First-order phase transitions: A study through the parallel tempering method

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We study the applicability of the parallel tempering (PT) method in the investigation of first-order phase transitions. In this method, replicas of the same system are simulated simultaneously at different temperatures, and the configurations of two randomly chosen replicas can occasionally be interchanged. We apply the PT method for the Blume-Emery-Griffiths model, which displays strong first-order transitions at low temperatures. A precise estimate of coexistence lines is obtained, revealing that the PT method may be a successful tool for the characterization of discontinuous transitions.

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I. INTRODUCTION

Due to the absence of exact solutions on most systems, Monte Carlo methods play an important role not only in statistical physics and critical phenomena but also in other areas. Usually, the Metropolis [1] and the Glauber [2] algorithms are used to lead the system to the Gibbs distribution. Despite their simplicity and generality, difficulties appear in studying the emergence of phase transitions when these algorithms are used to generate the microscopic configurations. Several techniques have been proposed to circumvent these difficulties, such as the multicanonical technique [3], cluster algorithms (which work properly not only for reducing critical slowing down [4], but also for eliminating metastability in first-order transitions [5–7]), the Wang-Landau method [8], simulated tempering [9], and replica exchange, also named *parallel tempering* (PT) *methods* [10,11].

Special attention has been devoted to this last approach, due to its relative simplicity in comparison with other approaches, and its enormous applicability for several systems in the framework of both statistical mechanics [12–15] and molecular dynamics [15,16]. Essentially, the PT method consists of simulating simultaneously a given set of replicas of the same system at different temperatures and, occasionally, interchanging the configuration of two randomly chosen elements of those replicas. This exchange between pairs of replicas allows for the implementation of an ergodic walk in the configuration space when the elements of the pair are separated by large free-energy barriers.

Although the PT method has been widely used in several contexts, an open question concerns its applicability for the investigation of first-order phase transitions [10]. In fact, since in discontinuous transitions a gap in the energy might lead to a small probability of accepting exchanges between replicas, this appears not to be a favorable scenario for PT.

In this paper, we give a further step in this direction by applying the PT method to study and characterize first-order transitions. We will consider the well known spin-1 Blume-Emery-Griffiths (BEG) model [17], which possesses a rather rich phase diagram with different structures, including first-order transitions in the regime of low temperatures. As we shall see, the PT method can be applied because thermodynamic properties are actually described by continuous functions when finite systems are simulated. In fact, the discontinuity of thermodynamic properties occurs only in the thermodynamic limit. However, smooth curves are obtained only when one uses a dynamics yielding a correct sampling of the configuration space [5,7,8]. In particular, the use of the PT method allows for application of a new finite-size procedure for the study of first-order phase transitions, as proposed in Ref. [7]. It is worth mentioning that a PT-based analysis of first-order transitions has recently been proposed by Neuhaus *et al.* [18]. That approach is, however, rather different from the one adopted here.

This paper is organized as follows. In Sec. II we present the model, in Sec. III we describe the PT method, in Sec. IV we discuss the numerical results, and in Sec. V we give the conclusions.

II. MODEL

The spin-1 BEG model is described by the following Hamiltonian:

$$\mathcal{H} = -J\sum_{(i,j)} \sigma_i\sigma_j - K\sum_{(i,j)} \sigma_i^2\sigma_j^2 + D\sum_i \sigma_i^2, \qquad (1)$$

where σ_i denotes the spin variable of the ith site of the lattice, which assumes the values ± 1 and 0, and the sums run over the nearest-neighbor spins on a d-dimensional lattice with $V=L^d$ sites. The parameters J,K are the nearest-neighbor spin couplings and D is the quadrupole moment. We have two order parameters defined as follows: $q=\langle\Sigma_{i=1}^V \sigma_i^2\rangle/V$ and $m=\langle\Sigma_{i=1}^V \sigma_i\rangle/V$. The BEG model will be considered for a square lattice and periodic boundary conditions.

III. PARALLEL TEMPERING METHOD

In the parallel tempering method, configurations at high temperatures are used to perform an ergodic walk at low temperatures. To this end, we simulate, for fixed values of D, a set of N replicas in the interval of temperatures $\{T_1,\ldots,T_N\}$, where T_1 and T_N are extreme temperatures.

