

## Configurational entropy for adsorbed linear species ( $k$ -mers)

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The configurational entropy of interacting linear molecules ( $k$ -mers) adsorbed on a regular lattice is addressed through analytical as well as numerical methods. The general definitions for computational exact calculations of  $k$ -mers lattice-gas entropy are presented. In addition, theoretical basis for accurate analytical estimations of the entropy of reference states are given. The coverage and temperature dependence of the configurational entropy of interacting adsorbed dimers on one and two-dimensional lattices are obtained. A novel phase behavior of  $k$ -mers lattice-gas is shown and discussed. © 2001 American Institute of Physics. [DOI: 10.1063/1.1372187]

### I. INTRODUCTION

Computational as well as analytical accurate calculations of configurational entropy and free energy are of major significance to develop a complete picture of generalized lattice-gas thermodynamics of adsorbates. We refer to generalized lattice-gas as the one in which ad-particles are polyatomic, having more than one constituting unit and, hence, occupying several lattice sites.

The advantages of Monte Carlo (MC) methods to calculate thermal averages of physical observables such as the total energy, energy fluctuations, density, etc., are well-known. However, the calculation of other quantities, like the entropy and the free energy, poses a much higher difficulty.<sup>1,2</sup> Among the available methods, thermodynamic integration is widely used and practically applicable.<sup>3,4</sup> However, in order to obtain the entropy,  $S$ , of a given state, the entropy,  $S_0$ , of a reference state must be known. The lack of knowledge of  $S_0$  is a major limitation for the application of thermodynamic integration to many physical models. Two methodologies (one numerical and one analytical) are presented here to calculate  $S_0$  for polyatomic gases.

For a lattice-gas, the more elaborated the model is, the more difficult it becomes to get  $S_0$ , either exactly or by means of analytical approximations. In particular, the lattice-gas properties of  $k$ -mers (dimers, trimers, and longer species) are not well-known because of the difficulties arising in the calculation of their thermodynamic functions.

Although, adsorption of polyatomic species (or the isomorphous problem of binary solution of a polymer phase and a monoatomic solvent) has been addressed long ago<sup>5-7</sup> in ideal systems, the correct density dependence of configurational entropy of a simple system such as noninteracting dimers on a two-dimensional regular lattice is still unknown. The properties of interacting particles have been less studied in detail and approximations relying on mean-field assumptions are the most usual theoretical treatments.<sup>6-8</sup>

In this work, the thermodynamics of simple adsorbed polyatomic gases is addressed through computational as well as analytical techniques. A computational methodology for highly accurate entropy calculations of interacting adsorbed  $k$ -mers is introduced, which relies upon the definition of an artificial Hamiltonian associated with the system of interest for which the entropy of a reference state can be exactly known. Thermodynamic integration is then applied to obtain the entropy in a given state of the system of interest.

In addition, the general relationship between surface coverage and chemical potential in statistical mechanics is reinterpreted as to provide a straightforward way for the calculation of the entropy of the reference state.

Hereforth, the basis for calculations of  $S$  in  $k$ -mers lattice-gas are presented by means of thermodynamic integration from a reference state of an artificial system to a state of the system of interest through the high temperature region of the thermodynamic space. The general definitions of an artificial system related to the system of interest are given in Secs. II and III. A new analytical approximation to calculate the entropy of the reference state is presented in Sec. IV. The accuracy of the method is checked against exact analytical calculations in one-dimensional lattices. Then, in Sec. V, the behavior of the entropy as a function of coverage and temperature is discussed for dimers.

