

Statistical thermodynamics and transport of linear adsorbates

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The exact lattice-gas solution for thermodynamics functions, jump and chemical diffusion coefficients of linear adsorbates in a one-dimensional space is presented. Results are compared with corresponding ones from the Flory's approximation. Significant quantitative and qualitative discrepancies are shown and discussed. The results may be applicable to adsorption and transport of polyatomic molecules in low-dimensional systems such as carbon nanotubes. All calculations are further extended to higher dimensions (higher connectivity) based upon the exact forms in one dimension and a connectivity ansatz. The resulting thermodynamic description is much improved with respect to the known standard approximations. [S0163-1829(99)06311-0]

I. INTRODUCTION

Adsorption with multisite occupancy is a topic being increasingly considered in surface science because of its straightforward relevance to practical situations such as gas and hydrocarbon separation, streams and pollution control, heterogeneous catalysis, etc.. Most adsorbates, except noble gases, are polyatomic. Furthermore, surfaces generally present inhomogeneities due to irregular arrangement of surface and bulk atoms, the presence of various chemical species, etc., which can significantly affect the entropic contribution to the adsorbate's free energy. Typical examples are O_2, N_2, CO, CO_2 absorbed in carbon and zeolite molecular sieves¹⁻³ and oligomers in activated carbons.^{4,5} In spite of the obvious significance of polyatomic adsorption, most developments in adsorption theory have mainly dealt with monoatomic adsorption.⁵⁻⁷ Valuable contributions have recently been presented in terms of lattice-gas approximations.⁸⁻¹³

The inherent complexity of this system still represents a major difficulty to the development of approximate solutions for the thermodynamic functions, which certainly hampers their analysis. To this respect, simple solvable models of adsorption on homogeneous surfaces are useful as basis for alternative approaches for heterogeneous surfaces.^{5,6,9,13}

Recently, the advent of modern techniques for building single and multiwalled carbon nanotubes¹⁴⁻¹⁹ has considerably encouraged the investigation of the gas-solid interaction (adsorption and transport of simple and polyatomic adsorbates) in such a low dimensional confining adsorption potentials.

The design of carbon tubules, as well as of synthetic zeolites and aluminophosphates such as $AlPO_4^5$ (Ref. 20) having narrow channels, literally provides a way to the experimental realization of one-dimensional adsorbents.

Many studies on conductivity, electronic structure, mechanical strength, etc. of carbon nanotubes are being currently carried out. However the amount of theoretical and experimental work done on the interaction and thermodynamics of simple gases adsorbed in nanotubes is still very limited.²¹⁻²³ No experimental adsorption of isotherms have been reported yet; however, this type of result will presumably be soon available because of the proceeding develop-

ment of this field (a number of very interesting experiments on adsorption and diffusion of gases in nanotubes²⁴⁻²⁶ (have recently appeared).

One outstanding feature of the gas-solid interaction in single-walled nanotubes (SWN) is that the adsorption potential is significantly strengthened with respect to the one on a planar layer of bulk graphite. This has recently been observed for atomic hydrogen whose isosteric heat of adsorption in a SWN is roughly four times larger (19.5 KJ/mol) than on graphite (4.9 KJ/mol).²⁷ Concerning the transport of gases in narrow nanocylinders, a leading experimental contribution has recently been reported where the diffusion coefficient of polyatomic adsorbates was measured by incoherent quasielastic neutron scattering.²⁰

For theoretical purposes, adsorption in the narrowest nanotubes can be treated in the one-dimensional lattice-gas approach. This is, of course, an approximation to the state of real adsorbata in nanotubes, which is justified because thermodynamics and transport coefficient can be analytically resolved in these conditions. This is of much qualitative value and may be thought feasible for monoatomic species strongly bonded to the nanopores's wall, as well as for polyatomics where the distance between their building units does not seriously mismatch the separation between adsorption potential minima for single units.

However, it should be pointed out that polyatomic adsorbates such as hydrocarbons within nanopores cannot be simply described by a lattice-gas approximation as shown by Refs. 28, 29, and 30.

Here, we present the exact solution for the thermodynamics functions of adsorbed linear chains (k -mers) of arbitrary length in a infinite one-dimensional space. The thermodynamic functions are further extended to higher dimensions based upon their exact form in one dimension and a connectivity ansatz. Although adsorption of monoatomic species have been long studied, it appears necessary to obtain rigorous results for polyatomic adsorbates. An early seminal contribution to this subject was the well-known Flory's approximation for adsorption of binary liquids in two dimensions.³¹ It is worth mentioning that, in the framework of the lattice-gas approach, adsorption of pure linear molecules is isomorphous to polymer mixture adsorption (linear polymer-monoatomic solvent). Thus, all results presented here can be

straightforwardly applied to the corresponding polymer solution case. Adsorption of chains on regular lattices is a long-standing problem in which modified forms of Flory's approximation³²⁻³⁴ have been also proposed. A comprehensive discussion on this subject is included in the book of Des Cloizeaux and Jannink³⁵ and Ref. 36.

Monte Carlo simulations of polymer-solvent mixtures in three dimensions³⁷ have shown that critical temperatures are expected to be largely overestimated by Flory's approach and the phase diagram appreciably distorted. However, Monte Carlo simulations of very large polymers ($k > 50$) at high concentrations are still highly demanding even with modern computational resources.

There are two main contributions in this chemical work: (a) the rigorous form of the adsorption isotherm and diffusion coefficient (and remaining thermodynamics functions) of linear adsorbates (sometimes referred here as k -mers) which may be applicable to adsorption and transport in narrow nanotubes; (b) the extension of the calculations to higher dimensions by using the exact forms in one dimension and a connectivity ansatz, that performs appreciably better than the standard Flory's approach.

In addition, the importance of the one-dimensional solution goes beyond the example cited here. There exist various phenomena that can be looked upon as adsorption on one-dimensional chain, namely, adsorption on linear polymers or on a protein chain.³⁸

Rigorous expressions for the chemical potential (adsorption isotherm), free energy, entropy, and spreading pressure of linear adsorbates in one dimension are given in Sec. II. In Sec. III, approximate forms for the thermodynamic functions in higher dimensions are proposed based upon the one-dimensional exact solution and a connectivity ansatz that incorporates the influence of higher connectivities on the partition function.

