Surface diffusion of *k*-mers in one-dimensional systems

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Abstract

The surface diffusion of interacting *k*-mers is studied both through analytical and Monte Carlo simulation methods in one-dimensional systems. Adsorption isotherms, jump diffusion coefficients and collective diffusion coefficients are obtained for attractive and repulsive *k*-mers, showing a variety of behaviors as a function of the size of particles, *k*. The following main results are found: (a) diffusion coefficients increase with *k* for non-interacting particles; (b) for fixed *k*, diffusion coefficients increase as the interaction energy increases from negative (attractive) to positive (repulsive) values; (c) for attractive interactions diffusion coefficients increase with *k* in the whole range of coverage; (d) for repulsive interactions diffusion coefficients decrease with *k* up to moderately high coverage and increase with *k* at high coverage. Results are rationalized in terms of the behavior of the vacancy probability distribution.
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1. Introduction

One-dimensional systems appear in a variety of physical phenomena, as different as, for example, the kinetics of laser-induced excitons in TMMC crystals [1], conduction in quantum wires [2,3], as well as biological phenomena, like for example the adsorption of molecules on ARN chains. Another source of interest in these low-dimensional systems is that it is not unusual to find that many processes (for example reaction-diffusion processes) may present novel behaviors as compared to the same processes in higher dimensions [4].

Simple phenomena, like adsorption and surface diffusion of particles are at the basis of many more complex processes occurring in such systems. The study of these phenomena have been usually restricted to monomers, i.e., particles occupying a single site [5]. When the involved particles are *k*-mers, i.e., particles occupying *k* > 1 sites, the site-vacancy symmetry is lost and the statistical thermodynamics of adsorbed layers becomes more complex. For this reason there

has been only a relatively low number of studies related to multisite occupancy adsorption [6–10], and almost none dedicated specifically to surface diffusion, in spite of the fact that this is the case of greater interest for applications.

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 [10–15]. Many studies on conductivity, electronic structure, mechanical strength, etc. of carbon nanotubes are being carried out. However, still a very limited amount of theoretical and experimental work has been carried out on the interaction and properties of simple gases adsorbed in nanotubes [16–22]. Thus, it is an open problem whether gases will adsorb with a strongly localized or rather mobile character. A leading experimental contribution has recently been reported in which transport of a polyatomic adsorbate in cylindrical nanopores has been measured by incoherent quasi-elastic neutron scattering [23]. Large adsorbates, like neopentane, appear to have mobility through activated jumps.

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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 adsorbates in nanotubes, which is justified because thermodynamics and transport coefficient can be analytically resolved in these conditions. This is helpful and may be applied 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.

In this context, our objective here is to study the properties of surface diffusion of interacting k-mers in one-dimensional systems. It is worth noticing that although lateral interactions are introduced in the present model, the system does not show a phase transition at finite temperature (it is well-known that no phase transition develops in a one-dimensional lattice when weak coupling between neighboring particles exists). If interactions are important and phase transitions are possible, modeling diffusion becomes significantly harder. In this sense, important approaches to diffusion of interacting particles have been recently reported. Among them, Giacomin et al. [24–26] developed a rigorous statistical mechanical theory of non-equilibrium phase transitions. This theory provides a fundamental theoretical background for modeling the evolution of non-equilibrium coexisting phases. More recently, a new approach to molecular diffusion of interacting particles was developed by Aranovich and Donohue [27]. The calculations were derived using density functionals for fluxes and the Metropolis algorithm in the mass balance equation.

The paper is organized as follows. In Section 2 we outline the model and the calculation method, both trough exact analytical equations and Monte Carlo simulations. Results are presented and discussed in Section 3 and conclusions are given in Section 4.

2. Model and calculation methods

2.1. Theory

We consider a substrate consisting of a chain of M adsorption sites, all with the same adsorption energy ε_0, which can be taken equal to zero without loss of generality. Particles from a gas phase at chemical potential μ and temperature T can be adsorbed on the chain, in such a way that each particle occupies k consecutive sites: i, $i+1,\ldots,$ $i+k-1$. Particles interact with each other through a nearest-neighbor (NN) interaction energy, w, which can be either attractive ($w < 0$) or repulsive ($w > 0$).

