

Adsorption of asymmetric rigid rods or heteronuclear diatomic molecules on homogeneous surfaces

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We treat the adsorption on homogeneous surfaces of asymmetric rigid rods (like for instance heteronuclear diatomic molecules). We show that the $n \rightarrow 0$ vector spin formalism is well suited to describe such a problem. We establish an isomorphism between the coupling constants of the magnetic Hamiltonian and the adsorption parameters of the rigid rods. By solving this Hamiltonian within a mean-field approximation, we obtain analytical expressions for the densities of the different rod's configurations, both isotherm and isobar adsorption curves. The most probable configurations of the molecules (normal or parallel to the surface) which depends on temperature and energy parameters are summarized in a diagram. We derive that the variation of Q_v , the heat of adsorption at constant volume, with the temperature is a direct signature of the adsorbed molecules configuration change. We show that this formalism can be generalized to more complicated problems such as for instance the adsorption of symmetric and asymmetric rigid rods mixtures in the presence or not of interactions.

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I. INTRODUCTION

Adsorption with multisite occupancy (MSO) is an important topic of surface science because of its key role in a broad range of industrial processes such as adhesion, wetting, monolayers, gas and hydrocarbon separation, streams and pollution control.¹ For instance, the adsorption of rigid rod-like molecules, including liquid crystals and liquid crystalline is essential to applications in displays. Other examples of multisite adsorption processes are for instance, O_2 , N_2 , CO adsorbed in carbons and zeolite molecular sieves or oligomers in activated carbons.² Despite the practical importance of MSO adsorption, most theoretical developments have been limited to monosite (i.e., monoatomic) adsorption. In contrast to monoatomic adsorption, treating exactly the statistics of MSO is a very challenging theoretical problem because of the existence of statistical correlations. Indeed in this case, statistical equivalence between vacancies and occupied sites does no longer hold. Thus, an occupied site has two different possible configurations depending on whether the diatomic molecule that occupies it, sticks perpendicular or parallel to the surface. Recall that in this latter case, at least one of its nearest-neighbor sites must be occupied by the other atom of the same molecule. Therefore, an isolated vacancy cannot serve to determine if that site can ever become occupied by a molecule parallel to the surface. Although an exact solution exists in one dimension both for gases and gases mixtures with MSO,³ extension to higher dimensions remains still difficult, even in the simplest non-interacting dimer adsorption. Moreover, no exact solution to Langmuir isotherms exists for two or more dimensions. That is why to analyze adsorption isotherms and heat of adsorption of dimers on homogeneous substrates, mean field, quasicheical or cluster approximations, and numerical Monte Carlo simulations are usually developed.⁴⁻¹²

The aim of this paper is to show that the $n \rightarrow 0$ dilute vector spin formalism, introduced originally by Wheeler and

co-workers¹³⁻¹⁵ for describing the polymerization phenomenon of liquid sulfur and of living polymers, is particularly suited for treating MSO adsorption. Solved within the mean-field approximation, this model permits to obtain analytical expressions, for instance, of: (i) the probability of the different configurations a molecule can adopt when it adsorbs and (ii) isotherm and isobar adsorption curves. In contrast to other approaches, such formalism may benefit from general methods used in theories of magnetism such as renormalization calculations. Besides, we show that it can easily be extended to treat the adsorption of diatomic molecules mixtures and interacting dimers.

II. ADSORPTION OF ASYMMETRIC RIGID MOLECULES ON HOMOGENEOUS SURFACES: STATISTICAL TREATMENT

To describe the adsorption of asymmetric rigid rods (or heteronuclear diatomic molecules) on homogeneous substrates, we use a lattice approach. The substrate is modeled as a two-dimensional (2D) lattice, whose M sites represent the different adsorption sites. On each site (i), are associated a magnetic vector spin \vec{S}_i whose dimension $n \rightarrow 0$ and an Ising number σ_i whose two possible values are 0 or 1.

Under these conditions, let us now consider the following magnetic Hamiltonian:

$$-\beta H = Q \cdot \sum S_{i,1}^2 \sigma_i + Q_o \cdot \sum S_{i,1}^2 (1 - \sigma_i) + K \sum_{\langle i,j \rangle} S_{i,1}^2 \sigma_i S_{j,1}^2 (1 - \sigma_j), \quad (1)$$

where the notation $\langle i,j \rangle$ recalls the fact that i and j are nearest-neighbor sites and where β is the Boltzmann's factor. For now, Q , Q_o , and K are numerical constants whose physical significance for the adsorption problem will be explained further in the text. By definition, the partition function asso-

ciated with this Hamiltonian is $Z = \langle \exp(-\beta H) \rangle_0$. The notation $\langle \cdot \rangle_0$ represents the average with no weight over all the n components of all spins $S_{i,\alpha}$ ($i=1,2,\dots,M$ and $\alpha=1,\dots,n$) and over all the possible values of $\{\sigma_i\}$. Another possible expression of Z can be obtained by expanding $\exp(-\beta H)$ in terms of powers of H and by averaging this expression with no weight over all the components of all spins $\tilde{S}_{i,\alpha}$ and all the possible Ising numbers σ_i :

$$\frac{Z}{M} = \langle 1 \rangle_0 - \beta \langle H \rangle_0 + \frac{\beta^2}{2} \langle H^2 \rangle_0 + \dots + \frac{(-\beta)^n}{n!} \langle H^n \rangle_0 + \dots \quad (2)$$

Usually, this expression cannot be computed because of its very complicated structure. However, when n tends to zero (which must only be considered as a mathematical trick), it turns out that it becomes much simpler because of the moment theorem (valid only in this limit) which states that¹⁶

$$\langle S_{i,\alpha} S_{j,\beta} \rangle_0 = \delta_{\alpha,\beta} \delta_{i,j}$$

and

$$\langle S_{i,\alpha}^k \rangle_0 = \delta_{0,k} + \delta_{2,k}. \quad (3)$$

Briefly, this expansion leads to a sum of polynomial expressions in power series of \tilde{S}_i and σ_i . In the $n \rightarrow 0$ limit, because of the moment theorem [see Eqs. (3)], the only nonvanishing contributions to Z correspond to polynomials containing for each site (i), a factor $S_{i,1}^k$ with $k=0$ or $k=2$. In this expansion because the averages are performed with no weight, terms involving more than one site (i.e., $i \neq j$) like, for instance, $\langle S_{i,\alpha}^m S_{j,\beta}^p \rangle_0$ reduce to $\langle S_{i,\alpha}^m \rangle_0 \langle S_{j,\beta}^p \rangle_0$ (Ref. 16) and can therefore be easily computed by using the moment theorem. Such calculations have already been treated in details in the literature.^{13–18} Following this procedure, it is then straightforward to show that Z is simply given by

$$Z(M) = \left\langle \prod_{i=1}^M [1 + Q_\circ S_{i,1}^2 (1 - \sigma_i)] \times \prod_{j=1}^M (1 + Q_\bullet S_{j,1}^2 \sigma_j) \prod_{\langle i,j \rangle} [1 + K S_{i,1}^2 \sigma_i S_{j,1}^2 (1 - \sigma_j)] \right\rangle_0 \quad (4)$$