The dynamics is composed of two parts. In the first part, each one of the N replicas is simulated according to the Metropolis algorithm. For the ith replica a given site k of the system is chosen at random and we select, with equal probability, one of the two other possible spin values σ_k' such

that $\sigma_k' \neq \sigma_k$. The spin variable σ_k is then replaced with σ_k' according to the Metropolis prescription: $p_k = \min\{1, \exp(-\beta\Delta\mathcal{H})\}$ [1], where $\Delta\mathcal{H} = \mathcal{H}(\sigma_k') - \mathcal{H}(\sigma_k)$ and $\beta = 1/k_B T$. In the second part of the dynamics, PT is implemented. After a given number of Monte Carlo steps, the exchange of configurations of two replicas at temperatures T_i and T_j is performed with the probability $p_{ij} = \min(1, \exp\{(\beta_i - \beta_j)[\mathcal{H}(\sigma_i) - \mathcal{H}(\sigma_j)]\})$, where $T_j > T_i$, $j = i + \delta$, and δ denotes the "distance" between two arbitrary replicas. The probability p_{ij} depends on $(\beta_i - \beta_j)$ and for this reason the performance of the method will depend on the distance between the replicas. If the difference is large enough, exchanges will hardly be performed and the PT method will not provide any improvement in the results.

In this paper, we adopt two independent procedures to choose the interval of temperatures. In the first one, the distance between adjacent temperatures obeys a geometric progression. Some authors have shown [19,20] that, while this procedure works well when specific heat of the system is about constant, at the emergence of a phase transition, when the specific heat diverges, its efficiency is reduced. For this reason, we adopted a second procedure, which consists in distributing temperatures in regular intervals between T_1 and T_N for a given small size system. By increasing L, we introduce additional temperatures between T_i and T_{i+1}. This procedure is necessary because the exchange probability in general decreases as L increases. We have verified that both procedures lead to the same results, within the statistical errors.

Concerning the replica exchanges, we also consider exchanges between nonadjacent sites. This is implemented in this work by allowing δ to range in the interval $\delta = 1, \ldots, 6$. As will be shown, although nonadjacent exchanges have been less studied [14,15], because the probability of performing a given exchange decreases when δ increases, they have been revealed to be essential mechanisms in eliminating hysteretic effects.

IV. NUMERICAL RESULTS

We have simulated three different values of K/J, given by $K/J = 0$, 3, and 3.3. Note that the first case $(K/J = 0)$ corresponds to the well known Blume-Capel model. Replicas are distributed in the intervals $T_1 = 1.5 \leqslant T \leqslant 2.2 = T_N$, for $K/J = 3$ and 3.3, and $T_1 = 0.4 \leqslant T \leqslant 0.62 = T_N$, for $K/J = 0$. We have simulated systems with size L ranging from $L = 10$ up to 40, and we considered 8×10^7 Monte Carlo (MC) steps to evaluate the appropriate quantities after equilibrating the system. For all values of K/J considered here, the system displays two ferromagnetic phases (rich in spins + and −) for small values of D. Also, a paramagnetic phase (rich in spins 0) occurs for high values of D. A strong first-order phase transition between the ferromagnetic and paramagnetic phases occurs for a given value of D that depends on K/J and T.

The first inspection of the applicability of PT for first-order transitions is shown in the inset of Fig. 1, where we compare the PT results with those obtained by using only the Metropolis algorithm. When only the Metropolis algorithm is used in the simulation, the system gets trapped in metastable states and even after 8×10^7 MC steps it does not undergo a transition to the stable phase. This effect does not occur when we use PT with nonlocal exchanges, since the system becomes able to pass from one phase to the other. The efficiency of the PT method is also corroborated by the agreement with results obtained from cluster algorithms [7], where a smooth curve is obtained for the order parameter. However, as mentioned previously, when one considers only exchanges of configurations between nearest-neighbor replicas, hysteresis is still present, as shown in Fig. 1.

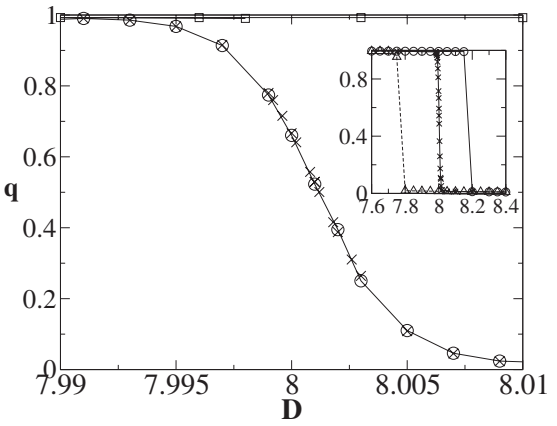

FIG. 1. Order parameter q as a function of D for $K/J = 3$, $T = 1.5$, and $L = 30$ obtained from parallel tempering (symbol ×) and cluster algorithms (circles). Squares correspond to data obtained from parallel tempering with exchanges only between nearest-neighbor replicas. In the inset, circles and triangles refer to the Metropolis algorithm, whereas the symbol × refers to the parallel tempering.

