J Math Chem (2010) 48:592–600
DOI 10.1007/s10910-010-9694-2

ORIGINAL PAPER

Configurational degeneracy of a set of dipoles in a quasi-two-dimensional system

P. L. Dammig Quiña · V. E. Pastor · I. M. Irurzun · E. E. Mola

Received: 29 October 2009 / Accepted: 26 April 2010 / Published online: 9 June 2010

Abstract The purpose of this paper is to provide an exact evaluation of the configurational degeneracy when an arbitrary number (k) of dipoles are placed in a quasi-two-dimensional space ($Q2D$). This $Q2D$ is made up of three contiguous diagonals $3 \times N$. Our $Q2D$ space gives to the central sites of the lattice their full coordination number of nearest neighboring compartments. We are going to determine the exact configurational degeneracy $W(k, N)$ when an arbitrary number k of the above mentioned particles are placed in this $3 \times N Q2D$ space. We found that $W(k, N)$ is exactly described by

$$W(k, N) = 8W(k-1, N-1) - 8W(k-2, N-2) + W(k, N-1)$$

$W(k, N)$ is a prerequisite to develop analytical methods to study the interaction between an arbitrary set of dipoles (or spins, magnetic domains, heterogeneous diatomic molecules, etc) placed in a $Q2D$ space.

Keywords Dipoles · Configurational degeneracy · Entropy · Partition function

1 Introduction

Many physical and chemical systems can be represented by the distribution of dipoles, spins, etc in a two-dimensional system ($2D$). Dipolar interactions can play a significant

P. L. D. Quiña · V. E. Pastor · I. M. Irurzun · E. E. Mola (✉)
Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, INIFTA. Consejo Nacional de Investigaciones Científicas y Técnicas, CONICET. Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, República Argentina
e-mail: eemola@inifta.unlp.edu.ar

E. E. Mola
Facultad de Química e Ingeniería, Fray Roger Bacon, Rosario Pontificia Universidad Católica Argentina, Buenos Aires, Argentina

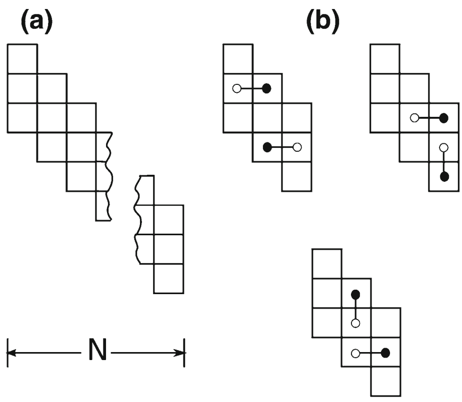

Fig. 1 **a** A $3 \times N$ diagonal array; **b** Three out of the 116 possible arrangements of two dipoles in a $3 \times 3 Q2D$ space

role in the structural properties of $2D$ systems. Representative examples include colloidal particles at an interface, electrorheological fluids, adsorption of molecules on a metal surface, magnetic thin films, nanocrystals deposited on a substrate, amphiphilic molecules adsorbed at an air-water interface, etc. [1–5].

Problems dealing with particles with distinguishable ends (dipoles, spins, magnetic domains, amphiphilic molecules, hetero-diatomic molecules, etc.) placed in a lattice have always been troublesome; unlike simple particles, there is no reciprocity between particles and vacancies. Therefore, as is generally true for problems of this nature, exact solutions are a difficult task.

In recent years we have made a considerable effort to develop analytical methods to find exact solutions to problems dealing with: (i) the kinetics of immobile adsorption of linear molecules on a two-dimensional lattice [6], (ii) a heterogeneous reaction exactly solved on a small lattice [7], (iii) how many Langmuirs are required for monolayer formation [8], (iv) the scaling properties in the average number of attempts until saturation in random sequential adsorption processes [9], (v) the branch counting probability approach to random sequential adsorption [10]. In the present paper we develop an analytical approach to find the configurational degeneracy when a set of particles with distinguishable ends are placed in a quasi-two-dimensional space.

