iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Histogram-based methodology for the determination of the critical point in condensation-evaporation systems

This content has been downloaded from IOPscience. Please scroll down to see the full text.

J. Stat. Mech. (2017) 073211

(http://iopscience.iop.org/1742-5468/2017/7/073211)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 128.59.222.107
This content was downloaded on 14/08/2017 at 13:36

Please note that terms and conditions apply.

You may also be interested in:

Phase behaviour of heteronuclear dimers in three-dimensional systems—a Monte Carlostudy
W Rysko and K Binder

Percolation and jamming in random sequential adsorption of linear k-mers on square lattices with the presence of impurities
P M Centres and A J Ramirez-Pastor

Inverse percolation by removing straight rigid rods from square lattices
L S Ramirez, P M Centres and A J Ramirez-Pastor

Dimer site-bond percolation on a triangular lattice
L S Ramirez, N De la Cruz Félix, P M Centres et al.

Jamming and percolation in random sequential adsorption of straight rigid rods on a two-dimensional triangular lattice
E J Perino, D A Matoz-Fernandez, P M Pasinetti et al.

Thermal percolation for interacting monomers adsorbed on square lattices
M C Giménez, F Nieto and A J Ramirez-Pastor

Applications of Monte Carlo methods to statistical physics
K Binder

Entropy-driven phase transition in a system of long rods on a square lattice
D H Linares, F Romá and A J Ramirez-Pastor

First-order phase transition in a 2D random-field Ising model with conflictingdynamics
Nuno Crokidakis

Journal of Statistical Mechanics: Theory and Experiment
An IOP and SISSA journal

PAPER: Classical statistical mechanics, equilibrium and non-equilibrium

Histogram-based methodology for the determination of the critical point in condensation-evaporation systems

G J dos Santos, D H Linares and A J Ramirez-Pastor

Departamento de Física, Instituto de Física Aplicada, Universidad Nacional de San Luis-CONICET, Ejército de Los Andes 950, D5700HHW, San Luis, Argentina
E-mail: dlinares@unsl.edu.ar

Received 24 May 2017
Accepted for publication 5 July 2017
Published 28 July 2017

Online at stacks.iop.org/JSTAT/2017/073211
https://doi.org/10.1088/1742-5468/aa7df2

J. Stat. Mech. (2017) 073211

Abstract. A methodology based on a combination of the histogram reweighting technique and the fourth order Binder cumulant was developed to determine the critical point in generalized condensation-evaporation systems. This methodology was applied, particularly, to the study of the critical point of the condensation transition for linear molecules adsorbed on square lattices. The results were obtained by means of grand canonical Monte Carlo simulations within the lattice gas model, along with finite size scaling. The method was tested in a system of interacting monomers, in which the critical point can be determined exactly. Furthermore, the application of this method to the determination of the critical point in dimer systems with attractive interactions, gave better results than the previous reported studies. In addition, the adsorption isotherms at different temperatures, as well as the phase diagrams for monomer and dimer systems were obtained, achieving significant improvements in the phase diagram for dimers.

Keywords: classical Monte Carlo simulations, classical phase transitions, discrete fluid models, finite-size scaling

1742-5468/17/073211+15$33.00

Contents

1. Introduction

The statistics and thermodynamics of adsorbed dimers have been an interesting problem in surface science and statistical mechanics [1–19]. An early seminal contribution to dimer statistics was made by Fowler and Rushbrooke [1], while an exact solution was found by Kasteleyn [2, 3], but only at close-packed density.

At intermediate coverage, an intriguing problem is the ordering of repulsive dimers on various lattices. Phares *et al* [7] studied interacting dimers on a semi-infinite square lattice using the transfer-matrix method. The authors concluded that there was a finite number of ordered structures for dimers with repulsive nearest-neighbor interactions. Later, the simulation analysis of the phase diagram of dimers with repulsive nearest-neighbor interactions on a square lattice [8] confirmed the presence of the two well-defined structures: a (4×2) ordered phase at $\theta = 1/2$ and a 'zigzag' (ZZ) order at $\theta = 2/3$, being θ the surface coverage.

In a later work [9], from the (4×2) phase appearing in dimers at half coverage, it was possible (1) to predict the existence of a $(2k \times 2)$ structure for k-mers at half coverage and (2) to obtain the critical temperature $T_{\rm c}(k)$ characterizing the transition from the disordered state to the $(2k \times 2)$ phase as a function of the size k of the adsorbed molecules. Pasinetti *et al* [10] went a step further, analysing the universality class of the phase transition at $\theta = 1/2$. The critical behaviour of the system was studied by using Monte Carlo (MC) simulations and finite-size scaling (FSS) analysis. The results obtained indicated that the nature of the phase transition occurring at half coverage in a system of repulsive rigid k-mers on a square lattice changes from second order for $k = 1$ to first order for $k \geqslant 2$.

The ZZ order corresponding to repulsive dimers on square lattices at $2/3$ coverage was studied by Romá *et al* [11]. The calculations were performed by using exchange MC simulations and FSS theory. The exhaustive determination of the complete set of static critical exponents, along with the behavior of Binder cumulants, confirmed previous results in the literature [7, 8] namely, the existence of a continuous phase transition at $2/3$ coverage. Although it was not possible to exclude the existence of a

J. Stat. Mech. (2017) 073211

more complex critical behaviour, the results suggest that the phase transition does not belong to the universality class of the two-dimensional Ising model.

In the case of attractive lateral interactions, the phase diagram corresponding to homonuclear dimers adsorbed on square lattices was studied by using MC simulations [8]. For temperatures below the critical value, the system underwent a first-order phase transition which was observed in the clear discontinuity in the adsorption isotherms. The critical temperature was obtained from the measurement of the maximum in the specific heat, which was calculated in the canonical ensemble for each surface coverage θ in the range $[0, 1]$. The resulting phase diagram is similar to that reported for a simple lattice gas of monomers (or equivalently, an Ising ferromagnet) with the critical temperature shifted to a higher value by a factor of ≈1.2. The critical temperature for the simple lattice gas is given by $k_{\mathrm{B}}T_{\mathrm{c}}/w \approx 0.567\,25$ [20] (k_{B} is the Boltzmann constant, T_{c} is the critical temperature and w is the magnitude of the lateral interaction energy).