### II. LATTICE-GAS MODEL FOR THE ADSORPTION OF POLYATOMIC MOLECULES

In our lattice-gas model for adsorption with multisite occupancy in the monolayer regime, we consider homonuclear linear  $k$ -mers on a lattice with constant connectivity (square lattices are used in this work). Adsorbate molecules are modeled as a linear array of  $k$  identical units with constant bond length equal to the lattice constant  $a$ . The  $k$ -mers can only lie flat on the surface occupying  $k$  lattice sites (each lattice site can only be singly-occupied). The surface is represented by an array of  $M$  adsorptive sites. The Hamiltonian of  $N$   $k$ -mers adsorbed on  $M$  sites at a given temperature  $T$  is described by the occupation variables  $c_i$   $\{i=1, \dots, M\}$ , which can take the values  $c_i=0$  or 1, if the site  $i$  is empty or

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occupied by a  $k$ -mer unit, respectively. Assuming that a  $k$ -mer retains its structure upon adsorption and desorption, the Hamiltonian is given by

$$H = \frac{w}{2} \sum_{(i,j)'} c_i c_j - N(k-1)w + \epsilon_o \sum_i c_i, \quad (1)$$

where  $w$  is the nearest neighbor (NN) interaction energy corresponding to repulsive (attractive) interaction for  $w > 0$  ( $w < 0$ ),  $(i,j)'$  represents pairs of NN sites, and  $\epsilon_o$  is the adsorption energy of a  $k$ -mer unit. The term  $N(k-1)w$  is subtracted in Eq. (1) because the summation over all the pairs of NN sites overestimates the total energy by including  $N(k-1)$  bonds belonging to the  $N$  adsorbed dimers. Finally,  $\epsilon_o$  is set equal zero for simplicity, without any loss of generality.

### III. CONFIGURATIONAL ENTROPY FOR ADSORBED $K$ -MERS IN THE CANONICAL ENSEMBLE THROUGH THERMODYNAMIC INTEGRATION

Given a lattice-gas of  $N$  interacting  $k$ -mers, each of which occupies  $k$  sites on a regular lattice with  $M$  sites at temperature  $T$ , from the basic relationship

$$(\partial S / \partial T)_{N,M} = \frac{1}{T} (\partial U / \partial T)_{N,M} \quad (2)$$

it follows

$$S(N, M, T) = S(N, M, \infty) + \int_{\infty}^T \frac{dU}{T}. \quad (3)$$

$S(N, M, T)$  is readily calculated if  $S(N, M, \infty)$  (reference state) is known, given that the integral in the second term can be accurately estimated by MC simulation. Since  $S(N, M, \infty) \forall N, M$  cannot be exactly calculated for  $k$ -mer adsorption by analytical means [it is worth mentioning that only for monoatomic lattice-gas  $S(N, M, \infty)$  is known], in the following we present a general numerical methodology to obtain the entropy of generalized lattice-gas in a reference state.

If an artificial lattice-gas is defined from the system of interest (henceforth referred to as the original system) such that it fulfills the condition,

$$\begin{aligned} \tilde{S}_A(N, M, \infty) &= \lim_{T \rightarrow \infty} \frac{S_A(N, M, T)}{M} = \lim_{T \rightarrow \infty} \frac{S(N, M, T)}{M} \\ &= \tilde{S}(N, M, \infty), \end{aligned} \quad (4)$$

where  $\tilde{S}_A$  and  $\tilde{S}$  denote the entropy per site of the artificial and original systems, respectively, then the integral in Eq. (3) can be separated into two terms. Thus,

$$\begin{aligned} \tilde{S}(N, M, T) &= \tilde{S}_A(N, M, \infty) + \int_{\infty}^T d\tilde{U}/T \\ &= \tilde{S}_A(N, M, 0) + \int_0^{\infty} d\tilde{U}_A/T + \int_{\infty}^T d\tilde{U}/T, \end{aligned} \quad (5)$$

where  $\tilde{U}_A$  and  $\tilde{U}$  are the mean total energy per site of the artificial and original system, respectively (both integrals can