The exact expression of the free energy per site, $f(\theta, T)$, for N adsorbed particles resulting in a coverage $\theta = N/M$, was obtained through a transformation consisting in mapping the system of N k-mers adsorbed on M sites onto a system of N monomers adsorbed on $N + M - kN$ sites [28–30] as

$$
\begin{aligned}
f(\theta, T) = {} & w\left[\frac{\theta}{k} - \alpha\right] \\
& - k_{\mathrm{B}}T\left[\frac{\theta}{k}\ln\frac{\theta}{k} + (1-\theta)\ln(1-\theta) - 2\alpha\ln\alpha\right] \\
& - k_{\mathrm{B}}T\left\{-\left[\frac{\theta}{k} - \alpha\right]\ln\left[\frac{\theta}{k} - \alpha\right]\right. \\
& \left. - (1 - \theta - \alpha)\ln(1 - \theta - \alpha)\right\}
\end{aligned}
\tag{1}
$$

where

$$
\alpha = \frac{2\theta(1-\theta)}{k\left[1 - \frac{k-1}{k}\theta + \beta\right]};
$$

$$
\beta = \left\{\left[1 - \frac{k-1}{k}\theta\right]^2 - \frac{4}{k}(1 - e^{-w/k_{\mathrm{B}}T})(\theta - \theta^2)\right\}^{1/2}
\tag{2}
$$

From these equations, and the differential form of f in the canonical ensemble, all equilibrium properties of the adsorbate can be calculated. In particular, the chemical potential, μ, and the entropy per site, s, are obtained as

$$
\begin{aligned}
\frac{\mu}{k_{\mathrm{B}}T} &= k\left(\frac{\partial f}{\partial \theta}\right)_{\mathrm{T}} \\
&= \frac{w}{k_{\mathrm{B}}T} + \ln[k(\beta - 1 + \theta) + \theta] + (k-1) \\
&\quad \times \ln\left[1 - \frac{k-1}{k}\theta + \beta\right] + (k-1)\ln k \\
&\quad - \ln[k(\beta + 1 - \theta) - \theta]
\end{aligned}
\tag{3}
$$

$$
\begin{aligned}
\frac{s}{k_{\mathrm{B}}} &= -\left(\frac{\partial f}{\partial T}\right)_{\theta} \\
&= \frac{\theta}{k}\ln\frac{\theta}{k} + (1-\theta)\ln(1-\theta) \\
&\quad - 2\alpha\ln\alpha - \left(\frac{\theta}{k} - \alpha\right)\ln\left(\frac{\theta}{k} - \alpha\right) \\
&\quad - (1 - \theta - \alpha)\ln(1 - \theta - \alpha)
\end{aligned}
\tag{4}
$$

It is worth to recall that, as it has been already shown [28–30], even in absence of inter-particle interactions, the predictions of these exact results are quite different from the predictions of the classical Flory–Huggins approximation [31,32].

Adsorbed k-mers are assumed to diffuse through thermally activated jumps to a NN position, i.e., they can move over a distance of only one lattice constant either to the left or to the right, provided that the corresponding NN site is empty. Although the surface migration of large molecules can, in many cases, involve large jumps, keeping this restriction will allow us to obtain exact expressions for the coverage dependence of diffusion coefficients, still preserving the main characteristics of their behavior.

It is well known [33–36] that the displacement $\vec{r}$ of a simple particle occupying a single site (a monomer) on a one-dimensional chain follows the time dependence $\langle r^2(t)\rangle \propto t^{1/2}$, and therefore the tracer diffusion coefficient vanishes at long times for diffusion on an infinitely long

chain. However, the displacement of the center of mass of a number of particles in one dimension (collective motion), $\vec{R}$, at a finite coverage, θ, behaves as $\langle R^2(t) \rangle \propto t$, where the proportionality constant, $D_j(\theta)$, depends on the coverage and is known as the *jump diffusion coefficient*. It is easy to show that the same behavior also holds for the diffusion of k-mers on one-dimensional chains with jumps to NN sites.

We are interested in the study of another kind of collective diffusion coefficient, the *chemical diffusion coefficient*, $D(\theta)$, which is phenomenologically defined through Fick's law. This coefficient is given in terms of the jump diffusion coefficient, $D_j(\theta)$, and the thermodynamic factor, Th(θ), through the phenomenological Reed–Ehrlich equation as [36,37]:

$$D(\theta) = D_j(\theta)\text{Th}(\theta) \tag{5}$$

where the thermodynamic factor, defined by

$$\text{Th}(\theta) = \left[\frac{\partial \mu / k_B T}{\partial \ln \theta} \right]_T \tag{6}$$

can be obtained by differentiation from Eq. (3). $D(\theta)$ can be alternatively written as

$$D(\theta) = \Gamma(\theta) \left[\frac{\partial \exp(\mu / k_B T)}{\partial \theta} \right]_T \tag{7}$$

where

$$\Gamma(\theta) = D_j(\theta)\theta \exp(-\mu / k_B T) \tag{8}$$

is known as the *effective jump rate* [36,37], representing the rate for jumps of k-mers into NN empty sites at coverage θ. This rate can be written as

$$\Gamma(\theta) = \sum_{v=0}^{2} \frac{2-v}{2} P_v \Gamma_v \tag{9}$$

where P_v is the probability that a k-mer be surrounded by v other NN k-mers and Γ_v is the jump rate of such a k-mer, which can be written as

$$\Gamma_v = \Gamma(0) \exp(vw / k_B T) \tag{10}$$

Here $\Gamma(0)$ represents the jump rate at zero coverage and can be arbitrarily taken as $= 1$ without loss of generality. On the other hand, inspired in the quasi-chemical approximation [38,39] for monomers, which is exact in one dimension, we propose for P_v the following expression:

$$P_v = \binom{2}{v} \frac{\eta^v}{(1+\eta)^2} \tag{11}$$

where η is an undetermined parameter depending on the coverage, the temperature and the size k of particles, i.e., $\eta = \eta(\theta, T, k)$.