As first noticed by de Gennes,¹⁶ all successive nonvanishing polynomials can be represented by graphs on the lattice. The exponent k of the prefactor $S_{i,1}^k$ indicates whether the site (i) is occupied ($k=2$) or not ($k=0$). Now, let us recall that to each site one associates an Ising number which can take two different values (0 or 1). Therefore, each lattice site can be occupied by two different species that we, respectively, represent on the graphs by open ($\sigma_i=0$) and closed ($\sigma_i=1$) circles (see Fig. 1). Thus, the presence of a term, $S_{i,1}^2 (1 - \sigma_i)$ in a nonvanishing polynomial expressions of Z , indicates that the site (i) is occupied by an open circle, since this prefactor is different from 0 only if $\sigma_i=0$. Because of the nature of the Hamiltonian and because of the moment theorem, such a prefactor comes from a first-order expansion of $\exp(-\beta H)$. Therefore, it either arises from a term $Q_\circ S_{i,1}^2 (1 - \sigma_i)$

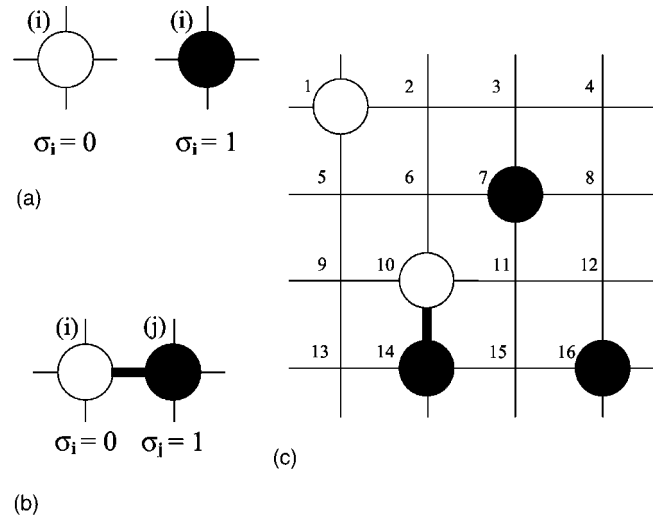


FIG. 1. (a) Shown are the representations of an open circle and close circle monomers. Such monomers are, respectively, related to a prefactor $Q_\circ S_{i,1}^2 (1 - \sigma_i)$ and $Q_\bullet S_{i,1}^2 \sigma_i$ in the polynomial expansion of Z . (b) Shown is the schematic representation of a dimer which is associated to a prefactor $K S_{i,1}^2 \sigma_i S_{j,1}^2 (1 - \sigma_j)$, in the polynomial expansion of Z . Such nonvanishing dimers link an open circle to a close adjacent circle. (c) Lattice representation of a configuration consisting of one “open circle” monomer (site 1), two “close circle” monomers (sites 7 and 16), and a dimer occupying both sites 10 and 14. By using the moment theorem, valid in the $n \rightarrow 0$ limit, this corresponding configuration is associated to a term: $Q_\circ (Q_\bullet)^2 K$.

or $K S_{i,1}^2 \sigma_i S_{j,1}^2 (1 - \sigma_j)$ [see Eq. (4)]. Similarly, a prefactor, $S_{i,1}^2 \sigma_i$, indicating that site (i) is occupied by a close circle, arises either from a term $Q_\bullet S_{i,1}^2 \sigma_i$ or $K S_{i,1}^2 \sigma_i S_{j,1}^2 (1 - \sigma_j)$. Now, if to each term, $K S_{i,1}^2 S_{j,1}^2$, one associates a continuous line between sites (i) and (j), each nonvanishing polynomial expressions contributing to Z can be represented by a diagram, made of isolated open and close circles (monomers) and continuous lines linking an open to a close adjacent circle (dimers) (Fig. 1). Note that lines connecting more than two sites do not contribute to the partition function since they require the presence of at least a term $\langle S_{i,1}^{2m} \rangle_0$ with $m > 1$, which cancels the polynomial expression associated to such a configuration. Besides, dimers made of two adjacent sites of same nature (open or close circles) do not contribute to the partition function. Recall that the prefactor $S_{i,1}^2 S_{j,1}^2 \sigma_i (1 - \sigma_j)$ associated to dimers vanishes whenever $\sigma_i = \sigma_j$. Following these considerations, the partition function Z can be expressed as

$$Z(N_\circ, N_\bullet, N_{\circ\bullet}, M) = \sum_{N_\circ} \sum_{N_\bullet} \sum_{N_{\circ\bullet}} \Gamma(N_\circ, N_\bullet, N_{\circ\bullet}, M) Q_\circ^{N_\circ} Q_\bullet^{N_\bullet} K^{N_{\circ\bullet}}, \quad (5)$$

where $\Gamma(N_\circ, N_\bullet, N_{\circ\bullet}, M)$ represents the number of ways to place on the M sites of the lattice: N_\circ monomers (\circ), N_\bullet monomers (\bullet), and $N_{\circ\bullet}$ dimers ($\circ\bullet$).

In what follows, we show that an isomorphism can be drawn between the magnetic partition function Z derived previously and the grand-partition function Ξ describing the

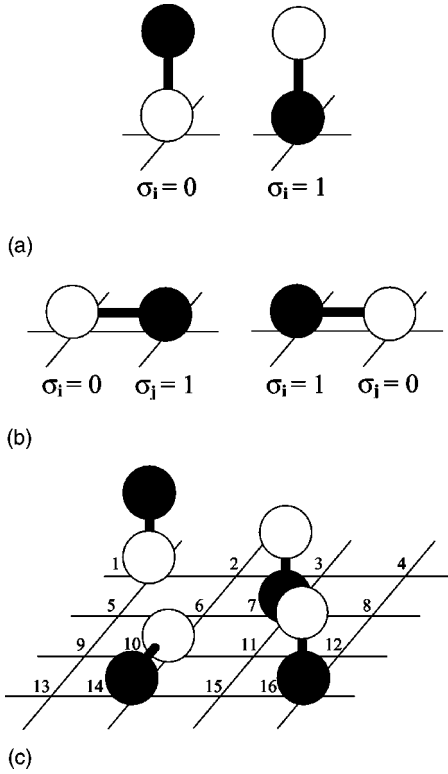


FIG. 2. Schematic representation of the three different main configurations a heteronuclear molecule (or asymmetric rigid rod) can adopt when it adsorbs on the surface. (a) When a molecule sticks normal to the surface, and occupies a site (i) a factor $Q_{\bullet} S_{i,1}^2 \sigma_i$ or $Q_{\circ} S_{i,1}^2 (1 - \sigma_i)$ is associated to it, depending on which one of its two extremities, namely, \bullet or \circ , sticks to the surface. A factor $K S_{i,1}^2 \sigma_i S_{j,1}^2 (1 - \sigma_j)$ is associated to a molecule lying parallel to the surface (b), and therefore occupying two adjacent sites (i) and (j). Such a factor is different from zero only if $\sigma_i \neq \sigma_j$. This condition ensures that the nonvanishing dimers have two different extremities (i.e., the molecules are heteronuclear). For instance, if $\sigma_i = 1$ and $\sigma_j = 0$, the extremity \bullet of the molecule is on site (i) and the other extremity \circ is on site (j). (c) Shown is a given lattice configuration consisting of three different molecules adsorbed perpendicular to the surface (two of which are adsorbed by the \bullet extremity and the other one by the \circ extremity) and one adsorbed molecule sticking parallel to the surface. In the $n \rightarrow 0$ limit, the corresponding configuration has a prefactor $(Q_{\bullet})^2 Q_{\circ} K$ and its total energy is $2\epsilon_{\bullet} + \epsilon_{\circ} + \epsilon_{\bullet\circ}$.

