Dimer adsorption on square nanotubes with first- and second-neighbor interactions

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Abstract. The thermodynamic properties of dimer adsorption on square \( M \) sites wide terraces, with first- and second-neighbor adsorbate-adsorbate interaction energies, were recently numerically obtained using an extension of the transfer matrix technique developed by the authors in 1993. The rank of the transfer matrix increases rapidly with size \( M \), and required the development of an efficient algorithm for its construction at any temperature of the system, and for all possible values of the adsorbate-adsorbate and adsorbate-substrate interaction energies. This article presents the non-trivial generalization of this algorithm for the study of dimer adsorption problems on a square lattice nanotube surface, with \( M \) sites on its circular normal section.

1. Introduction: Problem setup

Molecules in a medium (a gas or a solution) are adsorbed on a square-lattice nanotube surface (the substrate) as dimers bound to two first-neighbor sites, at thermodynamic equilibrium, with no overlapping. Pairwise interactions between dimers include first- and second-neighbors. The nanotube is viewed as vertical, assembled by wrapping on a vertical cylinder a square-lattice terrace, with \( M \) sites in its horizontal width, such that the 1st site on the right is a first-neighbor with the \( M \)th site on the left. The parameters are: the absolute temperature \( T \); the chemical potential energy \( \mu \) of the molecules in the medium; the adsorbate-substrate interaction energy \( V_0 \), and the adsorbate-adsorbate first- and second-neighbor energies, \( V \) and \( W \). There are four relevant activities, with \( k_B \) indicating Boltzmann’s constant:

\[
x = \exp[(\mu + V_0)/k_B T] , \quad y = \exp[V_0/k_B T] , \quad z = \exp[W/k_B T] .
\]  

Statistical thermodynamics provides all of the adsorption properties from the knowledge of the partition function \( Z \) associated with the system, which depends in this case on the three activities identified above.

Our approach is to construct a transfer matrix that depends on the activities, and whose eigenvalues provide the partition function of the system, from which all of its thermodynamic properties can then be computed. The set, \( \{ \theta_0, \theta, \beta \} \), of the statistical averages of the coverage of the surface, \( \theta_0 \), of the numbers per site of first-neighbors, \( \theta \), and second-neighbors, \( \beta \), describe the occupational state of the system. Phases correspond to dimers locked into a given distribution,
\{\theta_0, \theta, \beta\}, in a perfect order (zero entropy) or partial order (non-zero entropy), over a relatively wide range of values of \(\mu\). Phases gradually disappear with increasing temperature. All possible phases of a given adsorption system occur at relatively low temperatures. The temperature-energy phase space associated with the adsorption system is 4-dimensional with variables \((\mu+V_0), V, W, \text{ and } T\).

The transfer matrix method provides all of the phases that exist in the temperature-energy phase diagram which may be used as a guide in analyzing experimental data. Phases observed experimentally correspond to a specific temperature-energy region of the phase diagram, leading to information on adsorbate-adsorbate and adsorbate-substrate interaction energies, and on the range of values of \(T\) and \(\mu\) for which the phases may be observed. The phase diagram also provides the conditions under which transitions between phases may occur.

2. Transfer matrix

The energy of the system relies on the count of the number of dimers on the lattice, the number of dimer ends that are first- and second-neighbors. The counting proceeds along each strip of \(M\) horizontal sites, and these are added for all of the strips in the vertical length of the nanotube. A dimer is counted as a member of a strip when both of its ends are in that strip, or when its other end is in the site below (if below, it belongs to the lower strip). The numbers of first- and second-neighbors belonging to a given strip are those between dimers both members of that strip, or one belonging to that strip and the other to the strip below.

There is a one-to-one correspondence between a matrix element of the transfer matrix and the states of two consecutive strips, referred to as “lower” and “upper” strips [1, 2, 3]. The row-index of an element is associated with the state of the lower strip, and the column-index with the state of the upper strip. A vertical dimer belonging to the lower strip cannot have its upper end in the upper strip if that site is occupied by one end of a dimer since overlapping is excluded. A matrix element is zero when overlapping between the states of the lower and upper strips occurs; otherwise it is of the form \(x^ay^bz^c\), where \(a, b, \text{ and } c\) are the numbers of dimers, and the numbers of first- and second-neighbors, respectively, following the counting procedure described above.

A site may be in one of five states indicated by a number \(\alpha\). This number is (0) if the site is vacant. If the site is occupied by one end of a dimer, its state is indicated as (1) when its other end is in the site below, (2) when its other end is above, (3) when its other end is to its left, or (4) when to its right. The problem consists of locating the zero elements and, for every non-zero element, of determining exponents \(a, b, \text{ and } c\).

