC algorithms of the Metropolis importance sample and Wang-Landau and Wolff cluster algorithms (after [9]). The agreement among all these MC methods is very good, although some small discrepancies are clearly evidenced in the inset panel, where these same dependencies were represented with lower energy and inverse temperature scales in order to appreciate better the mathematical behavior of these curves near PT.

from the application of the formula (32). This procedure was already employed in our previous work [9], whose results are also shown here in Fig. 5. Although these estimations are still affected by incidence of finite size effects, the same ones are very small (see comparative study shown in Fig. 3 of Ref. [2]). Moreover, the same procedure provides a direct estimation for entropy derivatives of higher order. In addition, one can still obtain better improvements of formulas (22)–(24) by including higher-order correlations of the system fluctuating behavior (see additional comments in the Appendix, Sec. A 1).

For comparison purposes, we show in Fig. 6 different estimations of microcanonical caloric curve of this same model system using the extended versions of canonical MC algorithms of Metropolis importance sampling, and cluster algorithms of Swendsen-Wang and Wolff, as well as two runs of the Wang-Landau method of different lengths.[2] According to results shown in the main panel of this figure, the agreement among all these MC methods is very good. Nevertheless, one can verify the existence of small discrepancies in the inset panel. In principle, the results obtained from all these MC methods should converge among them. Therefore, the observed discrepancies reveal an insufficient convergence of these MC simulations. It is noteworthy that the existing discrepancies are more significant inside the energy region that contains PT of this model system, which is not a casual fact. According to Eq. (27) for the minimal total dispersion $\Delta_T^2$, statistical uncertainties during determination of microcanonical caloric curve $\beta(U)$ are larger where microcanonical curvature curve $\kappa(U) = -N\partial^2 S(U)/\partial U^2$ exhibits its lower values. In other words, statistical uncertainties associated with estimation of microcanonical caloric curve are *nonuniform*.

Extended canonical MC algorithms explore a small energy region in each simulation run because of the use of Gaussian ensemble (15) with optimal parameters. Consequently, the length of simulations can locally be increased to achieve the necessary accuracy for each energy region. Such a goal can be fulfilled using estimation (29) for the number $M$ of MC steps. The increase of the length of simulations using the Wang-Landau method involves an increase in the number of visits in regions where convergence of point statistical estimations (22) was already achieved. Perhaps, the exigency of *flat energy histograms* (31) should be replaced by another mathematical form that increases the number of visits in those energy regions where microcanonical curvature curve $\kappa(U)$ exhibits its lower values. For example, such a goal can be achieved by the following ansatz:

$$H(U) \propto f_\kappa(U) = 1 + [\sqrt{1+\kappa^2(U)} - \kappa(U)]^2, \qquad (42)$$

where $f_\kappa(U)$ arises as a *redistribution factor* in the probabilistic weight of multicanonical ensemble

$$\omega_\kappa(U) = A \exp[-S(U)]\, f_\kappa(U). \qquad (43)$$

Unfortunately, a complete analysis and implementation of this type of modifications is beyond the scope of this work. By themselves, these questions deserve a more comprehensive analysis in future works.

[2]For implementing the Wang-Landau multicanonical method, we have considered a minimum entry of 95% of the mean value for histogram of energies visited. First simulation run with $M = 2 \times 10^7$ steps was extended until parameter $f$ reaches the value $f = \exp(10^{-7})$. Second simulation run with $M = 1.1 \times 10^8$ steps was extended until parameter $f$ reaches the value $f = \exp(10^{-8})$.

## III. IMPROVING ACCURACY

### A. Application of the multihistograms method

A main goal of the multihistograms method is the estimation of the number of states $W(U)$. Originally, this method was proposed to extract information of histograms obtained from MC simulations based on the canonical ensemble [13]. However, its relevant expressions admit a direct extension for any probability weight. The energy distribution $p_G(U|\theta)$ associated with Gaussian ensemble (15) is given by

$$p_G(U|\theta) = \omega_G(U|\theta) W(U). \tag{44}$$

Formally, the number of states $W(U)$ is obtained from the energy distribution $p_G(U|\theta)$ as follows:

$$W(U) = p_G(U|\theta)/\omega_G(U|\theta). \tag{45}$$

The probability distribution $p_G(U|\theta)$ can be estimated using the energy histogram $\hat{p}_G(U|\theta)$ of a given simulation:

$$p_G(U|\theta) \simeq \hat{p}_G(U|\theta) = H(U|\theta)/M, \tag{46}$$

where $H(U|\theta)$ is the number of MC moves with final energy $U$, and $M = \sum_U H(U|\theta)$ is the total number of MC moves. The energy histogram $\hat{p}_G(U|\theta)$ is a random quantity with the following mean and variance [13]:

$$\langle \hat{p}_G(U|\theta)\rangle = p_G(U|\theta) \text{ and } \left\langle \delta \hat{p}^2(U|\theta)\right\rangle = p_G(U|\theta)/\mathcal{N}, \tag{47}$$

where $\mathcal{N} = M/\tau$ is the effective number of independent MC moves, with $\tau$ being the decorrelation time [12]. According to the relative error

$$\frac{\Delta p_G(U|\theta)}{p_G(U|\theta)} = \frac{1}{\sqrt{\mathcal{N} p_G(U|\theta)}}, \tag{48}$$

this procedure only allows a reliable estimation of $p_G(U|\theta)$ for a small region near most probable energy $U_e$. This difficulty is avoided combining the information of independent MC runs with different values of control parameters $\theta$. One can employ the estimator $\hat{W}(U)$:

$$\hat{W}(U) = \mathcal{H}(U)/\mathcal{W}(U) \tag{49}$$

for the number of states $W(U)$, while its error can be evaluated as

$$\langle \delta W^2(U)\rangle \simeq \mathcal{H}(U)/\mathcal{W}^2(U). \tag{50}$$