adsorption on a homogeneous surface of asymmetric rigid rods (for instance, heteronuclear diatomic molecules). In such a problem, the molecules are in exchange chemical equilibrium between a large reservoir (gas or liquid) and the substrate. In general, an adsorbed rigid rod may assume an infinite number of orientations relative to surface. However, following classical lattice approaches^{12,19,20} and for simplicity's sake, we restrict the possible rod orientations to either parallel and normal to the surface (Fig. 2). When an adsorbed molecule is arranged parallel to the surface, it occupies two adjacent sites whereas when it is adsorbed normal to the surface, it occupies only one site. However, because of its asymmetry, a molecule arranged normal or parallel to the surface exhibits two different configurations. The adsorption

energies associated with each molecule configuration are of the order of the thermal energy, so that the adsorbed molecules (or rods) can change the configurations depending on the adsorbed amounts. We first consider the grand-partition function Ξ of the substrate. Let N_{\bullet} be the number of adsorbed molecules arranged parallel to the substrate and N_{\circ} and $N_{\bullet\circ}$ the numbers of molecules arranged normal to the surface associated, respectively, with the two possible configurations due to the molecule asymmetry (see Fig. 2). Under these circumstances, Ξ can be written as

$$\Xi = \sum \sum \sum \Gamma(N_{\bullet}, N_{\circ}, N_{\bullet\circ}, M) z^{(N_{\bullet} + N_{\circ} + N_{\bullet\circ})} q_{\circ}^{N_{\circ}} q_{\bullet}^{N_{\bullet}} q_{\bullet\circ}^{N_{\bullet\circ}}. \quad (6)$$

In Eq. (6), $\Gamma(N_{\bullet}, N_{\circ}, N_{\bullet\circ}, M)$ represents the number of ways to accommodate on the M sites of the substrate, $N_{\bullet} + N_{\circ} + N_{\bullet\circ}$ molecules with, respectively, N_{\bullet} and $N_{\circ} + N_{\bullet\circ}$ molecules adsorbed parallel and normal to the surface. q_{\circ} , q_{\bullet} , and $q_{\bullet\circ}$ are, respectively, the individual partition function corresponding to the three configurations a molecule can adopt when it adsorbs on the surface and z stands for the fugacity of molecules. This expression is quite similar to that of Eq. (5). Indeed, an isomorphism between the magnetic partition function Z and the grand canonical partition function Ξ describing the adsorption of asymmetric rigid rods or heteronuclear diatomic molecules on homogeneous surfaces can be drawn by considering the following relations:

$$Q_{\circ} = q_{\circ} z, \quad Q_{\bullet} = q_{\bullet} z, \quad K = q_{\bullet\circ} z. \quad (7)$$

Now, by taking the contributions to the adsorbed molecule's partition function of the internal degree of freedom, namely, vibration (which exists only for diatomic molecules and not for rigid rods) and rotation modes, the relations given in Eq. (7) become

$$\begin{aligned} Q_{\circ} &= q_{\circ}^{vib} q_{\circ}^{rot} e^{\beta(\mu - \epsilon_{\circ})}, \\ Q_{\bullet} &= q_{\bullet}^{vib} q_{\bullet}^{rot} e^{\beta(\mu - \epsilon_{\bullet})}, \\ K &= q_{\bullet\circ}^{vib} q_{\bullet\circ}^{rot} e^{\beta(\mu - \epsilon_{\bullet\circ})}, \end{aligned} \quad (8)$$

where μ is the molecule's chemical potential. ϵ_{\circ} , ϵ_{\bullet} , and $\epsilon_{\bullet\circ}$ are the adsorption energies associated to the three different configurations a molecule can adopt when it adsorbs on the surface (see Fig. 2) and where q^{rot} and q^{vib} , respectively, stand for the rotational and the vibrational individual partition function of an adsorbed molecule.

III. MEAN-FIELD RESULTS AND DISCUSSION

Let us denote $f(\vec{S}, \sigma)$ the mean-field probability function describing the distribution of a single site in terms of the Ising number σ and the spin vector \vec{S} . In the mean-field approximation, the Helmholtz free energy per cell site F/M of the Hamiltonian given in Eq. (1) can be written as follows:

$$\frac{\beta F}{M} = \frac{\langle \beta H \rangle}{M} + \sum_{\sigma=0}^1 \int f(\vec{S}, \sigma) \ln[f(\vec{S}, \sigma)] d^n \vec{S}, \quad (9)$$

where the notation $\langle \cdot \rangle$ refer to a mean-field thermal average.²¹

The energy per cell site is

$$\frac{\langle \beta H \rangle}{M} = Q_o \langle S_1^2 \sigma \rangle + Q_o \langle S_1^2 (1 - \sigma) \rangle + \frac{Kq}{2} \langle S_1^2 \sigma \rangle \langle S_1^2 (1 - \sigma) \rangle, \quad (10)$$

with q the lattice coordination number. Furthermore, the probability function f must satisfy the normalization condition that is

$$\sum_{\sigma=0}^1 \int f(\vec{S}, \sigma) d^n \vec{S} = 1. \quad (11)$$

Owing to Eqs. (9)–(11), by minimizing Eq. (9) with respect to f , it can be shown that

$$f(\vec{S}, \sigma) = \frac{1}{C} \exp \left[Q_o S_1^2 \sigma + Q_o S_1^2 (1 - \sigma) + \frac{Kq}{2} S_1^2 \sigma \langle S_1^2 (1 - \sigma) \rangle + \frac{Kq}{2} S_1^2 (1 - \sigma) \langle S_1^2 \sigma \rangle \right], \quad (12)$$

where C is a numerical constant given by

$$C = \left[2 + Q_o + Q_o + \frac{Kq}{2} \langle S_1^2 \sigma \rangle + \frac{Kq}{2} \langle S_1^2 (1 - \sigma) \rangle \right]. \quad (13)$$

If now, by using the moment theorem associated with the special statistics in the vanishing $n \rightarrow 0$ limit,¹⁶ one computes the two quantities $\langle S_1^2 \sigma \rangle$ and $\langle S_1^2 (1 - \sigma) \rangle$, it is straightforward to derive that C satisfies the following second-order equation which admits two mathematical solutions:

$$C^2 - C[2 + Q_o + Q_o] - qK = 0. \quad (14)$$

The physical solution which minimizes the magnetic free energy, given in Eq. (9), is given by

$$C = \frac{2 + Q_o + Q_o + \sqrt{(2 + Q_o + Q_o)^2 + 4qK}}{2}. \quad (15)$$

Using the previous relations, the magnetic free energy per site can then be written as

$$\frac{\beta F}{M} = -\ln \left(\frac{2 + Q_o + Q_o + \sqrt{(2 + Q_o + Q_o)^2 + 4qK}}{2} \right) + \frac{2qK}{(2 + Q_o + Q_o + \sqrt{(2 + Q_o + Q_o)^2 + 4qK})^2}. \quad (16)$$

From this expression, the numbers of molecules adsorbed on the substrate, according to the three different possible configurations, are, respectively, given by

$$\langle N_o \rangle = Q_o \frac{\partial \ln Z}{\partial Q_o} = -Q_o \frac{\partial (\beta F)}{\partial Q_o}, \quad (17a)$$

$$\langle N_o \rangle = Q_o \frac{\partial \ln Z}{\partial Q_o} = -Q_o \frac{\partial (\beta F)}{\partial Q_o}, \quad (17b)$$

and

$$\langle N_{o\bullet} \rangle = K \frac{\partial \ln Z}{\partial K} = -K \frac{\partial (\beta F)}{\partial K}. \quad (17c)$$