The state of the \(i^{th}\) site in a strip of \(M\) sites is denoted \(\alpha_i\), randomly picking one of the sites to be the first. Let \(D(M)\) be the number of states of the strip, with no dimer with its ends in the \(1^{st}\) and \(M^{th}\) sites; thus excluding \((\alpha_1, \alpha_M) = (4, 3)\), which is the case for a terrace. In each of the cases \(\alpha_i = (0), (1), \text{ or } (2)\), the number of states is \(D(M-1)\); and, when \(\alpha_i = (3)\), it is \(D(M-2)\) since \((\alpha_2, \alpha_{M-1}) = (4,3)\) is excluded. Therefore, \(D(M) = 3D(M-1) + D(M-2)\). The number of states with \((\alpha_1, \alpha_M) = (4, 3)\) is \(D(M-2)\). Thus the total number, \(R(M)\), of states is given by the recursive relations:

\[
R(M) = 3D(M-1) + 2D(M-2) ; \quad D(M) = 3D(M-1) + D(M-2) .
\]

For \(M = 10\), \(R(10) = 154451\) while for a terrace \(D(10) = 141481\).

3. Recursive construction of the transfer matrix

The row-indices of the transfer matrix \(\text{NT}(M)\) are associated with an state of the lower strip given by the list \(\{\alpha_i\}\); similarly, the column-indices of \(\text{NT}(M)\) are associated with an state of the upper strip given by the list \(\{\beta_i\}\). Thus a (row, column)-matrix element is indicated as the \((\{\alpha_i\}, \{\beta_i\})\)-matrix element.
Block-matrices are extracted from the transfer matrix $\mathbf{NT}(M)$ by selecting a number of $(\{\alpha_i\}, \{\beta_j\})$-matrix elements. The selection is based on considering the states in the lower and upper strips of $M$ sites from $i = 1$ to $(M - k)$ in a given state, allowing all of the remaining $k$ sites to be in all of the possible states. In this manner, one identifies, for every $k$, eight families of block-matrices indicated as $\mathbf{T}$, $\mathbf{P}$, $\mathbf{K}$, $\mathbf{L}$, $\mathbf{T}'$, $\mathbf{P}'$, $\mathbf{K}'$, and $\mathbf{L}'$. The unprimed block-matrices exclude the first sites in the lower and upper strips to be both in the state (4); and the primed block-matrices correspond to the case where both of these sites are in state (4). There are 6 exclude the first sites in the lower and upper strips to be both in the state (4); and the primed members in each of the unprimed families and 2 members in each of the primed families, for a total of 32 block-matrices for every $k$, indicated as $\mathbf{T}(n + 2m; k)$, $\mathbf{P}(n + 2m; k)$, $\mathbf{K}(n + 2m; k)$, $\mathbf{L}(n + 2m; k)$, $\mathbf{T}'(n; k)$, $\mathbf{P}'(n; k)$, $\mathbf{K}'(n; k)$, and $\mathbf{L}'(n; k)$, where $n$ may take on the values 1 or 2, and $m$ the values 1, 2, or 3. The unprimed matrices with $m = 0$ (a total of 8) are the only ones required to construct the transfer matrix for terraces.

Using the standard Kronecker-delta notation, matrices $\mathbf{T}(n + 2m; k)$, $\mathbf{P}(n + 2m; k)$, $\mathbf{T}'(n; k)$, and $\mathbf{P}'(n; k)$ are $D(k - \delta_{2m}) \times D(k - \delta_{1m})$ matrices; matrices $\mathbf{K}(n + 2m; k)$ and $\mathbf{K}'(n; k)$ are $D(k - \delta_{2m}) \times D(k - 1 - \delta_{1m})$; and matrices $\mathbf{L}(n + 2m; k)$, and $\mathbf{L}'(n; k)$ are $D(k - 1 - \delta_{2m}) \times D(k - \delta_{1m})$ matrices. One can then show that the unprimed (primed) matrices for a given $k$ are obtained from the unprimed (primed) matrices for lower values of $k$, thus setting up a recursive construction. The recursion relations for the unprimed matrices are found as:

$\mathbf{T}(n + 2m; k) = \begin{pmatrix}
T(1 + 2m; k - 1) & 0 & xz^{n-1} & xz^{n-1} \\
T(2 + 2n; k - 1) & 0 & xyz^{n-1} & xyz^{n-1} \\
0 & z^{n-1} & 0 & 0 \\
L(1 + 2m; k - 1) & 0 & xyz^{n-1} & x^{2}z^{n+1} \\
\end{pmatrix}$

(3)

$\mathbf{P}(n + 2m; k) = \begin{pmatrix}
T(1 + 2m; k - 1) & 0 & xz^{n-1} & xz^{n-1} \\
zT(2 + 2m; k - 1) & 0 & xy^{2}z^{n} & xy^{2}z^{n} \\
0 & yz^{n} & 0 & 0 \\
zL(1 + 2m; k - 1) & 0 & xy^{2}z^{n} & x^{3}z^{n+2} \\
\end{pmatrix}$

(4)