In order to determine η, we start from the internal energy per site $u(\theta)$, which is given by

$$u(\theta) = f(\theta) + Ts(\theta) \tag{12}$$

Now, from Eqs. (1) and (4) we have:

$$u(\theta) = w\left(\frac{\theta}{k} - \alpha \right) \tag{13}$$

On the other hand, $u(\theta)$ can also be written as

$$u(\theta) = w\overline{N}_{11} / M \tag{14}$$

where $\overline{N}_{11}$ is the mean number of pairs of occupied NN sites belonging to different k-mers. Taking into account that the probability of finding a set of k contiguous occupied sites on the chain is θ/k, the quantity $\overline{N}_{11}$ can be written in terms of the probabilities P_v as

$$\frac{\overline{N}_{11}}{M} = \frac{1}{2} \frac{\theta}{k} (P_1 + 2P_2) \tag{15}$$

where the factor 1/2 avoids the double counting of pairs. From Eqs. (11)–(15), the parameter η can be determined as

$$\eta(\theta, T, k) = \frac{k(b - 1 + \theta) + \theta}{2k(1 - \theta)} \tag{16}$$

Finally, the exact solution for the chemical diffusion coefficient can be written in the form:

$$D(\theta) = \frac{1 + \eta \exp(w / k_B T)}{(1 + \eta)^2} \left[\frac{\partial \mu / k_B T}{\partial \ln \theta} \right]_T \tag{17}$$

At this point it is interesting to note that in the limit case of non-interacting k-mers, for which $w = 0$, the dependence of D with θ and k is given by: $D(\theta) \propto [1 - (k-1)\theta/k]^{-2}$, which represents a remarkably weaker coverage dependence than that predicted by the Flory–Huggins approximation: $D(\theta) \propto [1 - (k-1)\theta/k]^{-k}$.

The above equations allow the exact calculation of the jump and the chemical diffusion coefficients for k-mers on a one-dimensional chain. The same quantities will also be obtained through Monte Carlo simulations. The comparison between analytical and simulation results bears a double check purpose: on one hand, to verify the accuracy of the analytical solution and, on the other hand, to verify the validity of the Reed–Ehrlich phenomenological approach for the process studied here. Two different simulations will be used to obtain separately the factors Th and D_j in Eq. (5), using a lattice of M sites with periodic boundary conditions.

2.2. Standard Monte Carlo method in the grand canonical ensemble: calculation of Th

The adsorption process is conveniently simulated by using a standard Monte Carlo method in the grand canonical ensemble [40]. For a given value of the temperature and the chemical potential, an initial configuration with $N = M/2k$ k-mers adsorbed at random positions is generated. Then, an adsorption–desorption chain of events is started by choosing a site at random and attempting to change its occupancy number according to the Metropolis transition probability [41]:

$$P = \min \left\{ 1, \exp \left(-\frac{\Delta H}{k_B T} \right) \right\} \qquad (18)$$

where $\Delta H = H_f - H_i$ is the difference between the Hamiltonian of the final and initial states, which is defined as

$$H = w \sum_{(i,j)} c_i c_j - N(k-1)w + \varepsilon_0 \sum_i c_i - \mu \sum_i c_i \qquad (19)$$

where c_i is the occupation number of site i (= 0 if vacant, = 1 if occupied) and (i,j) stands for summation over all pairs of NN sites. A Monte Carlo step (MCS) is achieved when M sites have been tested to change their occupancy state. The approximation to thermodynamic equilibrium is monitored through the fluctuations in the number N of adsorbed particles; this is usually reached in about $n' = 10^5$ MCS. After that averages are taken on the system through the next $n = 10^5$ MCS on non-correlated configurations. At high values of $w/k_B T$ up to 10^6 MCS had to be used in order to let the system to relax from metastable states.

Thermodynamic quantities such as the mean coverage, θ, and the mean energy, U, are obtained as simple averages:

$$\theta = \frac{1}{M} \sum_{i=1}^{M} \langle c_i \rangle; \quad U = \langle H \rangle \qquad (20)$$

where the bracket denotes average over n uncorrelated configurations. The thermodynamic factor, Th, is calculated through the average:

$$\mathrm{Th} = \left[\frac{\langle \delta N \rangle^2}{\langle N \rangle} \right]^{-1} \qquad (21)$$

and is equivalent to the factor:

$$\mathrm{Th} = \left[\frac{\partial(\mu/k_B T)}{\partial \ln \theta} \right]_T \qquad (22)$$

involved in the calculation of the collective diffusion coefficient.

