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Exactly solvable model of reversible adsorption on a disordered substrate

J. Talbot,[1] G. Tarjus,[2] and P. Viot[2]
[1]*Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, Pennsylvania 15282-1530, USA*
[2]*Laboratoire de Physique Théorique de la Matière Condensée, Université Pierre et Marie Curie,*
4, place Jussieu,75252 Paris Cedex, 05 France

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We consider the reversible adsorption of particles (monomers with exclusion nearest-neighbor sites) on a one-dimensional lattice, where adsorption occurs on a finite fraction of sites selected randomly. By comparing this one-dimensional system to the pure system where all sites are available for adsorption, we show that when the activity goes to infinity, there exists a mapping between this model and the pure system at the same density. By examining the susceptibilities, we demonstrate that there is no mapping at finite activity. However, when the site density is small or moderate, the mapping exists up to second order in site density. We also propose and evaluate approximate approaches that may be applied to systems where no analytic result is known.

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I. INTRODUCTION

Over the years a significant and sustained research effort has been directed at understanding the effect of disorder in adsorption processes [1,2]. This is commensurate with the widespread occurrence of disorder in many different kinds of adsorption: e.g., gases on solid surfaces and in porous media [3], biomolecules [4] and colloidal particles [5,6] adsorbing from solution onto solid surfaces, and catalysis [7–10].

From a theoretical perspective, the challenge is how to incorporate disorder into statistical mechanical descriptions of the equilibrium and kinetic properties. In the absence of exact results, it is desirable to develop approximate treatments, possibly by mapping the system containing disorder to a pure system with no disorder.

One way to represent disorder is the random site surface (RSS) in which adsorption sites are uniformly and randomly distributed on a plane. The adsorbent molecules, represented by hard spheres, bind to these immobile sites. Steric exclusion is incorporated in the model in that a site is available for adsorption only if the nearest occupied site is at least one particle diameter away. The model is characterized by the dimensionless site density.

This model was originally studied in the context of irreversible adsorption where it was shown that there exists a mapping to an irreversible adsorption process on a continuous surface [11]. The existence of this mapping, which is exact and valid in any dimension, means that from knowledge of the amount adsorbed as a function of time in a continuous space we can calculate the amount adsorbed on the RSS surface of a given site density at any time. Adamczyk and co-workers have successfully applied the model and its extensions (e.g., allowing for finite-size adsorption sites) to the adsorption of latex spheres on mica surfaces [5,6].

More recently, Oleyar and Talbot [12] studied the reversible version of the RSS model in which hard spheres adsorb and desorb from immobilized sites in a plane. Here the quantities of interest are the adsorption isotherm, i.e., the amount adsorbed as a function of the bulk phase activity of the solute and the structure of the adsorbed layer. Somewhat surprisingly, a theoretical description of the system in equilibrium (even when no phase transitions intervene) is more difficult than in the irreversible case since there appears to be no exact mapping to the reversible adsorption on a continuous surface. Moreover, in one dimension where the exact solution of the corresponding model without disorder—i.e., hard rods on a line is well known [13]—attempts to solve the equilibrium RSS have so far proved unsuccessful (despite the fact that many one-dimensional statistical mechanical models have exact solutions).

It is the purpose of this article to study a simpler model: the adsorption of monomers with exclusion of nearest-neighbor sites) on a one-dimensional lattice. Disorder is introduced by randomly eliminating a given fraction of the sites. The advantage of the lattice model is that essentially exact solutions are available for both the pure and disordered systems. This permits us to examine the existence of a possible mapping between the two. We show that there is a mapping in the limit of small and large activities, but not in general. In the absence of a full mapping it is still useful to investigate approximate approaches that permit an accurate description of the thermodynamics of the disordered system. We note that Oshanin *et al.* [7,8] studied a similar lattice model for the catalytic reaction $A+A\rightarrow 0$.

We show that the introduction of an effective activity leads to highly accurate estimates of the thermodynamic properties of the disordered system. This methodology can be generalized to more realistic, off-lattice models.

