Multisite-Occupancy Adsorption and Surface Diffusion of Linear Adsorbates in Low Dimensions: Rigorous Results for a Lattice Gas Model

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The rigorous statistical thermodynamics of interacting linear adsorbates (*k*-mers) on a discrete one-dimensional space is presented in the lattice gas approximation. The coverage and temperature dependence of the Helmholtz free energy, chemical potential, entropy, and specific heat are given. The chemical diffusion coefficient of the adlayer is calculated through collective relaxation of density fluctuations. Transport properties are discussed and related to features of the configurational entropy. The correspondence of the present model to adsorption in one-dimensional nanopores is addressed.

1. Introduction

The recent synthesis of single-walled and multiwalled carbon nanotubes is a major development in material science that has extraordinarily encouraged the study of vapors and liquids confined in low-dimensional adsorption potentials. This literally provides the route to the experimental realization of one-dimensional adsorbents.[1-5] Similarly, quasi-one-dimensional nanotubes are present in synthetic zeolites (AlPO$_4$-5, SAPO-5)[6] arranged in a crystalline hexagonal close-packed structure. With regard to the gas–solid interaction, the fundamental as well as technological outreach of these materials is to be traced to their uniques properties as reference systems, molecular sieves, and possibly gas-storage adsorbents.

Furthermore, most adsorbata involved in experiments are polyatomic; hence, the theoretical description of their thermodynamic properties is a topic of much interest in adsorption theory. Leading contributions to this subject, generically called multisite-occupancy adsorption, have been presented by Nitta et al.,[7] Flory,[8] Everett,[9] and more recently Rudzinski et al.,[10] through approximate treatments of chains adsorption on homogeneous and heterogeneous surfaces. One of the most important characteristics of multisite-occupancy adsorption is that thermodynamic equilibrium of the adlayer is significantly affected by the spatial correlation between energies of adsorption sites, even for molecules that do not interact laterally. Accordingly, multisite adsorption would provide an appropriate theoretical framework for determination of the adsorption potential characteristics.[10]

Both the increasing importance of quasi-one-dimensional adsorbents and the relevance of multisite-occupancy adsorption as an issue of current interest in adsorption theory encourage and justify the study of the equilibrium and transport of interacting linear species on a one-dimensional adsorbent addressed in this work. The study represents a natural generalization of thermodynamic functions and collective diffusion coefficient obtained for noninteracting linear species on a one-dimensional lattice.[11] It has recently been shown that accurate approximations can be developed for *k*-mers adsorption on homogeneous and heterogeneous adsorbents on the basis of the exact form of the *k*-mers's free energy in one dimension.[12]

Several studies on conductivity, electronic structure, and mechanical strength of nanotubes have already been carried out. However, the amount of theoretical and experimental research focused on the interaction, equilibrium, and dynamical properties of noble, simple, and polyatomic gases within quasi-one-dimensional nanotubes is still limited.[13-15]

Experimental adsorption isotherms have been reported for simple gases (Ar, N$_2$) in monodisperse nanotubes in aluminophosphates;[15] these types of measurements are presumably to be soon available also for monodisperse carbon nanotubes because of the intensive development of techniques for synthesis and separation of carbon-based nanoparticles.

One of the outstanding characteristics of the gas–solid interaction in single-walled carbon nanotubes is the significantly strengthened adsorption potential relative to the one on the planar surface of bulk graphite. It has recently been reported that atomic hydrogen's isosteric heat of adsorption in single-walled carbon nanotubes is

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roughly four times larger (19.6 kJ/mol) than that on graphite (4.9 kJ/mol).[16] However, since the adsorption potential is expected to be less corrugated for nanotubes than for graphite, whether adlayers of simple or polyatomic gases will have a strongly localized or mobile character is still unknown. However, it is reasonable to presume that, at a given temperature, the adsorbate may behave much localized with respect to adsorption on a bulk phase of the same adsorbent. Transport of methane in cylindrical nanopores (7.3 Å) of $AlPO_4$-5, measured by incoherent quasi-elastic neutron scattering, shows relatively high mobility of the adlayer; however, larger molecules such as neopentane migrate through thermally activated jumps.[17]