By using MC simulations, multiple-histogram reweighting and finite size-scaling techniques, Rżysko and Borówko [12–19] studied a wide variety of systems in presence of multisite occupancy, including attracting dimers in the presence of energetic heterogeneity [12], heteronuclear dimers consisting of different segments, A and B, adsorbed on square lattices [13–17], and trimers with different structures adsorbed on square lattices and pores [18, 19]. In these papers, a rich variety of phase transitions was reported along with a detailed discussion about critical exponents and universality class. In the particular case of attractive homonuclear dimers on square lattices, the authors corroborated the results previously obtained by Phares *et al* [8].

The attractive phase diagram reported in [8] was obtained from the extrapolation of $T_{\mathrm{c}}(L)$ towards the thermodynamic limit, where $T_{\mathrm{c}}(L)$ is the temperature of the maximum in the specific heat for a $L \times L$ lattice. The calculations were performed in the canonical ensemble, using the coverage as the control parameter. This procedure does not allow us to simultaneously obtain critical coverage and critical temperature. In fact, the value of T_{c} reported in [8] was calculated at $1/2$ coverage, not at the critical coverage (which is expected to be shifted from 0.5). In addition, recent results in the literature [21, 22] show that fixing the density in models such as the one discussed here corresponds to introducing a constraint that renormalizes the critical parameters characterizing the phase transition.

To remedy this situation, we have developed a methodology that allows to obtain simultaneously the critical coverage and the critical temperature of a typical condensation-evaporation transition from Monte Carlo simulations in the grand canonical ensemble. We perform new Monte Carlo calculations in this ensemble, where the chemical potential is the control parameter, obtaining the fourth order Binder Cumulant with the aid of the Histogram Reweighting (HR) Technique [23–25]. We apply this methodology to the study of the phase transition occurring in a system of attractive dimers on square lattices.

It is quite obvious that the model considered here (described in section 2) is highly idealized and is not meant to reproduce a particular system experimentally studied. However the objectives of this work are (1) to introduce a new scenario to calculate the thermodynamic properties of attractive adsorbates; (2) to evaluate the accuracy and applicability of the new technique, comparing it with exact results for attractive monomers adsorbed on square lattices; and (3) to improve previous calculations of the transition point (temperature and coverage) for dimers on square lattices [8]. With

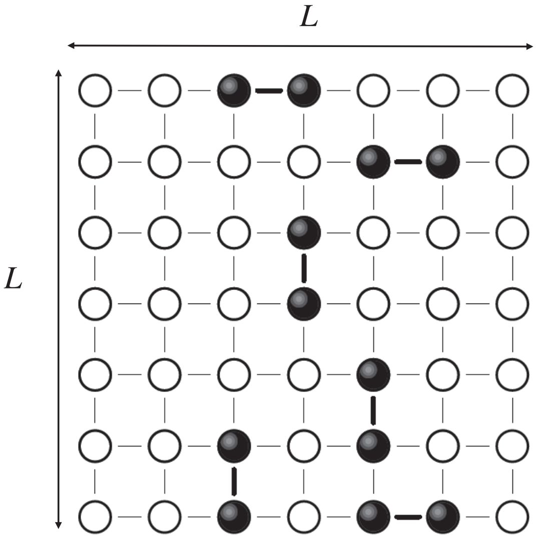

Figure 1. Lattice-gas model for the case of dimers $k = 2$. The surface is modelled by a square array of $L \times L$ adsorptive sites and each adsorbed k-mer will occupy k consecutive lattice sites. Full and empty circles represent dimer units and empty sites, respectively.

respect to the last objective, the shifting of the transition point from $\theta = 0.5$ has not been reported in previous studies.

This paper is organized as follows. The model is described in section 2. Details of the Monte Carlo simulations and the HR technique are presented in section 3. The developed methodology which is based in an adaptation of the HR technique applied to the fourth order Binder cumulant is given in section 4. Finally, section 5 presents the results and conclusions.

2. Model

The system consisting of N linear molecules adsorbing on a flat surface was modelled by k-mers adsorbing on a two-dimensional square lattice of linear size L using periodic boundary conditions (see figure 1). A k-mer of size k consists of k identical consecutive segments, each one occupying exactly one lattice site. The distance between k-mer segments is equal to the lattice constant, so each adsorbed k-mer will occupy k consecutive lattice sites and may be adsorbed in two perpendicular directions (x and y). Each segment of a k-mer interacts only with nearest neighbouring segments of other k-mers with interaction energy w. In order to characterize the occupancy state of each lattice site, the occupancy variable c_i was introduced, so that when site i is empty (occupied) $c_i = 0$ ($c_i = 1$). Then, the generalized grand canonical Hamiltonian is

$$H = \sum_{\langle i,j \rangle} w c_i c_j - N(k-1)w - \mu N + \varepsilon_0 \sum_i c_i \tag{1}$$

where w is the nearest-neighbor (NN) interaction and it is considered attractive (negative) and $\langle i, j \rangle$ denotes pairs of NN sites. This summation overestimates the number of pairs by $N(k-1)$, so the middle term $N(k-1)w$ corrects the total interaction energy.

Finally, μ is the chemical potential, and ε_0 represents the adsorption energy of one site. Since the surface is considered homogeneous, ε_0 is set equal zero, without any lost of generality. It is necessary to mention that w and μ are expressed in $k_{\mathrm{B}}T$ units, being k_{B} the Boltzmann constant and T the temperature.

3. Monte Carlo and histogram reweighting simulations

The problem was studied by means of grand canonical Monte Carlo simulations using a Parallel-Tempering algorithm [26–29] that allows the system to reach equilibrium in a considerable shorter time than the standard Monte Carlo simulations. The Parallel Tempering is applied on chemical potential (μ), generating a collection of N_{rep} replicas, each one at a different value of μ ranging from μ_0 to μ_f where N_{rep}, μ_0 and μ_f are parameters of the simulation. The algorithm selects one of the N_{rep} replicas at random and then a set of k consecutive sites (linear k-uple) is chosen randomly in that particular replica. Then, the operating dynamics consists in an attempt to change the occupancy state of the selected k-uple: if it is an 'empty k-uple', adsorption is carried out with probability $P=\min\{1,\exp(-\Delta H/k_{\mathrm{B}}T)\}$, and if it is an occupied k-uple, desorption is tried out with the same probability P. Where ΔH is the difference between the Hamiltonians of the initial and final states.