A thorough comparison of the coverage and chain-size dependence of thermodynamic functions arising from the exact solution, Flory's approximation, and Monte Carlo simulation, are carried out. Furthermore, dynamical properties of k -mers, such as the chemical and jump diffusion coefficients, are exactly calculated as well and discussed in Sec. IV. Conclusions are drawn in Sec. V.

II. EXACT THERMODYNAMIC FUNCTIONS IN ONE DIMENSION

Let us assume a one-dimensional lattice of M sites with lattice constant a ($M \rightarrow \infty$) where periodic boundary conditions apply. Under this condition all lattice sites are equivalent, hence border effects will not enter our derivation.

N -linear k -mers are adsorbed on the lattice such a way that each k -mer occupies one lattice site and double site occupancy is not allowed as to represent properties in the monolayer regime. Since different k -mers do not interact with each other through their ends, all configurations of N k -mers on M sites are equally probable; henceforth, the canonical partition function $Q(M, N, T)$ equals the total number of configurations, $\Omega(M, N)$, times a Boltzmann factor including the total interaction energy between k -mers and lattice sites, $E_k(N)$

$$Q(M, N, T) = \Omega(M, N) \exp\left[-\frac{E_k(N)}{k_B T}\right]. \quad (1)$$

Since the lattice is assumed homogeneous, $E_k(N)$ can be arbitrarily chosen equal to zero for all N without losing generality (i.e., the interaction energy between every unit forming a k -mer and the substrate is set to be zero).

$\Omega(M, N)$ can be readily calculated as the total number of permutations of the N indistinguishable k -mers out of n_e entities, being n_e

$$\begin{aligned} n_e &= \text{number of } k\text{-mers} + \text{number of empty sites} \\ &= N + M - kN = M - (k-1)N. \end{aligned} \quad (2)$$

Accordingly,

$$\Omega(M, N) = \binom{n_e}{N} = \frac{[M - (k-1)N]!}{N! [M - kN]!}. \quad (3)$$

(A particular solution for dimers was presented in Ref. 39.)

In the canonical ensemble the Helmholtz free energy $F(M, N, T)$ relates to $\Omega(M, N)$ through

$$\beta F(M, N, T) = -\ln Q(M, N, T) = -\ln \Omega(M, N), \quad (4)$$

where $\beta = 1/k_B T$.

The remaining thermodynamic functions can be obtained from the general differential form⁴⁰

$$dF = -SdT - \Pi dM + \mu dN, \quad (5)$$

where S , Π , and μ designate the entropy, spreading pressure, and chemical potential, respectively, which by definition are

$$S = -\left(\frac{\partial F}{\partial T}\right)_{M, N}, \quad \Pi = -\left(\frac{\partial F}{\partial M}\right)_{T, N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T, M}. \quad (6)$$

Thus, from Eqs. (3) and (4)

$$\begin{aligned} \beta F(M, N, T) &= -\{\ln[M - (k-1)N]! - \ln N! \\ &\quad - \ln[M - kN]!\}, \end{aligned} \quad (7)$$

which can be accurately written in terms of the Stirling approximation

$$\begin{aligned} \beta F(M, N, T) &= -[M - (k-1)N] \ln[M - (k-1)N] \\ &\quad + [M - (k-1)N] + [N \ln N - N] \\ &\quad + [(M - kN) \ln(M - kN) - (M - kN)] \\ &= -[M - (k-1)N] \ln[M - (k-1)N] \\ &\quad + N \ln N + (M - kN) \ln(M - kN). \end{aligned} \quad (8)$$

Henceforth, from Eqs. (6)

$$\begin{aligned} \frac{S(M, N)}{k_B} &= [M - (k-1)N] \ln[M - (k-1)N] \\ &\quad - N \ln N - (M - kN) \ln(M - kN), \end{aligned} \quad (9)$$

$$\beta \Pi = \ln[M - (k-1)N] - \ln[M - kN], \quad (10)$$

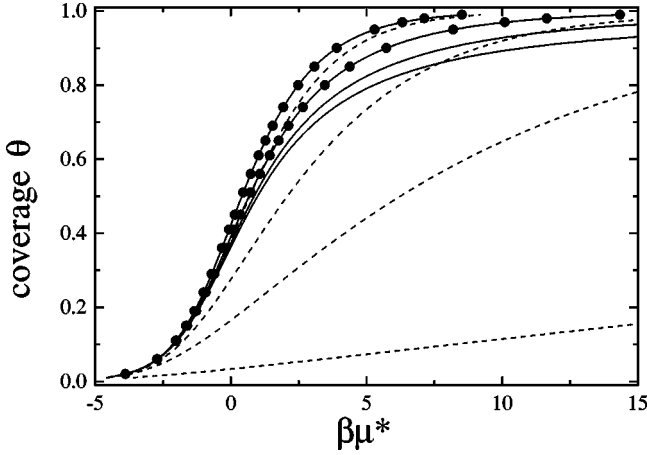


FIG. 1. Surface coverage $\theta = kN/M$ versus relative chemical potential $\beta\mu^* = \beta\mu + \ln C_k$. Comparison between adsorption isotherms for k -mers in one dimension from Flory's approximation (---) and exact solution (—) from Eq. (15) for dimers, 4-mers, 10-mers, and 100-mers (curves from top to bottom). MC simulation for $k=2$ and $k=4$ in one dimension are shown in full circles.

$$\beta\mu = \ln \frac{kN}{M} + (k-1) \ln \left[1 - (k-1) \frac{N}{M} \right] - k \ln \left[1 - \frac{kN}{M} \right]. \quad (11)$$