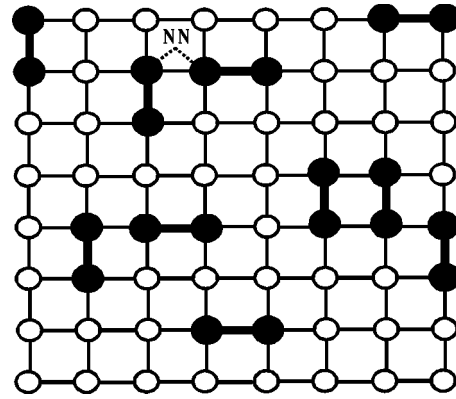


FIG. 1. Dimers ( $N=10$ ) adsorbed on a square lattice of  $M=64$  sites. Typical nearest neighbor (NN) units are labeled. This represents the system of interest (original).

be evaluated by MC in the canonical ensemble). The general definition of the artificial reference system follows.

Let us assume the original system to be a discrete system of  $N$  particles on  $M$  sites with Hamiltonian  $H(N, M, i) = E(N, M, i) \forall i \in \gamma$ ; where  $E(N, M, i) = \text{finite} \forall i \in \gamma$ , is the potential energy in the  $i$ th configuration among the set of accessible configurations  $\gamma$ . The original system can only have access to those configurations within  $\gamma$ ; the total amount of configurations in  $\gamma$  is  $G_T(N, M)$  {in a lattice gas of  $N$  monomers with single-site occupancy of  $M$  sites,  $G_T(N, M) = M! / [N!(M-N)!]$ }.

The Hamiltonian of the artificial system,  $H_A$ , follows from:

Definition 1:  $H_A$  is defined as  $H_A(N, M, j) = E_A(N, M, j) = \text{finite} \forall j \in \gamma_A$ , where  $E_A$  and  $\gamma_A = \gamma$  have analogous meanings to those given above for  $E$  and  $\gamma$ , respectively. This ensures that the set of accessible configurations for the original system and the artificial system are equal (although  $\gamma_A = \gamma$ , the energy of the configurations in the artificial system may be, in general, different from the one in the original system).

Definition 2: The potential energy of the accessible configurations ( $j \in \gamma_A$ ) for the artificial system take the following values:

$$\begin{aligned} E_A(N, M, j_o) &= 0 \quad j_o \in \gamma_A, \\ E_A(N, M, j) &> 0 \quad j \neq j_o \quad j \in \gamma_A. \end{aligned} \quad (6)$$

Definition 2 means that a given configuration (the  $j_o$ th) is selected arbitrarily from  $\gamma_A$  and defined as the nondegenerate ground state of the artificial lattice-gas; consequently  $S_A(N, M, 0) = 0$ . In practice, the configuration  $j_o$  can be easily chosen.

An example for adsorbed dimers follows in order to make this point clear. Let us consider adsorbed dimers on a square lattice with interaction between NN dimer's heads as shown in Fig. 1 (original system). For this system there is no rigorous expression of  $\tilde{S}(N, M, \infty)$  for  $N > 0$  in the thermodynamic limit ( $N \rightarrow \infty, N/M \rightarrow \text{constant}$ ).

To build up an artificial system fulfilling the Definitions (1) and (2), we take the following steps:

