Configurational Entropy in *k*-mer Adsorption

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The general basis for accurate calculations of *k*-mer lattice gases' configurational entropy is presented. The method relies on the definition of an artificial Hamiltonian from the system of interest. By Monte Carlo calculation of mean total energy followed by thermodynamic integration from a reference state of the artificial Hamiltonian, the entropy of a state of interest can be obtained for the physical system under consideration. Entropy of interacting dimers ($k = 2$) and linear trimers ($k = 3$) on one- and two-dimensional regular lattices are shown. The entropy of bended (L-shaped) trimers is investigated as well. Interesting characteristics of the coverage and temperature dependence of entropy in these systems are displayed and discussed.

1. Introduction

The importance of achieving very accurate calculations of free energy and entropy for elaborated lattice gases is major. Such accuracy would allow us to develop a computationally exact thermodynamics of generalized lattice gases. By computationally exact, we mean results obtained from rigorous thermodynamics within the statistical uncertainty of the simulation and the numerical methods that aid the calculations. The advantages of using Monte Carlo simulation to calculate thermal averages of thermodynamic observables are well-known.[1] The calculation of the total energy, energy fluctuations, correlation functions, etc., is rather straightforward; it is accomplished by averaging over a large number of microscopic configurations of the system. However, free energy and entropy are much more difficult to evaluate, and they cannot be directly computed. To calculate free energy and entropy, various methods have been developed.[2−8] Among them, the thermodynamic integration method is one of the most widely used and practically applicable.[9−12] The method relies upon integration of the total energy on temperature along a reversible path between an arbitrary reference state and the desired state of the system. Thus, for a system made of N particles on M lattice sites, from the thermodynamic relationship

$$\left(\frac{\partial S}{\partial T}\right)_{N,M} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{N,M} \qquad (1)$$

it follows that

$$S(N,T) = S(N,T_0) + \int_{T_0}^{T}\frac{\mathrm{d}U}{T} \qquad (2)$$

This calculation requires the knowledge of the entropy in a reference state, $S(N,T_0)$. In practice, the calculation of S in a reference state can be rigorously accomplished by analytical methods in only a very few cases. Although the entropy of some particular states is trivially known (for example, $S_{N\to 0} \to 0$), this knowledge is often computationally inconvenient in that it would require the simulation of a thermodynamically open system to obtain the entropy of a state at finite density. Alternatively, integration can be carried out through a thermodynamic path of a closed (mechanically isolated) system along a constant density path, if a proper reference state is defined for which $S(N,T_0)$ can be directly computed. Because the knowledge of S in a reference state represents the major limitation to the use of thermodynamic integration, we present here the basis for the calculation of entropy, S, and free energy, F, in discrete systems of interacting particles, for which no exact values of S or F in a reference state are known (section 2). We apply the methodology to *k*-mer adsorption on homogeneous lattices.

k-mers, assumed as either rigid or flexible chains containing *k* identical units (beds) with a bond length equal to the lattice constant, provide a simple model of polyatomic adsorbata such as *n*-alkenes, polymers, etc. The knowledge of thermodynamic properties and phase behavior of interacting polyatomic lattice gases is still limited, and it is a developing field of research in gas−solid interface science.[13−17] The coverage and temperature dependence of S for attractive and repulsive dimers and trimers adsorbed on one- and two-dimensional lattices are given in section 3. Effects of *k*-mer structure on the configurational entropy are studied by analyzing two

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trimer species (straight and bended trimers). Comparisons between numerical results from the method presented here and the analytical ones recently reported[17] are carried out and discussed. Novel behavior of S on coverage and temperature for interacting dimers and trimers is shown.

2. General Definition of Artificial Hamiltonians in Discrete Systems

The advantage of eq 2 is that it allows us to define integration paths through intermediate states of artificial systems whose Hamiltonians can differ from the one of the system under consideration. Hence, we define an artificial system whose Hamiltonian, H_A, is such that $\lim_{T \to 0} S_A(N,T)$ equals zero, $S_A(N,T)$ being its entropy. Because $\lim_{T \to \infty} S_A(N,T) = \lim_{T \to \infty} S(N,T)$ (as will be shown later), the entropy of a state of interest of our original system can be computed from eq 2 by integration through the high-temperature region of the thermodynamic space, starting from a reference state of the artificial system for which $S_A(N,T) = 0$.