Then, by defining the lattice coverage $\theta = kN/M$, molar-free energy $\tilde{F} = F/M$ and molar entropy $\tilde{S} = S/M$, Eqs. (8)–(11) can be rewritten in terms of the intensive variables θ and T ,

$$\beta\tilde{F}(\theta, T) = - \left\{ \left[1 - \frac{(k-1)}{k} \theta \right] \ln \left[1 - \frac{(k-1)}{k} \theta \right] - \frac{\theta}{k} \ln \frac{\theta}{k} - (1-\theta) \ln(1-\theta) \right\}, \quad (12)$$

$$\frac{\tilde{S}(\theta)}{k_B} = \left[1 - \frac{(k-1)}{k} \theta \right] \ln \left[1 - \frac{(k-1)}{k} \theta \right] - \frac{\theta}{k} \ln \frac{\theta}{k} - (1-\theta) \ln(1-\theta), \quad (13)$$

$$\exp(\beta\Pi) = \frac{\left[1 - \frac{(k-1)}{k} \theta \right]}{(1-\theta)}, \quad (14)$$

$$C_k \exp(\beta\mu) = \frac{\theta \left[1 - \frac{(k-1)}{k} \theta \right]^{k-1}}{(1-\theta)^k}, \quad (15)$$

where $C_k = k$

Equation (15) is the exact, so-called, isotherm equation for k -mers in one dimension that should be regarded as a generalization of the well-known equation

$$C_k \exp(\beta\mu_{Fl}) = \frac{\theta}{(1-\theta)^k} \quad (16)$$

(where μ_{Fl} holds for Flory's approximation) developed by Flory³¹ for polymer solutions when the solvent is monomeric

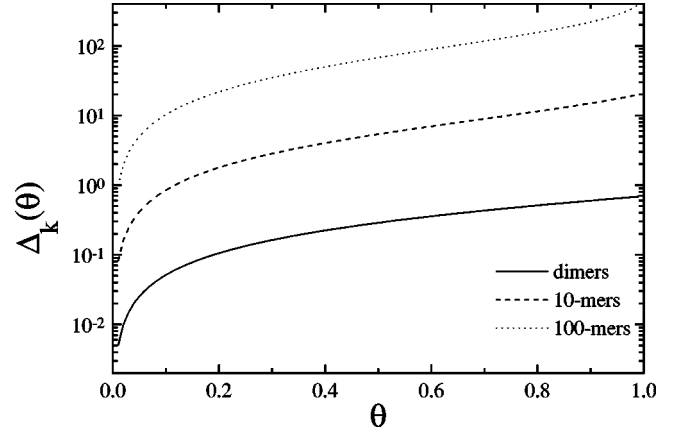


FIG. 2. Relative reduced chemical potential $\Delta_k(\theta) = \beta(\mu_{Fl} - \mu)$ versus surface coverage (log-linear plot) for various sizes of linear k -mers; (—), dimers ($k=2$); (---), 10-mers; (·····), 100-mers.

with unitary molar volume. This is indeed the case analyzed in the present paper, where the empty sites of the lattice formally correspond to the solvent's monomers in Flory's solution (see Appendix A).

Explicit forms for the molar-free energy and entropy from Flory's approximation are given in Appendix A.

In order to compare the adsorption isotherm Eqs. (15) and (16), it is worth to define a relative reduced chemical potential

$$\Delta_k(\theta) = \beta(\mu_{Fl} - \mu) = -(k-1) \ln \left[1 - \frac{(k-1)}{k} \theta \right], \quad (17)$$

which yields the limits $\Delta_k(\theta)_{\theta \rightarrow 0} = 0$; $\Delta_k(\theta)_{k \rightarrow \infty} = \infty$, for all $\theta > 0$.

An extensive comparison between the exact isotherm Eq. (15) and Flory's equation, along with MC simulations are shown in Figs. 1 and 2. Flory's approximation agrees fairly well with the exact result for very small k -mers (typically $k < 3$); however the disagreement turns out to be significantly large for larger chains.

The differences between both results can be much easily rationalized with the help of Fig. 2, where the coverage dependence of the reduced chemical potential has been depicted.

Concerning other thermodynamic functions such as the free energy, entropy, and spreading pressure, their exact forms present appreciable quantitative as well as qualitative discrepancies with Flory's approach. Particularly, the exact molar configurational entropy $\tilde{S}(\theta)$ behaves already quite differently for very small k -mers (dimers, trimers, etc.) at all coverages. The overall behavior can be summarized as follows: in the limits $\theta \rightarrow 0$ and $\theta \rightarrow 1$ the entropy tends to zero. For very low coverages $\tilde{S}(\theta)$ is an increasing function of θ , reaches a maximum at θ_m , then decreases monotonically to zero for $\theta > \theta_m$. The position of θ_m , which is $\theta_m = 0.5$ for $k=1$, shifts to higher coverages as the adsorbate size k gets larger. The maximum can be readily obtained from the condition $\partial \tilde{S}(\theta) / \partial \theta |_{\theta = \theta_m} = 0$.

Thus, from Eq. (13) we get

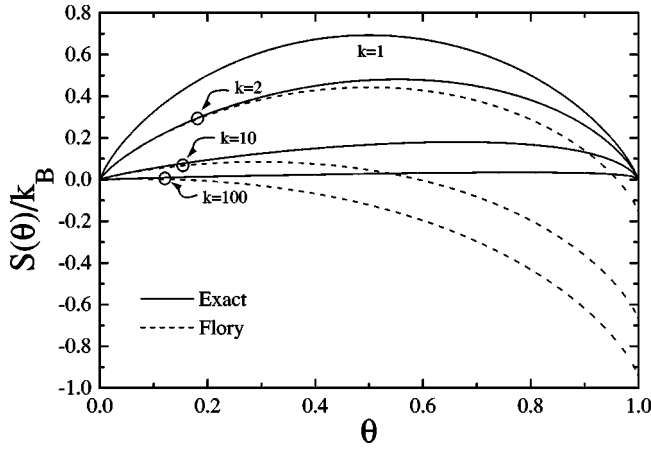


FIG. 3. Molar entropy $\tilde{S}(\theta)/k_B$ (in units of k_B) versus surface coverage. Comparison between exact results (—) and Flory's approach (- - -) for monomers ($k=1$), dimers ($k=2$), and polymers ($k=10$) and $k=100$). Curves from top to bottom (the case $k=1$ is common for both results).

$$(1-\theta)^k - \frac{\theta}{k} \left[1 - \frac{(k-1)}{k} \theta \right]^{k-1} = 0, \quad (18)$$

which is a polynomial of k th order with unique solution θ_m for all $k \geq 1$.

This represents a major distinction between the exact solution and the Flory's approach since in the latter, the larger the chain the more the maximum in the entropy shifts to lower coverages.