The role of nonlocal exchanges is analyzed in more detail by considering the time evolution of thermodynamic properties at the phase coexistence. In Fig. 2 we plot, for a single run, the order parameter q starting from two different initial

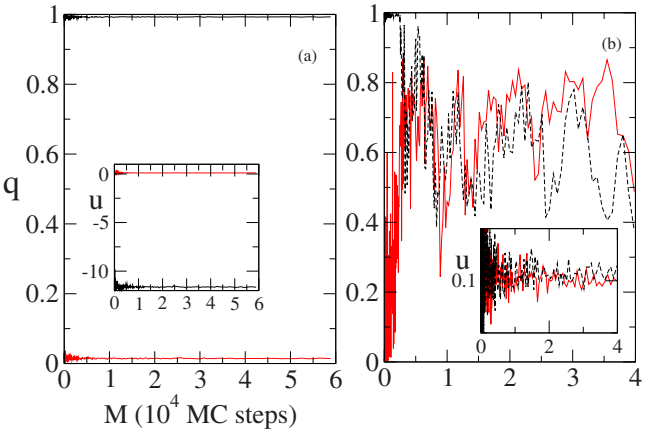

FIG. 2. (Color online) Time evolution of the order parameter q for a single run starting from two independent initial configurations simulated with (a) the Metropolis algorithm and (b) the PT method, for $L = 20$, $T = 1.5$, $D = 8.0$, and $K/J = 3$. In the insets the time evolution of the total energy per volume u is given for those initial configurations. In contrast with PT, until $M = 6 \times 10^4$ MC steps the Metropolis algorithm provides a nonergodic simulation.

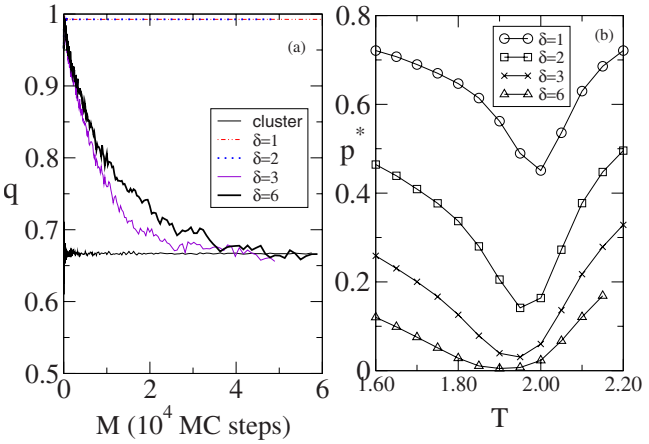

FIG. 3. (Color online) (a) Time evolution of the order parameter q simulated by cluster algorithm and PT with exchanges between i and its $(i+\delta)$th next-neighbor replica ($\delta=1$, 2, 3, and 6) for $L=20$ and 500 independent runs. (b) shows the mean probability p^* versus T for different δ.

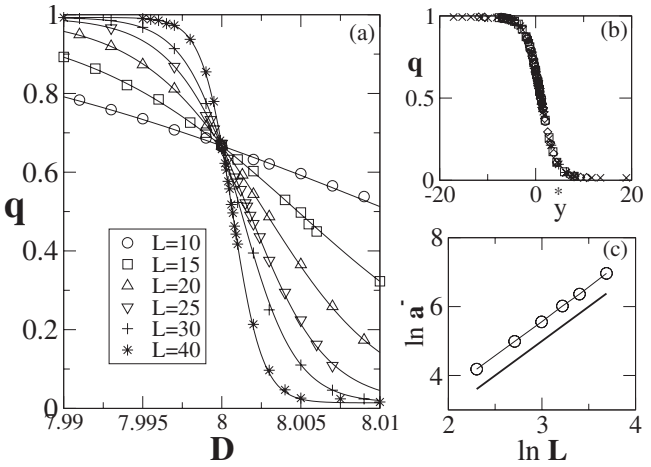

FIG. 4. Order parameter per volume q versus D for several values of the system size L for $K/J=3$ and $T=1.5$. Continuous lines correspond to the fittings defined by Eq. (2). In (b) we have a collapse of all data by using the relation $y^*=(D-D_0^*)L^2$. In (c) we have a log-log plot for the quantity $\bar{a}$ as a function of L. The straight line has slope 2.00(1).