Let us assume the real system to be a discrete system of N particles with Hamiltonian $H(N,i) = E(N,i)$ $i \in \gamma$, where $E(N,i)$ is the potential energy in the *i*th configuration among the total number of accessible configurations γ. $E(N,i) = $ finite $\forall i \in \gamma$.

The real system can access only those configurations within γ, that amount $G_T(N)$. For instance, in a lattice gas of N monomers with single occupancy of M sites, $G_T(N) = M!/[N!(M-N)!)]$. Let us now define the artificial system whose Hamiltonian is given from the following definitions.

Definition 1. The Hamiltonian of the artificial system, H_A, is defined as $H_A(N,j) = E_A(N,j) = $ finite $\forall j \in \gamma_A$, where E_A and $\gamma_A = \gamma$ have analogous meaning to that given above for E and γ, respectively. The equalities ensure that the set of accessible configurations for the real and the artificial systems are equal (although $\gamma_A = \gamma$, the energy of the configurations in the artificial system may be, in general, different from the ones in the real system).

Definition 2. Values are assigned to the potential energy of the accessible configurations ($j \in \gamma_A$) of the artificial system in the following way:

$$E_A(N,j) = 0 \quad j = j_o$$
$$E_A(N,j) > 0 \quad j \neq j_o \quad j, j_o \in \gamma_A \qquad (3)$$

Equation 3 means that one configuration, the j_oth, is picked up from the set γ_A and defined as the ground state of the artificial Hamiltonian. Arbitrary values larger than zero are assigned to the potential energy of the remaining configurations in γ_A (the election of one particular configuration j_o out of γ_A is dictated only by computational convenience). By following definitions 1 and 2, we find it is always possible to define an artificial Hamiltonian associated to a system of interest having a finite number of accessible states. From definition 2, it is obvious that $\lim_{T \to 0} S_A(N,T) = 0$ (nondegenerated ground state). Furthermore, in the canonical ensemble, it holds that

$$S(N,T) = k_B \ln Z(N,T) + \frac{U(N,T)}{T} \qquad (4)$$

where $Z(N,T) = \sum_{i \in \gamma} \exp[-\beta E(N,i)]$; $U(N,T) = \sum_{i \in \gamma} E(N,i) \exp[-\beta E(N,i)]/Z(N,T)$; $\beta = 1/k_B T$. Provided that $\lim_{T \to \infty} Z(N,T) = G_T(N)$, and $\gamma_A = \gamma$, the first term in eq 4 is identical for the artificial and real systems. From the second term,
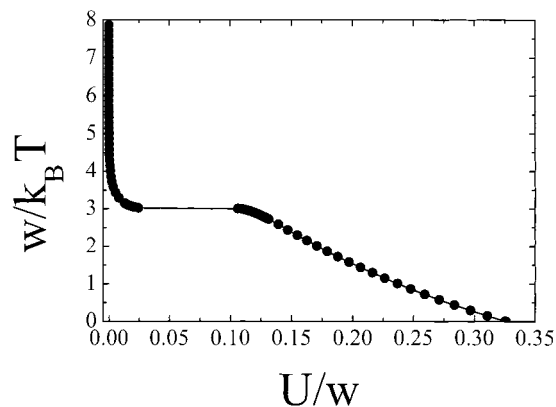

Figure 1. Mean total energy (in units of w) versus $w/k_B T$ for repulsive dimers in a square lattice at $\theta = 0.5$.

it follows that

$$\lim_{T \to \infty} U(N,T) = \frac{1}{G_T(N,T)} \sum_{i \in \gamma} E(N,i) = \text{finite} \qquad (5)$$

Although this limit is different in the artificial and real systems, $\lim_{T \to \infty} U(N,T)/T = 0$ for both. Ultimately, $\lim_{T \to \infty} S(N,T) = \lim_{T \to \infty} S_A(N,T)$, and

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

$$= S_A(N,\infty) + \int_\infty^T \frac{dU}{T}$$

$$= S_A(N,0) + \int_0^\infty \frac{dU_A}{T} + \int_\infty^T \frac{dU}{T} \qquad (6)$$

where the first and second integral are evaluated in the artificial and real systems, respectively. In the next section, we analyze the advantages and accuracy of this methodology in calculating adsorption entropy of dimers and trimers in one- and two-dimensional regular lattices.

