Exploiting a semi-analytic approach to study first order phase transitions

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In a previous contribution, Phys. Rev. Lett 107, 230601 (2011), we have proposed a method to treat first order phase transitions at low temperatures. It describes arbitrary order parameter through an analytical expression \( W \), which depends on few coefficients. Such coefficients can be calculated by simulating relatively small systems, hence with a low computational cost. The method determines the precise location of coexistence lines and arbitrary response functions (from proper derivatives of \( W \)). Here we exploit and extend the approach, discussing a more general condition for its validity. We show that in fact it works beyond the low \( T \) limit, provided the first order phase transition is strong enough. Thus, \( W \) can be used even to study athermal problems, as exemplified for a hard-core lattice gas. We furthermore demonstrate that other relevant thermodynamic quantities, as entropy and energy, are also obtained from \( W \). To clarify some important mathematical features of the method, we analyze in details an analytically solvable problem. Finally, we discuss different representative models, namely, Potts, Bell-Lavis, and associating gas-lattice, illustrating the procedure broad applicability.

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I. INTRODUCTION

First order phase transitions (FOPTs) occur in all sort of processes in nature [1], being extensively studied under different point of views and by a great diversity of approaches [2]. However, for strong FOPTs or at low temperatures, proper and reliable analysis still may be challenging [3, 4]. This is so because in such contexts many simulation methods either can face technical difficulties (e.g., associated to very slow convergence) or demand considerable computational efforts (e.g., due to the necessity to simulate large systems).

To overcome some of the above mentioned problems, in a recent short contribution [5] we have proposed a general semi-analytic method (a not so common approach in this area [6]) to deal with FOPTs at low \( T \)'s. The method combines simple ideas, resulting in an accurate “combo” protocol to study FOPTs. Briefly (details in Sec. II): (a) considering a special decomposition for the partition function at low \( T \)'s, an analytical expression \( W \) to characterize FOPTs (e.g., order parameter) is derived; (b) \( W \) depends on some coefficients, but which can be determined through few numerical simulations (thus, from a computationally inexpensive procedure); and (c) highly profiting from the analyticity of \( W \) and using finite scale analysis for rather small systems, location of the transition points, order parameters behavior, and response functions (like specific heats and compressibilities), are obtained with good precision.

In the original paper [5], we have demonstrated the framework power by means of different examples, including the analysis of complicated (and often hard to simulate) Hamiltonians which describe diverse effects, such as water-like anomalies and ferrimagnetic-ferromagnetic and ferromagnetic-ferromagnetic transitions. Nevertheless, distinct important aspects of the approach were not addressed in-depth.

Here we further explore the method, unveiling some of its mathematical and conceptual features. We address the approach extent of validity, demonstrating it can work fine beyond the originally derived regime of applicability, i.e., at low \( T \)'s. We propose a concrete condition (testable by simple simulations) which shows it can lead to good results in instances of strong FOPTs. Besides order parameters and their derivatives (i.e., generalized susceptibilities), we discuss examples of other relevant thermodynamic quantities, like entropy and energy, that around the phase transition are also well described by \( W \) (given that in such cases, the coefficients for \( W \) are properly determined).

The paper is organized as the following. The method main ideas and key expressions are summarized in Sec. II (for completeness, full derivations are presented in the Appendix). To clarify important technical aspects of the approach, an exactly solvable model [7] is discussed in Sec. III. In Sec. IV, an extensive analysis of representative models is carried out. The Potts model [8], displaying extreme FOPTs for large \( q \) values (and for which the transition points are known exactly), is thoroughly investigated, including entropy and energy. The method high numerical accuracy is illustrated with the Bell-Lavis model [9]. Taking the associating lattice gas (ALG) model [10, 11] as an example, it is shown that the approach can be used for higher temperatures, provided the phase transition is sufficiently strong. Considering a hard-core gas lattice model, it is demonstrated that even athermal problems can be studied with the method. Guided by the numerical simulations and straightforward thermodynamic arguments, a general condition setting the approach validity is proposed in Sec. V. Numerically, it is based on the calculation of the order parameter mul-
timodal probability distribution at the coexistence. Finally, remarks and conclusion are drawn in Sec. VI.

II. THE METHOD

A. Main ideas and results

The method start point is the fact that for finite systems at low temperatures and having \( \mathcal{N} \) coexisting stable phases, the partition function is well described by a sum of \( \mathcal{N} \) exponential terms, or \( \beta = 1/(kT) \)

\[
Z = \sum_{n=1}^{\mathcal{N}} \alpha_n \exp[-\beta V f_n]. \tag{1}
\]

For each phase \( n \), \( f_n \) is the free energy per volume \( V \) and \( \alpha_n \) the degeneracy (see also the Appendix).

Typically, relevant thermodynamic quantities have the form \( W = -(\beta V)^{-1} \left( \partial / \partial \xi \right) \ln[Z] \), with \( \xi \) an appropriate control parameter (e.g., chemical potential \( \mu \), temperature, etc.). For instance, if \( \xi = \mu \), the density follows directly from \( \rho(\mu, T) = -W \) and if \( \xi = \beta \), the energy per volume is \( u = \beta W \).

As discussed in details in the Appendix, close to the transition point \( \xi = \xi^* \) and considering Eq. (1), one finds very generally that \( W \) can be approximated by \( (y = \xi - \xi^*) \)

\[
W \approx (b_1 + \sum_{i=2}^{\mathcal{N}} b_i \exp[-a_i y])/(1 + \sum_{i=2}^{\mathcal{N}} c_i \exp[-a_i y]). \tag{2}
\]

The coefficients \( a_i, b_i \) and \( c_i \) are independent on the control parameter \( \xi \) and only the \( a_i \)'s are (linear) functions of \( V \). In this way, at the coexistence \( (y = 0) \), \( W \) is independent on the volume and for all \( V \) the curves \( W \times \xi \) cross at \( \xi = \xi^* \). Therefore, \( W \) in Eq. (2) does not only describe order parameters, but it also gives the thermodynamic limit estimate for the transition point \( \xi^* \).