2.3. n-Fold way Monte Carlo scheme: calculation of D_j

Simulations for the calculation of D_j are performed in the canonical ensemble, where the number N of particles is kept constant. Diffusion jumps are allowed only to NN vacant sites and the position of the center of mass, $\vec{R}(t)$, is monitored. In this way the jump diffusion coefficient is obtained as

$$D_j(\theta) = \lim_{t \to \infty} \frac{\langle R^2(t) \rangle}{2t} \qquad (23)$$

Our numerical simulations of D_j are performed by considering a fast kinetic Monte Carlo scheme based on the n-fold way-like algorithm (nFWMC) [35], which relies on the exact computation of the transition probabilities from each configuration of the system and the association of the time evolution to a random variable sampled from the waiting time distribution for these configurations. Therefore, the

Monte Carlo simulation of the diffusion process is performed by iterating the following two steps for any given configuration:

(i) The transition rates, $W_i (i = 1, 2, \ldots, 2N)$, where $2N$ is used to account for the two possible transitions (to the left or to the right) for each particle, are evaluated by using Eq. (10). Then, a random number ξ_1 uniformly distributed in $(0,1)$ is obtained and the jth event chosen from the condition:

$$\frac{1}{W} \sum_{i=1}^{j-1} W_i \prec \xi_1 \leqslant \frac{1}{W} \sum_{i=1}^{j} W_i; \quad W = \sum_{i=1}^{2N} W_i \qquad (24)$$

is performed.

(ii) A second random number ξ_2 is generated and the time t elapsed from the initial state is incremented through:

$$t = t + \Delta t = t - \frac{1}{W} \ln \xi_2 \qquad (25)$$

The advantage of using the nFWMC scheme for simulating the jump diffusion coefficient can be understood by taking into account that in the standard kinetic Monte Carlo simulation framework the number of trials for a successful jump scales as a function of time as $1/W_i$, while the efficiency of nFWMC is not affected by an increase in $w/k_B T$, since every trial produces a successful jump of some particle to a NN empty site. Henceforth, the dynamics of strongly interacting particles at very low temperatures can be readily achieved at a computational cost several orders of magnitude less (typically 10^{-3} for $w/k_B T \approx 5$) than that required by the Metropolis algorithm [41].

3. Results and discussion

We divide conveniently our results into three groups: (a) non-interacting k-mers ($k = 1$–5); (b) interacting dimers, with attractive and repulsive interactions; (c) k-mers ($k = 2$–5) with a given attractive and a given repulsive interaction. For each group, both simulation results (symbols) as well as exact solution results (continuous lines) are presented. An excellent agreement is obtained in all cases, for the adsorption isotherm, the jump diffusion coefficient, the chemical diffusion coefficients and the probabilities P_v, the latter being of great help for the understanding of the behavior of the diffusion coefficients. The agreement between analytical and simulation results confirms both the accuracy of the theory leading to the exact results and of the Reed–Ehrlich phenomenological formulation in the cases studied here.[1]

We begin with the case of non-interacting particles, which provides us with the basic understanding to analyze

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[1] The validity of the Reed–Ehrlich phenomenological formulation is objected for surface diffusion in two dimensions, where inter-particles interactions may produce real phase transitions.

the more complex cases. Adsorption isotherms are shown in Fig. 1. The case $k = 1$, representing the classical Langmuir isotherm for monomers is useful for comparison purposes. As k increases, the coverage grows faster at low μ and slower at high μ, which can be easily understood by considering the equilibrium between the adsorption and desorption processes. At low coverage only few adsorption attempts fail and each adsorption event produces a higher coverage for higher k, so that a lower pressure is necessary to produce the same equilibrium coverage. At high coverage the opposite situation occurs, since more adsorption attempts fail for higher k due to the surface crowding. Adsorption isotherms are smooth (no plateaus are formed), so that the thermodynamic factor will also be smooth and the behavior of the chemical diffusion coefficient will be dominated by the behavior of D_j. Fig. 2 shows the behavior of the jump diffusion coefficient (a) and the chemical diffusion coefficient (b), while Fig. 3 presents the NN occupancy probability P_v. Only P_0 and P_1 will contribute to the jumping rate, so that, in absence of interactions, the behavior of D_j is strongly related to that of $1 - P_2$ (the relationship is not direct due to the different factors in Eq. (9)). As it can be easily understood, P_2 increases with θ for all k, but for fixed θ it decreases with k (since it becomes more difficult to avoid inter-particles vacancies). Therefore, the behavior of D_j shown in Fig. 2(a) results, where it can be observed that the jump diffusion coefficient decreases with θ for all k and increases with k for fixed θ, which is similar to the behavior of $1 - P_2$. Multiplying D_j by the thermodynamic factor (which is related to the inverse of the derivative of the adsorption isotherm and therefore increases strongly with θ) the behavior of D shown in Fig. 2(b) results, producing a chemical diffusion coefficient which increases monotonically with θ for all k and increases with k for fixed θ.