3. k-mer Lattice Gas: Entropy of Interacting Dimers and Trimers

The simplest model of adsorption of a polyatomic species is that of homonuclear dimers on a one-dimensional regular lattice.[16] Here we deal with attractive as well as repulsive dimers. Only nearest-neighbor units of different k-mers interact, through an interaction energy w. Repulsive dimers show the richer phase behavior in one and more dimensions. The temperature dependence of $U_A(T)$ and $U(T)$ was calculated by Monte Carlo simulation in the canonical ensemble. A typical curve $U(T)$ is depicted in Figure 1 for repulsive dimers on a square lattice, where a smooth temperature dependence is observed as result of the large number of averaged configurations ($\approx 10^6$). Integration through eq 6 was carried out by standard methods after spline-fitting U_A and U versus T, respectively.

Given N dimers on a lattice of M sites, the surface coverage is defined by $\theta = 2N/M$. The election of the configuration j_o and the Hamiltonian of the artificial system is rather straightforward (for instance, in one dimension, site energy equal to zero is assigned to the leftmost $2N$ lattice sites, site energy greater than zero is given to the $M-2N$ remaining ones on the right, and the lateral interactions between k-mer units are switched off (i.e., set to $w = 0$). Then, the j_o configuration is taken as one in which N dimers lie on the $2N$ leftmost sites.). Hence,
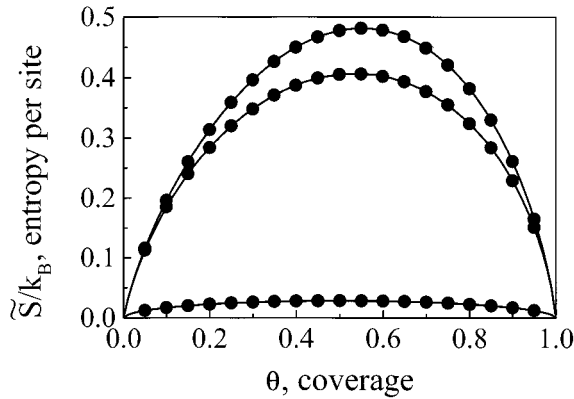
Figure 2. Entropy per site (in units of k_B) versus surface coverage for attractive dimers in one dimension. Curves, from top to bottom, correspond to the following: $w/k_B T = 0$; $w/k_B T = -2$; and $w/k_B T = -10$. Solid lines represent data from eq 7 (ref 17). Calculations from thermodynamic integration with an artificial Hamiltonian as described in this work are shown in filled circles.

the coverage dependence of entropy at infinite temperature, $S_A(\theta, T \to \infty)$, can be obtained as in eq 6. $S_A(\theta, \infty)$ provides the reference state for the calculation of $S(\theta, T)$ for finite T.

Results of thermodynamic integration with an artificial reference system are shown in Figure 2 for attractive dimers in a one-dimensional lattice. The high accuracy of this calculation can be asserted by comparison with exact analytical ones for $S(\theta, T)$ recently presented in refs 17 and 18 (shown in full line). The formula for entropy per site, $\tilde{S}(\theta, T)$, of interacting k-mers is[18]

$$\frac{\tilde{S}(\theta, T)}{k_B} = \frac{\theta}{k} \ln \frac{\theta}{k} + (1 - \theta) \ln(1 - \theta) - 2a \ln a - \left[\frac{\theta}{k} - a\right] \ln\left[\frac{\theta}{k} - a\right] - (1 - \theta - a) \ln(1 - \theta - a) \quad (7)$$

and

$$a = \frac{2\theta(1 - \theta)}{k\left[1 - \frac{(k-1)}{k}\theta + b\right]}; \; b = \left\{\left[1 - \frac{(k-1)}{k}\theta\right]^2 - \frac{4}{kA}(\theta - \theta^2)\right\}^{1/2} \quad (8)$$

$$A = [1 - \exp(-w/k_B T)]^{-1} \quad (9)$$

A remarkable agreement is obtained as shown in Figure 2. The behavior of repulsive dimers is reproduced throughout by the calculations of this work (as shown in Figure 3) for all the ratios $w/k_B T$ investigated. The local minimum of the entropy at $\theta = 2/3$ for strongly repulsive dimers is very well reproduced. This minimum corresponds to the developing of an ordered structure of alternating dimers as temperature decreases (see inset in Figure 3). However, this minimum does not correspond to a phase transition as expected for a one-dimensional lattice gas with short-ranged interactions.