Eloquent experimental evidence of the one-dimensional character of polyatomic adsorbates with globular morphology confined in narrow nanocylinders has recently been presented in leading experiments[18] and also addressed by molecular simulations.[19,20] In the best knowledge of the authors, there is still a lack of systematic experiments on sorption and diffusion of linear adsorbates in nanocylinders. Theoretical studies on desorption kinetics of linear adsorbates were presented earlier by Tobvin et al.[21]

The thermodynamical behavior of simple fluids (He, H) confined into the interstitials of carbon nanotube bundles has been recently predicted.[22,23] These interstitials can present an even more strongly corrugated adsorption potential than the interior of nanotubes such that the lattice gas approximation applies very well to this case.[22,23] It appears physically feasible to treat adsorption of linear molecules, whose elementary building unit's typical diameter are comparable to the nanotube's diameter, in the lattice gas approximation of interacting k-mers. Although this assumption is ultimately arbitrary, the analytical solution of thermodynamic functions in the discrete limit is of much value and shows qualitative accordance with the experimental behavior of fluids in nanocylinders found recently.[18]

The work is organized as follows. In section 2 the basis of the model of k-mers (linear chains) adsorption on a regular one-dimensional lattice is presented. In addition, the arguments for the rigorous calculation of the Helmholtz free energy in the canonical ensemble are given. The exact forms of chemical potential, configurational entropy, and specific heat are developed in section 3. The calculation of the coverage dependence of the chemical diffusion coefficient is carried out in section 4, assuming thermally activated jumps as the elementary diffusion mechanism. Conclusions are drawn in section 5.

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2. The Physical Model of One-Dimensional Adsorbents

As for theoretical purposes, the adsorption potential within the narrowest nanotubes can be matched to a homogeneous one-dimensional lattice L of adsorption sites. It has also been reported the one-dimensional character of adsorption in troughs of surface crystal planes of TiO_2.[24] Here, we address the general case of adsorbata assumed as linear molecules containing k identical units (k-mers), each of which occupies a lattice site. Small adsorbata with spherical symmetry would correspond to the monomers limit ($k = 1$). Two k-mers interact through their ends with an interaction energy that amounts to w when the ends are nearest-neighbors. The distance between k-mer units is assumed in registry with the lattice constant a; hence, exactly k sites are occupied by a k-mer when adsorbed. Without any loss of generality, we assume the interaction energy between a chain unit and a lattice site to be zero.

Let us assume N linear k-mers adsorbed on M sites with interaction energy w between nearest-neighbors k-mer ends. In this lattice the coverage is given by $\theta = kN/M$. We can now think of a mapping $\mathbf{L} \rightarrow \mathbf{L}'$ from the original lattice $\mathbf{L}$ to an effective lattice $\mathbf{L}'$ where each empty site of $\mathbf{L}$ transforms into an empty one of $\mathbf{L}'$, while each set of k sites occupied by a k-mer in $\mathbf{L}$ is represented by an occupied site in L'.[25] Thus, the total number of sites in $\mathbf{L}'$ is

$$M' = M + (k-1)N \quad (1)$$

and the coverage of $\mathbf{L}'$

$$\theta' = N/M' = (\theta/k) \bigg/ \left[1 - \frac{(k-1)}{k}\theta\right] \quad (2)$$

The canonical partition functions $Q(kN, M, T)$, $Q'(N, M', T)$ in the original and effective lattice must be equal. Thus

$$Q(kN, M, T) = \sum_{\{\mathbf{X}\}} \exp\left[-\frac{E(\mathbf{X})}{k_B T}\right] = Q'(N, M', T) =$$
$$\sum_{\{\mathbf{X}'\}} \exp\left[-\frac{E(\mathbf{X}')}{k_B T}\right] \quad (3)$$

where $\{\mathbf{X}\}$ and $\{\mathbf{X}'\}$ refer to a sum over all possible configurations in $\mathbf{L}$ and $\mathbf{L}'$, respectively.