After a few calculations given into Appendix A, it is possible to obtain the following analytical relations:

$$\left\langle \frac{N_o}{M} \right\rangle = \frac{Q_o}{2 + Q_o + Q_o + \sqrt{(2 + Q_o + Q_o)^2 + 4qK}},$$

$$\left\langle \frac{N_{o\bullet}}{M} \right\rangle = \frac{Q_o}{2 + Q_o + Q_o + \sqrt{(2 + Q_o + Q_o)^2 + 4qK}},$$

and

$$\left\langle \frac{N_{o\bullet}}{M} \right\rangle = \frac{qK}{[(2 + Q_o + Q_o) + \sqrt{(2 + Q_o + Q_o)^2 + 4qK}]}. \quad (18)$$

The fraction of occupied sites Θ is therefore given by

$$\Theta = \left\langle \frac{N_o + N_{o\bullet} + 2N_{o\bullet}}{M} \right\rangle = 1 - \frac{4}{(2 + Q_o + Q_o) + \sqrt{(2 + Q_o + Q_o)^2 + 4qK}}. \quad (19)$$

Prior to discussing heteronuclear molecule adsorption results, let us first note that by taking $Q_o = Q_o = Q = e^{\beta(\mu - \varepsilon)}$ and $K = 0$ in the mean-field solution of our model leads to the well-known relation found by Langmuir for monoatomic adsorption,²² namely, $\theta = 1/(1 + Q)$. Note also that this model permits to treat adsorption of homonuclear molecules by simply taking $Q_o = Q_o = Q = q^{vib} q^{rot} e^{\beta(\mu - \varepsilon_{\perp})}$ and $K = q^{vib} q^{rot} e^{\beta(\mu - \varepsilon_{\parallel})}$, where ε_{\perp} and ε_{\parallel} , respectively, represent the energy for a molecule sticking normal and parallel to the surface. Following the same mean-field treatment as previously described, the fractions of the adsorbed molecules sticking normal (N_{\perp}) and parallel (N_{\parallel}) to the surface and the fraction of occupied sites are, respectively, given by

$$\left\langle \frac{N_{\parallel}}{M} \right\rangle = \frac{qK}{2[(1 + Q) + \sqrt{(1 + Q)^2 + qK}]}, \quad (20a)$$

$$\left\langle \frac{N_{\perp}}{M} \right\rangle = \frac{Q}{1 + Q + \sqrt{(1 + Q)^2 + qK}}, \quad (20b)$$

and

$$\Theta = \left\langle \frac{N_{\perp} + 2N_{\parallel}}{M} \right\rangle = 1 - \frac{2}{(1 + Q) + \sqrt{(1 + Q)^2 + qK}}. \quad (21)$$

Now let us go back to the results obtained for the adsorption of heteronuclear molecules. Another quantity very important in adsorption experiments is, Q_v , the heat of adsorption at constant volume and temperature.²³ Such a quantity which provides information regarding the driving forces for adsorption is defined accordingly to

$$Q_v = \frac{\partial E_{tot}}{\partial N_{ad}}, \quad (22)$$

where $E_{tot} = E_{gas} + E_{ad}$ and $N_{ad} = \langle N_o + N_* + N_{**} \rangle$, respectively, stand for the total energy of the system (gas + adsorbate) and the number of adsorbed molecules. After a few steps (developed into details in the Appendix B), it is possible to derive that

$$Q_v = \frac{de_{ad}}{dn_{as}} - e_{gaz}, \quad (23)$$

where e_{gaz} and e_{ad} , respectively, represent the energy per molecule in the gas phase and the mean energy per adsorption site and where n_{ad} is defined as N_{ad}/M . Following a classical statistical treatment, it can be shown for a perfect gas that

$$e_{gas} = - \left[\frac{\partial \ln q^{trans}}{\partial \beta} + \frac{\partial \ln q^{rot}}{\partial \beta} + \frac{\partial \ln q^{vib}}{\partial \beta} \right], \quad (24)$$

and for adsorption with no interaction between adsorbed molecules other than excluded volume that

$$e_{ad} = \left\langle \frac{N_o}{M} \right\rangle \left[\epsilon_o - \frac{\partial \ln(q_o^{vib} q_o^{rot})}{\partial T} \right] + \left\langle \frac{N_*}{M} \right\rangle \left[\epsilon_* - \frac{\partial \ln(q_*^{vib} q_*^{rot})}{\partial \beta} \right] + \left\langle \frac{N_{**}}{M} \right\rangle \left[\epsilon_{**} - \frac{\partial \ln(q_{**}^{vib} q_{**}^{rot})}{\partial \beta} \right]. \quad (25)$$

Now, let us focus on both isobar and isotherm adsorption curves found for diatomic adsorption in the mean-field approximation. For simplicity's sake, we assume the following:

(i) The reservoir gas behaves as a perfect diatomic gas (i.e., the molecules do not interact but have rotation and vibration modes).

(ii) The molecule's vibration modes are not affected by adsorption.

(iii) The adsorbed molecules cannot rotate (i.e., their rotation modes are frozen).

Let us then comment the typical shapes of the isobar adsorption curves, found with these assumptions. In Fig. 3, shown are several isobar curves found when the values of ϵ_* and ϵ_o are identical, but the value of ϵ_{**} is different. In these curves, Θ , the fraction of occupied sites and the proportions of the three different molecule's configurations on the substrate are plotted as a function of T , the temperature, for the same gas pressure fixed to $P = 10^5$ Pa. In order to do so, for each chosen temperature T , we calculate the value of the corresponding chemical potential using the expression of the perfect gas for diatomic molecules, $\mu(T, P)$, and replace it in Eqs. (18) and (19). Provided that $\epsilon_{**} \leq \text{Sup}(\epsilon_*, \epsilon_o)/2$, at $T \approx 0$, all the sites of the substrate are occupied by molecules sticking normal to the surface and having the most energetic configuration per site. Contrary to monoatomic adsorption, when the temperature increases, all the sites of the substrate remain occupied until a temperature: $T = T_1$, is reached. However for $T_1 \leq T \leq T_2$, a close look reveals that the number of

molecules adsorbed normal to the surface decreases whereas that of molecules adsorbed parallel increases and reaches a maximum at a temperature T_2 . Indeed, the entropy related to this disorder compensates the loss of adsorption energy due to the presence on the substrate of molecules having less favorable energetic configurations (since the total number of adsorbed molecules decreases, some molecules are therefore released in the reservoir). For higher temperatures (i.e., for $T > T_2$), the total number of adsorbed molecules decreases as the temperature increases. This phenomenon induces a noticeable kink for the total number of adsorbed molecules versus T which obviously does not exist in monoatomic adsorption curves. However, the variation of Θ versus T does not exhibit such a kink. For temperatures larger than T_2 , when $\epsilon_{**} > \text{Sup}(\epsilon_*, \epsilon_o)$, most of the adsorbed molecules are lying parallel to the surface and their number now decreases as the temperature increases. In this case, the last molecules leaving the substrate are those lying parallel to the surface since such molecule's configuration requires the highest desorption barrier energy. Finally, for a given set $\{\epsilon_*, \epsilon_o\}$ of energy parameters, solving our model within a mean-field approximation makes it possible to predict how the configurations of adsorbed molecules vary with T and ϵ_{**} (Fig. 4).