Here, we have considered the superposition functions of probabilistic weights $\mathcal{W}(U)$:

$$\mathcal{W}(U) = \sum_n \mathcal{N}_k \omega_G(U|\theta_k) \tag{51}$$

and the energy histograms $\mathcal{H}(U)$:

$$\mathcal{H}(U) = \sum_k \mathcal{N}_k \hat{p}_G(U|\theta_k), \tag{52}$$

where $\mathcal{N}_k$ is the effective number of independent MC moves for $k$th simulation run. As expected, normalization function $f_k = f(\theta_k)$ of Gaussian ensemble (15) with control parameters $\theta_k$ should be obtained by self-consistency:

$$\exp(-f_k) = \sum_U \exp\left[-\phi(U|\theta_k)\right] \hat{W}(U). \tag{53}$$

Numerical resolution of problem (53) can be carried out using some type of *scheme of successive iterations*, such as the one described in the Appendix, Sec. A 2.

The success of the present methodology relies on a fine tuning of control parameters $(U_s,\beta_s,\lambda_s)$ of Gaussian ensemble (15). As already commented, their optimal values depend on microcanonical estimates $(U_e,\beta_e,\kappa_e)$, whose calculation is precisely the goal of MC simulation. A practical recipe is to use the microcanonical estimates $(U_e^j,\beta_e^j,\kappa_e^j)$ obtained from a previous MC simulation run, whose energy $U_e^i$ is close to energy value of interest $U_e^{j+1}$. We shall employ the following iterative scheme [9]:

$$\begin{aligned} U_s^{j+1} &= U_e^j + \varepsilon_j; \\ \beta_s^{j+1} &= \beta_e^j - \kappa_e^j \varepsilon_j \quad \text{and} \quad \lambda_s^{j+1} = \lambda_\Delta\left(\kappa_e^j\right), \end{aligned} \tag{54}$$

with $\varepsilon_j$ being a variable small energy step. The initial values of the control parameters $(U_s,\beta_s,\lambda_s)$ could be estimated from any canonical MC algorithm far enough from the region of temperature-driven PT. On the other hand, the success of the multihistograms method crucially depends on full coverage of region of interest by energy histograms. To guarantee the overlap between neighboring energy histograms, one can employ the energy dispersion $\Delta U = \sqrt{\langle \delta U^2\rangle}$ of the previous MC simulation $\varepsilon_j = \nu \Delta U_j$, where $\nu$ is a fraction in the interval $0 < \nu < 2$.

Once the estimation of the number of states $\hat{W}(U)$ is obtained, microcanonical entropy $S(U)$ can be evaluated using Boltzmann definition $\hat{S}(U) = \ln \hat{W}(U)$. The calculation of microcanonical dependencies (19) can be performed using the point statistical estimation formulas (22) and (23), where expectation values are evaluated using expression (32). Calculation of microcanonical dependencies (19) demands a good choice of control parameters $\theta$ for each energy. A simple way to achieve this goal is using a simple recalculation procedure. Essentially, roughly values of microcanonical estimates $(U_e^j,\beta_e^j,\kappa_e^j)$ are considered to provide new values for control parameters $\theta^j$:

$$U_s^{j+1} = U_e^j, \quad \beta_s^{j+1} = \beta_e^j, \quad \text{and} \quad \lambda_s^{j+1} = \lambda_\Delta\left(\kappa_e^j\right). \tag{55}$$

The control parameters $\theta^j$ are employed to provide a new estimation of microcanonical estimates $(U_e^{j+1},\beta_e^{j+1},\kappa_e^{j+1})$. This procedure is repeated until microcanonical estimates reach the convergence with a sufficient accuracy. Final values $(U_e,\beta_e,\kappa_e)$ of this procedure are employed to provide a rough estimation of control parameters for other energy values of interest using the scheme (54), where energy step $\varepsilon$ is small but arbitrary. This procedure is repeated until we obtain a smooth estimation of microcanonical dependencies (19) along the energy region of interest.