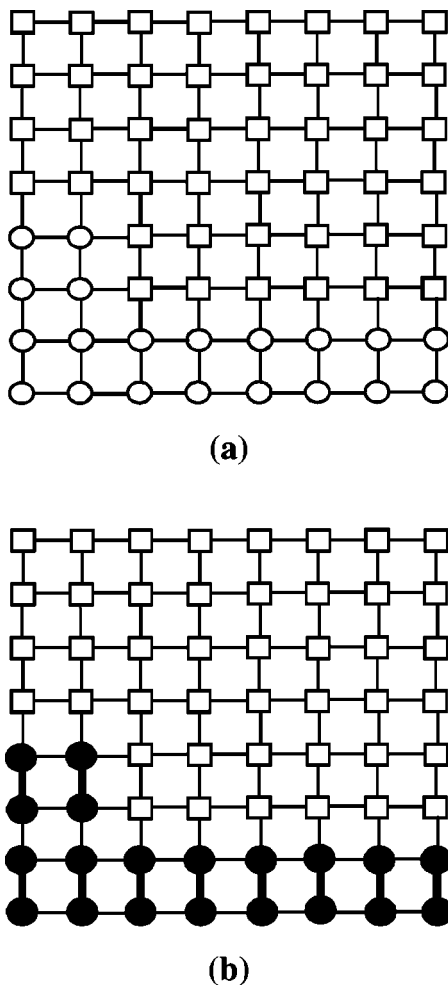


FIG. 2. (a) Square lattice of  $M=64$  sites representing the lattice of the artificial system; strong and weak sites are symbolized by circles and squares, respectively. (b) Configuration of  $N=10$  dimers in the lowest energy state (ground state) according to the artificial Hamiltonian of Eq. (7).

- (i) The number of particles, size and geometry of the lattice is kept as in the original system.
- (ii) The interaction energy between NN units is set to zero.
- (iii) An adsorption energy is introduced for the lattice sites (representing, for each site, the interaction between the lattice and the unit of the dimer adsorbed on it, in the artificial system), in such a way that two types of sites are defined, strong and weak, with energies  $\epsilon_S$  and  $\epsilon_W$ , respectively, being  $\epsilon_S < \epsilon_W$ . For  $N$  adsorbed dimers we choose  $2N$  strong sites conveniently on the lattice. For instance, in Fig. 2(a) a possible distribution of strong and weak sites is depicted, where circles and squares are sites of energy  $\epsilon_S$  and  $\epsilon_W$ , respectively.
- (iv) It is assumed that dimers in a particular direction are energetically favored. This is formally handled by introducing a virtual external field such that the interaction energy between the dimers and the field is  $w_n = -1$  if the  $n$ th dimer is vertically aligned and  $w_n = 0$  otherwise (this choice is obviously arbitrary). Care must be taken if periodic boundary conditions

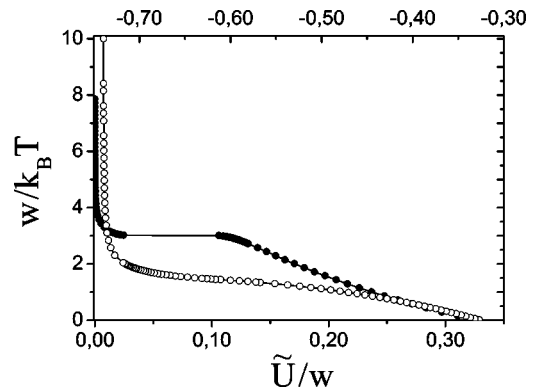


FIG. 3. Mean total energy per site (in units of the interaction energy  $w$ ) for dimers on a square lattice with nearest neighbor interaction energy  $w$  at fixed coverage  $\theta=0.5$ . (a) Open circles and top x-axis correspond to attractive dimers. (b) Full circles and bottom x-axis correspond to repulsive dimers. Simulations were carried out in the canonical ensemble and symbols represent averages over typically  $10^6$  MC configurations, after  $10^5$ – $10^6$  equilibration steps.

are applied to ensure that the state of minimum energy is unique. Then, the Hamiltonian of the artificial system for this example is given by

$$H_A = \sum_{i=1}^M \epsilon_i c_i + \sum_{n=1}^N w_n, \quad (7)$$

where  $\epsilon_i = \epsilon_S = -1$  if the site is strong and  $\epsilon_i = \epsilon_W = 0$  if the site is weak.

Thus, the ground state of the artificial system is the one shown in Figure 2(b), which is nondegenerate, giving  $\tilde{S}_A(N, M, 0) = 0$ .