configurations for $K/J=3$, $T=1.5$, and $L=20$. In the inset of each graph, we plot the time evolution of the total energy per volume u for the same initial configurations. In contrast with PT, until $M=6\times10^4$ MC steps, the simulation is not ergodic when the system is simulated with the Metropolis algorithm. Next, in Fig. 3(a) the time evolution of the system simulated via PT with local and nonlocal exchanges is compared with the results provided by cluster algorithms. Note that, for $\delta>2$ and $M>3\times10^4$ MC steps, the time evolution of the PT simulation for q converges to $q\approx2/3$ (as will be explained later), in agreement with cluster algorithm simulations. A similar behavior is obtained in all cases for the quantity m. In Fig. 3(b) we show the exchange mean probability $p^*=\langle\min(1,\exp\{(\beta_i-\beta_j)[\mathcal{H}(\sigma_i)-\mathcal{H}(\sigma_j)]\})\rangle$ [14] as a function of T for different distances δ between replicas, and $L=20$. Except for $\delta=1$, the minimum in p^* occurs at $T\approx1.95$, indicating the coexistence between the ferromagnetic phases, a paramagnetic phase rich with spins 0, and a disordered phase, that takes place in the limit of high temperatures [17]. Our results show that, although nonlocal exchanges are performed less frequently than local ones, they are fundamental for ensuring an ergodic simulation of the system. Next, we will describe the methodology employed in determining coexistence lines. Their location will be derived from finite-size analysis for both the order parameter q and the susceptibility χ_T.

Although a discontinuous phase transition is characterized by a jump in the order parameter, the discontinuity takes place only in the thermodynamic limit. For finite systems, not only the order parameter but also other quantities are described by continuous functions [7,8]. In this case, the behavior of physical quantities scales with the volume of the system [22,23]. In Fig. 4, the order parameter q is shown as a function of D for several values of L.

Although isotherms present strong dependence on the system size, they intersect one another at the point $D=D_0^*=8.0000(1)$ and $q\approx2/3$. As explained in Refs. [7,24], by means of two different lines of reasoning, the point where all isotherms cross is independent of the lattice size. This can be understood by recalling that in the regime of low temperatures two ferromagnetic phases ($q\approx1$) coexist with a paramagnetic phase rich in spins zero ($q\approx0$) at $D=D_0^*$, yielding $q\approx2/3$ for all system sizes. Therefore, the crossing point can be used as a criterion to estimate the transition point. As will be shown later, the estimate of D_0^* agrees very well with the value D_∞^* obtained from finite-size analysis for the susceptibility χ_T. In Fig. 4(b), we describe the collapse of all data by the expression $y^*=(D-D_0^*)L^2$, confirming the dependence on the volume. At low temperatures, the relation between q and the system size L and D is expressed by the following equation [7,25]:

$$q=\frac{b+ce^{-\bar{a}z}}{1+de^{-\bar{a}z}}, \tag{2}$$

where $\bar{a}$, b, c, and d are fitting parameters and $z\equiv D-D_0^*$. In Fig. 4(a), continuous lines correspond to the fittings proposed by Eq. (2). The parameter $\bar{a}$ scales with the volume, as shown in Fig. 4(c). In the thermodynamic limit $L\to\infty$, while the quantity $\bar{a}$ diverges, the order parameter q does not. According to Eq. (2), in the ferromagnetic phase, which occurs in the region $D-D_0^*<0$, we have that $q\to c/d$ as $L\to\infty$. On the other hand, in the paramagnetic phase, which appears for $D-D_0^*>0$, $q\to b$ as $L\to\infty$. For $D=D_0^*$, we have a jump in q, indicating a discontinuous phase transition.