Maragakis and co-workers have employed in Ref. [44] a superposition of Gaussian functions similar to expression (51) in the framework of Gaussian-mixture umbrella sampling method. However, such a superposition of Gaussians was proposed to estimate a probability distribution using the

reweighted statistics from several previous simulations. The result of this fitting procedure is employed to introduce the so-called biasing potential. In contrast, superposition of Gaussian functions (51) naturally arises here as a consequence of the multihistograms method, specifically, when one combines histograms obtained from independent MC simulations that implement Gaussian ensemble (15). Its introduction does not involve any fitting procedure because of the number of Gaussian weights and their respective control parameters $\theta_k$ were already prefixed by simulations. Only normalization functions $f_k$ of Gaussian ensemble (15) are determined during application of the multihistograms method, but their estimation obeys a self-consistent requirement (53). Gaussian-mixture umbrella sampling was introduced to reconstruct free energy landscapes, while the main purpose of the present methodology is to estimate first derivatives of microcanonical entropy (19).

### B. An application example

We consider the $q$-state Potts model [4]

$$H = -\sum_{(i,j)} \delta_{\sigma_i \sigma_j} \tag{56}$$

defined on the square lattice $L \times L$ with periodic boundary conditions, where $\sigma_i = (1,2,\ldots,q)$ is the spin variable of the $i$th site, while the sum in (56) runs over all nearest neighbors. This family of toy models undergoes both continuous and discontinuous PT at $\beta_s = \ln(1+\sqrt{q})$ in the thermodynamic limit $L \to \infty$. Their MC study can be performed using different canonical MC algorithms, such as the Metropolis importance sample and Swendsen-Wang and Wolff cluster algorithms [3–5], which enable us to perform a comparative study among them. Additionally, we have also considered the Wang-Landau multicanonical MC method [7], whose results are employed here as reference to compare with other microcanonical calculations.

To test the accuracy of the present improvements of Velazquez and Curilef methodology, let us reconsider the study of the same model system of our previous work: the four-state Potts model [9]. According to Baxter's exact results [20], this model undergoes a temperature-driven continuous PT at $\beta_c \simeq 1.0986$ in thermodynamic limit $L \to +\infty$. For the sake of simplicity, let us restrict this discussion to the cases of extended Wolff cluster algorithm [9] and the usual canonical Swendsen-Wang cluster algorithm. We have considered a variable number of MC steps for each calculated point: $M = 9.8 \times 10^4 \eta$ (extended Wolff) and $M = 4.0 \times 10^4 \tau$ (Swendsen-Wang), with $\eta$ and $\tau$ being efficiency factor and correlation time a given run, respectively. Typical values for fraction $\nu$ in control parameters scheme (54): $\nu = 0.05$ for $L = 16$–$22$ and $\nu = 0.5$ for $L = 32$–$90$.

We show in Fig. 7 results of MC simulations for the particular case of lattice size $L = 32$. We have also included microcanonical estimates obtained from the Wang-Landau method using the same data shown in Fig. 6 for $M = 1.1 \times 10^8$. According to dependencies shown in Fig. 7(d), the extended Wolff algorithm exhibits the lower values of efficiency factor $\eta$ and correlation time $\tau$ for the whole energy region considered in this study. This extended canonical MC algorithm exhibits a greater performance in regard to the usual Swendsen-Wang cluster algorithm. Although the canonical ensemble is a particular case of Gaussian ensemble with $\lambda_s = 0$, any MC methods based on the canonical ensemble fails to predict microcanonical dependencies $\beta(u)$ and $\kappa(u)$ near a critical point using point statistical estimation (22). This fact is clearly shown in Figs. 7(a) and 7(b). These systematic deviations of microcanonical estimates obtained from the Swendsen-Wang MC method rely on the failure of Gaussian approximation of canonical energy distributions near a critical point. Such a non-Gaussian behavior of canonical distributions is observed in energy histograms obtained from the Swendsen-Wang MC method, which is shown in Fig. 7(c). On the contrary, Gaussian approximation is fulfilled when one employs Gaussian ensemble (15) with optimal values of control parameters $\theta = (U_s, \beta_s, \lambda_s)$. This fact is also shown in Fig. 7(c) throughout Gaussian shape of energy distribution obtained from the extended Wolff cluster algorithm.

All energy distribution (or histograms) obtained from the extended Wolff and usual Swendsen-Wang MC algorithms were combined using multihistograms method to estimate microcanonical entropy per site $s(u)$. Additionally, we have considered estimation $\hat{s}(u)$ of microcanonical entropy per site obtained from the Wang-Landau method. All these estimations were combined with recalculation procedure to obtain microcanonical dependencies $\beta(u) = \partial s(u)/\partial u$ and $\kappa(u) = -\partial^2 s(u)/\partial u^2$. As clearly evidenced in Figs. 7(a) and 7(b), one observes a full agreement among microcanonical dependencies obtained from the multihistograms method, the point statistical estimates using the extended Wolff algorithm, as well as estimations obtained from the Wang-Landau method. According to the inset panel of Fig. 7(a), the greater discrepancies among all these MC estimations of microcanonical caloric curve $\beta(u)$ are observed near the inverse temperature of PT, which are of order $\Delta\beta \simeq 10^{-4}$.