We now study how diffusion is affected by interactions for fixed k. We choose the case of interacting dimers ($k = 2$), which deserves special attention. Fig. 4 shows adsorption isotherms for attractive and repulsive interac-
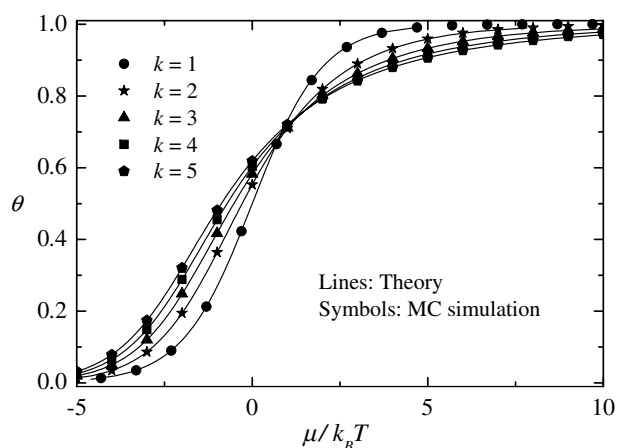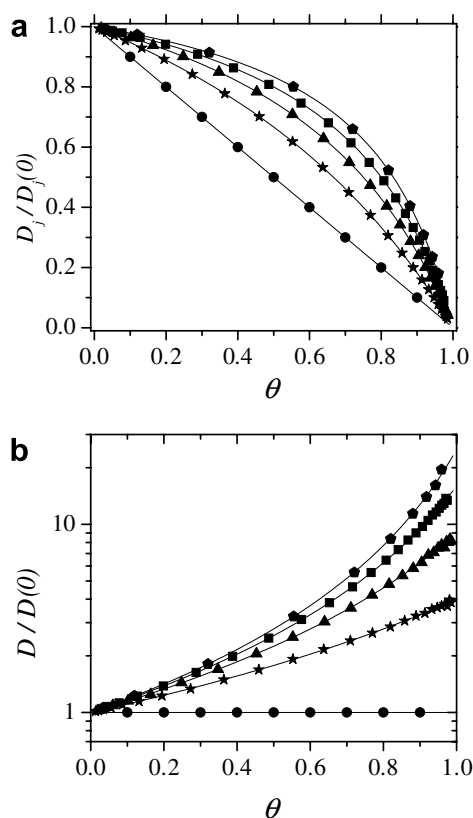
Fig. 2. Normalized jump (a) and chemical (b) diffusion coefficients for non-interacting k-mers. Symbols are as in Fig. 1.

tions ($w/k_B T$ ranges from -3 to 10 in steps of 1). We see that when the interaction energy is highly repulsive, a plateau appears in the isotherm around $\theta = 2/3$, which will produce a peak in the thermodynamic factor, the sharper the higher the energy. This peak will influence the chemical diffusion coefficient. Fig. 5 shows the jump (a) and the chemical (b) diffusion coefficients for the whole range of interaction energy, while Fig. 6 shows the P_v for repulsive interactions and Fig. 7 does the same for attractive interactions. We analyze in first place the case of repulsive interactions. Just as explained above for non-interacting k-mers, at low coverage the behavior of D_j is mainly determined by that of $1 - P_2$, Fig. 6(a). Therefore the jump diffusion coefficient increases slowly in this region, which extends up to approximately $\theta = 2/3$, due to the effect of repulsive interactions acting through Γ_v in Eq. (9). At this coverage, for sufficiently strong repulsive interactions, an ordered structure is formed (although there is no real thermodynamic phase transition), where pairs of NN dimers are surrounded by vacant sites on both sides. This ordered structure is evidenced by the plateau in the adsorption isotherm, Fig. 4, and the sharp increase and maximum in P_1, Fig. 6(b). In this region of coverage P_0 is low and P_1 acts in Eq. (9) with an enhanced weight $\Gamma_1 \gg 1$, therefore the behavior of P_1 dominates and determines the sharp increase in D_j observed in Fig. 5(a). As D_j is multiplied by the thermodynamic factor to obtain D, and given that Th
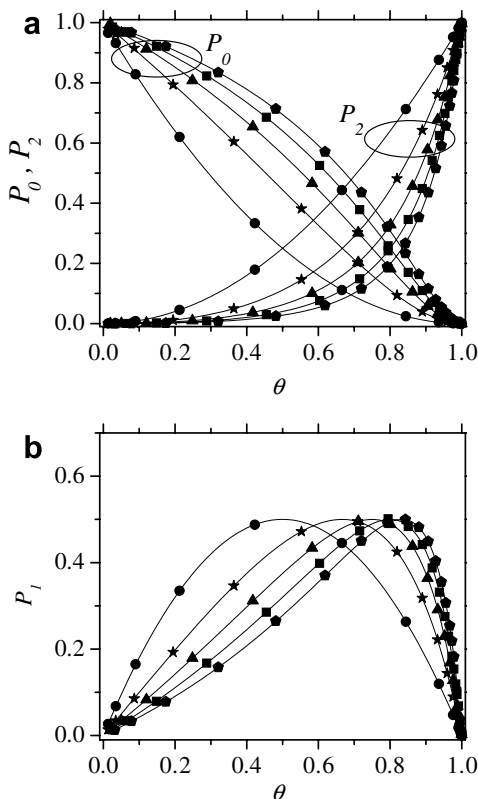
Fig. 1. Adsorption isotherms of non-interacting k-mers.