The calculation of  $\tilde{S}(N, M, T)$  through Eq. (5) is straightforward and computationally simple, since the temperature dependence of  $\tilde{U}_A(T)$  and  $\tilde{U}(T)$  is evaluated at constant coverage for various values of  $T$  following the standard procedure of Monte Carlo simulation in the canonical ensemble (based on the Metropolis scheme<sup>9</sup>). Then,  $\tilde{U}_A(T)$  and  $\tilde{U}(T)$  are spline-fitted and numerically integrated. It should be mentioned that  $\tilde{U}_A(T)$  and  $\tilde{U}(T)$  are obtained by using the Hamiltonians of Eqs. (7) and (1), respectively, in the transition probabilities of the Monte Carlo procedure. Two typical curves of  $1/k_B T$  vs  $\tilde{U}$  are shown in Fig. 3, for attractive and repulsive dimers on a square lattice. In order to evaluate the accuracy of the methodology, we calculate the coverage and temperature dependence of the entropy of interacting dimers on one and two-dimensional lattices and compare the results with analytical solutions and MC results of earlier studies.<sup>10–13</sup>

#### IV. ANALYTICAL APPROXIMATION FOR THE ENTROPY OF THE REFERENCE STATE: OCCUPATION BALANCE

The analytical treatment is an alternative way to estimate the entropy in a reference state. However, one of the bottlenecks in the estimation of  $\tilde{S}(N, M, T)$  for polyatomic lattice-gas is the lack of simple strategies to approximate the

counting of configurational degeneracy at finite coverage. This is one major reason for the relative underdevelopment of statistical thermodynamics of  $k$ -mers.

Here we propose an approximation to  $\tilde{S}$  for dimers on a regular lattice at infinite temperature, based on general arguments leading to very accurate results.

The mean number of particles in the adlayer,  $\bar{N}$ , and the chemical potential,  $\mu$ , are related through the following general relationship in the grand canonical ensemble,

$$\bar{N} = \lambda \left[ \frac{\partial \ln \Xi(M, \lambda)}{\partial \lambda} \right]_M, \quad (8)$$

where  $\lambda = \exp(\mu/k_B T)$  and  $\Xi$  is the grand partition function. By solving for  $\lambda^{-1}$  in Eq. (8), we get

$$\lambda^{-1} = \frac{1}{\bar{N}} \left[ \frac{\partial \ln \Xi(M, \lambda)}{\partial \lambda} \right]_M = \frac{\bar{R}(M, \lambda)}{\bar{N}}, \quad (9)$$

where the quantity  $\bar{R}(M, \lambda)$  can be proven to be the mean number of states available to a particle on  $M$  sites at  $\lambda$ . If  $Y_i(M, N)$  and  $R_i(M, N)$  denote the total number of distinguishable configurations of  $N$  particles on  $M$  sites and the number of states available to the  $(N+1)$ th particle in the  $i$ th configuration [out of  $Y_i(M, N)$ ], respectively, then

$$Y_i(M, N+1) = \sum_{i=1}^{Y_i(M, N)} R_i(M, N). \quad (10)$$

The total number of indistinguishable configurations of  $(N+1)$  particles on  $M$  sites can be obtained from Eq. (10) as

$$\begin{aligned} G_i(M, N+1) &= \frac{Y_i(M, N+1)}{(N+1)!} = \frac{\sum_{i=1}^{Y_i(M, N)} R_i(M, N)}{(N+1)!} \\ &= \frac{N!}{(N+1)!} \sum_{i=1}^{G_i(M, N)} R_i(M, N) \\ &= \frac{1}{N+1} \sum_{i=1}^{G_i(M, N)} R_i(M, N). \end{aligned} \quad (11)$$

The average of  $R_i(M, N)$  over a grand canonical ensemble is

$$\begin{aligned} \bar{R}(M, \lambda) &= \langle R_i(M, N) \rangle = \frac{1}{\Xi} \sum_{N=0}^{N_m} \left\{ \lambda^N \sum_{i=1}^{G_i} R_i(M, N) \right\} \\ &= \frac{1}{\Xi} \sum_{N=0}^{N_m-1} (N+1) \lambda^N G_i(M, N+1) \\ &= \frac{\lambda^{-1}}{\Xi} \sum_{N'=1}^{N_m} \lambda^{N'} N' G_i(M, N') = \frac{\bar{N}}{\lambda}, \end{aligned} \quad (12)$$

as already advanced in Eq. (9).  $N' = N+1$ ,  $N_m$  is the maximum number of particles that fit in the lattice, and  $R_i(M, N_m) = 0$ .

