Exact Matrix Treatment of the Statistical Mechanics of Adsorption of Large Aromatic Molecules on Graphene.

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Abstract

Experimental studies of adsorption from solution of the large aromatic molecules 1,2-dihydroxybenzene (catechol) and phenyl hydroquinone on graphene nanoplatelets show that at low coverage adsorption is followed by a transition which occurs from adsorbed molecules in flat to more vertically oriented states. Catechol adsorption isotherms exhibit 2 plateaus while phenyl hydroquinone shows 3 plateaus indicating 2 and 3 active conformers respectively participating in the adsorption process. Modelling such adsorption isotherms presents a challenge. Here, an exact matrix treatment of the statistical mechanics of a one-dimensional model of adsorption of catechol and dihydroquinone on graphene nanoplatelets is presented. The theoretical adsorption isotherms successfully reproduce all the features of both the catechol and dihydroquinone experimental adsorption isotherms. As suggested by the experimentalists, our theoretical model demonstrates that adsorbed phenyl hydroquinone molecules adopt a flat orientation at low concentrations and an edge orientation at higher coverage before eventually adopting a vertical configuration. Both catechol and phenyl hydroquinone can be described by our interconvertible monomer-dimer-trimer model. The theoretical adsorption isotherms obtained show several plateaus reflecting the types of conformer on the graphene surface.

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Introduction

The orientation of adsorbed molecules at surfaces continues to be of intense interest as orientational dependence plays a significant role in a wide range of interfacial phenomena[1,2,3,4,5,6]. Methods to determine molecular orientations of adsorbed species at interfaces are well developed[7,8]. Yet, the theoretical prediction of adsorption isotherms of assemblies of adsorbed molecules undergoing conformational transitions is less advanced and presents a number of challenges. Methods for describing conformational transitions in adsorbed monolayers at the air/water interface have been extensively studied[9,10,11] and related to this are investigations of conformational transitions of molecules adsorbed in zeolites.[12,13] Here, we present a new methodology for the calculation of adsorption isotherms of large aromatic molecules occupying several conformations on an adsorbing substrate, such as graphene nanoparticles. Our aim is to present an exactly solvable lattice model using semiempirical parameters which correctly models the trends in the unusual shapes of the adsorption isotherms of large aromatic molecules on graphene nanoplatelets[14,15]. This enables a confirmation of the underlying molecular behaviour suggested by experimentalists.

The properties of graphene have been extensively studied and its unusually high electrical transport and mechanical strength features have attracted strong interest. Graphene based sensors and electrodes are also of intense attention. Electron transfer rates at interfaces depend very sensitively on molecular orientations.

Although small polyatomic molecule adsorption on graphene has been well studied much less is known in detail about the orientational features of the adsorption of larger essentially aromatic 'metallic molecules' which exhibit strong intermolecular interactions with a graphene substrate. Hubbard at al [16,17,18, 19] have investigated numerous aromatic compounds adsorbed on metallic (Pt) surfaces and found that at low coverage molecules adsorb in a horizontal configuration but reorientate to stand vertically at higher coverage.

Compton and co-workers[14,15] have studied 1,2-dihydroxybenzene (catechol) and phenyl hydroquinone adsorbed on graphene nanoplatelets and observe that at low coverage Langmuir type adsorption is followed while at higher concentrations a transition occurs from adsorbed molecules in extended to vertically oriented states.

The adsorption isotherms obtained show several plateaus reflecting the types of conformer at the graphene/aqueous phase interface. Catechol shows 2 plateaus while phenyl hydroquinone shows 3 plateaus reflecting 2 and 3 active conformers in each case.

Adsorbed Phenyl hydroquinone molecules adopt a flat orientation at low concentrations and an edge orientation at higher coverage before eventually adopting a vertical configuration. For catechol, we model this as an interconvertible monomer-dimer model and for phenyl hydroquinone as an interconvertible monomer-dimer-trimer model.

Thus far, theoretical models which describe the broad features of these adsorption isotherms are lacking. There is a challenge to formulate a theoretical treatment which allows for a range of conformers in various reorientational states. Certain widely used molecular simulation strategies, such as Monte-Carlo Simulation, while useful, are expensive, time consuming and do not provide a method for rapidly calculating adsorption isotherms. The lattice model proved to be extremely efficient even for predicting mixture adsorption isotherms[20]. There, we parametrised the lattice model adsorption isotherms for gaseous mixture adsorption against the predictions of Monte-Carlo Simulations. This is the advantage of the lattice model in addition to providing a simple molecular description of the phenomena and approximate expressions for adsorption isotherms as discussed below in the corresponding section. Recent developments in Classical Density Functional Theory (see for example reference [21] which has relevant references) have enabled the computation of adsorption isotherms of mixtures of methane and n-butane. It may be possible in future to use Classical Density Functional Theory for the challenge of studying adsorption from solution of large aromatic molecules where conformational transitions take place on the surface of graphene nanoplatelets.