After $M=L\times L$ attempts of changing different k-uple states, an attempt of interchanging configurations between neighboring replicas is done by following the general method described in [29], where the acceptance criteria for swapping two replicas is $P=\min\{1,\exp(\Delta\beta\Delta U-\Delta(\beta\mu)\Delta N)\}$. In the present work, the simulations are performed at constant T. Then, $\Delta\beta=0$, $\Delta(\beta\mu)=\beta\Delta\mu$, and the swapping probability results $P=\min\{1,\exp(-\beta\Delta\mu\Delta N)\}$. ΔN is the difference in the number of molecules and $\Delta\mu$ is the difference in chemical potential between the two interchanging replicas.

A Monte Carlo Step (MCS) consist of $L\times L$ attempts per replica of changing a k-uple occupation state, i.e. $MCS=L\times L\times N_{\mathrm{rep}}$, where the linear dimensions of the system L ranges between 20 and 120.

For each replica a random initial configuration is generated, and it was checked that equilibrium was reached after $r=2\times10^6$ MCS; the next 2×10^6 MCS were used to compute averages.

The Parallel Tempering algorithm is used mainly to unblock freezing states using a given number of replicas of the system. The number of replicas in the simulations must be one such that the exchange probability is large, typically greater than 0.5. On the other hand, this number should not be too large to compromise the calculation time. Given the above, the simulations of the present work were run with a hundred replicas ($N_{\mathrm{rep}}=100$).

Typical quantities monitored in the simulations are the surface coverage θ and energy per site ϵ which are calculated as simple averages,

$$\theta=\frac{1}{M}\sum_{i}^{M}\langle c_i\rangle, \tag{2}$$

https://doi.org/10.1088/1742-5468/aa7df2

$$E = \frac{1}{M}\langle H\rangle \tag{3}$$

where $\langle\ldots\rangle$ means time average over the Monte Carlo simulation.

Histogram reweighting methods are great tools for extracting as much information as possible from a single simulation. This technique is well detailed elsewhere [23–25], so here we will provide a short explanation of the subject.

Near first or second order phase transitions, some thermodynamical quantities or their derivatives, such as specific heat or, in our case, the lattice coverage, show pronounced peaks or discontinuities. This effect is a big obstacle when trying to obtain results from direct simulations. In condensation transitions, such as in this work, the isotherms show a sharp jump between the two states near the critical temperature.

This jump makes it very difficult to obtain information of the system in that region from a direct simulation, since little variations in the chemical potential lead to very large changes in the lattice coverage. In addition, due to the fluctuations, it is necessary to take several samples in order to minimize the statistical error, which has a high computational cost. It is here when the single-HR technique is very useful.

From a grand canonical simulation of J steps run at $\mu=\mu_0$ and $T=T_0$, one can create a two-dimensional histogram $H_{T_0,\mu_0}(U,N)$, where U is the total energy and N is the number of molecules. The probability distribution is related to the histogram in the following way: $P(U,N,T_0,\mu_0)=H_{T_0,\mu_0}(U,N)/J$

The single-HR technique allows us to obtain the probability distribution at a slightly. different μ and T from

$$P(U,N,T,\mu) = \frac{H_{T_0,\mu_0}(N,U)\exp[-(\beta-\beta_0)U+N(\beta\mu-\beta_0\mu_0)]}{\sum_N\sum_U H_{T_0,\mu_0}(N,U)\exp[-(\beta-\beta_0)U+N(\beta\mu-\beta_0\mu_0)]}, \tag{4}$$

where $\beta=1/(k_\mathrm{B}T)$.

This is a very powerful relationship, since the average values of any function of N and U can be estimated from

$$\langle A\rangle = \sum_N\sum_U A(U)P(N,U,T,\mu). \tag{5}$$

4. Histogram-based methodology: determination of the critical point

In order to determine the condensation critical temperature, the fourth order Binder cumulant [30] of the order parameter m was calculated using the HR techniques, where the Binder cumulant is defined as

$$\langle U\rangle_L = 1-\frac{\langle m\rangle^4}{3\langle m^2\rangle^2}, \tag{6}$$

where $\langle\ldots\rangle$ denotes average over configurations, and $m=\theta-\langle\theta\rangle$ is the standard order parameter for liquid–vapor transition. Plotting U_L versus T for different system sizes (L), the curves will meet in an intersection point where the cumulant takes a fixed universal value U^*. The temperature at which this intersection occurs is the critical temperature.

J. Stat. Mech. (2017) 073211

The simulations were performed in the grand canonical ensemble at different temperatures, so m_L as well as U_L are functions of T and also functions of μ. Thus, the cumulant intersection plot U_L versus T, is a projection of a (μ, T, U_L) graphic onto a (T, U_L) plane.

The question that naturally arises is which are the values of μ that give the correct intersection plot projection. At low temperatures the isotherms show a discontinuity for a given μ that highlights the condensation phase transition occurring in the system. As the temperature increases, the size of the discontinuity decreases. At the precise temperature at which this discontinuity becomes a point, the system goes from experiencing a first order phase transition to experiencing a second order phase transition, the system being at the so-called critical point. Correspondingly, the isotherms go from having a discontinuity to having an inflection point. It is for this reason that if we move in the plane (μ, T) following a trajectory $Z\,(\mu, T) = 0$ (or $\mu = h(T)$) defined by the inflection point of the different isotherms, we will eventually encounter the critical point. We can evaluate the U_L cumulant along this trajectory finding a three-dimensional curve in a space ($\mu, T,\ U_L$). Due to the scale invariance of $U_L(T_{\rm c})$, if we repeat this procedure for the different sizes of the system L, we will find a family of curves that intersect at a given point, 'the critical point'. Because of the previously established relationship between μ and T, $Z(\mu, T) = 0$, we can detach from a degree of freedom and work with a single independent variable: T. Therefore, to find $T_{\rm c}$, it would be enough to draw the curves in the bidimensional space (T, U_L) for each L and find the intersection point.

In order to find the location of the inflection point for a given isotherm, the second derivative of the isotherm should be obtained. It is known that to obtain an accurate enough derivative of a function, it is necessary for the primitive to consist of a very large number of points, so the case of a second derivative requires even more points, demanding a very large computational cost since the isotherms typically show very sharp increases near first-order phase transitions. On the other hand, figure 2 shows that over an isotherm (fixed T) the fourth order Binder cumulant experiences a maximum at the same point where the isotherm's inflection point occurs, providing us a method to obtain the value of $\mu^*(T)$ and hence the value of $U_L(\mu^*(T), T)$[1]. Repeating this procedure for a group of isotherms of a system of size L, we can obtain a $U_L(T)$ curve as shown in figure 3. If the procedure is repeated for the different system sizes L, we will obtain a family of curves $U_{L_i}(T)$ whose intersection point determines the critical temperature $T_{\rm c}$.