Besides the above, two other aspects of the method, relevant for applications, are the following. First, the explicit dependence of \( Z \) on the free energy at low \( T \)'s, Eq. (1). Close to \( \xi^* \), it makes both \( f \) and the entropy per volume \( s \) (once \( s = (u - f)/T \)) also to have the same functional form of Eq. (2). Second, analytical derivatives of Eq. (2), e.g., leading to specific heat, susceptibility, and order parameters which are not necessarily first order derivatives of the free-energy, are easily calculated.

Lastly, an important advantage of the present procedure is that Eq. (2) is valid for any volume. So, by considering relatively small \( V \)'s we can obtain the parameters \( a \)'s, \( b \)'s, and \( c \)'s with a low computational cost (see below). It allows to describe a first order phase transition (at low temperatures) with a direct, accurate and numerically cheap method. Moreover, as we are also going to show below, the approach in fact can be applied to broader situations than that initially assumed to derive Eq. (2), namely, of low \( T \)'s.

B. Numerical simulations

Equation (2) is an analytical expression to describe proper order parameters (as well other thermodynamic functions) around the phase transition. Nevertheless, the coefficients \( a \)'s, \( b \)'s, and \( c \)'s need to be determined. Although approximated expressions for these parameters do exist (Appendix), much better results are obtained direct from numerics. The protocol is then: to use some simulation method to generate the sought thermodynamic quantity for different values of \( \xi \); to compare with the corresponding curve \( W \); and to determine the coefficients by fitting. In particular, the actual general shape of \( W \) requires only few points for a proper adjustment, making the numerics rather fast. Finally, once the coefficients are known, finite size scale analysis, crossing determination, calculation of derivatives, etc, can all be performed analytically.

As a condition to choose any simulation approach to fit the coefficients of \( W \), one should guarantee it is appropriate for the system at hands. Then, in this work we consider the parallel tempering (PT), which is general, simple to use and very efficient for low and intermediate system sizes, even for strong FOPTs \([3, 13, 14]\). Such features also qualify full simulations from the PT as good benchmarks to test Eq. (2).

For completeness, we briefly describe how to implement the PT in our examples (for a very detailed discussion, explaining each step in the method and its application to FOPT see, for instance, Ref. [2]. Basically, the PT (an enhanced sampling method) uses configurations from high to perform an ergodic walk at low \( T \)'s. It simultaneously simulates a set of \( R \) replicas – in the temperature interval \( \{ T_1, \ldots, T_R \} \) – by means of a standard algorithm (e.g., Metropolis, cluster, etc). When evolving any replica \( i \) at a temperature \( T_i \) (through an one-flip procedure), a given site \( k \) is chosen randomly and its state variable \( \sigma_k \) may change to a new value \( \sigma_k' \) according to the probability \( p_k = \min\{1, \exp[-\beta_i (\Delta H)]\} \), where \( \Delta H = \mathcal{H}(\sigma'^{\prime}) - \mathcal{H}(\sigma') \) is the energy change due to the transition. Moreover, from time to time a pair of replicas (say, at \( T_i \) and \( T_j \) with medium or high \( T \)'s) may undergo a temperature switching, drawn from the probability

\[
P_{T_i \leftrightarrow T_j} = \min\{1, \exp[(\beta_i - \beta_j)(\mathcal{H}(\sigma') - \mathcal{H}(\sigma'^{\prime}))]\}. \tag{3}
\]

Typically, the number of replicas does not need to be very high. For the concrete calculations in this work we set \( R = 12 \). We also consider adjacent and non-adjacent replica exchanges.

For the Potts model (Sec. IV.A), which presents strong discontinuous transition for large \( q \)'s, we replace the one above-flip step by the Wolff cluster algorithm [15]. In short, initially a seed site \( k \) (in the state \( \sigma_k \) ) is chosen at will. Then, with probability \( p_i = (1 - \exp[-\beta J]) \delta_{\sigma_k \sigma_i} \) (for \( J \) the two neighbor sites interaction energy when both are at \( \sigma_k \) ) \( k \) is connected to each nearest neighbor site \( l \). This is repeated for all the new sites of the cluster.
III. AN EXACTLY SOLVABLE MODEL

We begin with an analytical example, very instructive to unveil certain mathematical aspects of the present method. Thus, we discuss a prototype model proposed in [11], which although simple, displays all the essential aspects associated to first order phase transitions. The problem grand-partition function is given by [7]

\[ Z = (1 + z)^V (1 + z^{rV}), \]

(4)

where \( r \) is an arbitrary parameter and \( z = \exp[\beta \mu] \) is the fugacity. In the thermodynamic limit of \( V \to \infty \), \( Z \) has a real root at \( z = 1 \) (i.e., \( \beta \mu = 0 \)), which according to the Yang-Lee theory [10] characterizes a FOPT between two phases (\( N = 2 \)).

Here, an appropriate order parameter is the density

\[ \rho = \frac{1}{\beta V} \frac{\partial}{\partial \mu} \ln[Z] = \frac{z}{1 + z} + \frac{rz^{rV}}{1 + z^{rV}}. \]

(5)

Indeed, for \( V \to \infty \) \( \rho \) has a gap of \( r \) since in such limit \( \rho(z = 1^-) = 1/2 \) and \( \rho(z = 1^+) = 1/2 + r \). Moreover, \( \rho(z = 1) = (1 + r)/2 \) regardless of \( V \).