In this paper, we present a formalism, which allows rapid calculations in a single theory of adsorption isotherms for catechol and phenyl hydroquinone on graphene nanoplatelets. In our approach, we do not primarily seek quantitative agreement between theory and experiment in such complicated system. Rather, we attempt to establish the "signature" of the model with a view to confirming the molecular picture of the adsorption behaviour proposed in references[14,15]

Quasi-one Dimensional Model of Aromatic Molecule Adsorption on Graphene in the Constant Pressure Partition Function.

In this paper, we consider a model of 3 types of adsorbed species. These are a monomer, dimer and trimer occupying 1, 2, 3 sites respectively[14,22]. This is suggested by the conformers shown in Fig. 1 taken from reference[14,15] reproduced with permission. We consider an ensemble where the independent thermodynamic variables for aromatic species adsorption on graphene are the temperature T, the number of adsorbing unit cells M on the graphene surface, the pressure π and the

chemical potentials μ of the adsorbed species. The model is a development of previous theoretical studies of monolayers at the air/water interface[23].
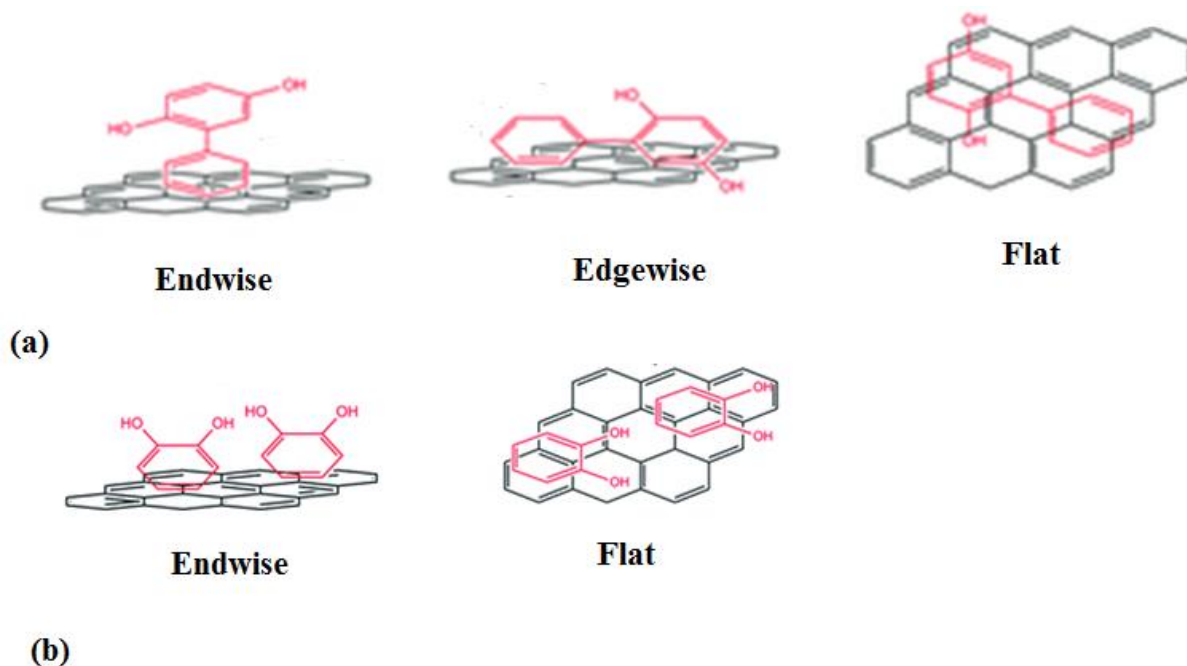

Fig. 1(a) Three possible coarse-grained conformations of hydroquinone adsorbed on a graphene layer. The 'endwise' and 'edgewise' conformers are assumed to occupy 1 and 2 lattice sites respectively, while the 'flat' conformer occupies 3 lattice sites.