II. EXACT SOLUTIONS

A. Pure model

The system consists of adsorbed particles which are in equilibrium with a bulk phase containing an adsorbate at activity λ. The particles bind to sites of a one-dimensional lattice. Occupancy of one site by a particle center excludes occupancy of the nearest-neighbor sites by another particle center: See Fig. 1. We note that this model is isomorphic to the adsorption of dimers on the dual lattice [14]. For a system consisting of N adsorption sites the adsorbed phase can be formally described by the "grand canonical" partition function

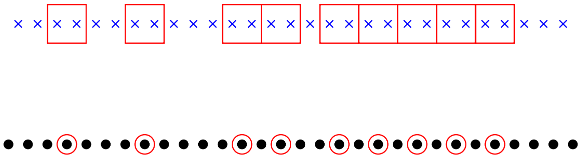

FIG. 1. (Color online) Adsorption of particles (with exclusion of the nearest-neighbor sites) on a pure lattice (bottom line) and equivalent representation with dimers on the dual lattice (top line). Solid circles or crosses represent adsorption sites, large open circles show adsorbed monomers, and squares correspond to dimers.

$$\Xi^*(N,\lambda) = \sum_{\{\tau_i=0,1\}} \lambda^{\tau_N} \prod_{i=1}^{N-1} \lambda^{\tau_i}(1-\tau_i\tau_{i+1}). \qquad (1)$$

Here τ_i is the occupancy of the site i, $\lambda \exp(\beta\mu)$ is the activity, and free boundary conditions are imposed. We use the superscript $*$ to denote a pure system—i.e., one in the absence of disorder. The exact calculation of the partition function is a simple exercise using the transfer matrix approach: See the Appendix.

The result can be expressed as

$$\Xi^*(N,\lambda) = 1 + \sum_{n=1}^{n_{\max}} \binom{N-n+1}{n} \lambda^n, \qquad (2)$$

where $n_{\max}=[(N+1)/2]$ is the maximum number of particles that can be adsorbed on the lattice of size N ($[x]$ represents the integer part of x) [7,8].

The average number of particles adsorbed on a chain of N sites at an activity λ is given by

$$\mathcal{N}_N(\lambda) = \lambda\left(\frac{\partial \ln \Xi^*(\lambda,N)}{\partial\lambda}\right), \qquad (3)$$

and the fraction of occupied sites can be computed as

$$\rho^*(N,\lambda) = \frac{\mathcal{N}_N(\lambda)}{N}, \qquad (4)$$

which in the thermodynamic limit is given by

$$\rho^*(\infty,\lambda) = \frac{2\lambda}{(1+\sqrt{1+4\lambda})\sqrt{1+4\lambda}}. \qquad (5)$$

This has the expected behavior in the limits of small (Langmuir isotherm) and large (half of the sites are occupied by particle centers) activities. The susceptibility, or fluctuation in the number of adsorbed molecules, is given by

$$\chi(\rho) = \frac{\langle n^2\rangle - \langle n\rangle^2}{N} = \lambda\frac{\partial\rho}{\partial\lambda}. \qquad (6)$$

After some calculations one obtains that, in the thermodynamic limit,

$$\chi^*(\rho) = \rho(1-\rho)(1-2\rho). \qquad (7)$$

FIG. 2. (Color online) Adsorption of particles (with exclusion of the nearest-neighbor sites) on a diluted lattice. The symbols are the same as in Fig. 1, and the points represent the lattice vacancies. Note that the equivalence to a dimer representation is no longer straightforward and is not shown here.

B. Model with disorder

We now consider a diluted site model in which only a fraction of randomly selected sites are present. The grand partition function in this case is given by

$$\Xi(\lambda,\{\eta\}) = \sum_{\{\tau_i=0,1\}} \lambda^{\tau_N\eta_N} \prod_{i=1}^{N-1} \lambda^{\tau_i\eta_i}(1-\tau_i\tau_{i+1}\eta_i\eta_{i+1}), \qquad (8)$$

where $\eta_i=0$ or 1 denotes the absence or presence of an adsorption site i. The probability of finding an adsorbing site is given by

$$P(\eta) = \rho_s\delta_{\eta,1} + (1-\rho_s)\delta_{\eta,0}. \qquad (9)$$

There are no correlations between sites. A sample configuration is shown in Fig. 2.