Figure 5 shows the variation of Q_v , numerically derived from Eqs. (22)–(24), versus T . Contrary to monoatomic adsorption process for which Q_v varies linearly with T [i.e., $Q_v(T) = \epsilon - 3k_B T/2$], such a curve (Fig. 5) exhibits two linear branches with the same slope $-5k_B/2$, separated by an inflexion point located at $T \approx T_2$. The shape of this curve can be easily understood if one takes a look at Fig. 3. For low temperatures, namely, for $T \ll T_2$, since the predominant population of adsorbed molecules is $\langle N_* \rangle$, it results that: $n_{ad} \approx \langle N_* \rangle / M$ since. By using Eqs. (23)–(25) with our model's assumptions, it is therefore possible to derive that Q_v varies linearly with T in this regime, accordingly, to

$$Q_v(T) \approx \epsilon_* - 5k_B T/2. \quad (26a)$$

On the other hand, for: $T \gg T_2$, most of the adsorbed molecules lay parallel to the surface and therefore: $n_{ad} \approx \langle N_{**} \rangle / M$. A similar calculation to the previous one, leads now to

$$Q_v(T) \approx \epsilon_{**} - 5k_B T/2. \quad (26b)$$

Let us notice that ΔQ_v , the amplitude of the continuous jump between the two asymptotic branches, respectively, described by Eqs. (26a) and (26b) is roughly equal to $(\epsilon_{**} - \epsilon_*)$. Consequently, these results show that if ΔQ_v is large enough, both $(\epsilon_{**} - \epsilon_*)$ and T_2 can be experimentally estimated.

Now, let us focus on a typical isotherm adsorption curves, calculated using the same mean-field approximation of our model. To determine these curves (Fig. 6), we proceed by analogy as for Fig. 3. We fix the value of T and for each chosen pressure P we calculate the value of the corresponding chemical potential (using the expression of the perfect gas for diatomic molecules) $\mu(T, P)$ and replace it in Eqs. (18) and (19). Figure 6 shows the variations of Θ and of the proportions of the three possible molecule's configurations as a function of pressure in the case where $\epsilon_{**} > \text{Sup}(\epsilon_*, \epsilon_o)$. As

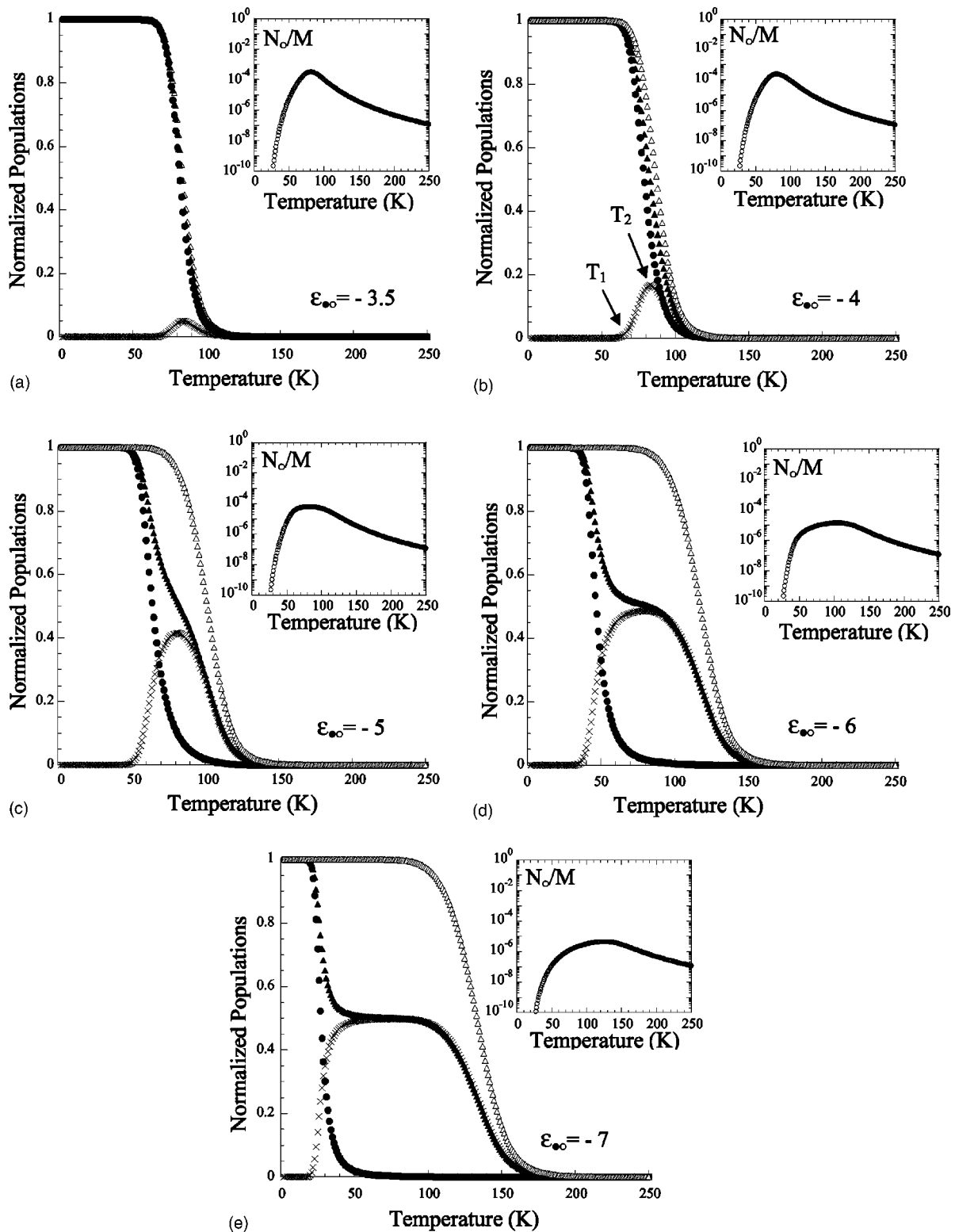


FIG. 3. Shown are several isobar adsorption ($P=10^5$ Pa) curves found in the mean-field approximation for the same set of adsorption parameters, namely, $\epsilon_s=-4$, $\epsilon_o=-2$, but different values of $\epsilon_{\infty\infty}$ (the unit of energy is $k_B T_0$, where $T_0=300$ K). The different values of $\epsilon_{\infty\infty}$ are: (a) $\epsilon_{\infty\infty}=-3.5$, (b) $\epsilon_{\infty\infty}=-4$, (c) $\epsilon_{\infty\infty}=-5$, (d) $\epsilon_{\infty\infty}=-6$, and (e) $\epsilon_{\infty\infty}=-7$. The molecule's weight is $m=4.10^{-26}$ kg and the vibration and rotation temperatures are, respectively, $T_{vib}=3000$ K and $T_{rot}=20$ K. The pressure and the coordination number are, respectively, $P=10^5$ Pa and $q=6$. Below, is the significance of the different symbols: (closed circles) N_o/M , (crosses) N_*/M , (closed triangles) Θ , and (open triangles) $(N_* + N_* + N_o)/M$. Inset: shown is the evolution of N_o/M (open circles).