Now, consider a finite \( \mu \). So, low temperatures correspond to large values for \( \beta \mu \) and a good approximation for Eq. (4) is \( Z \approx \exp[\beta \mu V] + \exp[\beta (r + 1) \mu V] \), which obviously is in the general form of Eq. (1). However, the phase transition takes place at \( z = 1 \). For \( z \approx 1 \) in Eq. (4), we can consider \( 1 + z \approx 2\sqrt{z} \), getting

\[ Z \approx \exp[-\beta V f_0] + \exp[-\beta V f_r], \]

(6)

with

\[ f_0 = -\frac{1}{\beta} (\frac{\beta \mu}{2} + \ln[2]), \quad f_r = -\frac{1}{\beta} ((r + 1) \beta \mu + \ln[2]). \]

(7)

Notice that again \( Z \) takes the form of Eq. (I). Hence, although being a particular model, it shows that Eq. (I) and so Eq. (2) can hold true in more general instances than just that of low \( T \)'s (see the discussion in Sec. V).

As mentioned in Sec. II, the density is given by \( \rho = -V \) with \( \xi = \mu \). Thus, using the analytical relations for the coefficients of Eq. (2) in the Appendix, one finds that for the present case: \( c_2 = 1, b_1 = -1/2, b_2 = -(r + 1/2) \), and \( a_2 = r\beta V \). Therefore, close to the phase transition point it follows from Eq. (2) an approximation for \( \rho \), or

\[ \rho_{z \to 1} = \frac{1}{2} + \frac{rz^{rV}}{1 + z^{rV}}, \]

(8)

which yields the correct limits once \( \rho_{z \to 1}(z = 1) = \rho(z = 1) \) does not depend on \( V \) and \( \rho(z \to 1)^+ = -b_1/c_1 = -b_2/c_2 = -\rho(1^+) = -\rho(1^-) \) for \( V \to \infty \).

In Fig. 1 we show the exact \( \rho \) vs. \( \beta \mu \) for different volumes \( V = L \times L \) and \( r = 1/2 \). We compare such curves with Eq. (8) and also with Eq. (2) for the \( c_2 \), \( b_1 \), and \( b_2 \) as above and \( a_2/\beta \) given by the best numerical fitting to Eq. (5) (see Table I). For all the volumes, we observe a very good agreement between the exact \( \rho \) and the approximations, especially in the case where \( a_2/\beta \) is fitted. This latter demonstrates that the general Eq. (2) — with the coefficients obtained from numerical simulations — is an accurate procedure to calculate FOPTs order parameters.

As a final analysis, we recall that the probability to be in phase \( x \) (for \( x = 0 \) or \( r \) is \( P_x = w_x/Z \), with \( Z = w_0 + w_x \) and \( w_x \) the proper weight of phase \( x \). Also, in the thermodynamic limit the term \( rz^{rV}/(1 + z^{rV}) \) in the exact \( \rho \), Eq. (5), is just the Heaviside function \( \Theta(z - 1) \) times the parameter \( r \). Hence, it is the term \( z/(1 + z) \) in Eq. (5) that actually gives the density variation with respect to the fugacity. Thus, considering Eqs. (6)-(7) close to the transition point — but still at the phase \( x -
the probability and density, as function of $z$, read

$$P_x \approx \frac{1}{Z} \exp[-\beta V f_x] = \frac{z^x V}{1 + z^V}, \quad \rho_x \approx \frac{x + z}{1 + z}. \quad (9)$$

By isolating $z$ in Eq. (9) one obtains $P_x(\rho_x)$, which gives (around $z \approx 1$) the probability to be in phase $x$ with the density value $\rho_x$. Plots for two distinct $V$’s and $r = 1/2$ are shown in the right inset of Fig. 1. It is interesting to observe that although $P_x(\rho_x)$ becomes broader for lower $V$’s, even for a so small volume of $V = 4 \times 4$ the density distributions of the two phases do not overlap if $r = 1/2$. On the other hand, by decreasing $r$, $P_0$ and $P_1$ start to intersect each other. But $r$ measures the jump in the order parameter, consequently how strong is the phase transition. Thus, a weaker phase transition leads to a larger overlap between the probability distributions of the order parameter close to the transition point. As it will be discussed in Sec. V, this result illustrates a general and important fact to set the method validity.

IV. NUMERICAL APPLICATIONS

A. Potts model

Widely studied in statistical mechanics, both analytically [17–20] and numerically [21–23], the Potts model is a fine test for the present method, specially given its transition points are exactly known [8].

Consider each site of a regular lattice associated to a spin variable $\sigma$, which assume the values $0, 1, \ldots, q - 1$. If two adjacent sites have different (same) spin, their interaction energy is null ($-J$). Thus, the Hamiltonian reads

$$\mathcal{H} = -J \sum_{(i,j)} \delta_{\sigma_i, \sigma_j}. \quad (10)$$

In the limit of very low temperatures, the system is constrained to an ordered phase, becoming disordered as $T$ increases. For any $q$, the order-disorder transition takes place at $T_c = 1/\ln[1 + \sqrt{q}]$, that in two dimensions is second-order for $q \leq 4$ and first-order for $q \geq 5$. An appropriate order parameter is

$$\phi = \frac{q(V_{\text{max}}/V) - 1}{q - 1}, \quad (11)$$

where $V_{\text{max}}$ is the volume occupied by the spins in a state $\sigma$ of largest population and $V = L^2$ (in 2D) is the total volume [13–19].

| $L$, where $V = L \times L$ | $a_2/\beta = rV$ | $a_2/\beta$ (numerical fitting) |
|--------------------------|-----------------|-----------------------------|
| $L = 4$                  | 8               | 10.016233                   |
| $L = 6$                  | 18              | 20.073368                   |
| $L = 8$                  | 32              | 34.164822                   |
| $L = 12$                 | 72              | 75.295494                   |

TABLE I. The values of $a_2/\beta$ used in Figure 1.