This methodology is further detailed as follows:

- For a given temperature, a histogram is obtained directly from the simulation at a chemical potential as near as we can find it from the inflection point.
- Using the HR technique, the cumulant $\langle U\rangle_L = 1 - \frac{\langle m\rangle^4}{3\langle m^2\rangle^2}$ is calculated for different values of μ near the original one, tuning the chemical potential.

---

[1] The coincidence between the inflection point of the isotherm and the maximum value of the cumulant has been confirmed in several adsorption systems: monomers, dimers, linear and bent trimers, linear and tortuous tetramers, and anisotropic phases of aligned rigid rods (data not shown here for brevity). A rigorous demonstration of this finding, based on the characteristics of the distribution function of the density, is in progress and will be reported in a separate article.

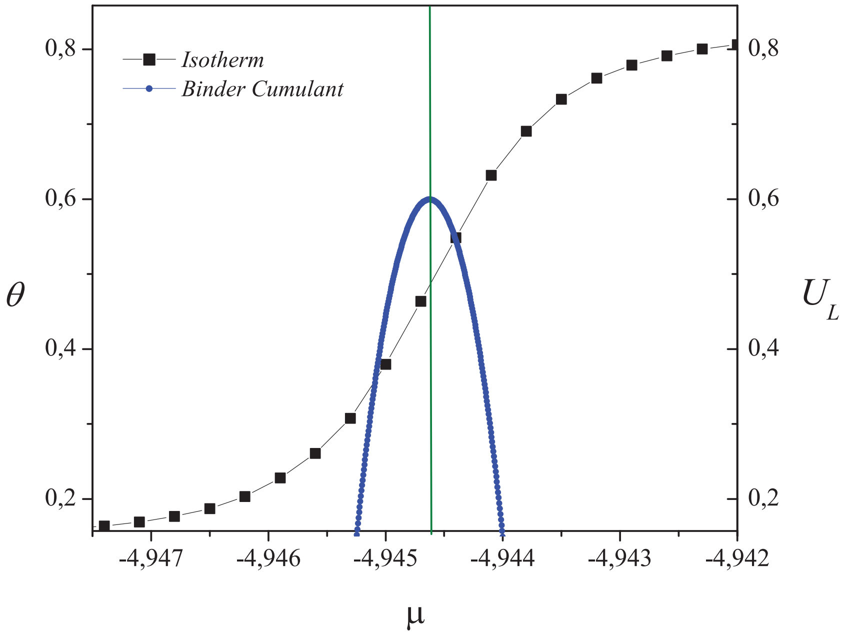

Figure 2. Dimers adsorption isotherm on a square lattice with $L = 80$, along with the fourth order Binder cumulant plotted against the chemical potential μ with fixed $w = -1, 44$. The straight line indicates the location of the inflection point of the isotherm, showing that it occurs when the cumulant takes its maximum value.

- The maximum value of U_L is taken from a U_L versus μ plot.
- We repeat this sequence for different temperatures and finally build the U_L versus T plot for different lattice sizes (L) finding the intersection point(figure 3).

Once we have found the critical temperature, we use the HR technique one more time to calculate the critical isotherm. By finding the inflection point of this isotherm we find the critical coverage (θ_c).

In order to obtain the ($T - \theta$) phase diagram, the two-state approximation was used [31] along with the HR technique. For a given isotherm, obtained at a temperature T on a lattice of size L, we construct a histogram for a value of the chemical potential as near as possible to the inflection point. Now, the reweighting method is applied to this histogram, and then the chemical potential is tuned until the areas under the two peaks becomes equal (see figure 4, where $T = 0.6896$ and $L = 80$). The two density values at which these peaks occur are the equilibrium points in the coexistence curve $\theta_1(L)$ and $\theta_2(L)$.

The procedure in figure 4 is repeated for different values of L ranging between 20 and 120 (these results are not shown here for brevity). From extrapolations, it is possible to obtain $\theta_1 \equiv \theta_1(L \to \infty)$ and $\theta_2 \equiv \theta_2(L \to \infty)$. In the case of the figure, $\theta_1 \approx 0.160$ and $\theta_2 \approx 0.816$.

5. Results and conclusions

A methodology based on a combination of the Binder cumulant and the HR technique was developed in order to find the critical point in a evaporation-condensation system. Monte Carlo simulations along with the HR technique were performed to determine the