For a given site configuration $\{\eta_i\}$, the number of clusters of exactly l contiguous adsorption sites is given by

$$n_l(\{\eta_i\}) = \sum_{i=1}^{N} (1-\eta_{i-1})\eta_i \cdots \eta_{i+l}(1-\eta_{i+l+1}). \qquad (10)$$

The mean number of clusters of size l is then given by

$$\overline{n_l} = N(1-\rho_s)^2\rho_s^l. \qquad (11)$$

One can check that the sum rule characterizing the total number of occupied sites is verified; namely,

$$\sum_{l=1}^{\infty} l\overline{n_l} = N\rho_s. \qquad (12)$$

Note that the thermodynamic limit has been taken in the two equations: corrections for a finite system occur for $1-\rho_s \simeq 1/N$ and need not be included in these calculations.

Since the adsorption-site occupancies are quenched variables, the average over disorder is taken over the logarithm of the partition function, with the following result:

$$\overline{\ln[\Xi(\rho_s,\lambda)]} = \sum_{l=1}^{\infty} \overline{n_l} \ln \Xi^*(l,\lambda), \qquad (13)$$

where we have used the result for the partition function of a finite lattice of l connected sites (i.e., the pure model) with free boundary conditions. The mean density of adsorbed particles is given by

$$\rho(\rho_s,\lambda) = \frac{\lambda}{N}\left(\frac{\partial\overline{\ln[\Xi(\rho_s,\lambda)]}}{\partial\lambda}\right) = \frac{1}{N}\sum_{l=1}^{\infty}\overline{n_l}\mathcal{N}_l(\lambda), \qquad (14)$$

where

$$\mathcal{N}_l(\lambda) = \lambda \frac{\partial \ln[\Xi^*(l,\lambda)]}{\partial \lambda} \tag{15}$$

is the average number of particles on a (full) lattice of size l with free boundary conditions.

For low site density, one easily obtains

$$\begin{aligned}\rho(\rho_s,\lambda) &= \frac{\lambda}{1+\lambda}\rho_s - 2\frac{\lambda^2}{(1+\lambda)(1+2\lambda)}\rho_s^2 \\ &\quad + \frac{(3+2\lambda)\lambda^3}{(1+2\lambda)(1+3\lambda+\lambda^2)(1+\lambda)}\rho_s^3 \\ &\quad - 2\frac{\lambda^4(3\lambda+2)}{(1+4\lambda+3\lambda^2)(1+3\lambda+\lambda^2)(1+2\lambda)}\rho_s^4 + O(\rho_s^5).\end{aligned} \tag{16}$$

On the other hand, whatever the site density, when the activity $\lambda \to \infty$, $\mathcal{N}_l(\lambda) \to p$ for $l=2p$ and $\mathcal{N}_l(\lambda) \to p+1$ for $l=2p+1$, so that one obtains

$$\rho(\rho_s,\infty) = (1-\rho_s)^2 \sum_{p=1}^{\infty} p\rho_s^{2p}\left(1+\frac{1}{\rho_s}\right), \tag{17}$$

which gives

$$\rho(\rho_s,\infty) = \frac{\rho_s}{\rho_s+1}, \tag{18}$$

a result identical to the case of hard rods onto a line with random sites [15]. (Note, however, that ρ_s cannot take any positive real value and is bounded by 1.)

In order to investigate the existence of a mapping between this model and the pure model, we consider the thermodynamic quantities; in particular, we focus on the susceptibility.

In the presence of quenched disorder, there are two kinds of susceptibility: the "connected" susceptibility $\chi_c(\rho_s,\lambda)$ describing the thermal fluctuations of the density of adsorbed particles and the "disconnected" susceptibility $\chi_d(\rho_s,\lambda)$ describing the disorder-induced fluctuations of the density of adsorbed particles [16].