An even more remarkable behavior comes from Flory's approach for the molar entropy in one dimension, which attains negative values for all $k > 1$. The range of θ where $\tilde{S}_{Fl}(\theta)$ becomes negative broadens as k increases. In the nomenclature of random mixing of polymer solutions, the difference $\Delta\tilde{S}(\theta)$ between $\tilde{S}(\theta)$ and the entropy of the pure polymer, rather than $\tilde{S}(\theta)$, is considered. Rigorously, this difference is expected to behave as $\Delta\tilde{S}(\theta)_{k \rightarrow \infty} \rightarrow 0$ for all θ . On the other hand, in the Flory's approach it tends to a limiting concave curve from above for $k \rightarrow \infty$.⁴⁰ In either case, the qualitative discordance is remarkable (Fig. 3).

Further comparison is carried out in Fig. 4 for the spreading pressure, which is a monotonically increasing function of θ over the range $[0,1]$.

Adsorption of linear adsorbates (i.e., dimers, oligomers, etc.), in very narrow carbon nanotubes or cylindrical pores of aluminophosphates, can be thought as a physical system to which the present thermodynamic results may apply.

Although no experimental adsorption isotherms are available yet to test the applicability of the exact isotherm Eq. (15) to this system, they will very likely be soon available owing to the increasing interest in the synthesis of monodisperse nanotubes and their adsorption properties.

III. FURTHER EXTENSION TO HIGHER DIMENSIONS

Hereafter, we address the calculation of approximated thermodynamical functions of linear chains adsorbed on lattices with connectivity c higher than 2 (i.e., dimensions higher than one).

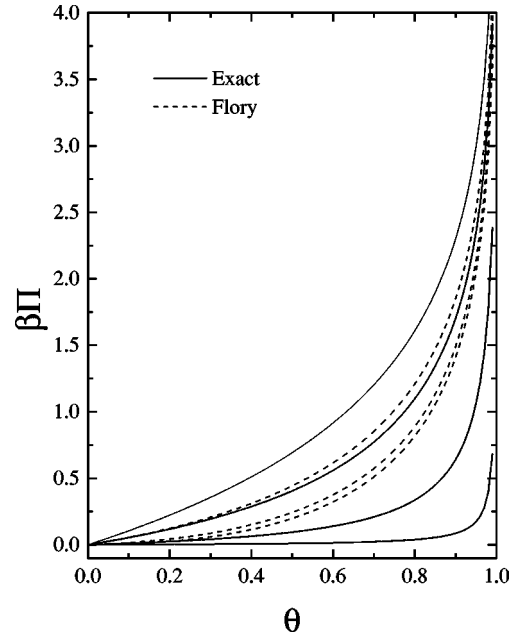


FIG. 4. Spreading pressure $\Pi(\theta)$ in units of $1/\beta$ versus surface coverage. Comparison between exact results (—) and Flory's approach (- - -) for monomers ($k=1$), dimers ($k=2$), and polymers ($k=10$ and $k=100$). Curves from top to bottom (the case $k=1$ is common for both results).

In general, the number of states Ω for fixed M and N will be also the function of the lattice connectivity; henceforth $\Omega \equiv \Omega(M, N, c)$.

In order to derive an explicit form for the $\Omega(M, N, c)$ that bears the advantages of the exact solution in one dimension with respect to the standard Flory's approximation, we assume the following connectivity ansatz (see Appendix C for further discussion)

$$\frac{\Omega(M, N, c)}{\Omega(M, N, c')} = \left[\frac{c-1}{c'-1} \right]^{N(k-1)} = \frac{\Omega_{Fl}(M, N, c)}{\Omega_{Fl}(M, N, c')}, \quad (19)$$

where Ω_{Fl} is given by Eq. (A.1). Accordingly, we resolve $\ln \Omega(M, N, c)$ by setting $c'=2$ and using $\ln \Omega(M, N, 2)$ from Eqs. (4) and (8)

$$\ln \Omega(M, N, c) = \ln \Omega(M, N, 2) + N(k-1) \ln(c-1). \quad (20)$$

It is straightforward from Eqs. (4), (6)–(15), and (20) that

$$\beta f_c = \beta f - \theta \frac{(k-1)}{k} \ln(c-1) \quad (21)$$

$$\frac{S_c}{k_B} = \frac{S}{k_B} + \theta \frac{(k-1)}{k} \ln(c-1), \quad (22)$$

$$\exp(\beta \Pi_c) = \frac{\left[1 - \frac{(k-1)}{k} \theta \right]}{(1-\theta)}, \quad (23)$$

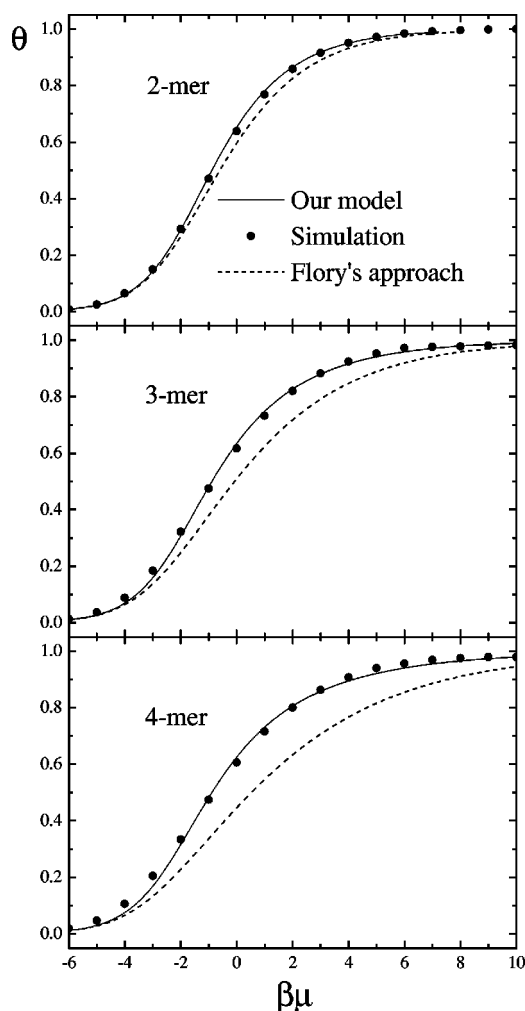


FIG. 5. Surface coverage θ versus relative chemical potential $\beta\mu^* = \beta\mu + \ln C_{k,c}$ for linear k -mers in a square lattice ($c=4$), our model from Eq. (24) (—), Flory's approximation (---). The isotherms for dimers, 3-mers, and 4-mers are shown in both cases (curves from top to bottom). MC simulations are shown in full circles.

$$C_{k,c} \exp(\beta\mu_c) = \frac{\theta \left[1 - \frac{(k-1)}{k} \theta \right]^{k-1}}{(1-\theta)^k}, \quad (24)$$

where the subindex c holds for the thermodynamic quantities in regular lattices with connectivity c , and the constant C_k of Eq. (15) has the general expression $C_{k,c} = k(c-1)^{k-1}$ (thus, $C_k = C_{k,2}$ for consistency).