The advantage of using Eq. (9) to calculate the coverage dependence of the fugacity  $\lambda$  can be visualized by considering the adsorption of dimers in the monolayer regime.  $\bar{R}[M, \lambda(\bar{N})] = \bar{R}(M, \bar{N})$  for dimers (occupying two nearest

neighbor lattice sites) is, to first order,<sup>14</sup>  $\bar{R}(M, \bar{N}) \approx cM/2 - (2c-1)\bar{N}$ , where the second terms account for the mean number of states excluded by the adsorbed dimers on a lattice with connectivity  $c$ . Thus,

$$\lim_{M \rightarrow \infty} \lambda^{-1} \approx \lim_{M \rightarrow \infty} \frac{cM/2 - (2c-1)\bar{N}}{\bar{N}} = \frac{c}{\theta} - (2c-1), \quad (13)$$

where  $\lim_{M \rightarrow \infty} 2\bar{N}/M = \theta$ .

The term  $(2c-1)$  overestimates the number of excluded states because of simultaneous exclusion of neighboring particles. Then, the approximation can be further refined by considering the mean number of states that are simultaneously excluded by  $\bar{N}$  dimers,  $\bar{L}(M, \bar{N})$ . It is possible to demonstrate that, in general,  $\bar{R}(M, \bar{N}) = cM/2 - (2c-1)\bar{N} + \bar{L}(M, \bar{N})$  for straight  $k$ -mers. In addition,  $\bar{L}(M, \bar{N}) \approx N(N-1)\bar{L}(M, 2)/2$ , where  $\bar{L}(M, 2)$  is the number of states simultaneously excluded by pairs of dimers (which can be calculated from the two-body partition function). Then, for  $c=4$  it follows

$$\begin{aligned} \lim_{M \rightarrow \infty} \lambda^{-1} &= \lim_{M \rightarrow \infty} \frac{2M - 7\bar{N} + \bar{L}(M, \bar{N})}{\bar{N}} \\ &\approx \lim_{M \rightarrow \infty} \frac{1}{\bar{N}} \left[ 2M - 7\bar{N} + \frac{9\bar{N}(\bar{N}-1)}{(2M-7)} \right] \\ &\approx \frac{4}{\theta} - 7 + \frac{9}{4}\theta + O(\theta^2). \end{aligned} \quad (14)$$

Finally,

$$\lambda^{-1} \approx \frac{4}{\theta} - 7 + \frac{9}{4}\theta + a\theta^2, \quad (15)$$

where the constant  $a = 3/4$  is determined from the limit condition  $\lambda \rightarrow \infty$  for  $\theta \rightarrow 1$ .

From the thermodynamic relationship  $\mu = (\partial F / \partial N)_{M, T}$  ( $F$  denotes the Helmholtz free energy), the entropy per lattice site  $\tilde{S}(\theta)$  can be evaluated in the limit  $T \rightarrow \infty$  as follows:

$$\begin{aligned} \frac{\mu}{k_B T} = \ln \lambda &= -\frac{1}{k_B} \lim_{M, T \rightarrow \infty} \left[ \frac{\partial S(M, N, T)}{\partial N} \right]_{M, T} \\ &= -\frac{2}{k_B} \left[ \frac{d\tilde{S}(\theta)}{d\theta} \right]. \end{aligned} \quad (16)$$

Then

$$\frac{\tilde{S}(\theta)}{k_B} = -\frac{1}{2} \int_0^\theta \ln \lambda(\theta') d\theta'. \quad (17)$$