Accordingly, the Helmholtz free energies per site in $\mathbf{L}$ and $\mathbf{L}'$, $\tilde{F}$ and $\tilde{F}'$, respectively, are related through

$$\tilde{F}(kN, M, T) = -\frac{k_B T}{M} \ln[Q(kN, M, T)]$$

$$= -\frac{k_B T}{M} \ln[Q'(N, M', T)]$$

$$= \frac{M'}{M} \tilde{F}'(N, M', T)$$

$$\tilde{F}(kN, M, T) = \frac{M'}{M}\tilde{F}' = \left\{1 + \left[\frac{(k-1)}{k}\theta\right]\right\} \tilde{F}'(N, M', T) \quad (4)$$

This relationship makes complete the mapping from the original problem of k-mer adsorption on $\mathbf{L}$ to an

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effective Ising-like one (monomer adsorption) on $\mathbf{L}'$. $\tilde{F}'$ can then be written in terms of the probability y of having two nearest-neighbor sites occupied in $\mathbf{L}'$, by means of the cumulant variation method,[26,27] as

$$\tilde{F}\!\left(\frac{N}{M},\,T\right) = wy - k_B T\,[\theta' \ln \theta' + (1 - \theta') \ln (1 - \theta') -$$
$$y \ln y] - k_B T\,[-2\,(\theta' - y) \ln (\theta' - y) -$$
$$(1 - 2\theta' - y) \ln (1 - 2\theta' - y)] \quad (5)$$

For each set of values θ' and T, y is obtained by minimizing $\tilde{F}$. Thus,

$$y = \theta' - \left(\frac{A}{2}\right) + \left[\frac{A^2}{4} - \theta'(1 - \theta')A\right]^{1/2} \quad (6)$$

where $A = [1 - \exp(-w/k_B T)]^{-1}$. In the infinite temperature limit $w/k_B T \to 0$, $A \approx k_B T/w$ and $y \approx \theta'^2 + O(w/k_B T)$, as expected for a totally random distribution of units on the lattice. For infinitely repulsive interactions $w/k_B T \to \infty$, $A \to 1$, and $y = 0$ if $\theta' \leq \frac{1}{2}$. (i.e, no two nearest-neighbor occupied sites are present on the lattice), or $y = 2\theta' - 1$ if $\theta' \geq \frac{1}{2}$. For infinitely attractive interactions, $w/k_B T \to -\infty$, it yields $y = \theta'$, as physically expected.

By using the relationship between θ' and θ (from eq 2) in eq 6 and replacing eq 6 in eq 5, the exact form of $\tilde{F}$ is obtained

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

where α is given by

$$\alpha = \frac{2\theta(1 - \theta)}{k\left[1 - \dfrac{(k-1)}{k}\theta + b\right]} \quad \text{and}$$
$$b = \left\{\left[1 - \frac{(k-1)}{k}\theta\right]^2 - \frac{4}{kA}\,(\theta - \theta^2)\right\}^{1/2} \quad (8)$$

3. Equilibrium Adsorption

All the equilibrium properties of the adlayer can be deduced from eq 7 along with the differential form of $F = M\tilde{F}$ in the canonical ensemble

$$dF = -S\,dT - \Pi\,dM + \mu\,dN \quad (9)$$

where

$$S = -\left(\frac{\partial F}{\partial T}\right)_{M,N} \quad \Pi = -\left(\frac{\partial F}{\partial M}\right)_{T,N} \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{M,T} \quad (10)$$

Then the coverage dependence of the chemical potential and the entropy per site $\tilde{S}$ are straightforward from eqs 7, 8, and 10