Curiously, all these MC estimations are consistent in predicting an S bend of microcanonical caloric curve of this model system outside the thermodynamic limit. This mathematical behavior indicates the existence of a small region where microcanonical curvature $\kappa(u) = -\partial^2 s(u)/\partial u^2$ is negative, that is, the existence of an energy region with *negative heat capacities*. The Wang-Landau method fails to predict the branch with negative values of microcanonical curvature curve using direct point statistical estimation (22), while its associated microcanonical caloric curve evidences the S bend. Although the observed deviation is very small, this inconsistency suggests that the Wang-Landau estimation of entropy per site $\hat{s}(u)$ does not fulfill the necessary accuracy to obtain a more precise point statistical estimation of microcanonical curvature. In fact, we have obtained a better estimation of this last dependency by applying a direct numerical differentiation on its microcanonical caloric curve $\beta(u) = \partial s(u)/\partial u$. This second procedure now predicts a branch with negative values of microcanonical curvature curve and its results exhibit a better agreement with estimates obtained from the multihistograms method.

As discussed elsewhere [17], the existence of a branch with negative heat capacity is a typical behavior of *finite systems that undergo a temperature-driven discontinuous PT*. In fact, this mathematical behavior of microcanonical dependencies

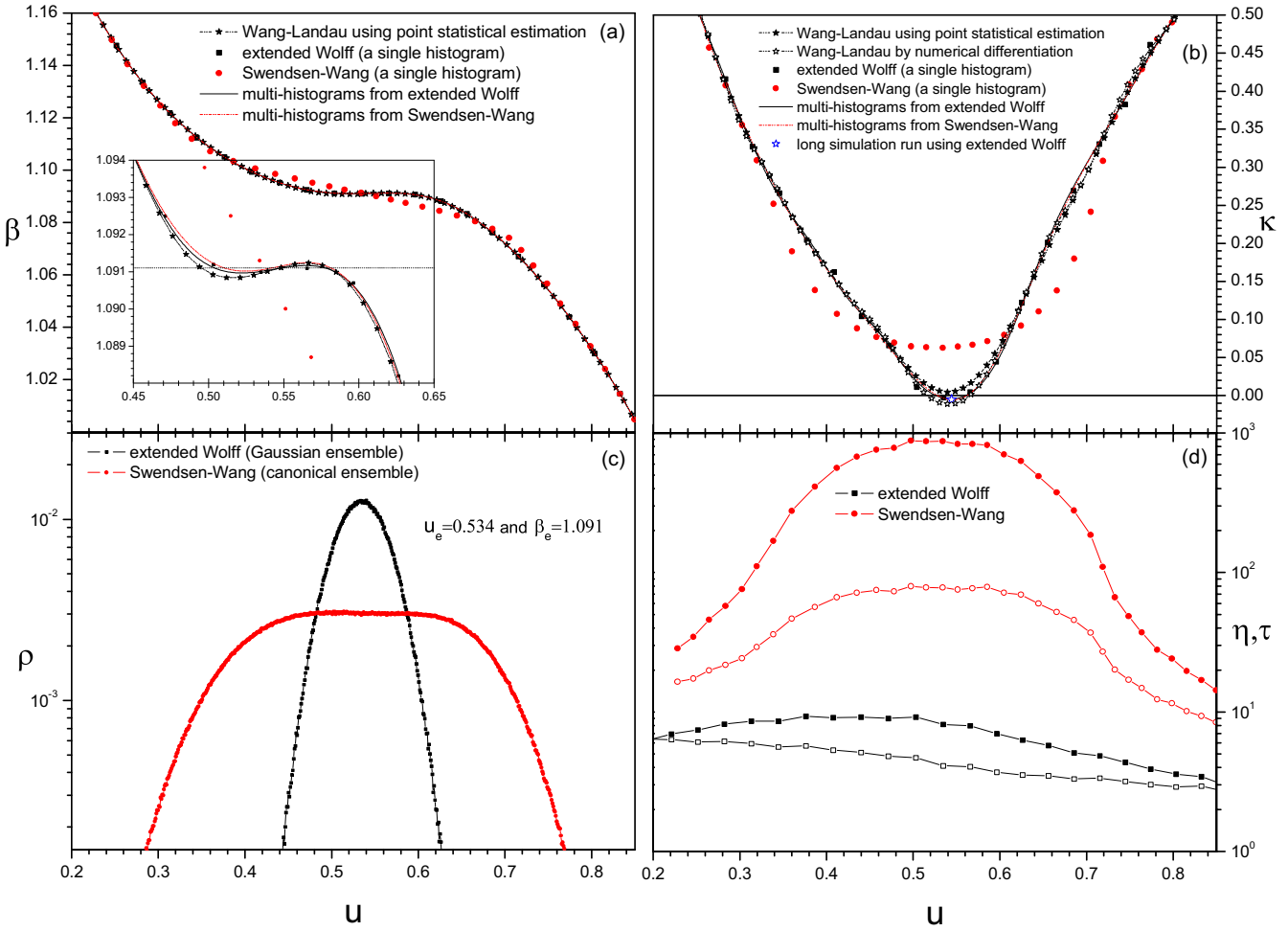


FIG. 7. (Color online) Comparison among results obtained from MC simulations using extended Wolff and usual Swendsen-Wang cluster algorithms. Results from the Wang-Landau method are employed here as reference. (a), (b) Microcanonical dependencies $\beta(u) = \partial s(u)/\partial u$ and $\kappa(u) = -\partial^2 s(u)/\partial u^2$ estimated using point statistical estimation (22), where $u = U/N$ and $s = S/N$ are energy and entropy per site, respectively. Squares and circles are the punctual values of these dependencies using a single energy histogram, while solid and dashed-dotted lines are smooth estimations using recalculation procedure once obtained microcanonical entropy per site $\hat{s}(u)$ derived from the multihistograms method. To check prediction of the multihistograms method for states with minimum curvature, the blue star point corresponds