For the numerics we set $q = 20$ and $q = 30$, values which characterize strong first-order phase transitions. In Fig. 2 we show the order parameter, Eq. (11), as function of $T$. We clearly see that in all cases $\phi$ is well described by Eq. (2) (through proper parameters fitting). Moreover, in Fig. 2 the crossing points are at $T_0 = 0.5883(3)$ for $q = 20$ and at $T_0 = 0.5352(1)$ for $q = 30$. Such values are corroborated by finite size scaling obtained from $T_L$ versus $1/L^2$, with $T_L$ the temperature at the peaks of the response function $\chi = -(\partial/\partial T)\phi$. Indeed, extrapolating the plots of $T_L$ versus $1/L^2$ (insets of Fig. 2), we find $T_0 = 0.5881(1)$ for $q = 20$ and $T_0 = 0.5353(3)$ for $q = 30$. The estimations are in excellent agreement with the exact values $1/\ln[1 + \sqrt{20}] = 0.588349(\ldots)$ and $1/\ln[1 + \sqrt{30}] = 0.535248(\ldots)$.

As mentioned in the Sec. II.A, the mean energy and entropy, $u$ and $s$, per site are also described by an expression in the form of Eq. (2). In Fig. 3 (Fig. 4) we display the results for $q = 20$ ($q = 30$). Since entropy is not directly computed from standard thermodynamic averages, here we consider an indirect procedure, based on the transfer matrix method (for details refer, e.g., to [4–24]), to make the simulations and fit the coefficients of Eq. (2) in the case of $s$. We note that once more Eq. (2) indeed does describe quite well the relevant thermodynamic quantities and the crossing point (for a similar analysis for $u$ and $s$, but considering a different approach, see Ref. [24]). We also can perform finite size scaling from the specific heat $c_V = (\partial^2/\partial T^2)u$, plotting $T_c$ versus $1/L^2$, for the $T_L$’s the peak positions of the curves $c_V(T)$ for distinct $L$’s [12, 22] (insets of Figs. 3 and 4). From the $u$’s crossing and the $T_L$ extrapolation we find, respectively, $T_0 = 0.5882(2)$ and $T_0 = 0.5882(1)$ for $q = 20$ and $T_0 = 0.5353(4)$ and $T_0 = 0.5351(4)$ for $q = 30$, again consistent with the previous results.

Finally, in Fig. 5 we display histograms of $\phi$ for three different values of $q = 10, 20, 30$ at the coexistence. It illustrates that stronger the phase transition (i.e., higher the $q$’s), lesser the overlap between the peaks (centered
FIG. 3. The Potts model with $q = 20$ and different $L$'s. The continuous lines are from Eq. (2). (a) $u$ versus $T$, with the crossing at $T = 0.5882(2)$. The inset displays $T_L$ versus $1/L^2$, for $T_L$ the temperature at the peak of the specific heat $c_V = (\partial u/\partial T)|_V$. (b) $s/k_B$ versus $T$, with the inset showing the good coincidence of the crossing point.

FIG. 4. The same as Fig. 3, but for $q = 30$. For $u$, the curves cross at $T = 0.5353(4)$.

FIG. 5. For different Potts model $q$ values and $L = 10$, histograms of the order parameter probability $P_\phi$ versus $\phi$ at the coexistence.

FIG. 6. For the BL model, (a) $\rho$ versus $\mu$ for $T = 0.3$ and distinct $L$'s around the gas-LDL transition. All the continuous lines are properly obtained from Eq. (2). (b) The values of $\mu = \mu_L$ (for which $(\partial \rho/\partial \mu)|_\mu$ is maximum) versus $1/L^2$. (c) A blow up of (a) around the crossing point and the respective small error bars.

at the distinct phases $\phi$ values) of the order parameter bimodal distribution. In particular, observe a larger overlap for $q = 10$, for which we find from the present method a transition at $T_0 = 0.7016(9)$ (details not shown). The exact value is $1/\ln[1 + \sqrt{10}] = 0.701231(\ldots)$. Therefore, although still good, it is not so accurate as the previous examples.

B. Bell-Lavis model

The Bell-Lavis (BL) [9] is a lattice gas model able to reproduce liquid polymorphism and water-like anomalies. It is defined on a triangular lattice where each site is characterized by its occupation ($\sigma$) and orientation ($\tau$) states. Whether the site $i$ is or is not occupied by a water molecule, $\sigma_i = 1$ or $\sigma_i = 0$, respectively. Furthermore, if the site $i$ has an “arm” which is (is not) inert towards the adjacent site $j$, then $\tau_{ij}^i = 0$ ($\tau_{ij}^i = 1$).

Two nearest neighbor molecules $i$ and $j$ interact via a van-der-Waals energy $-\epsilon_{vdw}$. They also form a hydrogen bond (of energy $-\epsilon_{hb}$) when $\tau_i^j \tau_j^i = 1$. So, in the grand-canonical ensemble the BL is described by the Hamiltonian

$$H = -\sum_{<i,j>} \epsilon_{hb} \tau_i^j \tau_j^i + \epsilon_{vdw}) - \mu \sum \sigma_i.$$

The van-der-Waals interaction favors an increasing in the lattice density (a proper order parameter), whereas the hydrogen bond tends to form sublattices for which the molecules have opposite orientations.

For $\zeta = \epsilon_{vdw}/\epsilon_{hb} < 1/3$, the system presents three stable phases, named: gas, low-density-liquid (LDL), and high-density-liquid (HDL). For low $\mu$, the system is in
the gas phase. By increasing $\mu$ we go through the gas-LDL and then through the LDL-HDL phase transitions. At zero temperature both gas-LDL and LDL-HDL are of first order, taking place at $\mu_c = -3(1 + \zeta)/2$ and $\mu_c = -6\zeta$, respectively. For $T > 0$, the gas-LDL remains first-order (ending up in a tricritical point if $\zeta = 1/10$), but the LDL-HDL becomes second-order \cite{14,25,26}.