The connected susceptibility is given by the thermodynamic relation [17]

$$\chi_c(\rho_s,\lambda) = \lambda \frac{\partial \rho(\rho_s,\lambda)}{\partial \lambda}. \tag{19}$$

For large activities, the connected susceptibility goes to 0 as $1/\lambda$. This result has a simple physical interpretation. For a given realization of the disorder, the densest configuration is selected when $\lambda \to \infty$. In this limit fluctuations are suppressed, and the connected susceptibility vanishes.

The "disconnected" (sometimes called "blocking" in the context of fluids in porous media [3]) susceptibility is given by the second cumulant (in the average over the disorder) of the number of adsorbed particles for a given configuration of the disorder, $\Sigma_l n_l(\{\eta_i\})\mathcal{N}_l(\lambda)$:

$$\chi_d(\rho_s,\lambda) = \frac{1}{N}\sum_{l,l'=1}^{\infty} (\overline{n_l n_{l'}} - \overline{n_l}\,\overline{n_{l'}})\mathcal{N}_l(\lambda)\mathcal{N}_{l'}(\lambda). \tag{20}$$

The different terms of the disorder average $\overline{n_l n_{l'}}$ can be obtained by sorting out configurations of overlapping and nonoverlapping clusters.

(i) When $l=l'$, there is a contribution when the two clusters are in the same location, and $\overline{n_l n_{l'}} = \delta_{ll'}N(1-\rho_s)^2\rho_s^l$.

(ii) When two clusters have a boundary in common, $\overline{n_l n_{l'}} = 2N(1-\rho_s)^3\rho_s^{l+l'}$, the factor of 2 coming from the two possibilities, right and left.

(iii) When two clusters have overlapping sites, $\overline{n_l n_{l'}} = 0$ and the number of possibilities is equal to $(l+l'+1-\delta_{ll'})$.

(iv) For all other configurations, there is no overlap between clusters and $\overline{n_l n_{l'}} = \overline{n_l}\,\overline{n_{l'}}$: this corresponds to $N(N-l-l'-3)$ configurations.

After some calculations, one obtains that

$$\begin{aligned}\overline{n_l n_{l'}} - \overline{n_l}\,\overline{n_{l'}} = N(1-\rho_s)^2\rho_s^l[\delta_{ll'} + 2(1-\rho_s)\rho_s^{l'+1} \\ - (l+l'+1)(1-\rho_s)^2\rho_s^{l'}].\end{aligned} \tag{21}$$

In the large-activity limit $\lambda \to \infty$, one easily shows from Eqs. (2) and (3) that

$$\sum_{l=1}^{\infty} \rho_s \mathcal{N}_l(\infty) = \frac{\rho_s}{(1-\rho_s)^2(1+\rho_s)} \tag{22}$$

and

$$\sum_{l=1}^{\infty} l\rho_s \mathcal{N}_l(\infty) = \frac{\rho_s(1+\rho_s+2\rho_s^2)}{(1-\rho_s)^3(1+\rho_s)^2}. \tag{23}$$

From Eqs (20)–(23) the following expression of $\chi_d(\rho_s,\infty)$ now results:

$$\chi_d(\rho_s,\infty) = \frac{\rho_s(1-\rho_s)}{(1-\rho_s)^3}. \tag{24}$$

Finally, by inverting Eq. (18), the disconnected susceptibility is obtained as

$$\chi_d(\rho_s,\infty) = \rho(1-\rho)(1-2\rho), \tag{25}$$

which is *identical to the susceptibility in a pure system at the same density* [Eq. (7)]. Since $\chi_c(\rho_s,\infty)=0$, this result establishes that the *total* fluctuations of the adsorbed number of particles are the same in the disordered system at infinite activity and in the pure system at the same mean adsorbed density ρ. This points to the existence of an exact mapping between the two systems under these conditions. The mapping can actually be proven by extending the above considerations to the correlation functions.