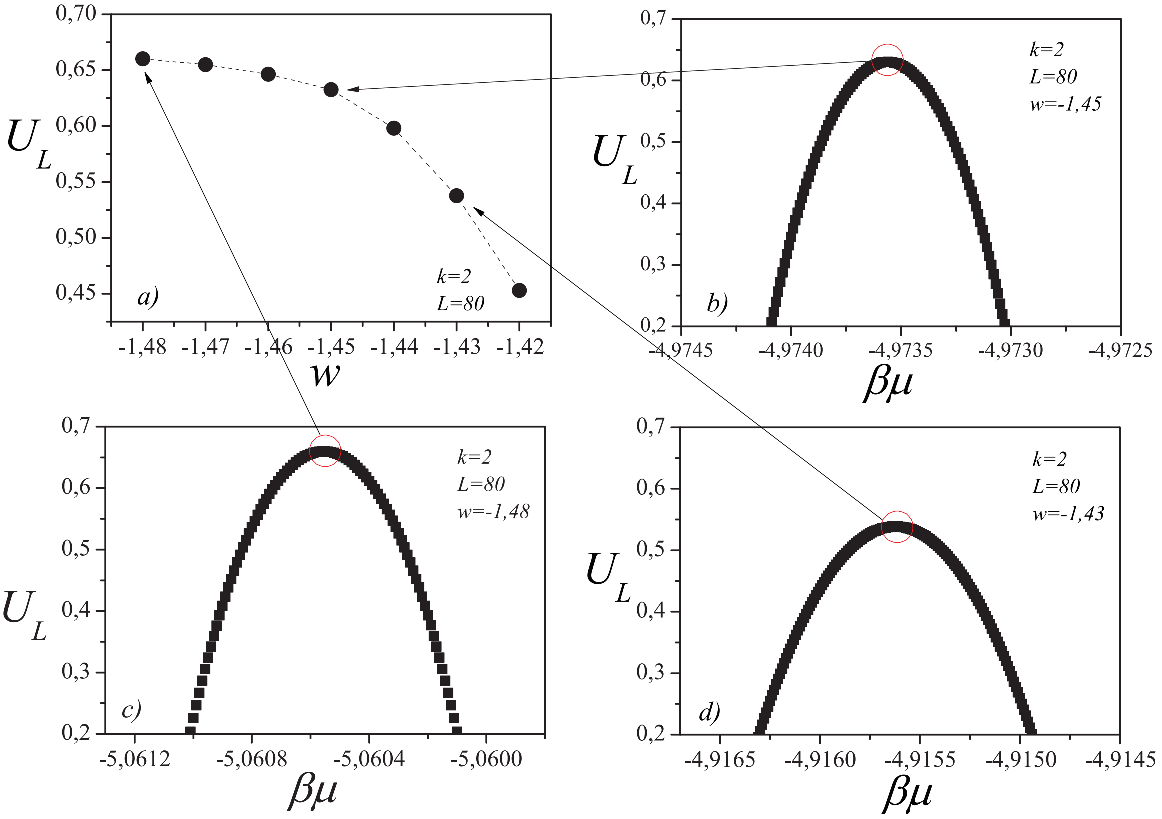

Figure 3. Schematic representation of the proposed methodology for obtaining the Binder cumulant curve as a function of w (in k_BT units).

critical temperature in two different ‘rod-like’ molecule condensation-evaporation systems. In order to test the methodology described in the last section, the case of monomer ($k = 1$) adsorption on square lattices was studied. It is well known that this problem has an exact solution [20], making it ideal for testing the accuracy of the method. For this purpose, we ran MC simulations for attractive monomers in different lattice sizes $L = 50, 60, 80, 100, 120$ and with various interaction energies $w = -1.70, -1.71... - 1.80$. The typical behavior of the adsorption isotherms at different values of w is shown in figure 5.

At first, the accuracy of the method was tested contrasting the value of the critical temperature given by the exact solution and the value obtained from the methodology presented here. From the two-dimensional histograms $H(N, U)$ obtained directly from the simulations employing the procedure described in section 4 the fourth order Binder cumulant was calculated as a function of temperature $U_L(T)$ for different lattice sizes as shown in figure 6.

It can be seen from figure 6, that the cumulants $U_L(T)$ corresponding to different lattice sizes (L) intersect at a well defined point, producing a value of the critical temperature of $T_c = 0.567\,21$. Since the exact value is $T_c^* = 0.567\,25$ [20], it can be concluded that the methodology is accurate enough, to be used in this type of systems. In addition, the critical density of this system was calculated by the methodology described previously, resulting in the value $\theta_c = 0.501$. Again, this result is in excellent agreement with the exact solution ($\theta_{\text{exact}} = 0.500$), and provides further confidence and

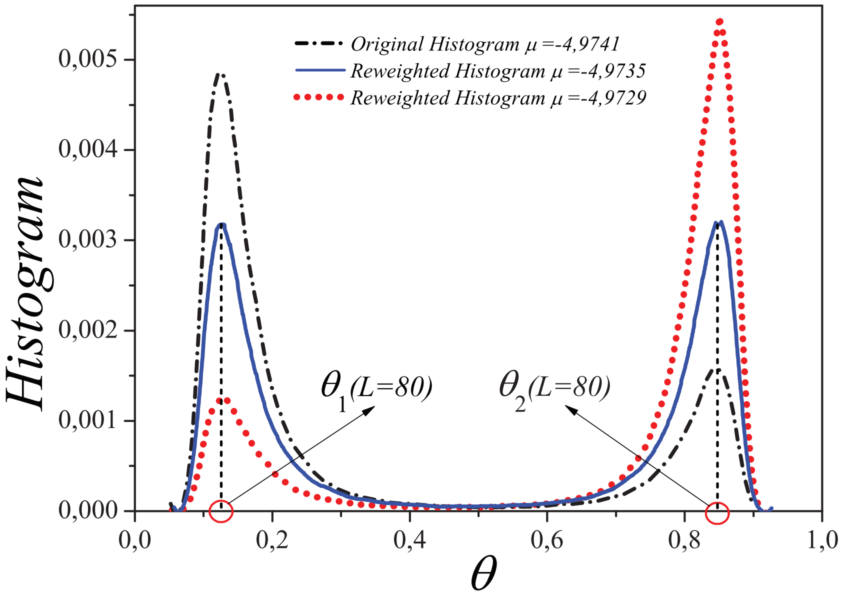

Figure 4. Reweighted lattice coverage histograms for dimers adsorption at fixed $w = -1,45$ and $L = 80$. The original histogram is obtained directly from the simulation and corresponds to a chemical potential $\mu = -4.9741$. Applying histogram reweighting technique, the chemical potential is 'tuned' until the resulting histogram curve is such that the areas under the two peaks is equal. The coverage values of the two maximum are the corresponding coverage values in the phase diagram for that given w or temperature.

evidence that the methodology presented here is valid to find characteristic behaviors of the critical point.

Once the validity and the accuracy of the methodology were tested, it was applied to the study of a system of attractive homonuclear dimers ($k = 2$) adsorbed on square lattices. The objective in this case is to revisit the study realized by Ramirez-Pastor *et al* [8] where the critical temperature of the phase transition of such a system was determined along with the corresponding phase diagram. In this work, the authors used canonical Monte Carlo simulations at a fixed value of lattice coverage $\theta = 0.5$ given that, for symmetry arguments, they assumed that the critical coverage should be the same as the one for the monomer case, i.e. $\theta = 0.5$. This assumption presupposes a symmetric phase diagram around $\theta = 0.5$, which is not correct since the phase diagram is actually slightly asymmetric. For the determination of the critical temperature the authors employed a method based on the extrapolation of the maximum of the specific heat. Although this is a valid method, it is not as precise as others, such as the crossing of the fourth order Binder cumulants. In addition, taking into account that what is being looked for is actually a critical point (T_c and θ_c and not only T_c), leaving the lattice coverage at the fixed value of 0.5 implies that the critical temperature found will be incorrect if the true critical coverage is other than $\theta_c = 0.5$.