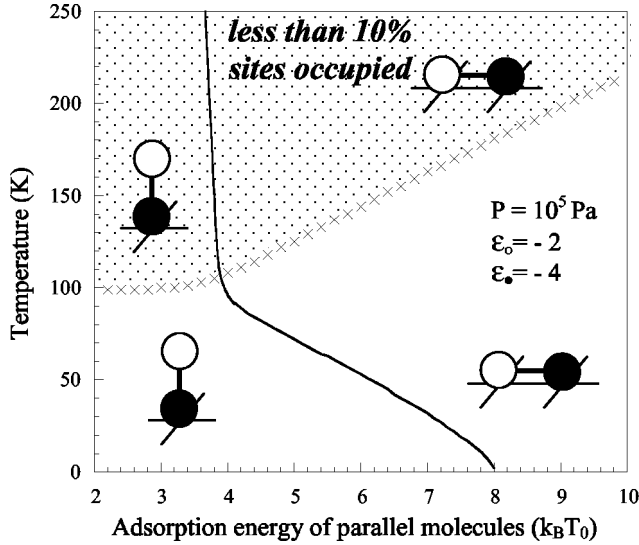


FIG. 4. Shown is a diagram giving the most probable configuration of adsorbed molecules in the (T, ϵ_{*o}) plane. The set of energy parameters is $\epsilon_{*o} = -4$ and $\epsilon_o = -2$ (given in $k_B T_0$ units). The continuous lines separating two different configurations correspond to the limit where these two configurations have the same probability. Although when $\Theta \leq 0.1$, we consider that the molecules are desorbed; in this region, we nevertheless indicates what is the most favorable configuration of the few molecules still adsorbed.

for monoatomic adsorption, at very high pressures, all the sites of the substrate are occupied by adsorbed molecules (i.e., $\Theta = 1$), lying normal to the surface. When the pressure decreases, their number decreases, whereas the number of molecules adsorbed parallel to the surface increases and reaches a maximum at a pressure P_1 . For pressures lower

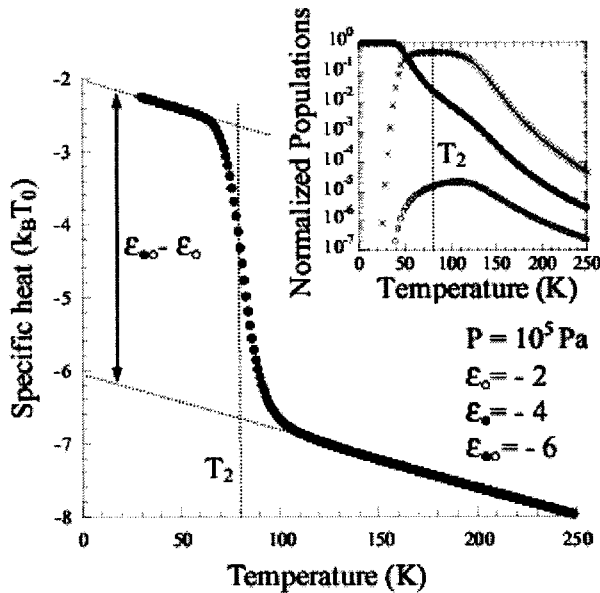


FIG. 5. Adsorption heat at constant temperature and volume, found in the mean-field approximation for the same molecular parameters than those of Fig. 3(d), as a function of temperature ($P = 10^5$ Pa). Inset: shown is the isobar adsorption. The symbols are identical to that of Fig. 3(d).

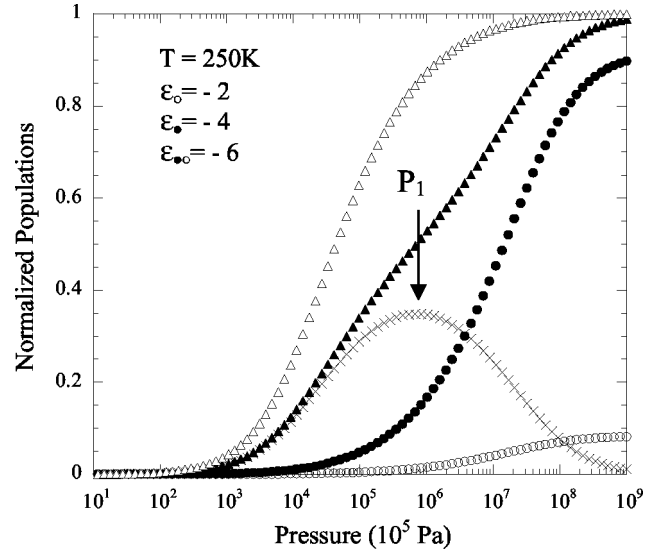


FIG. 6. Shown is the isotherm adsorption curve ($T = 250$ K), found in the mean-field approximation for the same molecular parameters than those of Fig. 3(d). The adsorption energies are $\epsilon_{*o} = -4$, $\epsilon_o = -2$, and $\epsilon_{*o} = -6$, where the units of energy is $k_B T_0$ with $T_0 = 300$ K. (Closed circles) N_{*}/M , (open circles) N_{*o}/M , (crosses) N_{*o}/M , (closed triangles) Θ , and (open triangles) $(N_{*o} + N_{*} + N_{*o})/M$.

than P_1 , note that most of the adsorbed molecules are sticking parallel to the surface and their number now decreases as the pressure decreases.

IV. GENERALIZATION TO NONINTERACTING GAS MIXTURES

Now, let us show that our $n \rightarrow 0$ vector spin Hamiltonian approach can easily be generalized to treat the adsorption of gas mixtures consisting of single atoms and/or diatomic (heteroatomic or homoatomic) molecules. Following the same approach previously used, a modification of our Hamiltonian permits to answer this problem. In order to illustrate this, let us consider a mixture made of two diatomic molecules, for example, a homonuclear (A_2) and a heteronuclear (BC) one. For instance, this can represent a mixture of CO and N_2 molecules. To each site (i) of the lattice, one still associates both a $n \rightarrow 0$ vector spin \vec{S}_i and an Ising number σ_i . However now, the possible values of σ_i are: 0, 1, or 2, depending on whether the corresponding site is, respectively, occupied by an atom A , B , or C . As before, we assume that both molecules can adsorb either perpendicular or parallel to the surface. When a molecule sticks perpendicular to the surface, only one of its two constituting atoms is adsorbed and the molecule occupies only one lattice site. However, when the same molecule sticks parallel to the surface, its two atoms are adsorbed and so this molecule occupies two adjacent sites. Let us consider the following Hamiltonian:

$$\begin{aligned}
 -\beta H = & Q_A \sum S_{i,1}^2 f_A(\sigma_i) + Q_B \sum S_{i,1}^2 f_B(\sigma_i) \\
 & + Q_C \sum S_{i,1}^2 f_C(\sigma_i) + K_{AA} \sum_{\langle i,j \rangle} S_{i,1}^2 f_A(\sigma_i) S_{j,1}^2 f_A(\sigma_j) \\
 & + K_{BC} \sum_{\langle i,j \rangle} S_{i,1}^2 f_B(\sigma_i) S_{j,1}^2 f_C(\sigma_j),
 \end{aligned} \quad (27)$$

where Q_A, Q_B, Q_C, K_{AA} , and K_{BC} are numerical constants and f_A, f_B , and f_C are the following polynomial functions:

$$\begin{aligned} f_A(\sigma) &= (\sigma - 1)(\sigma - 2)/2, \\ f_B(\sigma) &= \sigma(2 - \sigma), \\ f_C(\sigma) &= \sigma(\sigma - 1)/2. \end{aligned} \quad (28)$$

By expanding Z , the partition function, in power series of \tilde{S}_i , and using in the $n \rightarrow 0$ limit, the moment theorem,¹⁶ it is straightforward to show that

$$\begin{aligned} Z(N_A, N_B, N_C, N_{AA}, N_{BC}, M) \\ = \sum_{N_A} \sum_{N_B} \sum_{N_C} \sum_{N_{AA}} \sum_{N_{BC}} \Gamma(N_A, N_B, N_C, N_{AA}, N_{BC}, M) \\ \times Q_A^{N_A} Q_B^{N_B} Q_C^{N_C} K_{AA}^{N_{AA}} K_{BC}^{N_{BC}}, \end{aligned} \quad (29)$$

where $\Gamma(N_A, N_B, N_C, N_{AA}, N_{BC}, M)$ represents the number of ways to adsorb on the M sites of the substrate, $N_A + N_{AA}$ molecules A_2 and $N_B + N_C + N_{BC}$ molecules BC with, respectively, N_{AA} molecules A_2 and N_{BC} molecules BC sticking parallel to the surface (i.e., occupying two adjacent sites) and, respectively, N_A and $N_B + N_C$ molecules A_2 and BC adsorbed normal to the surface. Note that N_B and N_C correspond to the number of molecules BC , respectively, adsorbed on the substrate by their B or C atom.