Equilibrium thermodynamics of k-mer lattice gases in two dimensions is a challenging theoretical problem with applications to adsorption of polyatomic molecules on surfaces. In the simplest case of interacting dimers, a very limited knowledge about its phase behavior is currently
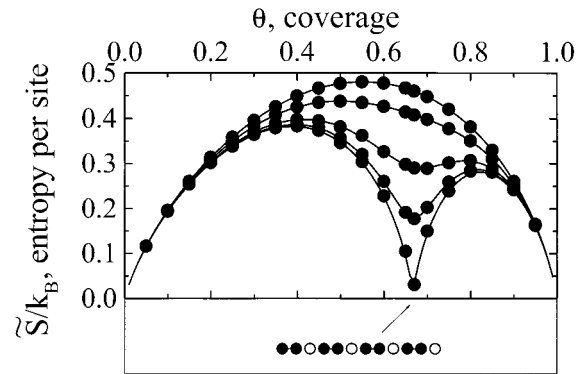

Figure 3. Entropy per site (in units of k_B) versus surface coverage for repulsive dimers in one dimension. Curves, from top to bottom, correspond to the following: $w/k_B T = 0$; $w/k_B T = 1.66$; $w/k_B T = 3.33$; $w/k_B T = 5.00$; and $w/k_B T = \infty$, respectively. Lines and symbols are as in Figure 2.
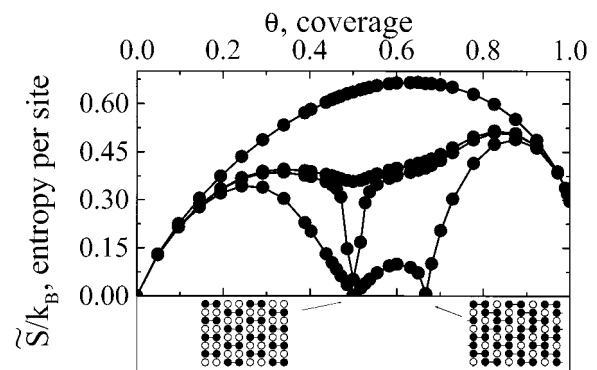

Figure 4. Entropy per site (in units of k_B) versus surface coverage for repulsive dimers in two dimensions. Curves, from top to bottom, correspond to the following: $w/k_B T = 0$; $w/k_B T = 2.94$; $w/k_B T = 3.13$; and $w/k_B T = \infty$, respectively. In this figure, lines connecting symbols are included for better visualization; however, they do not correspond to theoretical results as they do in Figures 2 and 3.

available.[19-21] By applying the method presented here, an accurate thermodynamic description of attractive and repulsive dimers in two dimensions can be achieved.

For calculations of dimer entropy in a square lattice, the reference artificial Hamiltonian was set up by choosing the configuration j_o as the one in which all dimers are packed on one side of the lattice and aligned in the same direction. Any other configuration has a larger energy. The results shown in Figures 4 and 5 correspond to a lattice size $M = 96 \times 96$. A detailed analysis of finite-size effects (not shown here for the sake of brevity) concluded that lattices of this typical size are appropriate to give results representative of the thermodynamic limit within one percent of uncertainty. The results shown and discussed below correspond to dimers and trimers on a square lattice.

For noninteracting as well as attractive dimers, $\tilde{S}(\theta, T)$ has a maximum at $\theta > 0.5$. The overall effect of the interactions is to decrease the entropy for all coverages. All these characteristics match the behavior of dimers in one dimension.[18] For repulsive dimers, $\tilde{S}(\theta, T)$ develops two local minima at $\theta = 1/2$ and $\theta = 2/3$ as T decreases. In the ground state, $\tilde{S}(1/2, 0) = \tilde{S}(2/3, 0) = 0$. These values