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$$\mu/k_B T = k\left(\frac{\partial \tilde{F}}{\partial \theta}\right)_{M,T} = w/k_B T + \ln\,[k(b - 1 + \theta) + \theta] +$$
$$(k - 1) \ln \left[1 - \frac{(k-1)}{k}\theta + b\right] + (k - 1) -$$
$$\ln k - \ln\,[k(b + 1 - \theta) - \theta] \quad (11)$$

$$\tilde{S}/k_B = -\left(\frac{\partial \tilde{F}}{\partial T}\right)_{M,N} = \frac{\theta}{k} \ln \frac{\theta}{k} +$$
$$(1 - \theta) \ln (1 - \theta) - 2\alpha \ln \alpha - \left[\frac{\theta}{k} - \alpha\right] \ln \left[\frac{\theta}{k} - \alpha\right] -$$
$$(1 - \theta - \alpha) \ln (1 - \theta - \alpha) \quad (12)$$

and finally the specific heat at constant volume

$$C_v/k_B = -\left(\frac{\partial^2 \tilde{F}}{\partial T^2}\right)_{M,N} =$$
$$\frac{4\theta^2(1 - \theta)^2}{bk^2\left[1 - \dfrac{(k-1)}{k}\theta + b\right]^2}\left[\frac{w}{k_B T}\right]^2 \exp\left[\frac{w}{k_B T}\right] \quad (13)$$

Equation 11 represents the exact form for the adsorption isotherm of interacting adsorbates (k-mers) in one dimension.

For noninteracting adsorbates ($w = 0$), we obtain from eq 11 the adsorption isotherm equation[11]

$$\exp(\mu/k_B T) = \left[1 - \frac{(k-1)}{k}\theta\right]^{k-1} \theta/(1 - \theta)^k \quad (14)$$

which contrasts significantly with the well-known Flory−Huggins (FH) approximation for linear chains on a one-dimensional lattice

$$\exp(\mu_{FH}/k_B T) = \theta/(1 - \theta)^k \quad (15)$$

because of the strong effect traced to the factor $[1 - \{(k-1)/k\}\theta]^{k-1}$ that is absent in the latter one. The differences observed in the adsorption isotherm are also significant for the entropy, leading to qualitative and quantitative disagreement of it in both approximations.

The coverage dependence of the chemical potential (adsorption isotherm), molar entropy, specific heat, and chemical diffusion coefficient are shown in Figures 1−4 for various k-mer's sizes and interaction energies [attractive ($w < 0$) as well as repulsive ($w > 0$)]. MC simulations in the grand canonical ensemble (shown in symbols in Figures 1−3) fully agree with the predictions from eqs 11−13.