The purpose of this paper is to provide an exact evaluation of the configurational degeneracy when an arbitrary number (k) of dipoles are placed in a quasi-two-dimensional space ($Q2D$). This $Q2D$ is made up of three contiguous diagonals $3 \times N$ as is shown in Fig. 1a. Our $Q2D$ gives to the central sites of the lattice their full coordination number of nearest neighboring compartments. In Sect. 2 we determine the exact configurational degeneracy $W(k, N)$ when an arbitrary number k of the above mentioned particles are placed in this $3 \times N Q2D$ space. Our conclusions are summarized in Sect. 3.

2 Exact dipole configurational degeneracy

We wish to determine a recursion relation for $W(k, N)$, the configurational degeneracy of k indistinguishable dipoles in a $3 \times N$ diagonal array of compartments. Figure 1b

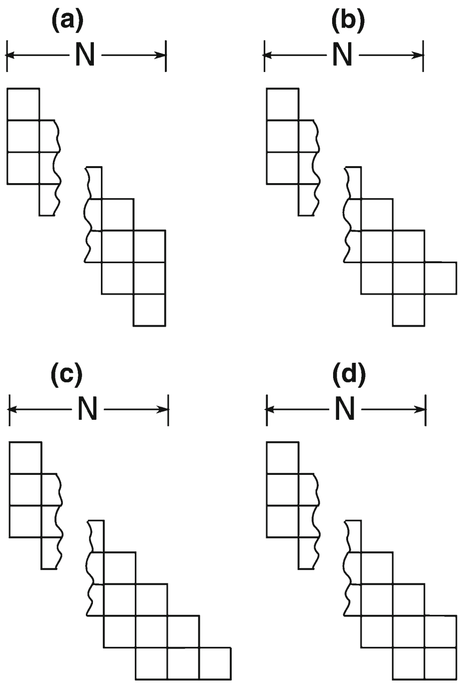

Fig. 2 **a** An $\omega(N)$ array, **b** a $\lambda(N)$ array, **c** a $\gamma(N)$ array, and **d** a $\delta(N)$ array

shows three out of the 116 possible arrangements of two dipoles in a $3 \times 3Q2D$ space. Let us first define the following arrays: (1) An $\omega(N)$ array, see Fig. 2a, is defined to be an array of sites arranged in three adjacent diagonals of N sites each; (2) a $\lambda(N)$ array, see Fig. 2b, is one in which the compartments are arranged in three adjacent diagonals of $(N + 1)$ compartments for the upper one and N compartments for the other two; (3) a $\gamma(N)$ array, see Fig. 2c, is an array of compartments arranged in three adjacent diagonals of $(N + 2)$, $(N + 1)$ and N compartments for the upper, central and lower diagonals respectively; (4) a $\delta(N)$ array, see Fig. 2d, is an array of three adjacent diagonals of $(N + 1)$, $(N + 1)$ and N compartments for the upper, central and lower diagonals, respectively.

Let $W(k, N)$ be the number of ways of arranging k indistinguishable spins in an $\omega(N)$ array, and $L(k, N)$, $G(k, N)$, $D(k, N)$ are the number of ways in which k indistinguishable dipoles can be arranged in a $\lambda(N)$, $\gamma(N)$ and $\delta(N)$ array, respectively.

Theorem I

$$G(k, N) = D(k, N) + 2L(k - 1, N) \tag{1}$$

Proof Let $g(k, N)$ be the set of all possible arrangements of k indistinguishable spins in a $\gamma(N)$ array; $d(k, N)$ is the subset of $g(k, N)$ where the only compartment of the $(N+2)th$ column is vacant and $l(k, N)$ is the subset of $g(k, N)$ in which that compartment is occupied. It should be noticed that this compartment can be occupied in two different ways. Then, every arrangement in $d(k, N)$ differs from every arrangement in $l(k, N)$ by the condition of occupation of the above mentioned compartment, i.e., $d(k, N) \bigcap l(k, N)$ is a null set. In addition, every member of $g(k, N)$ can be found either in $d(k, N)$ or $l(k, N)$, *i.e.*, $d(k, N) \bigcup l(k, N) = g(k, N)$.