to a point statistical estimation using a single histogram obtained from a very long simulation run with $M = 8.1 \times 10^7$ MC steps using extended Wolff algorithm. Additionally, we have included an estimation of microcanonical curvature by direct numerical differentiation of microcanonical caloric curve estimated from the Wang-Landau method in (a). (c) Energy histograms near critical point for each MC method. (d) Decorrelation time $\tau$ (open squares and circles) and efficiency factor $\eta = \tau \Delta_T^2$ (solid squares and circles) vs the most likely value of energy per particle $u_e$ for each simulation run.

is unambiguously observed in all cases of $q$-state Potts models on the square lattice $L \times L$ with $q > 4$ outside the thermodynamic limit [1,2,9]. To verify the accuracy of this prediction, we have reobtained a point statistical estimation of microcanonical inverse temperature and curvature at the energy with minimal value of microcanonical curvature curve. For this purpose, we have considered a single histogram obtained from a very large simulation with $M = 8.1 \times 10^7 \equiv 8.8 \times 10^6 \eta$ MC steps using the extended Wolff algorithm. Control parameters of Gaussian ensemble (15) for this particular calculation were prefixed using the microcanonical estimates of this notable point $u_s = 0.545$, $\beta_s = 1.0911$, and $\kappa_s = -0.0549$, which were previously estimated from the multihistograms method. Point statistical estimation obtained from this new simulation [the blue star point in Fig. 7(b)] is in full agreement with results already obtained from the multihistograms method.[3] According to estimations (29), statistical uncertainties in microcanonical caloric curve are of order $\Delta\beta < 10^{-5}$, while the ones of curvature are $\Delta\kappa <$

[3]According to results shown in Fig. 7(d), the efficiency factor $\eta$ of extended Wolff algorithm for $L = 32$ varies from 2.9 up to 9.2 in this energy region. Therefore, the number of steps $M_k$ of individual simulations using this cluster algorithm ranges as $M_k = (2.8 - 9.0) \times 10^5$ steps, with a total sum $\sum M_k = 1.4 \times 10^7$. The very large simulation with $M = 8.1 \times 10^7$ steps was not considered for calculations using the multihistograms method. This run was only employed to recalculate microcanonical quantities at the energy with minimum curvature $u \simeq 0.545$.