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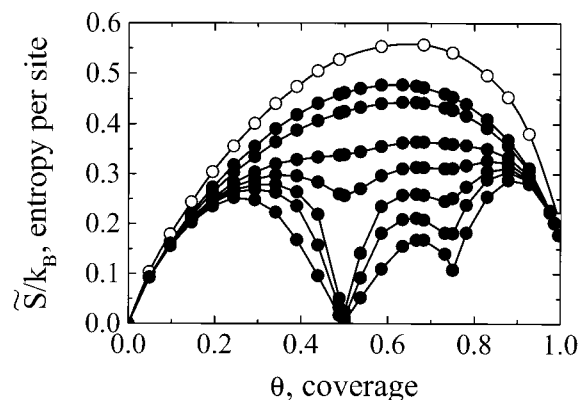(21) DiMarzio, E. A. *J. Chem. Phys.* **1961**, *35*, 658.

Figure 5. Entropy per site (in units of k_B) versus surface coverage for bended (L-shaped) and straight repulsive trimers in two dimensions. Curves with filled circles, from top to bottom, correspond to straight trimers with the following: $w/k_BT = 0$; $w/k_BT = 0.96$; $w/k_BT = 1.91$; $w/k_BT = 2.38$; $w/k_BT = 2.86$; $w/k_BT = 3.34$; and $w/k_BT = \infty$, respectively. Open circles correspond to bended trimers with $w/k_BT = 0$. Lines and symbols are as in Figure 4.

correspond to c(4 × 2) (see left inset in Figure 4) and zigzag (see right inset in Figure 4) ordered phases of dimers, respectively. The critical temperatures corresponding to the critical coverages $\theta = 1/2$ and 2/3 were estimated to be $T_c(1/2) \approx 0.33\,w/k_B$ and $T_c(2/3) \approx 0.20\,w/k_B$, in very good agreement with the values reported in ref 20 from finite-size analysis of order parameter cumulants. Our results confirm that only two out of the multiple minima arising from the transfer matrix approximation (TMA) for $\tilde{S}(\theta, T)$ of Phares et al.[19] are relevant. The others are artifacts of the TMA.

Linear trimers exhibit an intriguing behavior (see Figure 5 where $\tilde{S}(\theta, T)$ for noninteracting and repulsive straight and bended trimers are shown). From the comparison between noninteracting dimers and straight trimers in Figures 4 and 5, it arises that the maximum of $\tilde{S}(\theta, T)$ slightly approaches $\theta = 1/2$ from above as the k-mer size increases. For repulsive straight trimers, two minima appear. Other than the one at $\theta = 1/2$ with $\tilde{S}(1/2, 0) = 0$ corresponding to a $c(6 \times 2)$ ordered phase, it appears

to be a very degenerate state, with $\tilde{S}(3/4, 0) = $ finite at $\theta = 3/4$. This degeneracy remains as the ratio $w/k_BT \rightarrow \infty$ because trimers at this coverage can locally rearrange without any energy cost. This rearrangement is not possible for dimers in the zigzag phase at $\theta = 2/3$, and it makes a qualitative difference between the two cases. Whether this minimum traces to an order−disorder phase transition is still unknown.

The fact that trimers can have a bended configuration makes a significant influence on their configurational entropy. As displayed in Figure 5 for a pure phase of noninteracting bended trimers, $\tilde{S}(\theta, T)$ increases up to 20% at intermediate coverage with respect to a pure phase of straight trimers. The maximum also shifts appreciably to a higher coverage. Further analysis of the phase behavior, nature of phase transitions, and critical parameters is necessary in this case.

4. Concluding Remarks

A general definition of artificial Hamiltonians for polyatomic lattice gases, along with the thermodynamic integration method proposed here, were proven highly accurate for calculating $\tilde{S}(\theta, T)$. Comparisons with rigorous analytical results demonstrate the method's accuracy. This level of detail and accuracy cannot be ascertained by analytical approximations at the present. Novel features shown for dimer and trimer entropy are in favor of a very rich phase behavior of larger adsorbed particles. Similar calculations of free energy (coverage and temperature dependence) would allow a complete thermodynamic description of generalized lattice gases. A much more comprehensive report of the phase behavior of dimers and trimers will be presented elsewhere. Further applications to more complex problems in statistical physics, such as fractional statistics, polyatomic lattice gases, and generalized statistics, would in principle be feasible.