Therefore $\#g(k, N)$, the number of members of the set $g(k, N)$, is given by: $\#g(k, N) = \#d(k, N) + \#l(k, N) = G(k, N)$.

The compartment of the $(N + 2)th$ column is unoccupied in the set $d(k, N)$ so that by definition $\#d(k, N)$ is $D(k, N)$. If that compartment is occupied, then the adjacent one is also occupied. Hence, all other possible arrangements must involve the remaining $(k - 1)$ dipoles in the remainder of the array, which is a $\lambda(N)$ array. The number of elements in $l(k, N)$ therefore is $2L(k - 1, N)$, i.e., $\#l(k, N) = 2L(k - 1, N)$. The factor 2 is because the above mentioned compartment can be occupied in two different ways. Therefore we prove Eq (1). □

Theorem II

$$W(k, N) = D(k, N - 1) + 2L(k - 1, N - 1) \tag{2}$$

Proof Let $w(k, N)$ be the set of all possible arrangements of k indistinguishable dipoles in an $\omega(N)$ array; $d(k, N)$ is the subset of $w(k, N)$ where the lower compartment of the Nth column is vacant, and $l(k, N)$ is the subset of $w(k, N)$ in which that compartment is occupied. It should be noticed that this compartment can be occupied in two different ways. Then, every arrangement in $d(k, N)$ differs from every arrangement in $l(k, N)$ by the condition of occupation of the lower compartment of the Nth column, i.e., $d(k, N) \bigcap l(k, N)$ is a null set. In addition, every member of $w(k, N)$ can be found either in $d(k, N)$ or $l(k, N)$, i.e., $d(k, N) \bigcup l(k, N) = w(k, N)$. We conclude that $\#w(k, N)$, the number of members of the set $w(k, N)$, is given by: $\#w(k, N) = \#l(k, N) + \#d(k, N)$.

The lower compartment of the Nth column is unoccupied in the set $d(k, N)$, so that by definition, $\#d(k, N)$ is $D(k, N - 1)$. If that compartment is occupied, then the adjacent one is also occupied. Hence, all other possible arrangements must involve the remaining $(k - 1)$ dipoles in the remainder of the array, which is a $\lambda(N - 1)$ array. The number of elements in $l(k, N)$ therefore is $2L(k - 1, N - 1)$, i.e., $\#l(k, N) = 2L(k - 1, N - 1)$. The factor 2 is because the above mentioned compartment can be occupied in two different ways. Therefore we prove Eq. (2). □

Corollary 1

$$G(k, N - 1) = W(k, N) \tag{3}$$

Proof From Theorem I, by substituting N by $N - 1$ in Eq. (1) we obtain

$$G(k, N - 1) = D(k, N - 1) + 2L(k - 1, N - 1) \tag{4}$$

and the right hand side of Eq. (4) is $W(k, N)$ because of Theorem II. □

Theorem III

$$L(k, N) = W(k, N) + 2L(k-1, N-1) \tag{5}$$

Proof Let $l(k, N)$ be the set of all possible arrangements of k indistinguishable dipoles in a $\lambda(N)$ array; $w(k, N)$ is the subset of $l(k, N)$ in which the only compartment of the $(N+1)$th column is vacant, and $c(k, N)$ is the subset of $l(k, N)$ in which that compartment is occupied. It should be noticed that this compartment can be occupied in two different ways. Then, every arrangement in $w(k, N)$ differs from every arrangement in $c(k, N)$ by the condition of occupation of the only compartment of the $(N+1)$th column, i.e., $w(k, N) \bigcap c(k, N)$ is a null set. In addition, every member of $l(k, N)$ can be found either in $w(k, N)$ or $c(k, N)$, i.e., $w(k, N) \bigcup c(k, N) = l(k, N)$. We conclude that $\#l(k, N)$, the number of members of the set $l(k, N)$, is given by: $\#l(k, N) = \#w(k, N) + \#c(k, N)$.