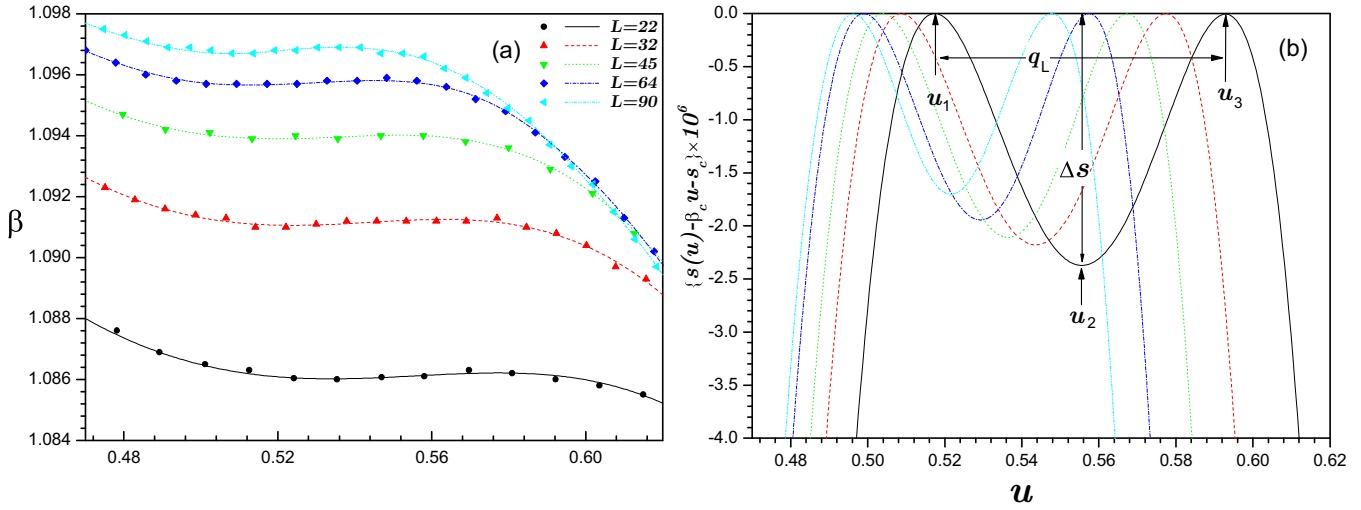


FIG. 8. (Color online) Some microcanonical dependencies of the four-state Potts model on the square lattice $L \times L$ with different $L$, which were estimated considering the multihistograms method combined with extended Wolff algorithm. (a) Microcanonical inverse temperature $\beta(u) = \partial s(u)/\partial u$. (b) Dependency $s^*(u) = s(u) - \beta_c u - s_c$ obtained from entropy per site $s(u)$ and inverse temperature $\beta_c$ corresponding to the temperature-driven PT. This auxiliary function reveals better the existence of a *convex intruder* for entropy per site $s(u)$, which is directly related to the existence of a branch with negative curvature $\kappa(u) = -\partial^2 s(u)/\partial u^2$ or, equivalently, states with negative heat capacities $C < 0$. Typical energies $(u_1,u_2,u_3)$ and entropy defect $\Delta s = s^*(u_1) - s^*(u_2)$ are employed to characterize this convex intruder region, in particular, to estimate the latent heat per site $q_L = u_3 - u_1$.

$3.2 \times 10^{-4}$. This precision allows us to claim that the existence of this S bend of microcanonical caloric curve cannot be attributed to a poor convergence of the data.

For a better understanding, microcanonical dependencies (19) were calculated for different values of the lattice size $L$. Because of our modest computational resources, we have restricted here to MC simulations with lattice sizes $L =$ 22–90 using the extended Wolff algorithm and multihistogram method. Microcanonical dependencies of inverse temperature $\beta(u)$ and entropy per site $s(u)$ are shown in Fig. 8. Again, these results confirm the existence of a branch with negative heat capacities in the four-state Potts model on the square lattice $L \times L$ outside the thermodynamic limit. As usual, the inverse temperature $\beta_c$ corresponding to this type of PT was estimated using the Maxwell area rule [30]

$$\int_{u_1}^{u_3} [\beta(u) - \beta_c]\, du = 0 \rightarrow s(u_3) - s(u_1) = \beta_c\,(u_3 - u_1) \tag{57}$$

in conjunction with conditions

$$\beta(u_1) = \beta(u_2) = \beta(u_3) = \beta_c. \tag{58}$$

Actually, dependence of entropy per site $s(u)$ was replaced in Fig. 9 by the auxiliary function $s^*(u) = s(u) - \beta_c u - s_c$, where $s_c$ is suitable constant. This auxiliary function reveals the existence of a *convex intruder* of microcanonical entropy per site $s(u)$. This energy region of convexity can be characterized by the three relevant energies $(u_1,u_2,u_3)$ and *entropy defect* $\Delta s = s^*(u_1) - s^*(u_2)$. The latent heat per site $q_L$ is evaluated as $q_L = u_3 - u_1$. These notable values are reported in Table II. Size dependencies of inverse temperature $\beta_c$ of the PT and latent heat per site $q_L$ are shown in Fig. 9.

At first glance, the present results are quite confusing. Baxter has demonstrated in the past [20] that latent heat of this model system vanishes. However, one can realize that there is no contradiction. Baxter's exact result only concerns the four-state Potts model on the square lattice in *thermodynamic limit* $L \rightarrow +\infty$. By itself, this result does not forbid the existence of macrostates with *negative heat capacities* for finite systems as the cases analyzed in this MC study. In fact, monotonous decreasing of the latent heat per site $q_L$ is compatible with an eventual vanishing of this quantity when $L \rightarrow +\infty$. Our MC estimations of latent heat per site $q_L$ are consistent with a power-law dependence $q_L(L) \propto (1/L)^z$ with

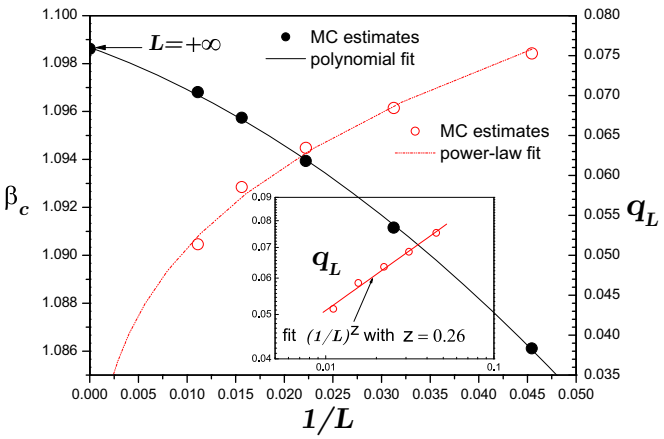


FIG. 9. (Color online) Dependence of inverse temperature $\beta_c$ (black circles) corresponding to temperature-driven PT and latent heat per site $q_L$ (red open circles) on the inverse lattice size $1/L$. Additionally, we have shown the extrapolation of these data when $1/L \rightarrow 0$ using polynomial fits (black line) for the inverse temperature $\beta_c(L)$ and a power-law fit for latent heat per site as $q_L(L) \propto (1/L)^z$ with $z = 0.26 \pm 0.02$, which is also shown in the inset panel using the log - log scale.