Equations (19)–(24) provide the basic thermodynamic functions for noninteracting linear adsorbates in lattices with general connectivity c .

It is worth noting that the isotherm Eq. (24), valid for lattices of arbitrary connectivity, shows coverage dependence identical to the exact one-dimensional one [Eq. (15)]. The lattice connectivity only enters in the constant $C_{k,c}$ [actually Eq. (15) is the only particular case in which Eq. (24) becomes exact].

A comparison between the adsorption isotherms of Eq. (24), Monte Carlo (MC) simulation, Flory's approach is carried out in Fig. 5 for adsorbates of different size on a square

lattice. For short chains (up to $k=4$), Eq. (24) agrees with MC appreciably better than it does with the other approaches.

MC simulation of larger linear adsorbates on regular two-dimensional lattices would be necessary to confirm this behavior. Nevertheless, Eq. (24) appears as a qualitatively and quantitatively better isotherm than other standard approaches³¹ for noninteracting chains. As usual, interaction between chain units can be incorporated into Eq. (24) by means of the mean-field approximation. Extension of these calculations to interacting chains *via* mean-field, quasichemical approximations, and exact counting of configuration are currently being worked out and are not included here to keep a reasonable length for this paper. A thorough analysis of adsorption of chains in higher dimensions and comparison with Flory's approximation will be given elsewhere.

IV. DYNAMICAL PROPERTIES: CHEMICAL DIFFUSION COEFFICIENT

Surface diffusion is one of the elementary mechanisms by which an adlayer reaches thermodynamic equilibrium with the adsorbent. Hence, it is expected to play a significant rate in surface processes such as catalysis, thermal desorption, film growth, roughening, etc..

Surface diffusion of monoatomic species has been addressed since long ago.^{41–44} However, the mathematical description of migration of polyatomic species on latticelike substrates has not been paid much attention.⁴⁵ Features of surface diffusion of interacting dimers in the monolayer regime have been recently reported.⁴⁶ The adsorbate size strongly affects the coverage dependence of the diffusion coefficient both for noninteracting and interacting molecules. This appears to be pertinent for strongly bound adsorbates as chemisorbed species [e.g., CO/Ni(111), Pt₂/W(110), W₂/W(110)]. On the other hand, a review on surface diffusion of physisorbed molecules can be found in Ref. 44, p. 451.

Hereafter, we address the exact solution for the chemical diffusion coefficient of polymers as a function of surface coverage, in the framework of the present description (one-dimensional space). Although here, we again address the collective diffusion in the lattice-gas approximation because of its simplicity and analytical tractability, it should be noted that in many situations diffusion of polyatomic species is significantly more complex and the model of migration through thermally activated jumps on a lattice-like substrate may not apply.⁴⁷ Even for monoatomic species in one-dimensional adsorption potentials, collective diffusion can take place by concerted motion of neighboring particles (clusters) rather than by individual groups as recently proposed in Ref. 48. We start the derivation by noting that small fluctuations (or linear perturbation) to the local surface coverage relax to equilibrium obeying the Fick's first law

$$\vec{J} = -D\nabla\rho, \quad (25)$$

where \vec{J} , ρ , and D are the net flux of mass through a unit area per unit of time, density, and chemical diffusion coefficient, respectively.

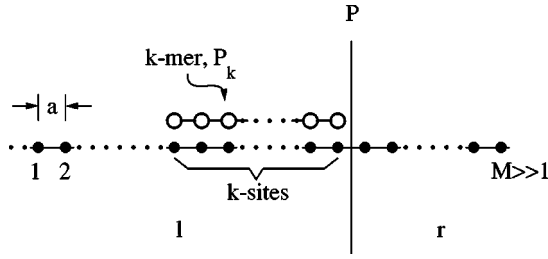


FIG. 6. One-dimensional chain of sites with lattice constant a and periodic boundary condition. The plane P , arbitrarily set between two nearest-neighbor sites, divides the lattice into two segments denoted by l (after left) and r (right), respectively. P_k designate the probability of k adjacent sites to be occupied by a k -mer.

Let us assume a plane P dividing the linear lattice in two segments l and r as shown in Fig. 6.

Let $J_{l \rightarrow r}$ be the mass per unit of time flowing through P from l to r . Since the lattice is assumed to be homogeneous and the diffusion a thermally activated process, the jump of an adsorbed k -mer to a nearest-neighbor position occurs with probability $W_{l \rightarrow r}$ given by

$$W_{l \rightarrow r} = \kappa \exp(\beta \Delta E_d) = W_{r \rightarrow l}, \quad (26)$$

where κ is a rate constant (the rate at which jumps are attempted) and ΔE_d the activation energy for diffusion (the energy barrier that a k -mer has to overcome to move right or left over a distance equal to one lattice constant). Thus,

$$J_{l \rightarrow r} = P_k P'_1 W_{l \rightarrow r}, \quad (27)$$

where P_k and P'_1 hold for the probability to have a k -mer adsorbed on k sites of l adjacent to P and an empty site adjacent to P in r , respectively. In order to relate Eq. (27) with Fick's first law, we can think of a periodically modulated chemical potential μ along the surface with wavelength $\lambda > ka$ and very small amplitude $\beta \Delta \mu_o \ll 1$. The surface coverage will therefore be modulated along the surface with small amplitude. Provided the adsorbed k -mers at l are assumed to be in equilibrium with its vapor at chemical potential μ ,

$$P_k = P'_k \exp(-\beta \Delta H_k), \quad (28)$$

where P'_k is the probability to have k adjacent empty sites and $\Delta H_k = \mathcal{E}_k - \mu$ is the change in the Hamiltonian upon the adsorption of a k -mer on k empty sites, \mathcal{E}_k being the k -mer-surface interaction energy. [$\mathcal{E}_k = 0$ had already been assumed after Eq. (1) without any loss of generality.] Accordingly,

$$P_k = P'_k \exp(\beta \mu). \quad (29)$$

From Eqs. (26)–(29) one obtains

$$\begin{aligned} J_{l \rightarrow r} &= P'_k P'_1 \kappa \exp(-\beta \Delta E_d) \exp(\beta \mu) \\ &= P'_{k+1} \kappa \exp(-\beta \Delta E_d) \exp(\beta \mu). \end{aligned} \quad (30)$$