The stronger the lateral interaction, the more steep the adsorption isotherm for attractive k-mers becomes. Qualitatively, no significant changes are observed as the k-mer size increases. However, the curves have a pronounced plateau at $\theta = (k-1)/k$ for strongly repulsive interactions, which smoothes out already for $w/k_B T = +2$. This type of isotherm has very recently been reported for Kr and CH_4 adsorbed in $AlPO_4$-5, where, very likely, the mismatch between the equilibrium separation of the intermolecular interaction and the lattice constant along the nanochannels gives rise to repulsive interaction between NN molecules as assumed in our calculations. It is worth noticing that although the double-steep isotherm may be indicative of a second-order phase transition (as speculated in ref 18), they may not be for an adsorbate whose size is comparable to the nanotube diameter that behaves as a one-dimensional confined fluid. It is well-known that no phase transition develops in a one-dimensional lattice when weak coupling between neighboring particles ex-
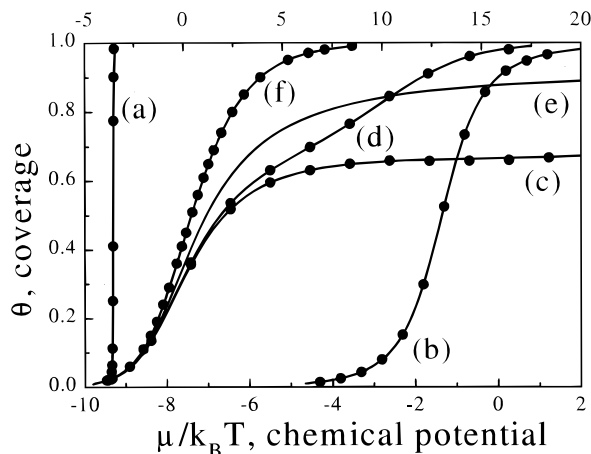
Figure 1. Lattice coverage θ versus relative chemical potential μ/k_BT for interacting (repulsive as well attractive) dimers and 10-mers: (a) $k = 2$, $w/k_BT = -10$; (b) $k = 2$, $w/k_BT = -2$; (c) $k = 2$, $w/k_BT = +10$; (d) $k = 2$, $w/k_BT = +2$; (e) $k = 10$, $w/k_BT = +10$; (f) $k = 2$, $w/k_BT = 0$. The symbols represent results from Monte Carlo simulation in the lattice gas model with the parameters specified in the respective case. The upper axis corresponds to μ/k_BT for the repulsive case ($w/k_BT > 0$).
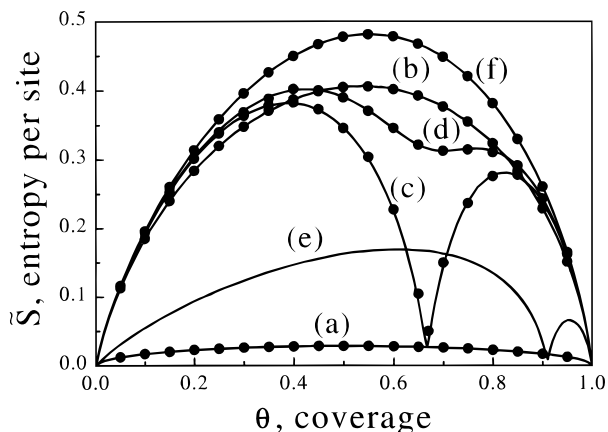

Figure 2. Entropy per site, $\tilde{S}(\theta)$, versus lattice coverage, θ; the curves denoted (a)−(f), correspond one-to-one to the cases displayed in Figure 1. Results from eq 10, where $\bar{E}(T, \theta)$ was calculated by Monte Carlo simulation in the canonical ensemble, are shown in symbols for the respective cases.

Figure 3. Specific heat in units of k_B (at constant volume) versus $4k_BT/|w|$ at $\theta = 0.5$: (a) monomers ($k = 1$); (b) dimers ($k = 2$); (c) trimers ($k = 3$); (d) 10-mers ($k = 10$). (a) and (b) correspond to the left-hand side axis, and (c) and (d) correspond to the right-hand side axis.

Figure 4. Relative chemical diffusion coefficient $D(\theta)/D_0$ versus lattice coverage θ (where D_0 denotes the zero-coverage diffusion coefficient, $D_0 = \lim_{\theta \to 0} D(\theta)$. The curves for repulsive and attractive nearest-neighbor interactions are shown in the upper and lower half of the figure, respectively, and are labeled as in Figure 1 according to the corresponding set of parameters.

ists.[27] Since our model of adsorbed k-mers is isomorphous to a one-dimensional Ising model, it will not present phase transition either. This is clearly seen in Figure 3 where the smooth dependence of the specific heat on temperature is depicted for various k-mers. More recently molecular simulations[19,20] of alkenes in AlPO$_4$-5 have also shown that a plateau in the adsorption isotherm arises along with a rearrangement of the adsorbate molecules within the channels. From isosteric heat of adsorption calculations is concluded that the plateau is due to a net repulsive potential felt by molecules. As the coverage approaches the typical value $\theta \approx {}^2/_3$, the molecules rearrange within the channel to increase their ads−ads interaction; however, this forces the molecules to occupy new adsorption sites where their interaction with the AlPO$_4$-5 framework diminishes (becomes more repulsive), giving a net decrease of the isosteric heat of adsorption.