TABLE II. Size dependence of some thermodynamic parameters that characterize the *convex intruder* of entropy per site $s(u)$ shown in Fig. 8(b).

| $L$ | $\beta_c$ | $u_1$ | $u_2$ | $u_3$ | $q_L$ | $\Delta s \times 10^6$ |
|---|---|---|---|---|---|---|
| 22 | 1.0861 | 0.5176 | 0.5553 | 0.5929 | 0.075 | 2.37 |
| 32 | 1.0912 | 0.5088 | 0.5437 | 0.5772 | 0.068 | 2.18 |
| 45 | 1.0939 | 0.5040 | 0.5365 | 0.5675 | 0.063 | 2.11 |
| 64 | 1.0957 | 0.4990 | 0.5293 | 0.5575 | 0.058 | 1.94 |
| 90 | 1.0968 | 0.4963 | 0.5216 | 0.5477 | 0.051 | 1.70 |
| $\infty$ | 1.0986 | | | | 0.000 | 0.00 |

$z = 0.26 \pm 0.02$. Of course, it would be desirable to extend the present microcanonical MC estimations for systems with larger lattice sizes $L > 90$, which is beyond our computational capability.

As already demonstrated by Baxter himself [20], the four-state Potts model on the infinite square lattice is a *marginal case*: cases with $q > 4$ exhibit a temperature-driven discontinuous PT, while cases with $q \leqslant 4$ undergo a continuous PT. According to our results, ambiguities in some behaviors can appear for the marginal case $q = 4$ outside the thermodynamic limit. For example, multimodal character of canonical energy distributions during the phase coexistence phenomenon (see example in Fig. 1) leads to an exponential dependence of decorrelation times $\tau(N) \propto \exp(\gamma N)$ with system size $N = L^2$ during MC simulations [12]. For the particular case of the four-state Potts model on the square lattice $L \times L$, canonical MC algorithms exhibit a power-law dependency of decorrelation times $\tau(N) \propto N^{w_\tau}$, whose critical exponents $w_\tau$ were already shown in Table I. As expected, such a power-law dependency of decorrelation times is a typical behavior of finite systems at critical temperature of continuous PT [12]. According to our results, the non-Gaussian form of canonical energy distribution at transition inverse temperature $\beta_c$, as the one shown in Fig. 7(c), is explained by the superposition of two close Gaussian peaks. The widths of these peaks are sufficiently large to hide the existence of a bimodal character of energy histogram within canonical ensemble. This behavior cannot be distinguished in canonical energy distribution of this figure because of defect $\Delta s$ of entropy convex intruder is very small. The proximity of these peaks is the reason why canonical MC algorithms do not follow an exponential dependence of decorrelation time $\tau(N) \propto \exp(\gamma N)$.

Barkema and de Boer presented in the past [45] an interesting Monte Carlo study about a dynamical model with parameters $(d^*,q^*)$ that resembles $d$-dimensional $q$-state Potts models for noninteger values. Curiously, these authors also reported a nonvanishing latent heat per site $q_L$ for the case $d^* = 2$ and $q^* = 4$ considering MC simulations with lattice size $L = 128$. Their estimated value $q_L = 0.019$ seems to be compatible with this study.[4] However, these authors do not attempt to analyze this particular finding because they were more interested in behavior of latent heat for noninteger values of parameter $q^*$ in the thermodynamic limit.

[4]A simple extrapolation of numerical results of Table II using power law $q_L(L) \propto (1/L)^z$ suggests the value $q_L \simeq 0.048$ for $L = 128$.

## IV. FINAL REMARKS

We have combined the extended canonical MC algorithms with the multihistograms method [13], which enable us to improve accuracy of microcanonical calculations using point statistical estimation formulas (22)–(24). The resulting technique is sufficiently accurate to detect subtle thermodynamical behaviors during MC simulations. As an example of application, we have applied this method to reveal the existence of a very small latent heat during occurrence of temperature-driven PT of the four-state Potts model on the square lattice $L \times L$ outside the thermodynamic limit. Our MC estimates of latent heat per site $q_L$ are consistent with a power-law dependence $q_L(L) \propto (1/L)^z$ with $z = 0.26 \pm 0.02$, which predicts a vanishing of this quantity when $L \to +\infty$. Accordingly, the present results are compatible with Baxter's exact result about continuous character of temperature-driven phase transition of this model in the thermodynamic limit $L \to +\infty$.

Velazquez and Curilef methodology [1,2,9] admits other improvements to increase the performance of extended canonical MC methods. A next step is the combination with rejection-free algorithms [46]. If possible, resulting algorithms could exhibit much greater performance. This methodology can also be extended to perform a MC study of systems with several control parameters besides energy and temperature. An important step to achieve this purpose was already done in Ref. [26], where equilibrium fluctuation relation (1) was extended to situations with several thermodynamic variables. As already discussed in this work, some arguments of this methodology could be useful to enhance potentialities of other MC methods, such as the multicanonical method and its variants [6–8]. Some of these questions will be discussed in forthcoming works.