The reverse jump, i.e., when the k -mer having one unit in the region r and $k-1$ units in l moves one lattice unit to the left, has a likelihood

$$J_{r \rightarrow l} = P'_{k+1} \kappa \exp(-\beta \Delta E_d) \exp(\beta \mu'), \quad (31)$$

where the chemical potential μ' differs slightly from μ because of the smooth modulation assumed above. Therefore,

$$\mu' \approx \mu + d\mu \approx \mu + \left(\frac{\partial \mu}{\partial x} \right)_T a, \quad (32)$$

where x is the coordinate along the chain of adsorption sites.

Hence, the net flux through P is

$$\begin{aligned} |\bar{J}| &= J = J_{l \rightarrow r} - J_{r \rightarrow l} = P'_{k+1} \kappa \exp(-\beta \Delta E_d) \\ &\times \exp(\beta \mu) \left\{ 1 - \exp \left[\beta \left(\frac{\partial \mu}{\partial x} \right)_T a \right] \right\}. \end{aligned} \quad (33)$$

Since we assumed a small periodical modulation of the equilibrium chemical potential,

$$\beta d\mu = \beta \left(\frac{\partial \mu}{\partial x} \right)_T a = \beta \left(\frac{\partial \mu}{\partial \theta} \right)_T \left(\frac{\partial \theta}{\partial x} \right)_T a \ll 1. \quad (34)$$

Equation (33) can be very well approximated by expanding the exponential function around zero. Then

$$J = -\beta P'_{k+1} \kappa \exp(-\beta \Delta E_d) \exp(\beta \mu) \left(\frac{\partial \mu}{\partial \theta} \right)_T \left(\frac{\partial \theta}{\partial x} \right)_T a, \quad (35)$$

which can be rewritten in terms of k -mers concentration $\rho = Nk/Ma = \theta/a$ as to give it the general form of Fick's first law

$$J = -a^2 P'_{k+1} \kappa \exp(-\beta \Delta E_d) \left\{ \frac{\partial [\exp(\beta \mu)]}{\partial \theta} \right\}_T \left(\frac{\partial \rho}{\partial x} \right)_T. \quad (36)$$

The chemical diffusion coefficient is identified by matching Eqs. (30) and (19),

$$D_k(\theta) = a^2 P'_{k+1} \kappa \exp(-\beta \Delta E_d) \left\{ \frac{\partial [\exp(\beta \mu)]}{\partial \theta} \right\}_T. \quad (37)$$

It is still necessary to get an exact form for the probability to have $k+1$ adjacent empty sites, P'_{k+1} , in order to give an analytical form for D_k as a function of surface coverage θ and temperature [an elegant calculation, due to one of the authors (T.P.E.), is presented in Appendix B]. By using Eqs. (15) and (B.12) in Eq. (37)

$$D_k(\theta) = a^2 \exp(-\beta \Delta E_d) \left[1 - \frac{(k-1)}{k} \theta \right]^{-2}. \quad (38)$$

For the sake of comparison, it is worth defining the ratio $R_k(\theta) = D_k(\theta)/D_k(0)$. Thus,

$$R_k(\theta) = \left[1 - \frac{(k-1)}{k} \theta \right]^{-2}. \quad (39)$$

$R_k(\theta)$ is a monotonous function of θ for all k -mers, with limits $R_k(0) = 1$ and $R_k(1) = k^2$. The general features of the dependence of $R_k(\theta)$ on θ are displayed in Fig. 7 for various polymers sizes. MC calculations of $R_k(\theta)$ were also carried out in order to compare with the exact solution for small

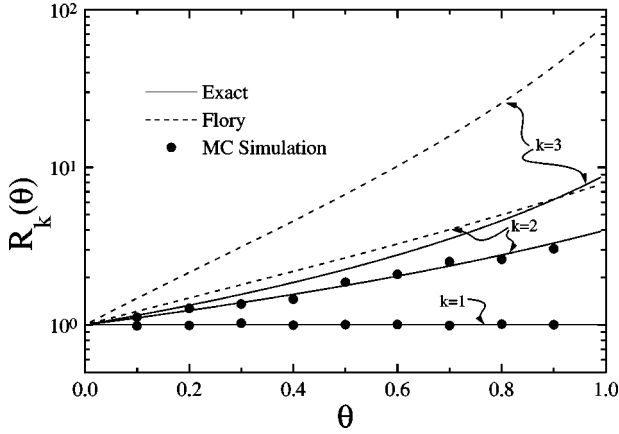


FIG. 7. Relative chemical diffusion coefficient $R_k(\theta)$ versus surface coverage. Solid lines (—) correspond to exact solution from Eq. (32) for $k=1, 2$, and 3 . Dashed lines (- -) arise from Flory's approximation for the chemical potential [Eq. (16)] in the general form of Eq. (37), which yields $R_{k,Fl}(\theta) = (1 + (k-1)\theta)[1 - (k-1)/k\theta]^{-k}$. MC simulations for monomers ($k=1$) and dimers ($k=2$) are displayed in full circles.

k -mers (namely, $k=1$ and $k=2$). Full agreement was found as expected. Further comparison is carried out in Fig. 7 between $R_k(\theta)$ from Eq. (39) (solid lines) and the corresponding to Flory's approximation, $R_{k,Fl}(\theta) = [1 + (k-1)\theta][1 - (k-1)/k\theta]^{-k}$ obtained by using Eq. (16) in the general form Eq. (37).