Is the mapping exact for finite activities? In order to answer this question, we compare $\chi(\rho(\rho_s,\lambda))$ and $\chi_c(\rho_s,\lambda)+\chi_d(\rho_s,\lambda)$ for small values of ρ_s. The first orders of the expansions read

$$\chi^{*}(\rho(\rho_s,\lambda)) = \frac{\lambda}{\lambda+1}\rho_s - \frac{\lambda^2(8\lambda+5)}{(1+2\lambda)(\lambda+1)^2}\rho_s^2 + \frac{\lambda^3(18\lambda^3+69\lambda^2+66\lambda+17)}{(1+2\lambda)(1+3\lambda+\lambda^2)(\lambda+1)^3}\rho_s^3 + O(\rho_s^4), \tag{26}$$

where we have combined Eqs. (7) and (16), and

$$\chi_c(\rho_s,\lambda) + \chi_d(\rho_s,\lambda) = \frac{\lambda}{\lambda+1}\rho_s - \frac{\lambda^2(8\lambda+5)}{(1+2\lambda)(\lambda+1)^2}\rho_s^2 + \frac{\lambda^3(18\lambda^2+49\lambda+17)}{(1+3\lambda+\lambda^2)(\lambda+1)^2(1+2\lambda)}\rho_s^3 + O(\rho_s^4). \tag{27}$$

It is noticeable that the expansions coincide at first and second order, but differ at third order and above. We conjecture that the absence of exact mapping at finite activities is independent of the model (monomers with k-nearest-neighbor exclusion, hard rods, …) and of the dimension. In addition, one can see that the two expansions approach the same limit when the activity is very large. This means that they differ maximally for intermediate values of the activity. In any case, the above considerations prove that no mapping exists between the correlation functions of the disordered system at finite activity and those of the pure system at the same density, $\rho(\rho_s,\lambda)$.

III. APPROXIMATE SCHEMES

The lattice model studied here is exceptional in that we know its exact solution, even when disorder is present. More often, we will have only a partial description: e.g., the cluster expansion that applies at low site density in the case of the RSS [12]. In these cases, we seek approximate schemes that can provide an accurate description of the adsorption isotherms for the full range of site densities and activities. In this section we propose two such schemes and evaluate their accuracy by comparing with the exact results.

One approach involves a partial resummation of the site density expansion of Eq. (14). Specifically, retaining explicitly the first term that appears at all orders we can write

$$\rho(\rho_s,\lambda) = \sum_{l=1}^{\infty}\left[-\left(\frac{-\lambda}{1+\lambda}\right)^{l} + F_l(\rho_s,\lambda)\right]\rho_s^{l}, \tag{28}$$

where $F_l(\rho_s,\lambda)$ represents the remaining terms in the exact expansion and, consistent with these terms, has the property that

$$F_l(\rho_s,\lambda) \to 0 \tag{29}$$

when $\lambda \to 0$ and $\lambda \to \infty$.

The simplest approximation is to set $F_l(\lambda)=0$, resulting in the approximate isotherm

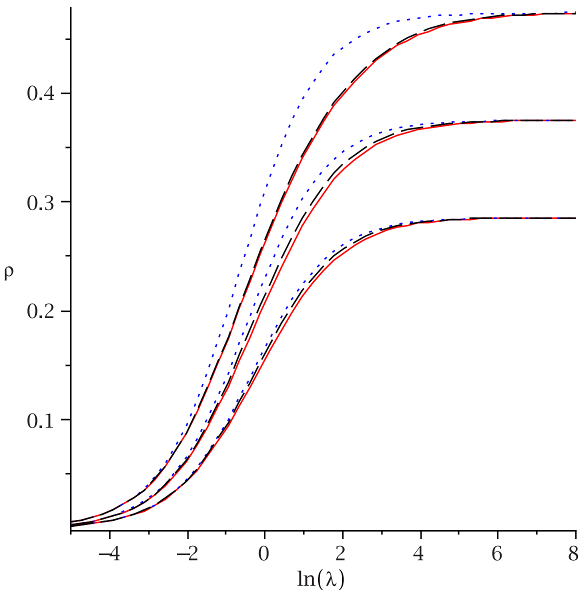

FIG. 3. (Color online) Density ρ as a function of activity λ for $\rho_s=0.4,0.6,0.9$ calculated via the exact formula, Eq. (14) (full curves), via Eq. (30) (dotted lines), and via Eq. (36) to the zeroth order $[f(\rho_s,\lambda)=1]$ (dashed curve) (see text).

$$\rho(\rho_s,\lambda) = \frac{\lambda\rho_s}{\lambda\rho_s+1+\lambda}, \tag{30}$$

which, as expected, has the correct behavior in the limits of small and large activities.