The general features of the coverage dependence of the entropy per site are the following (see Figure 2): for attractive interactions $\tilde{S}$ is symmetrical with a maximum at $\theta = 0.5$ for interacting as well as for noninteracting monomers ($k = 1$). For interacting k-mers ($k > 1$), the
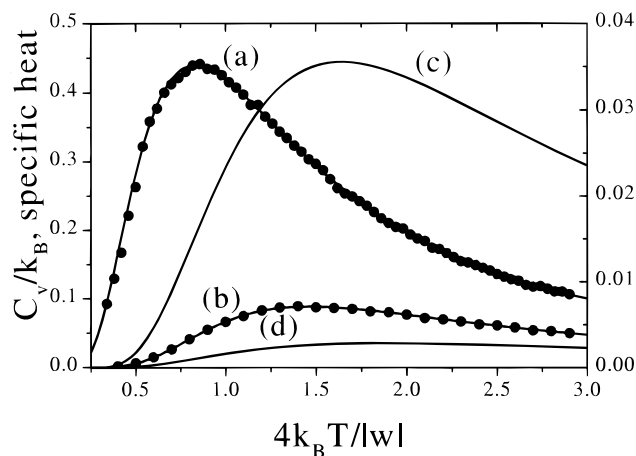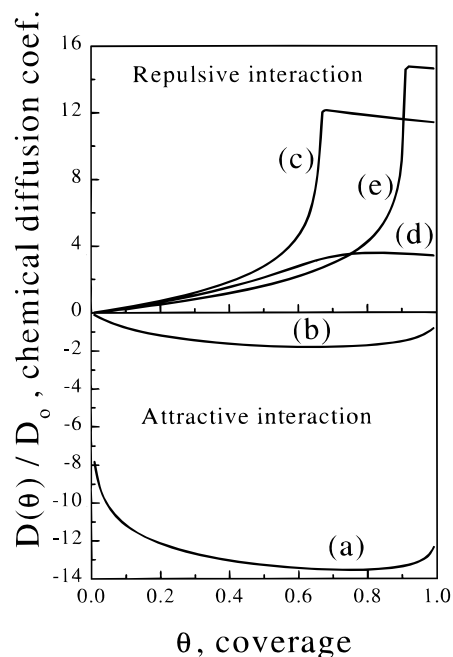
maximum shifts to higher coverages ($\theta > 0.5$). However, given a ratio $w/k_BT \leq 0$ the maximum shifts to higher coverages in such a way that the larger k, the further the maximum gets from $\theta = 0.5$. This result differs from the one-dimensional limit of noninteracting k-mers ($w/k_BT = 0$) in the Flory−Huggins[8,27] approximation for which the maximum of $\tilde{S}$ shifts to lower coverages as k increases. Given a k-mer size, the stronger the interaction the smaller the shift of the maximum from $\theta = 0.5$. For repulsive interactions, the entropy develops a local minimum at $\theta \geq 0.5$, which gets sharper as the ratio w/k_BT increases and shifts to higher coverages as the k-mer size increases. In all cases the minimum traces to a nondegenerate ground state where k-mers structure is an ordered sequence leaving one empty site between nearest-neighbor particles. None of the minima correspond to a second-order phase

transition as expected for particles with short-ranged interactions in one dimension. The position of this minimum also embodies valuable information about the collective transport of particles since, as shown later in Figure 4, it relates to the maximum of the chemical diffusion coefficient of repulsive *k*-mers. Comparisons between calculations of $\tilde{S}$ (from MC simulation and thermodynamic integration) and the analytical dependence from eq 12 are also shown in Figure 2. For any given temperature *T* and coverage θ

$$\frac{\tilde{S}}{k_B}(T, \theta) = \frac{\tilde{S}}{k_B}(\infty, \theta) + \frac{\bar{E}(T, \theta)}{k_B T} -$$
$$\int_{T=\infty}^{T} \bar{E}(T', \theta) \, d\left[\frac{1}{k_B T'}\right] \quad (16)$$