For $T = 0.3$, in Fig. 8 (a) we plot $\rho$ versus $\mu$ around the gas-LDL coexistence. As previously, the isotherms are well described by Eq. (2), with a crossing occurring at $\mu_0 = -1.6559(1)$ for $\rho \approx 0.516(2)$. Such $\rho$ is close to $1/2$, the exact result at $T = 0$ (understood recalling that at the coexistence both gas ($\rho = 0$) and LDL ($\rho = 2/3$) phases have equal weight and the LDL has degeneracy $\sigma_{L,DL} = 3$). In Fig. 8 (b) we display $\mu_L$ (the $\mu$ for which $(\partial/\partial \mu)\rho$ is a maximum) versus $1/L^2$. By taking the thermodynamic limit $L \to \infty$, we find the extrapolated value of $\mu_0 = -1.6560(1)$, in excellent agreement with the estimate in Fig. 8 (a). Finally, Fig. 8 (c) is a blow up of Fig. 8 (a) in the vicinity of the phase coexistence. The observed small error bars illustrate the good accuracy of the present method in locating the transition point.

We should stress that although this is the only instance where we present a more detailed error analysis, in all the other examples the error bars are likewise small.

C. Associating lattice-gas (ALG) model

Similarly to the BL, the symmetric associating lattice-gas (ALG) model \cite{10,11} can display liquid polimorphism and water anomalies. It is also defined on a triangular lattice, where each site is described by an occupation ($\sigma$) and orientation ($\tau$) state. But an important difference from the BL is that an energetic punishment exists for which the respective response functions, $(\partial/\partial \mu)\rho$ and $(\partial/\partial \mu)\phi$, present a maximum. Extrapolating to the thermodynamic limit we get the estimates $\mu_0 = -1.9999(1)$ and $\mu_0 = 0.0000(1)$, values very close to those from the crossing calculation. Lastly, the bi-

\begin{equation}
\mathcal{H} = 2u \sum_{<i,j>} \sigma_i \sigma_j [(1 - v/(2u)) - \tau^{ij}_i \tau^{ij}_j] - \mu \sum_i \sigma_i. \tag{13}
\end{equation}

The ALG presents a gas and two liquid, LDL and HDL, phases. In particular, for the LDL phase $3/4$ of the lattice is filled by water molecules forming the maximum number of hydrogen bonds \cite{11}. Another relevant distinction from the BL model is that here both gas-LDL and LDL-HDL transitions remain first-order for $T \neq 0$. At $T = 0$, the discontinuous transitions occur at $\mu/v = -2$ (gas-LDL) and $\mu/v = -6 + 8u/v$ (LDL-HDL).

Around the transitions gas-LDL, Fig. 7 (a), and LDL-HDL, Fig. 8 (a), we plot the order parameter versus $\mu$ for $T = 0.2$ and different $L$‘s. For the former, we simple take $\rho$ as the order parameter. However, since for LDL-HDL the density is never null, we set as the order parameter $\phi = (4\rho - 3)$. Both cases are completely described by Eq. (2), with the crossing occurring at $\mu_0 = -2.0000(2)$, gas-LDL, and $\mu_0 = 2.0000(2)$, LDL-HDL. These estimates (within the numerical uncertainties) are identical to their exact values at $T = 0$, a particularity of the ALG model. However, by increasing more the temperature, the $\mu_0$’s start to change as well. For instance, for gas-LDL (which has a shorter coexistence line than that for LDL-HDL \cite{11}) $\mu_0 = -1.9986(2)$ at $T = 0.3$ \cite{3}. On the other hand, for LDL-HDL it is necessary $T > 0.5$ for a sensible departure of $\mu_0$ from its value of 2 at $T = 0$ (see also Sec. V), e.g., for $T = 0.6$, we have found that $\mu_0 = 1.9970(5)$ (results not shown).

In Figs. 7 and 8 (b) we plot $\mu_L$ versus $1/L^2$, for $\mu_L$ the $\mu$ for which the respective response functions, $(\partial/\partial \mu)\rho$ and $(\partial/\partial \mu)\phi$, present a maximum. Extrapolating to the thermodynamic limit we get the estimates $\mu_0 = -1.9999(1)$ and $\mu_0 = 0.0000(1)$, values very close to those from the crossing calculation. Lastly, the bi-
modal density probability distributions, $P_\rho$ and $P_\phi$, are shown Figs. 4 and 5 (c). They present a very flat valley between the peaks (with each peak associated to an individual phase at the coexistence).

### D. Hard-core gas lattice model

As a last example, let us assume a 2D square lattice for the hard-core gas model introduced in [27] and recently revisited in [28, 29]. The interaction is entirely given by an exclusion range: a particle in a certain site prevents the occupation of all the surrounding sites. In the so called 3NN version, the one analyzed here, the excluded sites are those shown in Fig. 9 (a)-(b). In this case, the occupation of all the surrounding sites. In the so called 3NN version, the one analyzed here, the excluded sites are those shown in Fig. 9 (a)-(b). In this case, the exclusive structure in the maximum possible filling configuration has (d) an unitary cell with four vacant sites (in a total of five), resulting in a density of $\rho_{\text{max}} = 1/5$.

The sole control parameter is an effective chemical potential $\mu$, which determines the total number of particles in the system. Hence, temperature is not defined, characterizing an athermal problem. For a fixed $\mu$, the probability to have $n$ particles in a lattice of volume $V$ is given by $p(n) = \alpha_n \exp[\mu n]/Z$, for $Z = \sum_{n=0}^{N_{\text{max}}} \alpha_n \exp[\mu n]$, $N_{\text{max}} = V/5$, and $\alpha_n$ the number of distinct configurations of $n$ particles allowed by the hard-core potential. By decreasing (increasing) $\mu$, the system density decreases (increases). For lower $\mu$’s, the particles are basically randomly distributed – obeying the above restrictions – constituting a fluid phase. For higher $\mu$’s, the system starts to present a certain ordering so to accommodate larger numbers of particles (up to a maximum of $N_{\text{max}}$). The transition fluid-ordering is of first-order (actually, in the ordering regime there are two phases related to each other by a chiral transformation [28–30]).