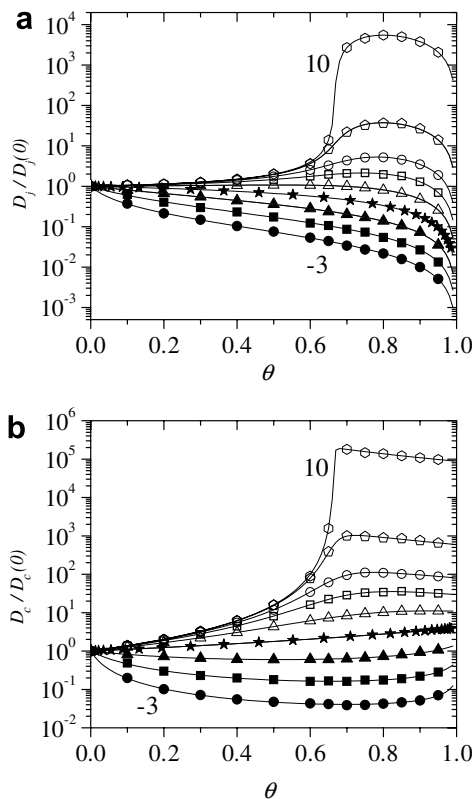Fig. 3. Vacancy probabilities for non-interacting k-mers: (a) P_0 and P_2; (b) P_1. Symbols are as in Fig. 1.
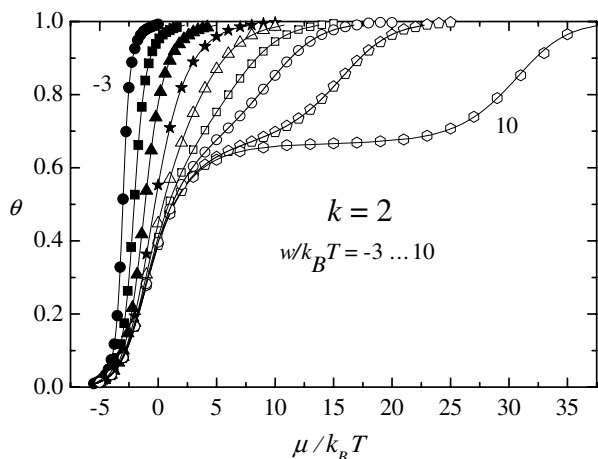

Fig. 4. Adsorption isotherms for interacting dimers. Curves from left to right correspond to: $w/k_BT = -3$; $w/k_BT = -2$; $w/k_BT = -1$; $w/k_BT = 0$; $w/k_BT = 1$; $w/k_BT = 2$; $w/k_BT = 3$; $w/k_BT = 5$ and $w/k_BT = 10$.

Fig. 5. Normalized jump (a) and chemical (b) diffusion coefficients for interacting dimers. Symbols are as in Fig. 4.

Fig. 6. Vacancy probabilities for dimers with repulsive interactions: (a) P_0 and P_2; (b) P_1. Symbols are as in Fig. 4.