where $\bar{E}(T', \theta)$ denotes the mean total energy per site (that is calculated by MC in the canonical ensemble) and $\tilde{S}/k_B(\infty, \theta)$ denotes the entropy per site of noninteracting *k*-mers ($w/k_B T = 0$) such that

$$\frac{\tilde{S}}{k_B}(\infty, \theta) = \left[1 - \left(\frac{k-1}{k}\right)\theta\right] \ln\left[1 - \left(\frac{k-1}{k}\right)\theta\right] -$$
$$\frac{\theta}{k} \ln \frac{\theta}{k} - (1-\theta) \ln(1-\theta) \quad (17)$$

by taking the limit $\alpha \to \infty$ in eqs 8 and 12. The agreement obtained is remarkable for weak as well as strong lateral interactions regarding the intrinsic difficulties of entropy calculation for polyatomic species at low temperatures. $S(\theta, T)$ is thoroughly reproduced by this calculation for attractive as well as repulsive interactions, as shown in Figure 2.

The specific heat, from eq 13, is compared with MC simulations at $\theta = 0.5$ (see Figure 3). A continuum variation of C_v/k_B on *T* is observed with a maximum that lowers and broadens as the *k*-mers size increases; accordingly no phase transition develops as expected.

4. Surface Diffusion

Concerning diffusion of interacting *k*-mers, we consider the elementary transport process to take place by thermally activated jump to nearest-neighbors positions (i.e, the *k*-mers can move over a distance of only one lattice constant either to the left or right if the final sites are empty). It is worth mentioning that a very interesting alternative mechanism of diffusion in one-dimensional systems has recently been proposed,[28] where the molecules move along one direction in concerted motion involving jump of a admolecules cluster rather than by individual jumps, because of the strong mismatching between the equilibrium separation of the intermolecular potential and the lattice spacing. Although this mechanism may account for the high mobility observed for single-file diffusion in AlPO₄-5,[28,29] the results are still hypothetical. It should be also mentioned that (as shown later) also nearest-neighbor repulsive interactions, owing to the mismatch between the molecular size and lattice spacing, also lead to a significant increase of the chemical diffusion coefficient at finite coverages. There exists evidence of this type of diffusion mechanism for polyatomic molecules adsorbed in nanocylindrical pores.[17] Although the migration of large molecules can, in many cases, show other jump mechanisms, the fact that the exact coverage dependence of the

diffusion constant can be obtained under this assumption justifies the following analysis.

It is known that the displacement of single particles in single-file diffusion follows the time dependence[30,31] $\langle r^2(t) \rangle \propto t^{1/2}$. Hence the tracer diffusion coefficient vanishes at long times for diffusion on an infinitely long lattice. However, it is known that the center of mass's mean-square displacement of monomers in one dimension (collective motion) at finite coverages obeys a time dependence[30,32] $\langle R^2(t) \rangle \propto t$, where the proportionality constant $D_j(\theta)$ is coverage dependent and called jump (or phenomenological) diffusion coefficient. It is straightforward to show that this behavior also holds for *k*-mers in one dimension that perform elementary jumps of length equal to one lattice constant.

From the Green–Kubo formalism,[33] the chemical diffusion coefficient is

$$D(\theta) = D_j(\theta) \, Th(\theta) \quad (18)$$

where

$$Th(\theta) = \left[\partial\left(\frac{\mu}{k_B T}\right)/\partial \ln \theta\right]_T \quad (19)$$

is called the thermodynamic factor, and it can be obtained from eq 11 by differentiation. $D(\theta)$ can be alternatively written as

$$D(\theta) = \Gamma(\theta)\left\{\partial\left[\exp\left(\frac{\mu}{k_B T}\right)\right]/\partial\theta\right\}_T \quad (20)$$

where

$$\Gamma(\theta) = D_j(\theta) \, \theta \, \exp\left[-\left(\frac{\mu}{k_B T}\right)\right] \quad (21)$$

is called the effective jump rate[34] and physically gives the rate of jumps of *k*-mers into nearest-neighbor empty sites at coverage θ.