In the second analysis, we determine the transition point by examining the susceptibility $\chi_T=\beta L^2(\langle q^2\rangle-\langle q\rangle^2)$. On increasing D toward the coexistence line, one observes a sharp peak in χ_T at D_L^* for all system sizes, as shown in Fig. 5(a). The deviation between D_L^* and its asymptotic value D_∞^* decays as L^{-2} in a first-order transition [22,23]. Our results satisfy this asymptotic relation, as can be seen in Fig. 5(b). From this law, we have obtained the extrapolated value $D_\infty^*=8.0000(1)$, which agrees with the estimate D_0^* obtained pre-

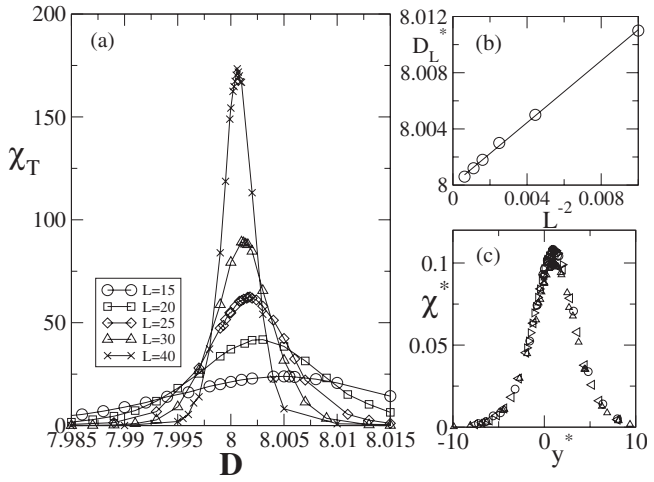

FIG. 5. Susceptibility χ_T versus D for several values of the system size L, $K/J=3$, and $T=1.5$. In (b), we plot the value of $D=D_L^*$ in which χ_T is maximum, as a function of L^{-2}. In (c) we have a collapse of all data using the relations $\chi^*=\chi_T/L^2$ and $y^*=(D-D_\infty^*)L^2$.

viously and also agrees with the result $\bar{D}=8.0000(1)$ obtained from a cluster algorithm for the BEG model [7]. In Fig. 5(c) we observe that all curves coalesce to $\chi^*=\chi_T/L^2$ and $y^*=(D_L^*-D_\infty^*)L^2$, confirming once again the scaling with volume.

It is worth emphasizing that, when one uses only the Metropolis algorithm to generate the configurations, neither the crossing among isotherms nor accurate finite-size analysis for smooth curves is possible, due to the presence of hysteresis effects, as can be seen in Fig. 1.

In Figs. 6 and 7, we repeat, for $K/J=3.3$ and $T=1.5$, both analyses presented above for determining phase coexistence. From the first procedure, where all isotherms are to be fitted by Eq. (2), the crossing is given by $q\approx 2/3$ and

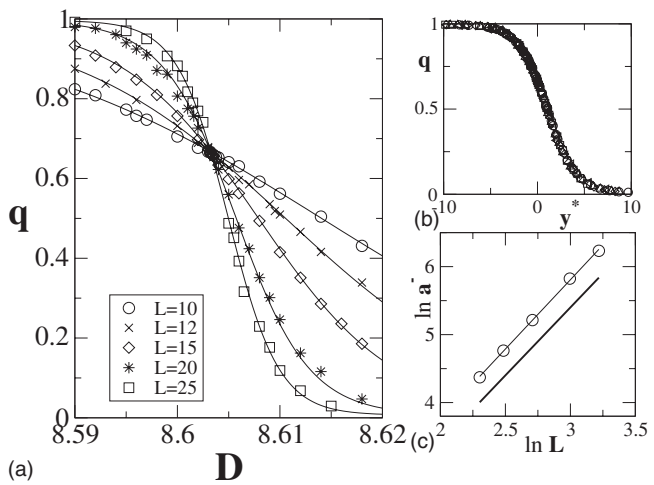

FIG. 6. Order parameter per volume q versus D for several values of the system size L for $K/J=3.3$ and $T=1.5$. Continuous lines stand for the fittings defined by Eq. (2). In (b) we have a collapse of all data using the relation $y^*=(D-D_0^*)L^2$. In (c) we have the log-log plot of $\bar{a}$ versus L. The straight line has slope 2.00(1).

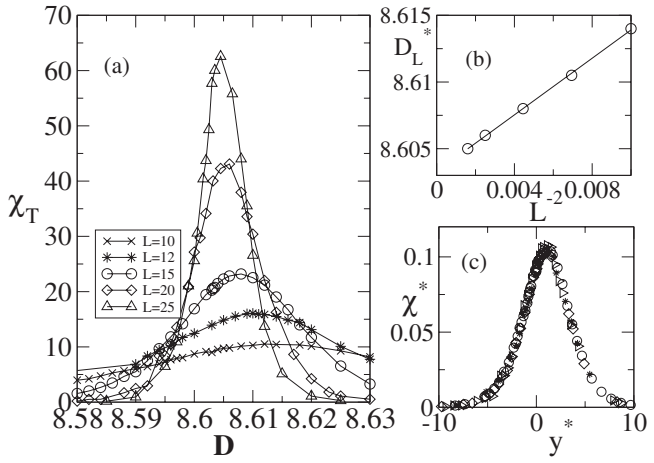

FIG. 7. Susceptibility χ_T versus D for several values of the system size L, $K/J=3.3$, and $T=1.5$. In (b), we plot the value of $D=D_L^*$ in which χ_T is maximum, as a function of L^{-2}. In (c) we have a collapse of all data using the relations $\chi^*=\chi_T/L^2$ and $y^*=(D-D_\infty^*)L^2$.