The differences between the two results are remarkably large, as it can be inferred from the limit $R_{k,Fl}(1) = k^{k+1}$ compared to $R_k(1) = k^2$, which yields a rapidly increasing ratio $R_{k,Fl}/R_k \propto k^{k-1}$ as a function of the adsorbate size. In summary, the approximate Flory's solution largely overestimates the chemical diffusion coefficient with respect to the exact result for all coverages and k -mers sizes.

In addition, the jump diffusion coefficient $D^J(\theta)$ can be derived from the general form of $D(\theta)$ in Eq. (32) and the Green-Kubo formula that relates $D(\theta)$ and $D^J(\theta)$ through⁴¹

$$D(\theta) = D^J(\theta) \left[\frac{\partial \beta \mu}{\partial \ln \theta} \right]_T, \quad (40)$$

where $D^J(\theta)$ relates to the time dependence of the center of mass's mean-square displacement $\langle R^2(t) \rangle$ ($R(t)$ refers to the center of mass of the whole set of adsorbed particles). It has been found by MC simulation⁴⁹ that $\langle R^2(t) \rangle \propto t$ for monomers in one dimension (this is also true for k -mers in one dimension). Hence, $D^J(\theta)$ can be obtained by simulation from

$$D^J(\theta) = \lim_{t \rightarrow \infty} \frac{\langle R^2(t) \rangle}{2t}. \quad (41)$$

On the other hand, $D^J(\theta)$ can be analytically solved from Eq. (40),

$$D^J(\theta) = D(\theta) \left[\frac{\partial \beta \mu}{\partial \ln \theta} \right]_T^{-1}. \quad (42)$$

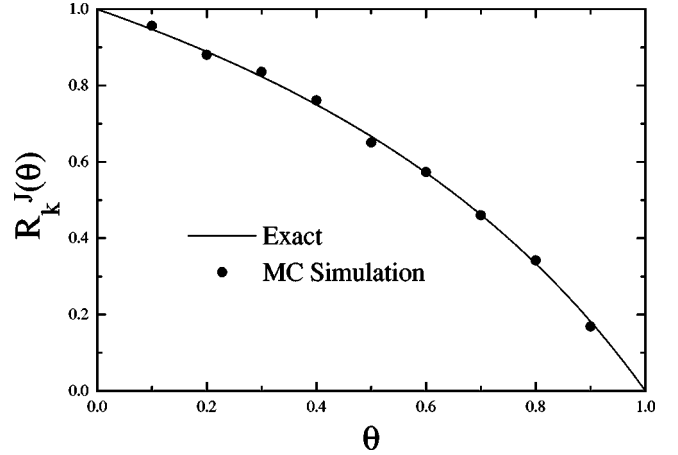


FIG. 8. Relative jump diffusion coefficient $R_k^J(\theta)$ versus surface coverage for dimers. Solid lines (—) correspond to exact solution from Eq. (44). MC simulations are displayed in full circles.

Replacing the first factor by Eq. (38), and solving the second one from Eq. (15) one gets

$$D^J(\theta) = a^2 \exp(-\beta \Delta E_d) (1-\theta) \left[1 - \frac{(k-1)}{k} \theta \right]^{-1}. \quad (43)$$

In this way one can observe the coverage dependence of the jump factor in the chemical diffusion coefficient regardless of the influence of the thermodynamic factor that relates to the density fluctuations in the adlayer.⁴¹

In Fig. 8, the coverage dependence of $D^J(\theta)$, relative to its zero-coverage limit, is represented by $R_k^J(\theta) = D^J(\theta)/D^J(0)$. As expected, $R_k^J(\theta)$ decays monotonically with coverage. Complete agreement between analytical and simulation results is observed for dimers.

It is worth noticing that our discussion concerned with the jump diffusion and chemical diffusion coefficient $D^J(\theta)$ and $D(\theta)$ is valid for lattices with one or more spatial dimensions. However, the mean-square displacement $\langle r^2(t) \rangle$ of single-particles in a one-dimensional lattice (single file-diffusion) does not vary linearly on time but $\langle r^2(t) \rangle \propto t^{1/2}$ so the tracer diffusion coefficient $[D^*(\theta)]$ is strictly zero, in contrast with the normal diffusion (in dimensions d larger than one) where $\langle r^2(t) \rangle = 2dD^*(\theta)t$. Although this is since long known,⁵⁰ the interest for the investigation of tracer diffusion in one-dimensional systems, where particles cannot overtake each other, has increased considerably in the last years by both theoretical and experimental studies.⁵¹

V. CONCLUSIONS

The exact forms of the thermodynamic functions for non-interacting linear adsorbates (k -mers) in a one-dimensional space were presented. Furthermore, the temperature and coverage dependence of the chemical and jump diffusion coefficients for chains of arbitrary size were calculated and analyzed.

The calculations may have interesting potential application in adsorption equilibrium and diffusion of polyatomic linear adsorbates in quasi-one-dimensional materials, like carbon nanotubes.

A thorough comparison with corresponding quantities from Flory's approximation was carried out. The results show that Flory's approximation becomes inadequate already at fairly low coverage. The exact configurational entropy is appreciably larger than that from Flory's solution for all coverages and adsorbate sizes. This discrepancy is extended to all thermodynamic functions as well. The analytical form of the chemical diffusion coefficient predicts a coverage and adsorbate size dependence extraordinary weaker than the one presumed by Flory's approximation. The artificial effects that this approximation induces on the thermodynamic functions can now be compared with exact results and rationalized.

Approximate analytical expressions for the thermodynamic functions in higher dimensions were given, based on the exact partition function for one dimension and a connectivity ansatz. Preliminary comparison with MC simulations shows approximate adsorption isotherm, in two and higher dimensions, highly adequate for describing adsorption with multisite occupancy on homogeneous surfaces in the lattice gas approximation.