As was mentioned in section 3 simulations in the present work were run in the grand canonical ensemble with the aim of studying the problem in a wide range of both temperature and density with the chemical potential as a control parameter, to determine the critical point accurately. The simulations for attractive dimers

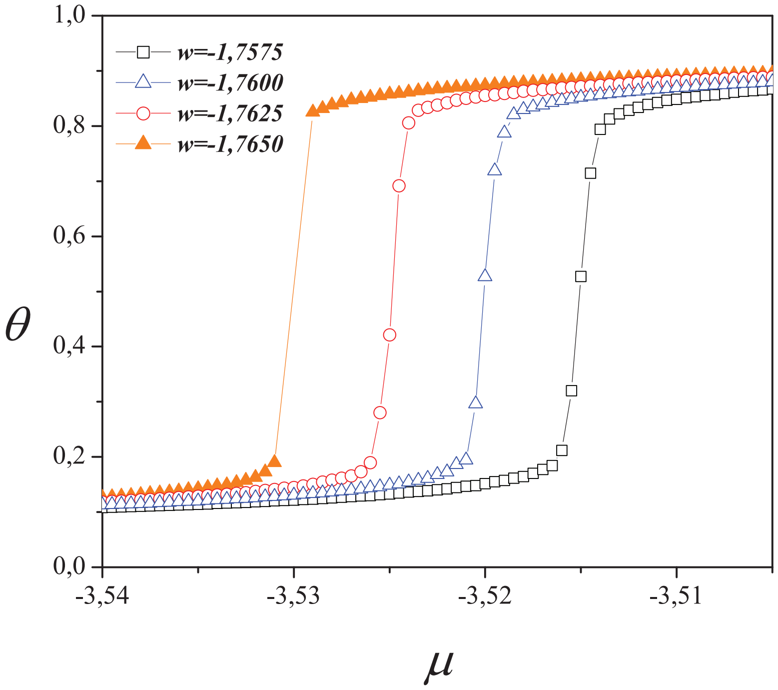

Figure 5. Monomers adsorption isotherms on a square lattice of size $M = 100 \times 100$ for different values of w. It can be seen the typical behaviour of the isotherm when the system experiences a first order phase transition for $w < -1,7625$. The different curves correspond to $w = -1,7575$ (empty squares), $w = -1,7600$ (empty triangles), $w = -1,7625$ (empty circles), $w = -1,7650$ (filled triangles).

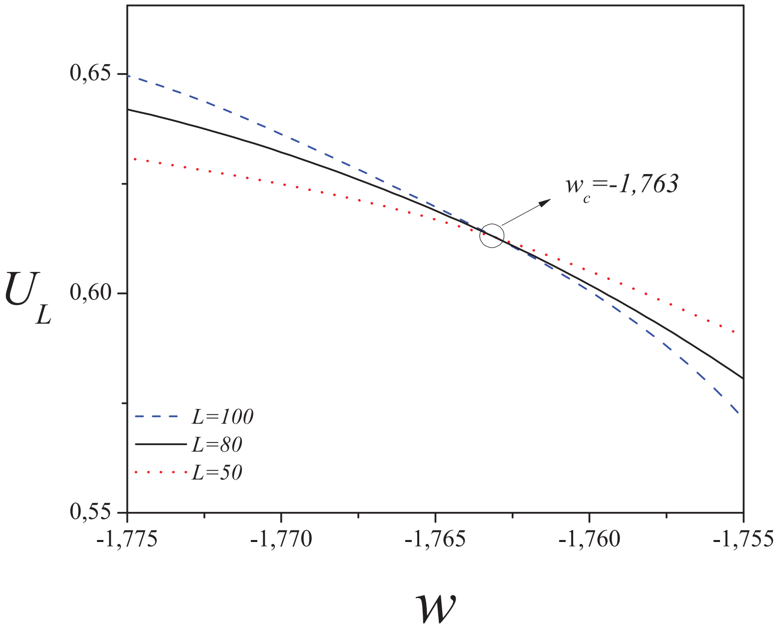

Figure 6. Intersection plot of the fourth order Binder cumulant for the monomer adsorption system. The critical interaction energy found $w_c = -1,763$, is related to the critical temperature by $T_c = 1/w_c = 0.567$.

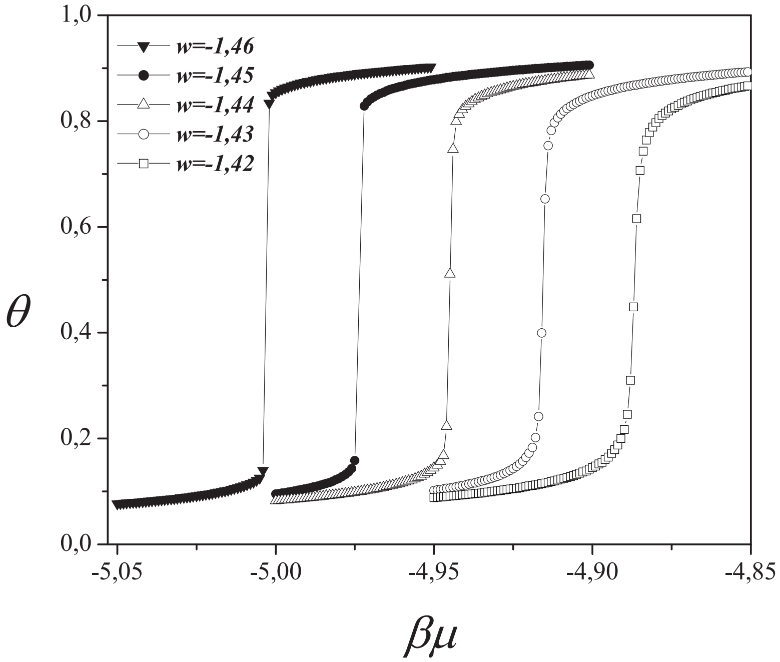

Figure 7. Simulation adsorption isotherms for dimers on square lattices with $L = 100$. Typical behavior of the adsorption isotherms with different lateral interactions near a first-order phase transition: $w = -1,42$ (empty squares); $w = -1,43$ (empty circles); $w = -1,44$ (empty triangles); $w = -1,45$ (filled circles); and $w = -1,46$ (filled triangles).

were run on square lattices of sizes $L = 20, 40, 60, ..., 120$, with interaction energies $w = -1.40, -1.41, ..., -1.50$.

At first, the dimer adsorption isotherms were obtained directly from the simulation for different lateral interaction energies as shown in figure 7. The figure highlights the typical jump that characterize a first order transition in a condensation-evaporation system.

Figure 8 shows the resulting Binder cumulant plot for the dimers case obtained by applying the technique presented in section 4. A well located intersection point for the determination of the critical interaction energy $w_c = -1,444$ corresponding to a critical temperature $T_c = -1/w_c = 0.692$ can be seen. The critical temperature found here corrects the previous values obtained by other authors (Ramirez-Pastor *et al* found $T_c = 0.689$ [8]) giving a slightly higher value than the preceding ones.