Since the usual density $\rho$ only vanishes for $\mu \to -\infty$ and the phase transition takes place for a finite $\mu$, a more appropriate order parameter $\phi$ should be considered. For so, we follow the approach in [29] and take the full lattice as composed of basic cells (sublattices) of 5 x 5 sites each, Fig. 10 (a). The sites in each row of a basic cell are labeled as $a_i$ ($i = 1, \ldots, 5$) and in total there are five different ways ($k = 0, \ldots, 4$) to name it (see Fig. 10 (b)). Thus, from such construction one can set $\phi$ as in [29] (just using a slight different notation), or

$$\phi = \langle |\phi_{k=3} - \phi_{k=0}| \rangle, \quad \phi_k = \frac{\rho_{\text{max}}}{4} \sum_{i,j=1;j>i}^5 |n_{a_i}^k - n_{a_j}^k| \quad (14)$$

Above, $\langle \ldots \rangle$ denotes average over all the lattice basic cells. Also, for a chosen labeling $k$, $n_{a_i}^k$ denotes the number of particles in the sites named $a_i$ of a basic cell. According to this definition, at the maximum filling $\phi_{k=0} = 0$ and $\phi_{k=3} = 1$, so $\phi = 1$. On the other hand, at low densities (fluid phase) $\phi_k$ tends to zero, consequently it does $\phi$.

The numerical simulation procedure is essentially that described in Sec. II.B. The only small differences are: (i) instead to define the replicas at distinct temperatures, they are defined at distinct $\mu$’s; (ii) the occupation...
the exchange of configuration between two replicas, is taken if the site is initially empty (occupied); finally (iii) the exchange of configuration between two replicas, say A and B, is performed according to the probability \( \min\{1, \exp[(\pm \mu)]\} \), where the signal + (−) is taken if the site is initially empty (occupied); finally (iii) the exchange of configuration between two replicas, say A and B, is performed according to the probability \( \min\{1, \exp[(\pm \mu_A)\Delta N]\} \), with \( \Delta N \) the difference of the number of particles of A and B.

We have simulated the model for system sizes ranging from \( L = 25 \) to \( L = 40 \), shown in Fig. 11. Note that all curves are very well described by Eq. (2), whose crossing point occurs at \( (\tilde{\mu}_0, \phi_0) = (3.6741(8), 0.835(6)) \). Thus, even for an uncommon (but appropriate) definition for the order parameter, Eq. (14), it is properly represented by our general function \( W \). In the inset of Fig. 11 we plot \( \tilde{\mu}_L \) versus \( 1/L^2 \), where \( \mu_L \) is the position of the peak of the “susceptibility” \( \chi = (\partial/\partial \mu)\phi \).

FIG. 11. For the 3NN hard-core gas model, the order parameter \( \phi \) versus the effective chemical potential \( \tilde{\mu} \) for different \( L \)'s. Continuous lines are from Eq. (2). The curves cross at \( \tilde{\mu}_0 = 3.6741(8) \). In the inset, \( \tilde{\mu}_L \) versus \( 1/L^2 \), where \( \mu_L \) is the position of the peak of the “susceptibility” \( \chi = (\partial/\partial \mu)\phi \).

state of a site (observing the exclusion rule) is changed according to \( \min\{1, \exp[\pm \mu]\} \), where the signal + (−) is taken if the site is initially empty (occupied); finally (iii) the exchange of configuration between two replicas, say A and B, is performed according to the probability \( \min\{1, \exp[(\pm \mu_A)\Delta N]\} \), with \( \Delta N \) the difference of the number of particles of A and B.

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V. THE METHOD APPLICABILITY

So far we have discussed five distinct examples: a prototype thermodynamic system, three representative lattice-gas models, and an interesting athermal problem. We have found that the present approach is able to describe FOPTs in all the different situations studied. Thus, a relevant issue is to enquire to what extent the method can give good results.

To address it, we first recall that the approach key point is the actual form of Eq. (11), i.e., to write \( Z \) as a sum of exponentials, where each term is uniquely associated to a particular phase. In other words, there are no terms involving overlapping between coexisting phases. The rigorous analysis in [12, 31] show that this decomposition is generally valid at low temperatures (see also the Appendix).

To understand in a more physical ground why of a such structure for the partition function, one might consider the following heuristic arguments (in the specific case we are close to a FOPT point):

(i) Assume in phase space a small region \( \Omega \) encompassing a point of coexistence of \( N \) phases. Moreover, for any \( n = 1, \ldots, N \), let \( \Omega_n \) be a portion of \( \Omega \ corresponding to the phase \( n \) (e.g., Fig. 13 (a)).

(ii) Within any \( \Omega_n \), \( F_n = -\ln[Z]/\beta \) is the phase \( n \) free energy. Then, suppose (at least formally) that in \( \Omega_n \) we can write \( Z \approx \exp[-\beta F_n]/(1 + Z_n) \), with a proper \( Z_n \), being very small in such region (in fact, we must have \( |Z_n/\beta| \ll F_n \)).

(iii) Thus, in each \( \Omega_n \): \( Z \approx \exp[-\beta F_n] + \) a small term.

FIG. 12. For the 3NN hard-core gas model and \( L = 30 \), histogram of the order parameter probability \( P_\phi \) at the coexistence.

FIG. 13. (a) In an arbitrary phase space \( \xi \times \zeta \), example of a small region \( \Omega \) around a point of coexistence of \( N \) phases (here, \( N = 6 \)). (b) Schematics of \( F \) versus \( \xi \) for \( \zeta = \zeta^* \). If \( \xi > \xi^* \), the system is in the phase \( n = 5 \) and the dashed line represents the functional form of \( F_1 \) extended into such region. From the inclination of \( F_5 \), the FOPT 1–5 would be stronger in (ii) than in (i). So, \( \Delta_{1,5}(\xi^*) = F_1(\xi^*) - F_5(\xi^*) \) would be larger in the case (ii).
Therefore, a tentative partition function for the whole \( \Omega \) can be \( Z \approx \sum_{n=1}^{N} \exp[-\beta F_n] \) (for simplicity neglecting possible degeneracies \( \alpha_n \)). This is just Eq. (1).