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APPENDIX A

The total number of configurations for a mixture of N k -mers and m molecules of a monoatomic solvent on a lattice with M sites and connectivity c is given in the Flory's approximation by³¹

$$\ln \Omega_{Fl}(M, N, m) = -N \ln N + N - m \ln m + m + M \ln M - M + N(k-1) \ln \left[\frac{(c-1)}{M} \right]. \quad (\text{A1})$$

Hereforth, the following definitions apply

$$\beta F_{Fl}(M, N, m) = -\ln \Omega_{Fl}(M, N, m), \quad (\text{A2})$$

$$dF_{Fl} = -S_{Fl}dT - \Pi_{Fl}dM + \mu_{Fl}dN, \quad (\text{A3})$$

$$\tilde{F}_{Fl} = \frac{F_{Fl}}{M}, \quad \tilde{S}_{Fl} = \frac{S_{Fl}}{M}. \quad (\text{A4})$$

For the purpose of comparison with the exact solution for a pure polymer adsorbed on a one-dimensional lattice, it should be noticed that $c=2$ and $m=M-kN \equiv$ numbers of empty sites. By rewriting the thermodynamic functions in terms of $\theta=kN/M$, we get

$$\beta \tilde{F}_{Fl}(\theta, T) = -\ln \Omega_{Fl} = - \left\{ \frac{\theta}{k} \left[1 - \ln \left(\frac{\theta}{k} \right) \right] - (1-\theta) \ln(1-\theta) - \theta \right\}. \quad (\text{A5})$$

Similarly for the molar entropy $\tilde{S}_{Fl}(\theta)$, spreading pressure Π_{Fl} and chemical potential μ_{Fl}

$$\frac{\tilde{S}_{Fl}(\theta)}{k_B} = \frac{\theta}{k} \left[1 - \ln \left(\frac{\theta}{k} \right) \right] - (1-\theta) \ln(1-\theta) - \theta, \quad (\text{A6})$$

$$\exp(\beta \Pi_{Fl}) = \frac{\exp \left[-\frac{(k-1)}{k} \theta \right]}{(1-\theta)}, \quad (\text{A7})$$

$$C_k \exp(\beta \mu_{Fl}) = \frac{\theta}{(1-\theta)^k}, \quad (\text{A8})$$

where $C_k=k$.

APPENDIX B

In order to calculate $P'_{n+1} \equiv$ probability to have $(n+1)$ adjacent empty sites on a one-dimensional lattice of M sites randomly covered by N k -mers ($\theta=kN/M$) we first define

$P_s \equiv$ probability to find s empty sites between

two consecutive k -mers. (B1)

Provided that all sets of $s \geq n+1$ contribute to P'_{n+1} , then

$$P'_{n+1} = \frac{N}{M} \sum_{s=n}^{\infty} g_{s,n+1} P_s = \frac{N}{M} \sum_{s=n}^{\infty} (s-n) P_s, \quad (\text{B2})$$

where $g_{s,n+1}$ denotes the number of ways $n+1$ adjacent empty sites can be taken out of a set of s adjacent empty sites lying between two k -mers. Since this is a typical waiting-time-like Poisson process, it will follow an exponential distribution of the stochastic variable s ,

$$P_s = ab^s. \quad (\text{B3})$$

The parameters a and b can be determined from the normalization condition

$$\sum_{s=0}^{\infty} P_s = a \sum_{s=0}^{\infty} b^s = \frac{a}{1-b} = 1 \quad (\text{B4})$$

and the fact that the total number of empty sites $M-kN$ can be written in terms of P_s as

$$M-kN = N \langle s \rangle, \quad (\text{B5})$$

where $\langle s \rangle$ is the statistical mean of s

$$\langle s \rangle = \sum_{s=0}^{\infty} s ab^s = ab \frac{\partial}{\partial b} \sum_{s=0}^{\infty} b^s = ab \frac{\partial}{\partial b} \left(\frac{1}{1-b} \right) = \frac{ab}{(1-b)^2} \quad (\text{B6})$$

from Eqs. (B3) and (B5)

$$a = 1-b, \quad (\text{B7})$$

$$b = \langle s \rangle \frac{(1-b)^2}{a}, \quad (\text{B8})$$

respectively.

Resolving $\langle s \rangle$ from Eq. (B4) and relacing it in Eq. (B7) along with a from Eq. (B6), one gets

$$b = \frac{\langle s \rangle}{1 + \langle s \rangle} = \frac{1 - \theta}{\left[1 - \frac{(n-1)\theta}{n} \right]}, \quad (\text{B9})$$

$$a = \frac{\theta}{\left[n - (n-1)\theta \right]}. \quad (\text{B10})$$

Finally, from Eqs. (B1)', (B2), (B8), and (B9)

$$P'_{n+1} = \frac{N}{M} \sum_{s=0}^{\infty} sab^{s+n-1} = \frac{N}{M} \frac{b^{n+1}}{(1-b)}, \quad (\text{B11})$$

$$P'_{n+1} = \frac{(1-\theta)^{n+1}}{\left[1 - \frac{(n-1)\theta}{n} \right]^n}. \quad (\text{B12})$$

Particularly for $n=k$ [which is the form necessary in Eq. (31)] it yields

$$P'_{k+1} = \frac{(1-\theta)^{k+1}}{\left[1 - \frac{(k-1)\theta}{k} \right]^k}. \quad (\text{B13})$$

APPENDIX C

We can think of the exact number of configuration for given M, N, k , and c , $\Omega(M, N, c)$ as being

$$\Omega(M, N, c) = \Omega_{Fl}(M, N, c) \cdot \Delta\Omega(M, N, c), \quad (\text{C1})$$

where $\Omega_{Fl}(M, N, c)$ stands for the Flory's counting strategy for the same set of parameters, and $\Delta\Omega$ does for the difference (which is actually unknown at this point). Thus, the ratio

$$\frac{\Omega(M, N, c)}{\Omega(M, N, c')} = \frac{\Omega_{Fl}(M, N, c)}{\Omega_{Fl}(M, N, c')} \cdot \frac{\Delta\Omega(M, N, c)}{\Delta\Omega(M, N, c')} \quad (\text{C2})$$

we now assume that $\Delta\Omega$ does not depend on c , so the Eq. (C2) becomes

$$\frac{\Omega(M, N, c)}{\Omega(M, N, c')} = \frac{\Omega_{Fl}(M, N, c)}{\Omega_{Fl}(M, N, c')} = \left[\frac{c-1}{c'-1} \right]^{N(k-1)} \quad (\text{C3})$$

then, Eq. (19) is recovered.

It should be noted that Eq. (C1) and the assumption $\Delta\Omega \equiv \Delta\Omega(M, N)$ is reminiscent of the way overcounting of configuration in the quasichemical approximation is handled.

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