From Eqs. (15) and (17) we obtain

$$\begin{aligned} \frac{\tilde{S}(\theta)}{k_B} &= \frac{\theta}{2} \left[ \ln \frac{3}{4} - \ln \theta - 2 \right] - \frac{(1-\theta)}{2} \ln(1-\theta) \\ &\quad - \frac{(A-\theta)}{2} \ln(A-\theta) \\ &\quad + \frac{(B+\theta)}{2} \ln(B+\theta) + \frac{A}{2} \ln A - \frac{B}{2} \ln B, \end{aligned} \quad (18)$$

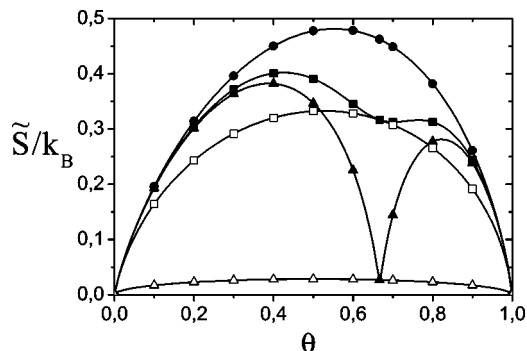


FIG. 4. Configurational entropy per site (in units of  $k_B$ ) vs the surface coverage for dimers on one-dimensional lattice. Symbols are results from thermodynamic integration using an artificial system as presented in this work; (a) full circles, noninteracting dimers ( $w/k_B T = 0$ ); (b) full squares, repulsive dimers  $w/k_B T = 3$ ; (c) full triangles, repulsive dimers  $w/k_B T = 10$ ; (d) open squares, attractive dimers  $w/k_B T = -3$ ; (e) open triangles, attractive dimers  $w/k_B T = -10$ . Lines are exact results from Ref. 12.

where  $A = 2(\sqrt{7/3} - 1)$  and  $B = 2(\sqrt{7/3} + 1)$ .

The coverage and temperature dependence of the entropy for attractive and repulsive dimers on one-dimensional and two-dimensional lattices are shown in Figs. 4 and 5 and discussed below in Sec. IV.

Analytical results from Eq. (18) are shown in Fig. 5 and compared with the corresponding ones from the thermodynamic integration method with an artificial reference system. A remarkable agreement between the occupation balance approximation and thermodynamic integration is observed.

It is worth pointing out that a similar degree of approximation within the formalism of the virial expansion yields significantly more limited result for  $\tilde{S}(\theta)$  (also shown in Fig. 5).

## V. RESULTS AND CONCLUSIONS

Attractive interacting  $k$ -mers in one dimension show asymmetry of  $\tilde{S}(\theta, T)$  with respect to  $\theta = 0.5$  for  $k > 1$  and the overall effect of the attraction is a decrease of  $\tilde{S}(\theta, T)$  for all coverage as  $|w|/k_B T$  increases. For repulsive dimers in

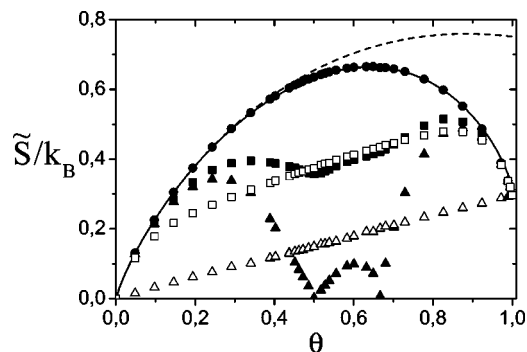


FIG. 5. Idem Fig. 4 for dimers on square lattice. Symbols are results from thermodynamic integration as presented here; (a) full circles, noninteracting dimers ( $w/k_B T = 0$ ); (b) full squares, repulsive dimers  $w/k_B T = 3$ ; (c) full triangles, repulsive dimers  $w/k_B T \rightarrow \infty$ ; (d) open squares, attractive dimers  $w/k_B T = -1.45$ ; (e) open triangles, attractive dimers  $w/k_B T \rightarrow -\infty$ . Dashed line corresponds to virial expansion up to order  $\theta^2$ ; full line is the result from occupation balance method [Eq. (18)].