(iv) But for the above to hold, a consistency condition is required. Notice that \( Z_n = \sum_{n' \neq n} \exp[-\beta \Delta_{n',n}] \), with \( \Delta_{n',n} = F_{n'} - F_n \) representing the difference between the free energy of phases \( n' \) and \( n \). So, \( Z_n \) to be small in \( \Omega_n \) implies that \( \forall n' \neq n \), \( \Delta_{n',n} \) is large in \( \Omega_n \).

From the above reasoning we reach the desired general validity condition for Eq. (1) (and so for \( W \) in Eq. (2)), namely,

\[
\beta \Delta_{n',n} \gg 1 \quad \text{in} \quad \Omega_n \quad \text{for any} \quad n \quad \text{and for all} \quad n' \neq n. \quad (15)
\]

Note that it explains why Eq. (1) is always valid at low \( T \)'s (at least close to phase transitions). Indeed, in such case even if the \( \Delta \)'s are not large, the product \( \beta \Delta \) can be very large if the temperature is sufficiently small.

But Eq. (15) is also true if the \( \Delta \)'s themselves are large (of course, with \( T \) not too high). As illustrated in Fig. 13 (b), this is the case in strong FOPTs, i.e., for the system displaying large discontinuities in the slop of the \( F \)'s across \( \xi^* \) or, equivalently, for a large jump in the value of the order parameter (for instance, as determined by the quantity \( r \) in the example of Sec. III).

Lastly, there is a practical and computationally inexpensive test to check the above relations. Equation (15) implies in very high entropic barriers across the transition point. Hence, even considering ubiquitous thermodynamic fluctuations (e.g., for finite systems) around such point it would be much more probable the order parameter to assume values typical of the single phases (corresponding to the \( F \)'s minima) than to present values in between (implying the system to cross the high \( F \)'s regions). So, one could calculate the probability distribution histogram for the order parameter at the coexistence for the different phases. The verification of Eq. (15) would result in well separated peaks, not overlapping each other. Indeed, this is exactly the case in the examples here, as observed in Figs. (right inset). 6 (c), 8 (c), and 12.

As a final illustration, we come back to the ALG model of Sec. III.C. However, we set \( T = 0.5 \), which is 2.5 times higher than the value in Figs. 7 (a) and 8. This case is interesting because now the gas-LDL (LDL-HDL) transition, Fig. 13 (Fig. 14), is well described by Eq. (2) only closer to the phases coexistence point. Indeed, compare the fitting quality and the \( \mu \) range considered in Figs. 7 and 13 and in Figs. 8 and 15. Important to emphasize that unlike Fig. 7 (c), in Fig. 13 (c) the probability distribution is not really a flat valley between the peaks for the gas-LDL. On the other hand, similar to Fig. 8 (c), for LDL-HDL the two peaks in Fig. 13 (c) do not intersect.

Nevertheless, the range in which \( W \) is valid is still large enough to allow a proper characterization of the FOPT in the gas-LDL case (for LDL-HDL, the range is even larger, see Fig. 15). From the crossing curves in Fig. 13 we get the estimate \( \mu_0 = -1.9360(5) \), in agreement with \( \mu_0 = -1.9365(5) \) from the position \( \mu_L \) of the peak of \( \chi = \langle \phi^2 \rangle - \langle \phi \rangle^2 \) vs. \( 1/L^2 \). Fig. 13 (b). We observe that since the fitting of \( \phi \) is not so good for a broader interval of \( \mu \)'s, we prefer to calculate \( \chi = \langle \phi^2 \rangle - \langle \phi \rangle^2 \) (thus numerically more reliable) instead to define \( \chi = (\partial/\partial \mu) \phi \).

For the LDL-HDL case, the curves crossing leads to the estimate \( \mu_0 = 1.9995(5) \), very close to the estimate \( \mu_0 = 1.9990(5) \), obtained from the peak of \( \chi = (\partial/\partial \mu) \phi \) (Fig. 15).

VI. REMARKS AND CONCLUSION

In this contribution we have clarified the main mathematical aspects, discussed the applicability condition and
extended the instances of usage of a recent proposed approach to treat FOPTs, which can be summarized as the following. From a special decomposition for the partition function $Z$, Eq. (1) – valid close to a FOPT whenever Eq. (15) holds – one can derive an analytical expression $W$, Eq. (2), which depends on few coefficients. By using simple numerical simulations to determine these coefficients, $W$ is able to describe quite well relevant thermodynamic quantities, like order parameter, energy, entropy, etc, around the transition point. In addition, there is a point where all curves $W$ (irrespect of $L$) cross. By considering relatively small system sizes $L$, the crossing can give the transition point thermodynamic value.

As it should be, the procedure agrees with other efficient schemes available [8, 12, 16, 22, 29]. However, it can give the transition point thermodynamic value.

The method validity condition can be tested from plots of multimodal probability distributions of the order parameter at the coexistence, calculated from straightforward simulations. A non-overlapping of the peaks (associated to the individual phases) indicates that it can be satisfactorily applied. In fact, such condition extends the protocol, originally derived [5] for the situation of low temperatures.

The method has been tested and shown to work fine for several lattice problems, including an exact solvable and the relevant Potts, Bell-Lavis, ALG, and athermal hard-core gas, models. But certainly, a natural question is if FOPTs taking place in off-lattice systems – with much larger phase spaces – could be studied in a similar fashion. In this respect, we first observe that some aspects of continuous systems displaying FOPTs at low $T$’s, (e.g., as for polymers in Ref. [32], analyzable in terms of finite-size scaling [33]) can be described by lattice models [34]. Obviously, in such cases the method could be directly applied. Second, note that the decomposition for the partition function $Z$, when valid, does not make restrictions regarding lattice or off-lattice systems. Thus, the only issue would be the use (in a continuous phase space) of a proper simulation sampling procedure to fit the parameters in Eq. (2). For instance, there are some implementations of the PT for off-lattices systems (see, e.g., Refs. [35]). With such implementations the approach should hold in the same way.