Only one compartment of the $(N+1)$th column is vacant in the set $w(k, N)$, so that by definition $\#w(k, N)$ is $W(k, N)$. If that compartment is occupied, then the adjacent one is also occupied. Hence, all other possible arrangements must involve the remaining $(k-1)$ dipoles in the remainder of the array, which is a $\lambda(N-1)$ array. The number of elements in $c(k, N)$ therefore is $2L(k-1, N-1)$, i.e., $\#c(k, N) = 2L(k-1, N-1)$. The factor 2 is because the above mentioned compartment can be occupied in two different ways. Therefore, we prove Eq. (5). □

Corollary 2

$$L(k, N) = \sum_{i=0}^{k} 2^i W(k-i, N-i) \tag{6}$$

Proof We can evaluate $L(k-1, N-1)$ by using Theorem III

$$L(k-1, N-1) = W(k-1, N-1) + 2L(k-2, N-2) \tag{7}$$

Substitution of this into the Theorem III yields

$$L(k, N) = E(k, N) + 2E(k-1, N-1) + 4L(k-2, N-2) \tag{8}$$

Repeated use of Eq. (7) gives

$$\begin{aligned} L(k, N) = {} & W(k, N) + 2W(k-1, N-1) + 2^2 W(k-2, N-2) + \cdots \\ & + 2^{k-1} W(1, N-k+1) + 2^k L(0, N-k) \end{aligned} \tag{9}$$

However, $L(0, N-k) = W(0, N-k)$. Therefore, we prove Eq. (6). □

Theorem IV

$$\begin{aligned} W(k, N) = {} & L(k, N-1) + 2L(k-1, N-1) + 2W(k-1, N-1) \\ & + 2G(k-1, N-2) \end{aligned} \tag{10}$$

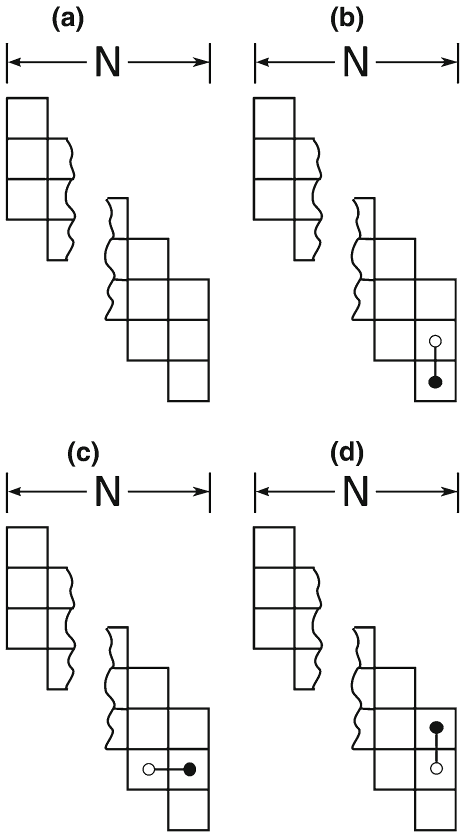

Fig. 3 The four possible states of occupation of the two lower compartments of the Nth column. **a**, **b**, **c** and **d**) stands for a_1, a_2, a_3 and a_4 respectively

Proof Let $w(k, N)$ be the set of all possible arrangements of k dipoles in an $\omega(N)$ array, and let $a_1(k, N)$, $a_2(k, N)$, $a_3(k, N)$ and $a_4(k, N)$ be subsets of $w(k, N)$ in which the lower two compartments of the Nth column of the $\omega(N)$ array are occupied in the manner shown in Fig. 3. In other words, the $a_i(k, N)$ are subsets defined on the basis of the manner in which those two compartments are occupied. Since every member of $a_i(k, N)$ differs from any and every member of $a_i(k, N)(i \neq j)$, we conclude that $a_i(k, N) \bigcap a_j(k, N) = \Phi, i \neq j$. Also, these four configurations clearly are the only one we can form with the above mentioned compartments, therefore,

$$\bigcup_{i=1}^{4} a_i(k, N) = w(k, N) \tag{11}$$

We conclude that

$$\#w(k, N) = \sum_{i=1}^{4} \#a_i(k, N) = W(k, N) \tag{12}$$

The set $a_1(k, N)$ contains only those arrangements in which those two compartments are vacant. All k dipoles are then arranged in the remaining $\lambda(N-1)$ array; hence $\#a_1(k, N) = L(k, N-1)$.