will have a sharp peak at the isotherm plateau, the behavior observed in Fig. 5(b) is obtained for strongly repulsive interactions. This effect of the ordered structure gradually disappears in D_j and D as the repulsive interaction decreases. The behavior of diffusion coefficients can be straightforwardly analyzed in a similar way for attractive interactions: the jump diffusion coefficient is mainly determined by the behavior of P_0 in Fig. 7(a), due to the
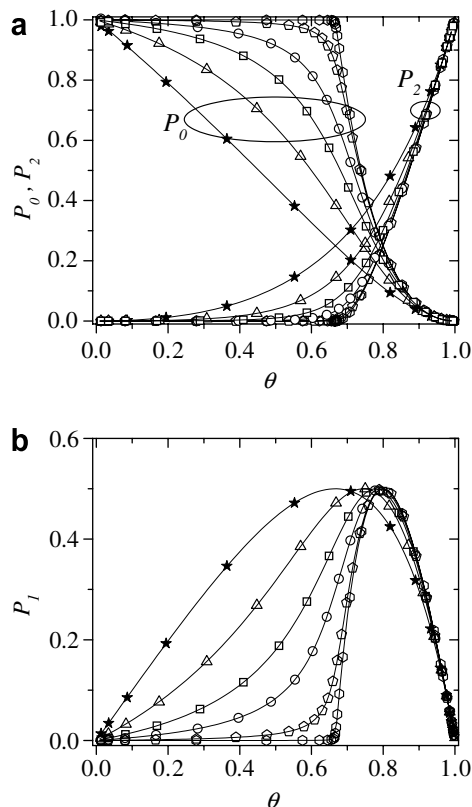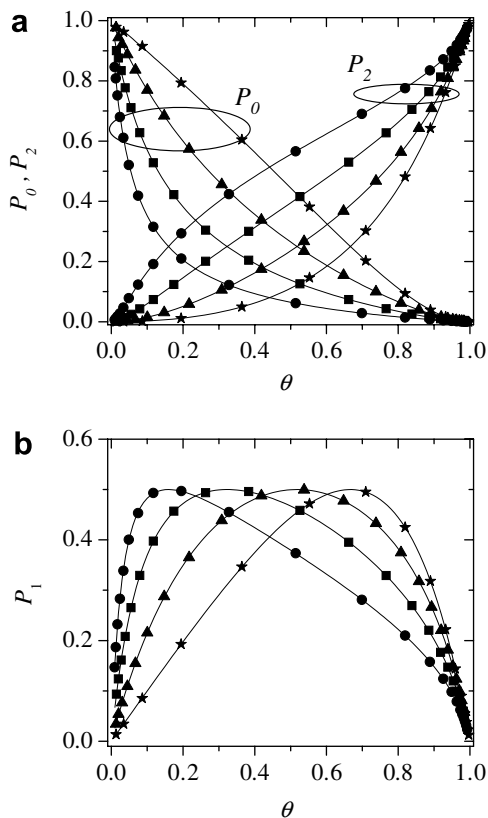
Fig. 7. Vacancy probabilities for dimers with attractive interactions: (a) P_0 and P_2; (b) P_1. Symbols are as in Fig. 4.
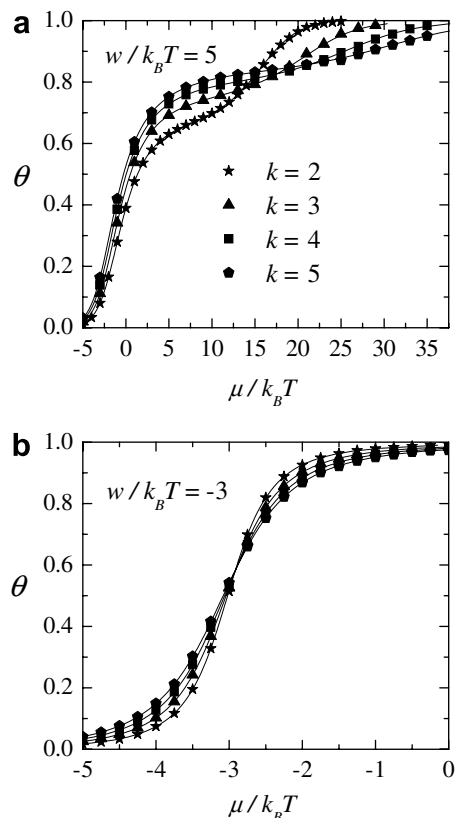

Fig. 8. Adsorption isotherms for interacting k-mers: (a) repulsive interactions; (b) attractive interactions.

depressing effect of $\Gamma_1 < 1$ on P_1, and the thermodynamic factor is smooth on the whole coverage range. As it can be easily understood, due to the effect of Γ_v in Eq. (9), both diffusion coefficients increase with w for any fixed coverage.

We finally analyze the case of fixed attractive and repulsive interactions (we choose $w/k_BT = 5$, for repulsive interactions, and $= -3$, for attractive interactions) and different values of $k = 2-5$. Adsorption isotherms are shown in Fig. 8 and diffusion coefficients in Fig. 9, while Figs. 10 and 11 present the probabilities P_v for repulsive and attractive interactions, respectively. After the analysis performed above for dimers, it is now easy to rationalize the shown results, so that we only highlight the main characteristics. Ordered structures, i.e., two NN k-mers surrounded by vacant sites on both sides, are again formed for strongly repulsive interactions, with the already discussed consequences. However, as it can be seen from the isotherms in Fig. 8(a) and from P_1 in Fig. 10(b), the ordered structure appears at higher coverage for higher k as it is to be expected. This produces a peak in D_j and D shifting to higher coverages for higher k. This is also the reason why, for repulsive interactions, both diffusion coefficients show two regions: the lower coverage region, where they decrease with k, and the higher coverage region, where they increase with k. For attractive interactions, on the contrary, both diffusion coefficients increase with k over the whole coverage range.
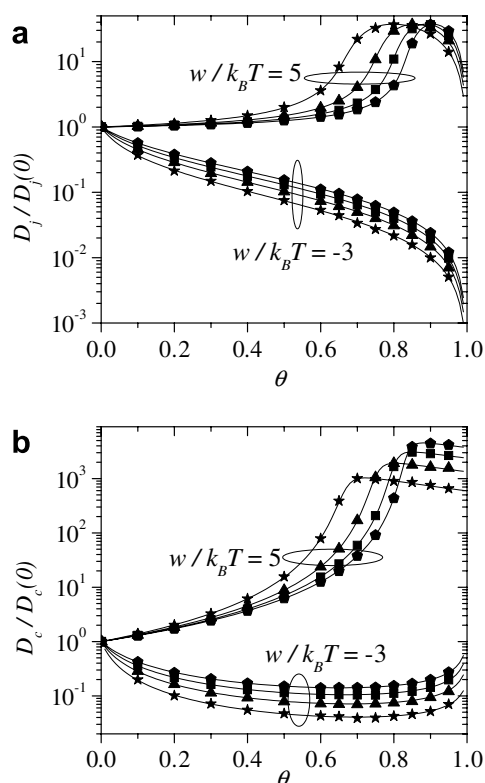