An isomorphism can therefore be drawn between Z and the grand-partition function describing the adsorption on the homogeneous substrate of the A_2/BC gas mixture, by considering the following relations:

$$Q_A = q_{AA,\perp}^{vib,rot} e^{\beta(\mu_{AA} - \varepsilon_A)}, \quad Q_B = q_{BC,\perp}^{vib,rot} e^{\beta(\mu_{BC} - \varepsilon_B)},$$

$$Q_C = q_{CB,\perp}^{vib,rot} e^{\beta(\mu_{BC} - \varepsilon_C)},$$

$$K_{AA} = q_{AA,\parallel}^{vib,rot} e^{\beta(\mu_{AA} - \varepsilon_{AA})}, \quad K_{BC} = q_{BC,\parallel}^{vib,rot} e^{\beta(\mu_{BC} - \varepsilon_{BC})}, \quad (30)$$

where μ_{AA} and μ_{BC} , respectively, stand for the chemical potentials of the molecules A_2 and BC ; and where ε_A and ε_{AA} (respectively, $\varepsilon_B, \varepsilon_C$, and ε_{BC}) represent the different configurations a molecule A_2 (or, respectively, BC) can adopt when it adsorbs. The notation $q^{vib,rot}$ stands for the vibration and rotation partition function of the different molecules configurations. The indexes \perp and \parallel indicate that the molecule is, respectively, adsorbed normal and parallel to the surface. For a molecule BC adsorbed normal to the surface, the notations $q_{BC,\perp}^{vib,rot}$ and $q_{CB,\perp}^{vib,rot}$ permit to differentiate between the two perpendicular configurations such a molecule (i.e., a molecule adsorbed to the surface by its B or C extremity) can adopt.

Following the mean-field approximation, described into details in Sec. III, one shows that the magnetic free energy F/M per site is now given by

$$\frac{\beta F}{M} = -\ln(C) + \frac{q(K_{AA} + K_{BC})}{2C^2} \quad (31)$$

with

$$C = \frac{3 + Q_A + Q_B + Q_C + \sqrt{(3 + Q_A + Q_B + Q_C)^2 + 4q(K_{AA} + K_{BC})}}{2}. \quad (32)$$

From this expression, the numbers of the molecules adsorbed on the substrate with each possible configurations can be estimated:

$$\langle N_A \rangle = Q_A \frac{\partial \ln Z}{\partial Q_A} = -Q_A \frac{\partial(\beta F)}{\partial Q_A},$$

$$\langle N_B \rangle = Q_B \frac{\partial \ln Z}{\partial Q_B} = -Q_B \frac{\partial(\beta F)}{\partial Q_B},$$

$$\langle N_C \rangle = Q_C \frac{\partial \ln Z}{\partial Q_C} = -Q_C \frac{\partial(\beta F)}{\partial Q_C},$$

$$\langle N_{AA} \rangle = K_{AA} \frac{\partial \ln Z}{\partial K_{AA}} = -K_{AA} \frac{\partial(\beta F)}{\partial K_{AA}},$$

and

$$\langle N_{BC} \rangle = K_{BC} \frac{\partial \ln Z}{\partial K_{BC}} = -K_{BC} \frac{\partial(\beta F)}{\partial K_{BC}}. \quad (33)$$

Following the same kind of calculations, previously described in Sec. III, one can derive mathematical expressions for the thermodynamic properties of such a mixture, as for instance, Q_v or isotherm and isobar adsorption curves.

V. CONCLUSION

We have presented a simple model, based on a dilute $n \rightarrow 0$ vector spin model, to describe the adsorption of asymmetric rigid rodlike molecules on homogenous surfaces. We have shown that this approach is particularly suited to treat multisite adsorption. In a first step, we have treated the case of noninteracting dimer adsorption and have shown that can easily be extended to the case of noninteracting or interacting polyatomic mixtures. As a final comment, it is interesting to

note that this model can also be extended to the case of adsorption mixture with chemical decomposition or interacting gas mixtures. Following the approach of Frumkin-Fowler and Guggenheim,²⁴ interactions can be included in the model, for instance, in the case of our A_2/BC gas mixtures, by adding the following term to the expression of the Hamiltonian [Eq. (27)]

$$\sum_{(i,j)} \chi_{AA} f_A(\sigma_i) f_A(\sigma_j) + \chi_{AB} f_A(\sigma_i) f_B(\sigma_j) + \chi_{AC} f_A(\sigma_i) f_C(\sigma_j) + \chi_{BC} f_B(\sigma_i) f_C(\sigma_j) + \chi_{BB} f_B(\sigma_i) f_B(\sigma_j) + \chi_{CC} f_C(\sigma_i) f_C(\sigma_j), \quad (34)$$

where the parameters χ_{AA} , χ_{AB} , χ_{AC} , χ_{BC} , χ_{BB} , and χ_{CC} represent the different interaction energies between two adjacent adsorbed atoms.²⁵ Moreover, our model can also be extended to the adsorption of a gas mixture containing mono or linear polyatomic molecules (such as for instance CO_2) by, respectively, adding to the Hamiltonian a term $S_{i,1}^2$ or $S_{i,1}^2 S_{j,1}^2 S_{k,1}^2$, where (j) and (k) are two nearest-neighbor sites of site (i). We therefore believe that this very versatile formalism will be used frequently to treat such physical problems and others.

To date, most available experiments on adsorption of diatomic molecules on solid surfaces always involve complex phenomena such as multilayer adsorption or heterogeneous substrates, which are difficult to analyze only within the framework of our model. Nevertheless, we strongly believe that the analytical formulae derived above [Eqs. (18) and (19)], will be of primary interest to experimentalists to understand and quantify the orientation of rigid rod molecules on homogeneous surfaces such as liquid-liquid or gas-liquid interfaces. Indeed a very active field of research is the adsorption of colloidal solid spheres on liquid-liquid surfaces as for instance the formation of colloidosomes,^{26,27} of pickering emulsions²⁸ or the adhesion of virus on cell^{29,30} and by no doubt these experiments will be extended to the adsorption of rigid rods.