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## APPENDIX: ADDITIONAL DISCUSSIONS

### 1. About point statistical estimation

Formally speaking, the point statistical estimation formulas (22)–(24) is an *inference procedure* to determine best guess for first entropy derivatives [43]. To fix some ideas, let us consider an energy histogram $H(U)$ obtained from a MC simulation based on the Gaussian ensemble (15):

$$H(U) \propto \omega_G(U|\theta) \exp[S(U)]. \tag{A1}$$

Entropy difference $S(U) - S(U_e)$ around the most likely value of energy $U_e$ can be approximated by the following polynomial:

$$P_e(U) = \beta_e \Delta U_e - \kappa_e \frac{\Delta U_e^2}{2N} + \zeta_e^3 \frac{\Delta U_e^3}{6N^2} + \zeta_e^4 \frac{\Delta U_e^4}{24N^3} \tag{A2}$$

with $\Delta U_e \equiv U - U_e$, which is the Taylor power expansion of entropy difference up to four orders of approximation. By definition, the energy $U_e$ obeys the *stationary condition*

$$\beta_\omega(U_e) = \beta_e, \tag{A3}$$

where $\beta_\omega(U)$ is given by the linear ansatz of Gaussian ensemble (14). Accordingly, the microcanonical inverse temperature parameter $\beta_e$ is fully determined by the knowledge of the energy $U_e$. Mathematical form of energy histograms $H(U)$ can be approximated by the following distribution:

$$H(U) \simeq A(\theta,\chi_e)\exp\left[-Q(U|\theta,\chi_e)\right], \tag{A4}$$

where $A(\theta,\chi_e)$ is a normalization constant and $Q(U|\theta,\chi_e)$ is the four-order polynomial

$$Q(U|\theta,\chi_e) = \phi(U|\theta) - P_e(U). \tag{A5}$$

As naturally expected, parametric distribution (A4) improves Gaussian approximation of energy distributions by including finite size $1/N$ effects. The unknown microcanonical parameters $\chi_e = (U_e,\kappa_e,\zeta_e^3,\zeta_e^4)$ can be obtained using suitable *estimators* [43]. In particular, point statistical estimation formulas (22)–(24) follow from the application of the known *method of moments* combined with a perturbative $1/N$ expansion. The idea is to perform calculation of energy moments of $n$ order:

$$\mu_n = \mathbf{E}\left(U^n\right) = \frac{\sum_U U^n \exp\left[-Q(U|\theta,\chi_e)\right]}{\sum_U \exp\left[-Q(U|\theta,\chi_e)\right]} = f_n(\chi_e|\theta) \tag{A6}$$

with $n = 1$–$4$. Afterwards, the concrete analytical expressions of functions $f_n(\chi_e|\theta)$ are inverted as follows:

$$\mu_n = f_n(\chi_e|\theta) \to \chi_e = g_e(\mu_1,\mu_2,\mu_3,\mu_4|\theta). \tag{A7}$$

Finally, the estimators $\hat{\chi}_e$ of microcanonical parameters $\chi_e$ are obtained replacing $\mu_n$ by the sample moments

$$\hat{\mu}_n = \frac{\sum_U U^n H(U)}{\sum_U H(U)}. \tag{A8}$$

Further details about this procedure are discussed in the appendix of Ref. [2].

### 2. Iterative scheme

First, it is convenient to notice that normalization functions $f_k$'s in self-consistent problem (53) are undetermined by an additive term. If the set of values $f = \{f_k\}$ represents a solution of this problem, the set $f^* = \{f_k^*\}$ with $f_k^* = f_k + C$ also represents a solution. This fact implies that the estimator $\hat{W}(U)$ is undetermined by a constant factor $\hat{W}^*(U) = \hat{W}(U)\exp(-C)$. This arbitrariness is not a problem because only entropy change $S(U) = \ln W(U)$ for different energies is thermodynamically relevant. Anyway, we shall impose the following constraint

$$\sum_k f_k = 0 \tag{A9}$$

to avoid this arbitrariness. Self-consistent problem (53) is solved in this work using the following *scheme of successive iterations*:

(1) A rough estimation $f^n = \{f_k^n\}$ is employed to obtain an estimation for number of states $\hat{W}^n(U)$.

(2) A tentative set of values $\check{f}^n = \{\check{f}_k^n\}$ is obtained from normalization condition

$$\exp\left(-\check{f}_k^n\right) = \sum_U A_k \exp\left[-\phi(U|\theta_k)\right]\hat{W}^n(U). \tag{A10}$$

(3) The set $\check{f}^n$ is displaced as follows:

$$\tilde{f}_k^n = \check{f}_k^n - \frac{1}{Q}\sum_n \check{f}_n^n \tag{A11}$$

to guarantee imposition of constraint (A9), with $Q$ being the number of histograms.

(4) A new approximation $f^{n+1} = \{f_k^{n+1}\}$ is obtained as follows:

$$f_k^{n+1} = f_k^n + \epsilon\left(\tilde{f}_k^n - f_k^n\right), \tag{A12}$$

where $\epsilon$ is a small positive number.

The present iterative scheme is repeated until the convergence error $\delta_n$,

$$\delta_n = \sqrt{\frac{1}{Q}\sum_k \left(\tilde{f}_k^n - f_k^n\right)^2}, \tag{A13}$$

reaches a desirable accuracy. Typically, we have employed the values $\epsilon = 0.1$ and $\delta_n < 10^{-6}$.


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