For the determination of the phase diagram for the dimer system we have employed, as was mentioned in section 4, the two-state approximation along with the HR technique. On the basis of the results of figure 4, we showed how the equilibrium points in the coexistence curve can be obtained for a given temperature ($T = 0.6896$ in the case of the figure) and $L \to \infty$. The study was repeated for other values of T: 0.6250, 0.6579, 0.6757, 0.6803, 0.6849 and 0.6920. The resulting phase diagram, shown in figure 9, is different from the one obtained by Ramirez-Pastor *et al* because this phase diagram is slightly asymmetric. In addition, the critical coverage obtained in the present work is $\theta_c = 0.489$ showing a small shift from the value $\theta_c^* = 0.5$ predicted by previous works.

Even though the numerical differences between the new values of (T_c, θ_c) and the previous ones [8] are small, the observed shifting of the transition coverage from

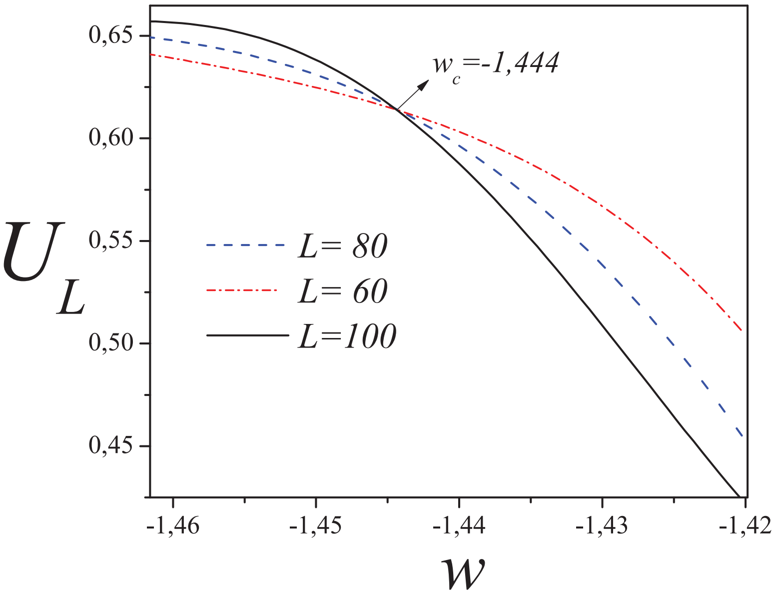

Figure 8. Intersection plot of the fourth order Binder cumulant for the dimer adsorption system. The critical interaction energy found $w_c = -1,444$, is related to the critical temperature by $T_c = 1/w_c = 0.692$.

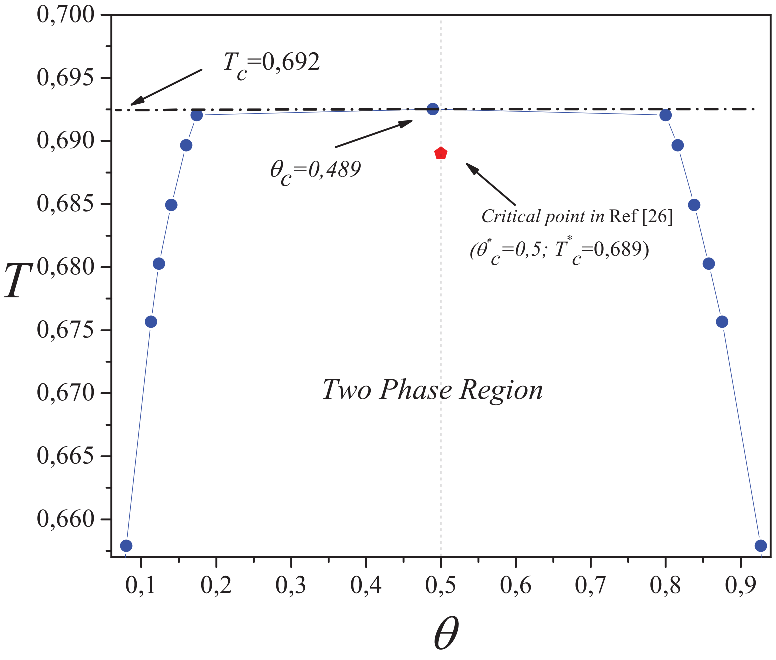

Figure 9. Phase diagram for dimers. The dashed line indicates the critical temperature. It can be seen, the slightly asymmetric character of the diagram, resulting in a critical coverage different from 0.5 ($\theta_c = 0.489$).

0.5 represents a qualitative improvement. This asymmetry has been reported in many experimental phase diagrams [32–36], and could be associated with the adsorption of particles occupying more than one site. In this sense, the present study encourages future research on real systems in the presence of multisite-occupancy adsorption.

In summary, we can conclude that the method presented is adequate to find the critical temperature in a condensation-evaporation system, since it was successfully tested in a monomer system with attractive interactions, which has an exact solution. The result obtained in this work was $T_c = 0.567\,21$, while the exact value is $T_{c_{\text{exact}}} = 0.567\,25$ [20], exhibiting an error less than 1/1000. Using this method, the critical temperature for dimers with attractive interactions was found to be $T_c = 0.692$, which was compared with Ramirez-Pastor *et al* [8], who reported a critical temperature $T_c = 0.689$, which in light of the accuracy of the method is clearly lower than the corresponding critical temperature reported in the present work. We believe that the value reported in this work is more accurate, not only because of the precision of the method used, but because Ramirez-Pastor *et al* [8], assume that the phase diagram is symmetric, so the critical density is assumed to be $\theta = 0.5$. From our studies we have been able to conclude that the diagram is asymmetric and that the critical density is approximately $\theta_c = 0.489$. The fact that the phase diagram is not symmetrical can be understood since there is no equivalence between occupied and empty sites in the case of dimers. The results obtained in the present work clearly correct and complement previous results in the literature. Finally, it is important to note that the particular behavior of the cumulant with respect to the adsorption isotherm observed in this study should be universal for this kind of transition. This finding indicates that the methodology proposed here is valid for any other type of adsorbate and/or substrate, and could be straightforwardly extended to other evaporation-condensation systems.