Thus

$$\Gamma(\theta) = \sum_{j=0}^{2}(2-j)/2 \, P^{(j)}\Gamma^{(j)} \quad (22)$$

where $P^{(j)}$ and $\Gamma^{(j)}$ are the probability that a *k*-mer has *j* nearest-neighbor *k*-mers and its jump rate, respectively. Within the quasi-chemical approximation (which is exact in one dimension)

$$P^{(j)} = (\eta\epsilon)^j/(1 + \eta\epsilon)^2 \quad (23)$$

where

$$\eta \equiv \exp(-w/k_B T) \quad \text{and}$$
$$\epsilon = [kb - k + k(k-1)\theta + 2\theta]/2\eta\theta \quad (24)$$

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The jump rate is defined by $\Gamma^{(j)} = \Gamma(0)\eta^{-j}$. Finally

$$D(\theta) = \frac{(1 + \epsilon)}{(1 + \eta\epsilon)^2}[\partial(\mu/k_B T)/\partial \ln \theta]_T \qquad (25)$$

(assuming $\Gamma(0) = 1$ arbitrarily).

It is worth noting the limit case of noninteracting k-mers for which $w = 0$ and $D(\theta) = [1 - \{(k-1)/k\}\theta]^{-2}$. This gives a remarkably much weaker coverage dependence for D than the one obtained by assuming the coverage dependence of the chemical potential from the FH approximation that predicts $D_{FH}(\theta) \propto [1 - \{(k-1)/k\}\theta]^{-k}$.

The coverage dependence for the chemical diffusion coefficient $D(\theta)$ of dimers and 10-mers is depicted in Figure 4 for repulsive (top) and attractive interactions (bottom). The general behavior for $D(\theta)$ is that a repulsive interaction leads to an increase of $D(\theta)$ for all θ. For large $w/k_B T \gg 1$, $D(\theta)$ varies significantly within an interval of θ around the one corresponding to the plateau in the adsorption isotherm shown in Figure 1. It reaches a maximum and then becomes approximately coverage independent up to full coverage, owing to a cancelation effect between $D_j(\theta)$ (that decreases with θ) and $Th(\theta)$ (that increases with θ).

As pointed out before, the net effect of repulsive interaction is the overall increase of chemical diffusion at high coverages. It should be mentioned that this situation may occur in quasi-one-dimensional pores where the mismatch of the adsorbate size and lattice constant can give rise to repulsive forces between nearest-neighbor units. Attractive interactions, in turn, decrease $D(\theta)$ for all θ, with respect to noninteracting k-mers, leading to a smooth coverage dependence, except for θ close to 0 and 1.

5. Conclusions

The statistical thermodynamic analysis of multisite-occupancy adsorption in a one-dimensional lattice provides an intuitive approach to linear molecules confined in quasi-one-dimensional nanotubes.

A comprehensive description of thermodynamic functions and their dependence on parameters as the type of interactions, adsorbate size, temperature, and surface coverage was given through their exact forms.

The model also provides a background to approximate the thermodynamic functions of more complex quasi-one-dimensional adsorbents as carbon nanotube bundles, where molecules within a channel can interact with their neighbors along the same channel, as well as with others adsorbed in neighboring channels because of the bundle packing. Transversal interactions can be easily accounted for by incorporating them through a mean-field in the free energy expression of eq 7.

Interesting results concerning transport properties on this model system have been presented by means of the exact calculation of the chemical diffusion constant representing the macroscopic relaxation of density fluctuations.

Features of the transport coefficients can be traced to similar ones of the thermodynamic functions, as the maximum in $D(\theta)$ for $w/(k_B t) \gg 1$ that traces to the minimum in $\tilde{S}$ to the same coverage.