The set $a_2(k, N)$ contains a dipole occupying both compartments, and the remaining $(k-1)$ dipoles are arranged in an array composed of the original array minus the two precluded compartments, i.e., in a $\lambda(N-1)$ array. We may then write $\#a_2(k, N) = 2L(k-1, N-1)$. The factor 2 is because of the two different ways in which a dipole can be placed in the two precluded compartments.

The set $a_3(k, N)$ has the upper compartment occupied and the lower one empty. The remaining end of the dipole occupies a compartment of the $(N-1)th$ column, the remaining $(k-1)$ dipoles are arranged in an array composed of the original array minus the three precluded compartments, i.e., in a $\gamma(N-2)$ array. We may then write $\#a_3(k, N) = 2G(k-1, N-2)$. The factor 2 is because of the two different ways in which the above mentioned dipole can be placed.

The set $a_4(k, N)$ has the upper compartment occupied and the lower one empty, the remaining end of the dipole occupies another compartment of the Nth column, and the remaining $(k-1)$ dipoles are arranged in a $\omega(N-1)$ array, i.e., $\#a_4(k, N) = 2W(k-1, N-1)$. The factor 2 is because of the two different ways in which we can place the dipole. Therefore by Eq. (12) we prove Theorem IV. □

Corollary 3

$$W(k, N) = 8W(k-1, N-1) - 8W(k-2, N-2) + W(k, N-1) \tag{13}$$

Proof By Corollary 1, Eq. (3), we evaluate $G(k-1, N-2)$;

$$G(k-1, N-2) = W(k-1, N-1) \tag{14}$$

We may then write Theorem IV as

$$W(k, N) = 4W(k-1, N-1) + L(k, N-1) + 2L(k-1, N-1) \tag{15}$$

Therefore

$$W(k-1, N-1) = 4W(k-2, N-2) + L(k-1, N-2) + 2L(k-2, N-2) \tag{16}$$

Let us now perform the difference $W(k, N) - 2W(k-1, N-1)$, from Eqs. (15) and (16) we obtain,

$$\begin{aligned} W(k, N) - 2W(k-1, N-1) = {} & 4W(k-1, N-1) - 8W(k-2, N-2) \\ & + L(k, N-1) - 2L(k-1, N-2) \\ & + 2L(k-1, N-1) - 4L(k-2, N-2) \end{aligned} \tag{17}$$

Table 1 Occupational degeneracy $W(k, N)$ when indistinguishable dipoles are placed in a $3 \times NQ2D$ space for N and k in the range 0–8

$N\backslash k$	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
0	1/2	1	1	1	1	1	1	1	1
1		4	12	20	28	36	44	52	60
2			28	116	268	484	764	1,108	1,516
3				192	1,024	3,008	6,656	12,480	20,992
4					1,312	8,576	30,496	79,872	173,600
5						8,960	69,376	289,280	875,008
6							61,184	547,584	261,7856
7								417,792	4,243,456
8									2,852,864

We then use Corollary 2, Eq. (6), to evaluate the differences $L(k, N-1) - 2L(k-1, N-2)$ and $2L(k-1, N-1) - 4L(k-2, N-2)$

$$\begin{aligned} L(k, N-1) - 2L(k-1, N-2) = {} & W(k, N-1) + 2W(k-1, N-2) \\ & + 2^2 W(k-2, N-3) + \cdots \\ & + 2^k W(0, N-1-k) - 2W(k-1, N-2) \\ & - 2^2 W(k-2, N-3) - \cdots \\ & - 2^k W(0, N-1-k) \end{aligned} \tag{18}$$

Therefore

$$L(k, N-1) - 2L(k-1, N-2) = W(k, N-1) \tag{19}$$

In an analogous way we can obtain the second difference using Corollary 2

$$2L(k-1, N-1) - 4L(k-2, N-2) = 2W(k-1, N-1) \tag{20}$$

By substituting the differences found in Eqs. (19) and (20) in Eq. (17) we found

$$\begin{aligned} W(k, N) - 2W(k-1, N-1) = {} & 4W(k-1, N-1) - 8W(k-2, N-2) \\ & + W(k, N-1) + 2W(k-1, N-1) \end{aligned} \tag{21}$$

Finally we found the exact recursion relationship for $W(k, N)$ given by Eq. (13).