$D_0^*=8.6032(1)$. This estimate agrees with the value $D_\infty^*=8.6033(1)$ obtained from finite-size analysis for the quantity χ_T, as shown in Fig. 7. These estimates, both obtained by using PT, are in good accordance with the value $\bar{D}=8.6032$ obtained by Rachadi and Benyoussef from cluster algorithms [6].

In the last analysis, we show in Fig. 8 numerical results for $K/J=0$ considering $T=0.4$. When all isotherms are fitted with Eq. (2), the intersection point turns out to be given by $q\approx 2/3$ and $D_0^*=1.9968(1)$. The collapse of data using this estimate of D_0^* confirms again the adequacy of this procedure for the estimation of the transition point. Repeating this procedure for $T=0.5$, we verify that all isotherms cross the abscissa at $D_0^*=1.9879(1)$, which is in fair agreement with the

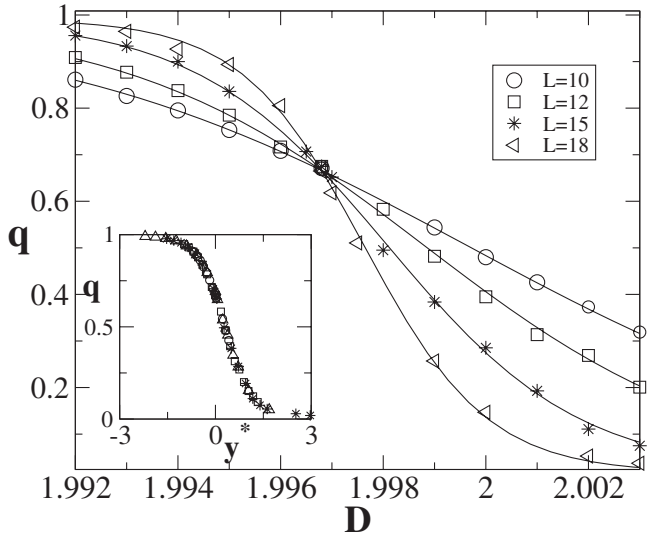

FIG. 8. Order parameter per volume q versus D for several values of system size L, for $K/J=0$ and $T=0.4$. Continuous lines stand for the fittings defined by Eq. (2). In the inset, we have a collapse of all data using the relation $y^*=(D-D_0^*)L^2$.

estimates $T=0.499(3)$ and $\bar{D}=1.992$ [21], by means of the Wang-Landau method.

V. CONCLUSIONS

In this paper, we have applied the parallel tempering method for the study of first-order transitions. We have considered different regions of the phase diagram of the BEG model, for which the usual Metropolis algorithm leads to strong hysteresis at phase coexistence, providing no reliable estimates of the coexistence lines. On the other hand, by using PT it was possible to circumvent the free-energy barriers and as a consequence hysteretic effects were eliminated. All results obtained via PT allowed us to locate the transition points precisely by means of two techniques, whose estimates agree with those obtained from other procedures, such as cluster algorithms and, in one case, with the Wang-Landau method. Although the agreement between results obtained from PT and cluster algorithms has been shown to be very good, cluster algorithms are more specialized, since each model requires a specific cluster algorithm that takes into account the appropriate transitions. On the other hand, PT is general and can be used, in principle, for any system. We remark that more studies of first-order transitions using parallel tempering are still required, in order to have a better comprehension of its performance.

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[24] C. E. Fiore, V. B. Henriques, and M. J. de Oliveira, J. Chem. Phys. **125**, 164509 (2006).
[25] The expression (2) is derived from the theory of Borgs and Kotecký, where it was shown that at low temperatures the partition function for two or more coexisting phases can be expressed in terms of the metastable free energy of each phase. By taking the derivative of the logarithm of the partition function with respect to D, one gets an expression for q, as given in Eq. (2). More details can be found in Ref. [7].