In order to highlight the deviations from the exact results, we have plotted in Fig. 3 the density ρ as a function of the activity λ for various values of the site density ρ_s. The approximate isotherms always overestimate the adsorbed density for all activities. The deviations increase with the site density and are most pronounced at intermediate activities. In order to understand the origin of this discrepancy, we have performed an asymptotic expansion of Eq. (14) at large activity,

$$\rho(\rho_s,\lambda) \simeq \frac{\rho_s}{1+\rho_s} - \frac{1}{6\lambda}\frac{\rho_s(-\rho_s^3+3\rho_s+6)}{(1+\rho_s)^3(1-\rho_s)} + \cdots, \tag{31}$$

and compared with that of Eq. (30),

$$\rho(\rho_s,\lambda) \simeq \frac{\rho_s}{1+\rho_s} - \frac{\rho_s}{\lambda(1+\rho_s)^2} + \cdots. \tag{32}$$

We note that when $\rho_s \to 0$, Eqs. (31) and (32) coincide. This explains the very accurate description of the approximate isotherm in this limit. Conversely, when $\rho_s \to 1$, one obtains

$$\rho(\rho_s,\lambda) \simeq \frac{\rho_s}{1+\rho_s} - \frac{1}{6(1-\rho_s)\lambda}, \tag{33}$$

whereas no such combination in $\lambda(1-\rho_s)$ appears in Eq. (32).

By including the leading term of the asymptotic behavior, Eq. (31), the agreement with the exact result is only correct up to intermediate ρ_s. It would be necessary to add additional

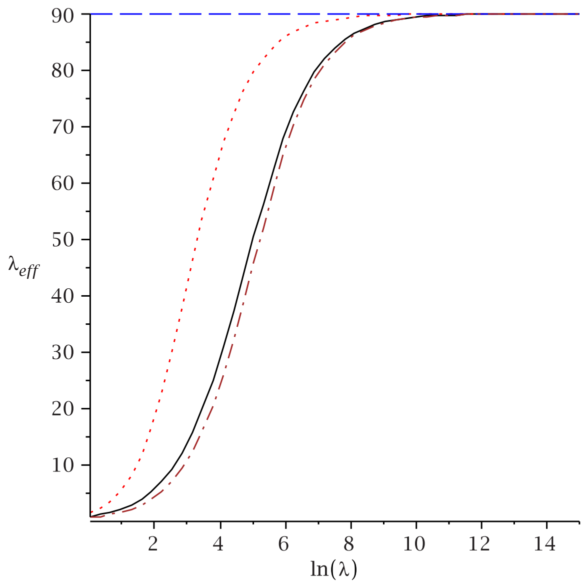

FIG. 4. (Color online) Effective activity λ_{eff} as a function of λ for $\rho_s=0.9$ calculated via the exact formula, Eq. (14) (solid curve), via Eq. (36) to the zeroth order (dotted curve) and to the first order, Eq. (37) (dot-dashed curve).

terms when ρ_s goes to 1 in order to have a good approximation of the isotherms. Such a procedure rapidly becomes very complicated and is not useful for more realistic models. The asymptotic analysis seems to indicate that the neglected terms of the series correspond to the existence of an asymptotic series whose variable is $[(1-\rho_s)\lambda]^{-1}$.