$\mathbf{K}(n + 2m; k) = \begin{pmatrix}
z^{n-1}T(1 + 2m; k - 1) & yz^{n}P(2 + 2m; k - 1) \\
yz^{n}P(2 + 2m; k - 1) & 0 \\
z^{n}L(2 + 2m; k - 1) & 0 \\
\end{pmatrix}$

(5)

$\mathbf{L}(n + 2m; k) = (z^{-n-1}T(2 + 2m; k - 1)) \begin{pmatrix}
zy^{n} \mathbf{P}(2 + 2m; k - 1) \\
xy^{n}z^{n} \mathbf{K}(2 + 2m; k - 1) \\
\end{pmatrix}$

(6)

There are conditions that must be met at the $M$-end of the lower and upper strips, when $k = 0$ or 1. These initial conditions for the $\mathbf{T}$- and $\mathbf{P}$-families are:

$\mathbf{T}(n; 0) = \mathbf{P}(n; 0) = \begin{pmatrix} 1 \\ 0 \end{pmatrix} ; \quad \mathbf{T}(n + 2; 1) = \begin{pmatrix} z^{-n-1} \\ yz^{n-1} \end{pmatrix} ; \quad \mathbf{P}(n + 2) = \begin{pmatrix} yz^{n-1} \\ y^{2}z^{n-1} \end{pmatrix} ; \quad \mathbf{T}(n + 4; 1) = \begin{pmatrix} 1 & 0 \end{pmatrix} ; \quad \mathbf{P}(n + 4; 1) = \begin{pmatrix} z & 0 \end{pmatrix} \begin{pmatrix} 0 & y^{2}z^{n} \end{pmatrix}$.
There are no $K(n+2m;0)$ or $L(n+2m;0)$ matrices, and $K(n+4;1) = y^n z^n$; $L(n+2;1) = y^n z^n$. More involved conditions must be met on the other end of the two strips to account for first- and second-neighbors across the boundary between the 1st and $M$th sites.

There are two members in each of the primed families of matrices, for which $m = 0$ and $n = 1$ or 2. The recursion relations among the primed matrices are the same as those among their unprimed counterparts (where $m$ is set to zero). Here the 1st and $M$th sites are restricted to be in the states $(\alpha_1, \alpha_M) = (\beta_1, \beta_M) = (4, 3)$. The only conditions to be satisfied are at $k = 0$ or 1: there are no $K'(n;0)$ or $L'(n;0)$, and $T'(n;0) = z^{n-1}$, $P'(n;0) = y z^n$, and

\[
K'(n;1) = \begin{pmatrix} y z^n \\ y^2 z^{n-1} \\ 0 \end{pmatrix}, \quad L'(n;1) = \begin{pmatrix} z^n \\ 0 \\ x y^{n+1} z^{n+2} \end{pmatrix}.
\]

The transfer matrix $NT(M)$ is divided into $5 \times 5$ block-matrices. The row-indices (or column-indices) of a block-matrix correspond to all of the possible states of the lower strip (or upper strip) restricting $\alpha_1$ (or $\beta_1$) to be in this order: (0), (1), (2), (3), or (4), leading to

\[
NT(M) = \begin{pmatrix}
T(1; M - 1) & 0 & xP(1; M - 1) & xK(1; M - 1) & xP(3; M - 2) \\
T(2; M - 1) & 0 & xyP(2; M - 1) & xyK(2; M - 1) & xyzP(4; M - 2) \\
P(2; M - 1) & 0 & 0 & 0 & 0 \\
L(1; M - 1) & 0 & xyL(2; M - 1) & xy^2 z^2 P(2; M - 1) & xyzL(4; M - 1) \\
T(6; M - 1) & 0 & xyzP(6; M - 1) & xyzK(6; M - 1) & xy^2 z^2 Q(M - 1)
\end{pmatrix}
\]

The $Q$-block in the lower right corner of $NT(M)$ is a square matrix of rank $D(M - 2)$ and is obtained recursively in terms of the families of primed matrices as follows:

\[
Q(M - 2) = \begin{pmatrix}
T'(1; M - 3) & 0 & xyz & xyz & xyz \\
z T'(2; M - 3) & 0 & xy^2 z^2 & xy^2 z^2 & xy^2 z^2 \\
0 & y z^2 & P'(2; M - 3) & P'(2; M - 3) & P'(2; M - 3) \\
z L'(1; M - 1) & 0 & xy^2 z^2 & xy^2 z^2 & xy^2 z^2
\end{pmatrix}
\]

The algorithm that results from this mathematical construction makes it possible to study dimer adsorption on nanotube surfaces with increasing diameter.

4. Discussion
We have written C language code to perform this algorithm which is similar to the code we wrote for dimers adsorbed on square terraces [1, 2]. The results for nanotubes will be valuable for comparison with experimental results. We plan to extend the algorithm for co-adsorption of two species in a manner similar co-adsorption of several monomer species [3].

References
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