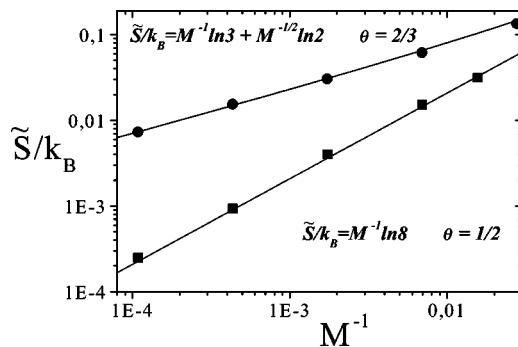


FIG. 6. Configurational entropy per site (in units of  $k_B$ ) vs the reciprocal of the lattice size,  $M^{-1}$ , for dimers on square lattice at  $\theta = 1/2$  and  $\theta = 2/3$ . Symbols are results from the simulation method presented in Sec. II; full squares, dimers at  $\theta = 1/2$ ; full circles, dimers at  $\theta = 2/3$ . Full lines correspond to exact analytical calculation of  $\tilde{S}/k_B$  at these particular coverages;  $\tilde{S}/k_B(\theta = 1/2) = M^{-1} \ln 8$  and  $\tilde{S}/k_B(\theta = 2/3) = M^{-1} \ln 3 + M^{-1/2} \ln 2$ .

one dimension,  $\tilde{S}(\theta, T)$  develops a sharp minimum at  $\theta = 2/3$  as  $T$  decreases, corresponding to a nondegenerate ground state  $\tilde{S}(2/3, 0) = 0$ . No phase transition are related to this minimum, as it is well-known for one-dimensional lattice-gas with short ranged interactions. As shown in Fig. 4, the results from the thermodynamic integration from an artificial system agree absolutely with exact calculations recently presented.<sup>13</sup>

On the other hand, the two minima for repulsive dimers on a square lattice (Fig. 5) represent a second-order phase transition with critical temperatures  $T_c(\theta = 1/2) \approx 0.33|w|/k_B$  and  $T_c(\theta = 2/3) \approx 0.20|w|/k_B$ , respectively, in full agreement with estimations from finite-size analysis of order-parameter cumulants.<sup>11</sup> Ground states with zero entropy per site correspond to the ordered structures at  $\theta = 1/2$  and  $\theta = 2/3$ , which was confirmed by means of finite-size analysis, as shown in Fig. 6 for dimers at  $\theta = 1/2$  and  $\theta = 2/3$ . These results show that the predictions of a ground state with finite entropy per lattice site for  $\theta = 2/3$  (and the appearance of additional minima for  $\theta > 2/3$ ), presented in Ref. 15 from transfer matrix approximation, are artifacts of the calculation technique.

$\tilde{S}(\theta, T)$  for attractive dimers (nearest neighbor interactions) is also shown for  $T > T_c$  and  $T < T_c$ . It should be noted that from the limiting coverages of the linear portion of  $\tilde{S}(\theta, T)$  vs  $\theta$  in Fig. 5, the coverages of the phase diagram lattice-gas/lattice-liquid can be obtained at the given temperature.

Computational as well analytical methodologies have been presented for the calculation of the entropy of the reference state. The detailed balance counting strategy appears to outperform significantly the virial formalism. In addition, the thermodynamic integration based on artificial Hamiltonian is a reliable methodology to gain insight into the critical properties and phase behavior of complex lattice-gas of short linear adsorbates. New features of adsorbed dimers have been reported from the coverage and temperature dependence analysis of configurational entropy.

## ACKNOWLEDGMENT

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