The study of off-lattice and polymers systems displaying FOPTs [32] is presently an ongoing work and will be reported in the due course.

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**APPENDIX A: THE DERIVATION OF $W$ AND SOME OF ITS PROPERTIES**

Consider a finite system at a low temperature and presenting $N$ coexisting stable phases (the meaning of “low” here is discussed in Section V). It has been rigorously shown [12, 31] that the problem partition function is well described by (with $\beta = (kT)^{-1}$ and $V$ the volume)

$$Z = \sum_{n=1}^{N} \alpha_n \exp[-\beta V f_n] + Z_{unst}. \quad (A1)$$

$Z_{unst}$ is associated to the possible existence of unstable phases – but which are exponentially damped, so negligible in Eq. (A1) – and $f_n$ is the $n$-th phase ($n = 1, \ldots, N$) free energy per volume [12].

The degeneracy parameters (or weights) $\alpha$’s result from eventual symmetries, so that $\alpha_n > 1$ would be due to distinct spatial configurations leading to a same phase $n$.

Now, let $\xi$ to be a proper phase transition control parameter, which we shall vary. From Eq. (A1) we define

$$W = \frac{1}{\beta V} \frac{\partial}{\partial \xi} \ln[Z] = \frac{\sum_{n=1}^{N} \alpha_n g_n \exp[-\beta V f_n]}{\sum_{n=1}^{N} \alpha_n \exp[-\beta V f_n]}, \quad (A2)$$

with

$$g_n = T \frac{\partial}{\partial \xi} \left( \frac{f_n}{T} \right). \quad (A3)$$

Note this the definition of $W$ is usually the start point to calculate relevant order parameters.

The system may have many other intensive parameters, which we generally denote by $\zeta$. So, suppose $\zeta$ kept fixed at proper values, such that the $N$ phases coexistence takes place at $\xi = \xi^*$ (usually with $\xi^*$ depending on $\zeta$, see Fig. 10). In this case, the $f_n$’s are single functions of $\xi$ and for $y = \xi - \xi^* \approx 0$ we consider a first order series expansion (possible due to the existence of smooth representations for the $f_n$’s [31]): $f_n \approx f^* + f_n^* y$, in an interval $W$.\[\] as finite-size scaling [33]) can be described by lattice models [34].
with \( f_n(\xi^*) = f^* \forall n \) (because the coexistence) and \( f_n^* = (\partial f_n/\partial \xi)|_{\xi=\xi^*} \). It leads to

\[
g_n \approx f_n^* - f^* \frac{\partial T}{T^*} \frac{\partial \xi}{\partial \xi^*},
\]

(A4)

where, obviously, \( \partial T/\partial \xi = 1 \) for \( \xi = T \) and zero otherwise. In deriving Eq. (A4), if the control parameter \( x \) is the temperature, one also must assume \( 1/T \approx 1/T^* \), a reasonable approximation provided \( |T| \ll 1 \). Next, for \( a_n = (f_n^* - f_1^*) V^\beta \) [or \( a_n = (f_n^* - f_1^*) V^\beta^* \) if \( \xi = T \)], \( b_n = (\alpha_n/\alpha_1) g_n \), and \( c_n = (\alpha_n/\alpha_1) \), we get

\[
W \approx \frac{b_1 + \sum_{n=2}^{N} b_n \exp[-a_n y]}{1 + \sum_{n=2}^{N} c_n \exp[-a_n y]}.
\]

(A5)

Above, the coefficients \( a_n \), \( b_n \), and \( c_n \) are independent on the control parameter and only the \( c_n \)'s depend (linearly) on the volume. Hence, at the coexistence (\( y = 0 \)) \( W \neq W(V) \) and all the curves \( W \) versus \( \xi \), regardless of \( V \), must cross at \( \xi = \xi^* \). Thus, Eq. (A5) not only describes generic thermodynamic quantities, but also yields the thermodynamic limit estimate for the transition point. Furthermore, by taking derivatives of Eq. (A5), one can obtain response functions and susceptibilities.

Finally, at \( \xi = \xi^* \) either from Eq. (A2) or from Eq. (A5) \( W \) reads

\[
W(\xi^*) = \sum_{n=1}^{N} p_n f_n^* - f^* \frac{\partial T}{T^*} \frac{\partial \xi}{\partial \xi^*}.
\]

(A6)

with

\[
p_n = \frac{\alpha_n}{\sum_{n=1}^{N} \alpha_n}.
\]

(A7)

Moreover, suppose the \( f \)'s ordered such that \( f_n^* = f_1^* \geq \ldots \geq f_{m+1}^* \geq \ldots \geq f_{k-1}^* < f_k^* = \ldots = f_N^* = f_2^* \). Assuming \( y \) small, we can consider Eq. (A4), if we take \( V \rightarrow \infty \) with \( y \) positive (case +) or \( y \) negative (case −), for \( v_+ = 1, u_+ = m, v_- = k, u_- = N \) we find (note a little misprint in Ref. [3])

\[
W_{\pm} = \frac{\sum_{n=1}^{v_{\pm}} b_n}{\sum_{n=v_{\pm}}^{u_{\pm}} c_n} = f_n^* - f^* \frac{\partial T}{T^*} \frac{\partial \xi}{\partial \xi^*}.
\]

(A8)

Equations (A6)-(A8) give the discontinuity of the order parameter across the phase transition in the thermodynamic limit. Numerically, such discontinuity is obtained from the coefficients \( b \)'s and \( c \)'s once, from Eq. (A8), we can write \( W_+ = b_1/c_1 \) and \( W_- = b_N/c_N \). In particular, for \( k = N (m = 1), W_+ (W_-) \) is given in terms of the sole phase which is immediately to the right (left) of \( \xi^* \). Also, the number of equal \( a_n \)'s correspond, at least in a first order approximation, to the number of phases which coexist over the line \( \xi \) in the vicinity of \( \xi^* \). This fact can be used to locate coexisting phase lines and triple points (an application for the present method to appear elsewhere).

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