Fig. 9. Normalized jump (a) and chemical (b) diffusion coefficients for interacting k-mers. Symbols are as in Fig. 8.
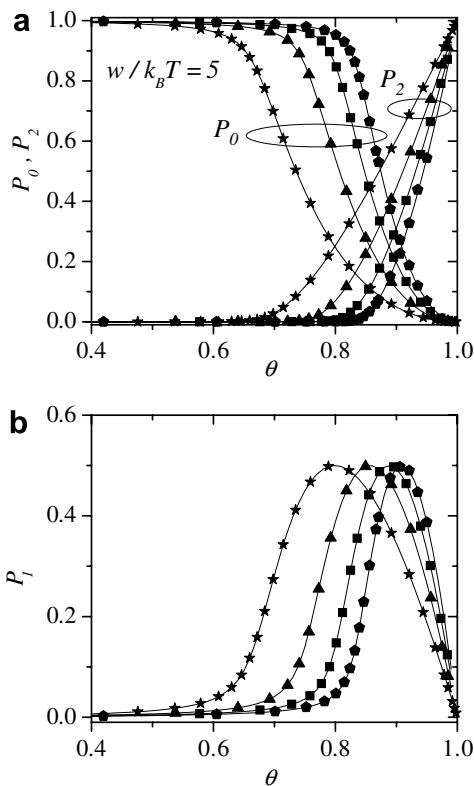
Fig. 10. Vacancy probabilities for k-mers with repulsive interactions: (a) P_0 and P_2; (b) P_1. Symbols are as in Fig. 8.
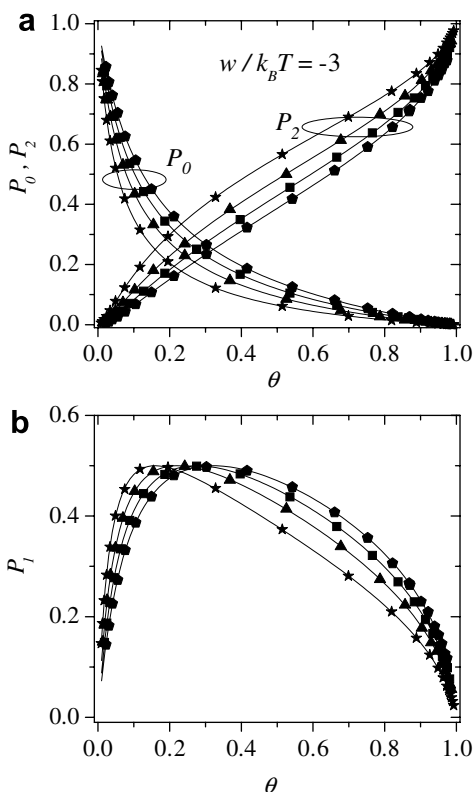

Fig. 11. Vacancy probabilities for k-mers with attractive interactions: (a) P_0 and P_2; (b) P_1. Symbols are as in Fig. 8.

4. Conclusions

We have developed an exact solution for the surface diffusion coefficients of interacting k-mers on one-dimensional chains, based on the phenomenological Reed–Ehrlich approach. This solution, together with Monte Carlo simulations, have been applied to study the behavior of diffusing k-mers, with an excellent agreement between the two methods in all cases.

According to the present study the diffusion of k-mers on one-dimensional chains is characterized by the following properties:

(a) diffusion coefficients increase with k for non-interacting particles;
(b) for fixed k, diffusion coefficients increase as the interaction energy increases from negative (attractive) to positive (repulsive) values;
(c) for attractive interactions diffusion coefficients increase with k in the whole range of coverage;
(d) for repulsive interactions diffusion coefficients decrease with k up to moderately high coverage and increase with k at high coverage.

The observed behavior is physically interpreted by making use of the vacancy probabilities P_v. These quantities have demonstrated to be very useful for the understanding of the process at a microscopic level.

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