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APPENDIX A

As seen in Eq. (16), the magnetic free energy per site can be written as

$$\frac{\beta F}{M} = -\ln(C) + \frac{qK}{2C^2}. \quad (A1)$$

Using Eqs. (17a) and (17b), it is then straightforward to show that

$$\langle N_\bullet \rangle = -Q_\bullet \frac{\partial(\beta F)}{\partial Q_\bullet} = M \frac{Q_\bullet}{C} \left[1 + \frac{qK}{C^2} \right] \frac{\partial C}{\partial Q_\bullet} \quad (A2a)$$

and

$$\langle N_\circ \rangle = -Q_\circ \frac{\partial(\beta F)}{\partial Q_\circ} = M \frac{Q_\circ}{C} \left[1 + \frac{qK}{C^2} \right] \frac{\partial C}{\partial Q_\circ}. \quad (A2b)$$

By deriving each terms of Eq. (14) with respect to Q_\bullet or Q_\circ , one obtains, respectively, that

$$\frac{\partial C}{\partial Q_\bullet} = \frac{\partial C}{\partial Q_\circ} = \frac{C}{2C - (2 + Q_\bullet + Q_\circ)}. \quad (A3)$$

Using Eq. (14), it is straightforward to show that

$$\frac{qK}{C^2} = \frac{C - (2 + Q_\bullet + Q_\circ)}{C}. \quad (A4)$$

Now, by inserting Eqs. (A3) and (A4) into the expressions (A2a) and (A2b) one obtains, the two following relations:

$$\left\langle \frac{N_\bullet}{M} \right\rangle = \frac{Q_\bullet}{C} = \frac{Q_\bullet}{2 + Q_\bullet + Q_\circ + \sqrt{(2 + Q_\bullet + Q_\circ)^2 + 4qK}} \quad (A5a)$$

and

$$\left\langle \frac{N_\circ}{M} \right\rangle = \frac{Q_\circ}{C} = \frac{Q_\circ}{2 + Q_\bullet + Q_\circ + \sqrt{(2 + Q_\bullet + Q_\circ)^2 + 4qK}}. \quad (A5b)$$

If one inserts the expression (A1) in Eq. (17c), it is possible to show that

$$\langle N_\bullet \rangle = -K \frac{\partial(\beta F)}{\partial K} = M \frac{K}{C} \left[\frac{\partial C}{\partial K} \left(1 + \frac{qK}{C^2} \right) - \frac{q}{2C} \right]. \quad (A6)$$

By deriving the two terms of Eq. (14) with respect to K , one obtains that

$$\frac{\partial C}{\partial K} = \frac{q}{2C - (2 + Q_\bullet + Q_\circ)}. \quad (A7)$$

If the expressions (A4) and (A7) are introduced into Eq. (A6), it is straightforward to derive that

$$\left\langle \frac{N_\bullet}{M} \right\rangle = \frac{qK}{2C} = \frac{qK}{[(2 + Q_\bullet + Q_\circ) + \sqrt{(2 + Q_\bullet + Q_\circ)^2 + 4qK}]}. \quad (A8)$$

From the previous expressions, it is straightforward to derive that Θ , the fraction of occupied is given by:

$$\Theta = 1 - \frac{2}{C} = 1 - \frac{4}{(2 + Q_\bullet + Q_\circ) + \sqrt{(2 + Q_\bullet + Q_\circ)^2 + 4qK}}. \quad (A9)$$

APPENDIX B

The total energy of the system is the sum of the energy of the gas and that of the adsorbed molecules

$$E_{tot} = E_{gas} + E_{ad}. \quad (B1)$$

Considering now that at the temperature T , the system composed of N molecules consists of N_{gas} molecules in the gas

phase and $N_{ad}=N-N_{gas}$ molecules adsorbed, the total energy can be written as

$$E_{tot} = N_{gas}e_{gas} + E_{ad}(N_{ad}, M) = (N - N_{ad})e_{gaz} + E_{ad}(N_{ad}, M), \quad (B2)$$

where e_{gas} represents the energy per molecule in the gas phase.

Consequently, Q_v , the heat of adsorption at constant volume and temperature is simply given by the following relation:

$$Q_v = \frac{dE_{tot}}{dN_{ad}} = \frac{de_{ad}}{dn_{ad}} - e_{gaz} \quad (B3)$$

with $e_{ad}=E_{ad}/M$ and $n_{ad}=N_{ad}/M$.

First of all, the total energy of the molecules adsorbed can be computed from the expression of the grand partition function describing adsorption on the surface, namely,

$$\Xi = \sum \sum \sum \Gamma(N_o, N_{\bullet}, N_{\bullet\bullet}, M) e^{\beta\mu(N_o+N_{\bullet}+N_{\bullet\bullet})} \times (q_o^{vib} q_o^{rot} e^{-\beta\epsilon_o})^{N_o} (q_{\bullet}^{vib} q_{\bullet}^{rot} e^{-\beta\epsilon_{\bullet}})^{N_{\bullet}} (q_{\bullet\bullet}^{vib} q_{\bullet\bullet}^{rot} e^{-\beta\epsilon_{\bullet\bullet}})^{N_{\bullet\bullet}}. \quad (B4)$$

In order to do so, let us recall that

$$E_{ad} - \mu N_{ad} = - \frac{\partial \ln \Xi}{\partial \beta} \quad (B5a)$$

and

$$N_{ad} = kT \frac{\partial \ln \Xi}{\partial \mu}. \quad (B5b)$$

Therefore, by replacing Eq. (B5b) in Eq. (B5a), one obtains the following relation:

$$E_{ad} = - \frac{\partial \ln \Xi}{\partial \beta} + \mu kT \frac{\partial \ln \Xi}{\partial \mu}. \quad (B6)$$

Now by taking for Ξ , the expression given in Eq. (B4), and inserting into Eq. (B6) leads to

$$E_{ad} = N_o \left[\epsilon_o - \frac{\partial \ln(q_o^{vib} q_o^{rot})}{\partial \beta} \right] + N_{\bullet} \left[\epsilon_{\bullet} - \frac{\partial \ln(q_{\bullet}^{vib} q_{\bullet}^{rot})}{\partial \beta} \right] + N_{\bullet\bullet} \left[\epsilon_{\bullet\bullet} - \frac{\partial \ln(q_{\bullet\bullet}^{vib} q_{\bullet\bullet}^{rot})}{\partial \beta} \right] \quad (B7a)$$

and, therefore, to

$$e_{ad} = \frac{N_o}{M} \left[\epsilon_o - \frac{\partial \ln(q_o^{vib} q_o^{rot})}{\partial \beta} \right] + \frac{N_{\bullet}}{M} \left[\epsilon_{\bullet} - \frac{\partial \ln(q_{\bullet}^{vib} q_{\bullet}^{rot})}{\partial \beta} \right] + \frac{N_{\bullet\bullet}}{M} \left[\epsilon_{\bullet\bullet} - \frac{\partial \ln(q_{\bullet\bullet}^{vib} q_{\bullet\bullet}^{rot})}{\partial \beta} \right]. \quad (B7b)$$

Following classical treatment, the total energy of the gas can be derived from the expression of Z_{gas} its partition function, accordingly to

$$E_{gaz} = - \frac{\partial \ln(Z_{gas})}{\partial \beta}. \quad (B8)$$

Now, if one recalls that for a perfect gas

$$Z_{gas} = \frac{1}{N_{gas}!} (q^{trans} q^{rot} q^{vib})^{N_{gas}}, \quad (B9)$$

where, q^{trans} , q^{rot} , and q^{vib} , respectively, stand for the translational, the rotational, and the vibrational partition function of an individual molecule, the relation (B8) leads straightforwardly to

$$e_{gaz} = \frac{E_{gas}}{N_{gas}} = - \frac{\partial \ln(q^{trans} q^{rot} q^{vib})}{\partial \beta}. \quad (B10)$$

For heteronuclear diatomic molecules, this relation gives

$$e_{gaz} = \frac{5}{2} k_B T + \frac{k_B T_{vib}}{2} \coth\left(\frac{T_{vib}}{2T}\right) \quad (B11)$$

with T_v the characteristic temperature vibration of the molecule, whereas for asymmetric rigid rods, it is only:

$$e_{gaz} = \frac{5}{2} k_B T. \quad (B12)$$

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