An alternative approach uses an effective activity λ_{eff} instead of $\rho(\rho_s,\lambda)$. The idea is to estimate the density in the disordered system with

$$\rho(\rho_s,\lambda)=\rho^*(\lambda_{\text{eff}}(\lambda,\rho_s)), \tag{34}$$

where ρ^* corresponds to the density at equilibrium given by Eq. (5). Note that, since there is no exact mapping to a pure system for a finite activity λ, even if we could find the function $\lambda_{\text{eff}}(\lambda,\rho_s)$ that satisfies Eq. (34), it would not give exact results for other thermodynamic quantities. There is, however, merit in this approach because, as we have shown in previous sections, there is a mapping in the limits of large and small activities. Thus, by using Eq. (31) with Eq. (5), one obtains the asymptotic expansion

$$\frac{1}{\lambda_{\text{eff}}}=\frac{(-1+\rho_s)^2}{\rho_s}+\frac{6+3\rho_s-\rho_s^3}{6\rho_s\lambda}+O(\lambda^{-2}). \tag{35}$$

The coefficient of the leading term of this expansion is a function of ρ_s which behaves simply in the two limits $\rho_s\to 0$ and $\rho_s\to 1$. By combining with the low-activity expansion $[1/\lambda_{\text{eff}}=1/(\lambda\rho_s)]$, we propose the following interpolation scheme:

$$\frac{1}{\lambda_{\text{eff}}}=\frac{(-1+\rho_s)^2}{\rho_s}+\frac{f(\lambda,\rho_s)}{\lambda\rho_s}, \tag{36}$$

where $f(\lambda,\rho_s)$ is an $[n,n]$ Padé approximant. The isotherms are then calculated using Eq. (34). As can be seen in Fig. 3, even to zeroth order $[f(\lambda,\rho_s)=1]$, this route gives a significantly better approximation than Eq. (30). By matching the exact asymptotic behavior, Eq. (33), as well as the second-order low-activity expansion, one obtains

$$f(\lambda,\rho_s)=\frac{1+a(\rho_s)\lambda}{1+b(\rho_s)\lambda}, \tag{37}$$

where

$$a(\rho_s)=\frac{6+2\rho_s^3+9\rho_s^2-\rho_s^5+9\rho_s-\rho_s^4}{6-3\rho_s-\rho_s^3} \tag{38}$$

and

$$b(\rho_s)=6\frac{\rho_s(1+\rho_s+\rho_s^2)}{6-3\rho_s-\rho_s^3}. \tag{39}$$

Since the zeroth-order approximation is practically indistinguishable from the exact result in the isotherm plot (Fig. 3), we highlight the differences between the two by plotting the effective activity versus the activity for high density ρ_s in Fig. 4. The horizontal line corresponds to the asymptotic value, the solid line to the exact result, the dotted line to the zeroth order, and the dashed line to the first order. We note that this method converges very rapidly to the exact result, even at high ρ_s, which is very encouraging for systems where no exact result is known.

We can thus conclude from the present study that (i) there is a mapping between the adsorbed configurations of particles (monomers with exclusion of the nearest-neighbor sites) on a diluted one-dimensional lattice and those on a full lattice at the same adsorbed density in the two limits of small and large activities; (ii) this mapping does not extend to finite activities. However, a successful approximation scheme is provided by considering a pseudomapping through the introduction of an effective activity. The scheme has been tested

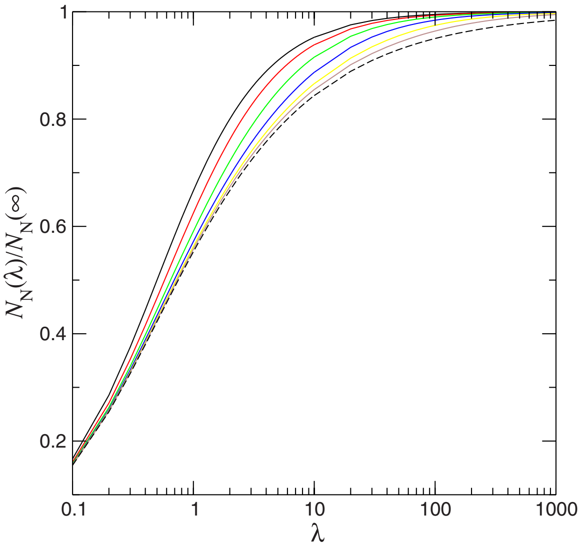

FIG. 5. (Color online) Adsorption isotherms on a pure chain of N sites ($N=2,4,8,16,32,64$, top to bottom). The dashed line is the thermodynamic limit.

on the present one-dimensional lattice system for which we have also obtained exact expressions, and work is in progress to apply it to more realistic situations.