Equation 13 has the following initial conditions: $W(0, 1) = 1$, $W(1, 1) = 4$, $W(0, 2) = 1$, $W(1, 2) = 12$ and $W(2, 2) = 28$. From those initial conditions we can derive $W(0, 0) = 1/2$. It should also be noticed that $W(k, N) = 0$ if $N < k < 0$ or $k > N$.

Table 1 shows the configurational degeneracy $W(k, N)$ of k indistinguishable dipoles in a $3 \times NQ2D$ space for k and N in the range 0–8, according to Eq. (13) with the stated boundary conditions. □

3 Conclusions

In the present paper we provide an exact evaluation of the configurational degeneracy when an arbitrary number (k) of dipoles are placed in a quasi-two-dimensional space ($Q2D$). This $Q2D$ space is made up of three contiguous diagonals $3 \times N$ as is shown in Fig 1a. Our $Q2D$ space gives to the central sites of the lattice their full coordination number of nearest neighboring compartments. We determine the exact configurational degeneracy $W(k, N)$ when an arbitrary number k of the above mentioned particles are placed in this $3 \times NQ2D$ space. We found that $W(k, N)$ is exactly described by

$$W(k, N) = 8W(k-1, N-1) - 8W(k-2, N-2) + W(k, N-1) \tag{22}$$

Table 1 shows the configurational degeneracy $W(k, N)$ when indistinguishable dipoles are placed in a $3 \times NQ2D$ space for N and K in the range 0–8.

From that table we learn that the configurational degeneracy $W(k, N)$ shows a maximum when $N > 5$. Work is in progress in La Plata to determine the characteristic of $W(k, N)$ when $N >> 1$, in particular if the dependence of $W(k, N)$ on k is either a broad or a sharp distribution. The analysis presented in this paper is a first step in order to unravel, through analytical methods, the role played by the configurational entropic contribution to these systems.

Acknowledgements This work was financially supported by Consejo Nacional de Investigaciones Cientificas y Tecnicas (CONICET), Universidad Nacional de La PLata (UNLP) y Agencia Nacional de Investigaciones Cientificas y Tecnologicas (ANPCyT)

References

1. T. Beier, H. Jahrreis, D. Pescia, Th. Woike, W. Gudat, Phys. Rev. Lett. **61**, 1875 (1988)
2. K. De Bell, A.B. MacIsaac, I.N. Booth, J.P. Whitehead, Phys. Rev. B. **55**, 15108 (1997)
3. E. Rastelli, S. Regina, A. Tassi, A. Carbognani, Phys. Rev. B. **65**, 094412 (2002)
4. R. Allenspach, A. Bischof, Phys. Rev. Lett. **69**, 3385 (1992)
5. M. Seul, M.J. Sammon, Phys. Rev. Lett. **64**, 1903 (1990)
6. A.E. Bea, A.V. Ranea, A.M. Irurzun, E.E. Mola, Chem. Phys. Lett. **401**, 342–346 (2005)
7. P. Bergero, V. Pastor, I.M. Irurzun, E.E. Mola, Chem. Phys. Lett. **449**, 115–119 (2007)
8. A.E. Bea, I.M. Irurzun, E.E. Mola, Langmuir **21**, 10871–10873 (2005)
9. A.E. Bea, I.M. Irurzun, E.E. Mola, Phys. Rev. E **73**, 051604 (2006)
10. I.M. Irurzun, V.A. Ranea, E.E. Mola, Chem. Phys. Lett. **408**, 19–24 (2005)