Acknowledgments

The authors thank support from Universidad Nacional de San Luis (Argentina) under project 322000, CONICET (Argentina) under project PIP 112-201101-00615 and the National Agency of Scientific and Technological Promotion (Argentina) under project PICT-2013-1678. The calculations were carried out using the BACO3 parallel cluster located at Instituto de Física Aplicada, CONICET-Universidad Nacional de San Luis, Argentina. The authors would also like to thank members of GAECI for their services and help.

References

[1] Fowler R H and Rushbrooke G S 1937 An attempt to extend the statistical theory of perfect solutions *Trans. Faraday Soc.* **33** 1272–94

[2] Kasteleyn P W 1961 The statistics of dimers on a lattice: I. The number of dimer arrangements on a quadratic lattice *Physica* **27** 1209–25

[3] Kasteleyn P W 1963 Dimer statistics and phase transitions *J. Math. Phys.* **4** 287–93

[4] Fisher M E 1961 Statistical mechanics of dimers on a plane lattice *Phys. Rev.* **124** 1664

[5] Nagle J F 1966 New series-expansion method for the dimer problem *Phys. Rev.* **152** 190

[6] Lieb E H 1967 Solution of the dimer problem by the transfer matrix method *J. Math. Phys.* **8** 2339–41

[7] Phares A J, Wunderlich F J, Grumbine D W and Curley J D 1993 The entropy curves for interacting dimers on a square lattice *Phys. Lett.* A **173** 365–8

[8] Ramirez-Pastor A J, Riccardo J L and Pereyra V D 1998 Monte Carlo study of dimer adsorption at monolayer on square lattices *Surf. Sci.* **411** 294–302

[9] Romá F, Ramirez-Pastor A J and Riccardo J L 2003 Critical behavior of repulsive linear k-mers on square lattices at half coverage: theory and Monte Carlo simulations *Phys. Rev.* B **68** 205407

[10] Pasinetti P M, Romá F and Ramirez-Pastor A J 2012 First-order phase transitions in repulsive rigid k-mers on two-dimensional lattices *J. Chem. Phys.* **136** 064113

[11] Romá F, Riccardo J L and Ramirez-Pastor A J 2008 Critical behavior of repulsive dimers on square lattices at 2/ 3 monolayer coverage *Phys. Rev.* B **77** 195401

[12] Borówko M and Rżysko W 2001 Critical behavior of dimers in monolayers adsorbed on heterogeneous solid surfaces *J. Colloid Interface Sci.* **244** 1–8

[13] Rżysko W and Borówko M 2002 Phase diagrams of heteronuclear dimers adsorbed on a square lattice *J. chem. phys.* **117** 4526–31

[14] Rżysko W and Borówko M 2002 Non-universal critical behaviour of heteronuclear dimers on a square lattice—a Monte Carlo study *Surf. sci.* **520** 151–7

[15] Rżysko W and Borowko M 2003 Monte Carlo study of adsorption of heteronuclear dimers on heterogeneous surfaces *Thin Solid Films* **425** 304–11

[16] Rżysko W and Borówko M 2006 Phase behavior of unsymmetrical dimers on a square lattice *Surf. sci.* **600** 890–6

[17] Rżysko W and Binder K 2008 Phase behaviour of heteronuclear dimers in three-dimensional systemsa Monte Carlo study *J. Phys.: Condens. Matter* **20** 415101

[18] Rżysko W and Borówko M 2003 Computer simulation of phase diagrams of trimers adsorbed on a square lattice *Phys. Rev.* B **67** 045403

[19] Borowko M, Rżysko W and Staszewski T 2004 Phase behavior of linear trimers confined to a narrow slit *Phys. Rev.* B **69** 014209

[20] Hill T L 1960 *An Introduction to Statistical Thermodynamics* (Reading, MA: Addison-Wesley)

[21] Almarza N G, Tavares J M and Telo da Gama M M 2010 Effect of polydispersity on the ordering transition of adsorbed self-assembled rigid rods *Phys. Rev.* E **82** 061117

[22] López L G, Linares D H and Ramirez-Pastor A J 2012 Comment on effect of polydispersity on the ordering transition of adsorbed self-assembled rigid rods *Phys. Rev.* E **85** 053101

[23] Panagiotopoulos A Z 2000 Monte Carlo methods for phase equilibria of fluids *J. Phys.: Condens. Matter* **12** R25

[24] Ferrenberg A M and Swendsen R H 1988 New Monte Carlo technique for studying phase transitions *Phys. rev. lett.* **61** 2635

[25] Ferrenberg A M and Swendsen R H 1989 Optimized Monte Carlo data analysis *Phys. Rev. Lett.* **63** 1195

[26] Swendsen R H and Wang J-S 1986 Replica Monte Carlo simulation of spin-glasses *Phys. Rev. Lett.* **57** 2607

[27] Earl D J and Deem M W 2005 Parallel tempering: theory, applications, and new perspectives *Phys. Chem. Chem. Phys.* **7** 3910–6

[28] Hukushima K and Nemoto K 1996 Exchange Monte Carlo method and application to spin glass simulations *J. Phys. Soc. Japan* **65** 1604–8

[29] Yan Q and de Pablo J J 1999 Hyper-parallel tempering Monte Carlo: application to the lennard-jones fluid and the restricted primitive model *J. chem. phys.* **111** 9509–16

[30] Binder K 1997 Applications of Monte Carlo methods to statistical physics *Rep. Prog. Phys.* **60** 487–559

[31] Hill T L 1962 *Thermodynamics of Small Systems* (New York: Dover)

[32] Boutin A, Pellenq R J-M and Nicholson D 1994 Molecular simulation of the stepped adsorption isotherm of methane in alpo4-5 *Chem. Phys. Lett.* **219** 484–90

[33] Lachet V, Boutin A, Pellenq R J-M, Nicholson D and Fuchs A H 1996 Molecular simulation study of the structural rearrangement of methane adsorbed in aluminophosphate alpo4-5 *J. Phys. Chem.* **100** 9006–13

[34] Radhakrishnan R and Gubbins K E 1997 Quasi-one-dimensional phase transitions in nanopores: pore-pore correlation effects *Phys. Rev. Lett.* **79** 2847

[35] Maris T, Vlugt T J H and Smit B 1998 Simulation of alkane adsorption in the aluminophosphate molecular sieve alpo4-5 *J. Phys. Chem.* B **102** 7183–9

[36] Martin C, Tosi-Pellenq N, Patarin J and Coulomb J P 1998 Sorption properties of alpo4-5 and sapo-5 zeolite-like materials *Langmuir* **14** 1774–8