APPENDIX: PURE MODEL

To obtain an analytic expression for the partition function of the pure system we use the transfer matrix method: see, e.g., [18]. Using this approach, Eq. (1) can be rewritten as

$$\Xi^*(\lambda,N) = \mathrm{Tr}(T^N A), \tag{A1}$$

where

$$T = \begin{pmatrix} 1 & 1 \\ \lambda & 0 \end{pmatrix} \tag{A2}$$

and

$$A = \begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix}. \tag{A3}$$

Performing the trace operation, the partition function becomes

$$\Xi^*(\lambda,N) = \frac{\lambda_1^{N+1} - \lambda_2^{N+1}}{\lambda_1 - \lambda_2} + \lambda \frac{\lambda_1^N - \lambda_2^N}{\lambda_1 - \lambda_2}, \tag{A4}$$

where λ_1 and λ_2 are the eigenvalues of the matrix T,

$$\lambda_{1,2} = \frac{1 \pm \sqrt{1+4\lambda}}{2}. \tag{A5}$$

For finite N the partition function is a polynomial in λ: e.g., $\Xi^*(\lambda,1)=1+\lambda$, $\Xi^*(\lambda,2)=1+2\lambda$, $\Xi^*(\lambda,3)=1+3\lambda+\lambda^2$, $\Xi^*(\lambda,4)=1+4\lambda+3\lambda^2,\ldots$. In the thermodynamic limit, only the largest eigenvalue contributes to the thermodynamic quantities and we have

$$\lim_{N\to\infty} \frac{\ln[\Xi^*(\lambda,N)]}{N} = \ln\left(\frac{1+\sqrt{1+4\lambda}}{2}\right). \tag{A6}$$

Some isotherms for different values of N are shown in Fig. 5. Note that the thermodynamic limit is approached rather slowly.

[1] W. Rudzinski and D. H. Everett, *Adsorption of Gases on Heterogeneous Surfaces* (Academic Press, New York, 1992).

[2] A. Dabrowski, Adv. Colloid Interface Sci. **93**, 135 (2001).

[3] E. Kierlik, M. L. Rosinberg, G. Tarjus, and P. A. Monson, J. Chem. Phys. **106**, 264 (1996).

[4] R. D. Johnson, Z. G. Wang, and F. H. Arnold, J. Phys. Chem. **100**, 5134 (1996).

[5] Z. Adamczyk, P. Weronski, and E. Musial, J. Chem. Phys. **116**, 4665 (2002).

[6] Z. Adamczyk, B. Siwek, P. Weronski, and E. Musial, Appl. Surf. Sci. **196**, 250 (2002).

[7] G. Oshanin, O. Bénichou, and A. Blumen, Europhys. Lett. **62**, 69 (2003).

[8] G. Oshanin, O. Bénichou, and A. Blumen, J. Stat. Phys. **112**, 541 (2003).

[9] G. Oshanin and S. F. Burlatsky, J. Phys. A **35**, L695 (2002).

[10] G. Oshanin and S. F. Burlatsky, Phys. Rev. E **67**, 016115 (2003).

[11] X. Jin, N. H. L. Wang, G. Tarjus, and J. Talbot, J. Phys. Chem. **97**, 4256 (1993).

[12] C. Oleyar and J. Talbot, Physica A **376**, 27 (2007).

[13] L. Tonks, Phys. Rev. **50**, 955 (1936).

[14] J. W. Evans, Rev. Mod. Phys. **65**, 1281 (1993).

[15] J. Talbot, G. Tarjus, and P. Viot (unpublished).

[16] *Spin Glasses and Random Fields*, edited by A. Young (World Scientific, Singapore, 1998).

[17] M. L. Rosinberg, G. Stell, and G. Tarjus, J. Chem. Phys. **100**, 5172 (1994).

[18] N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group, Frontiers in Physics* (Westview Press, Boulder, 1992).