1(b) Two possible coarse-grained conformations of 2 catechol molecules adsorbed on a graphene layer. The 'endwise' conformer is assumed to occupy 1 lattice site, while the 'flat' conformer occupies 2 lattice sites. Modified from refs[14,15]. Reproduced from Refs. [14,15] with permission from the PCCP Owner Societies.
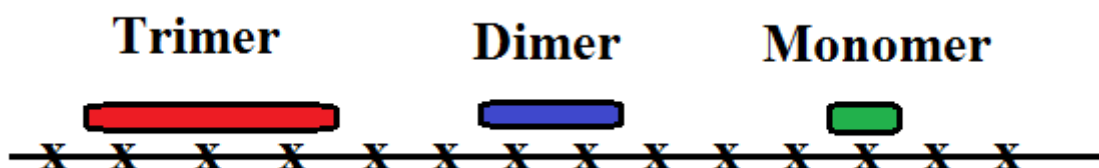

Fig.2 Monomers are shown in green (endwise catechol or endwise hydroquinone), Dimers are shown in blue (Flat catechol or edgewise hydroquinone), Trimers are shown in red(Flat hydroquinone) adsorbed on a one dimensional lattice of sites. The lattice sites are marked with an **x** and if vacant are referred to as 'holes'. Hydroquinone adsorption involves monomers, dimers and trimers whereas catechol adsorption only involves monomers and dimers.

We focus on a chain of M lattice sites. The chain has a small but finite cross-sectional area and is subjected to a pressure π directed along the horizontal chain axis as shown in Fig. 2. We consider

molecules, which can interconvert from occupying 3 sites (a trimer), 2 sites (a dimer) or a single site (a monomer). The basic unit occupies a volume v_0 which has been parameterised to be 100 Å^3. Following the widely used nomenclature in statistical mechanics, we call them monomers/dimers/trimers not to be confused with a similar terminology in polymer chemistry. They correspond to different configurations of the same molecule which occupy a different number of lattice site, one/two/three.

The adsorbed molecules occupying the cells are in equilibrium with those in solution at pressure P and temperature T. The mole fraction is denoted by X. The chemical potential[24] is given by $\mu = \mu^0 + kT \ln(X)$ where the standard chemical potential is μ^0. Modification for non-ideal behaviour is straightforwardly achieved by replacing concentration by fugacity

Each lattice site may be occupied by a single molecule or a part of a molecule so that all possible occupations and configurations are allowed in the model.

For an ensemble of species adsorbed in the one-dimensional chain of M lattice points, the Constant Pressure partition function $\Xi(N, \pi, T)$ may be expressed as[12, 25]

$$\Xi(N, \pi, T) = \sum_V \exp(-\frac{\pi V}{kT}) Q(N, V, T) \qquad (1)$$

The summation runs over the varying volume V. $Q(N,V,T)$ is the Canonical partition function for volume V. The Constant pressure partition function is obtained here from the logarithm of the maximum term. In our method, we calculate this exactly by a transfer matrix method thereby obtaining thermodynamic functions by using the method of the maximum term[26].

The method of the maximum term in which the logarithm of the sum in equation (1) is replaced by the logarithm of the maximum term can be used to evaluate the Constant pressure potential without making any error for all practical purposes to thermodynamic quantities[26]. Thus, the logarithm of the maximum term may be written as

$$\ln \Xi = -\frac{\pi V^*}{kT} + \ln Q(N, V^*, T) \qquad (2)$$

where $*$ signifies the optimum value.

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Each lattice site may be occupied by a single molecule or a part of a molecule so that all possible occupations and configurations are allowed in the model.

The optimum value V^* must simultaneously satisfy the extremum condition

$$\left(\frac{\partial \ln \Xi}{\partial V}\right) = \frac{-\pi}{kT} + \left(\frac{\partial \ln Q}{\partial V}\right) = 0 \qquad (3)$$

The Reader will recognize this equation as that for pressure in a canonical ensemble. This demonstrates that by using the method of the Maximum term the Constant pressure ensemble has degenerated as expected into a Canonical ensemble as discussed for Generalized Ensembles by Hill[26]. Equation (2) in differential form is:

$$-d(kT \ln \Xi) = V^* d\pi - SdT + \mu dN \qquad (4)$$

which yields the following relations for the optimum value:

$$V^* = -kT\left(\frac{\partial \ln \Xi}{\partial \pi}\right) \qquad (5).$$

$\ln \Xi$ will be evaluated by a transfer matrix method which we describe in the next section.

Transfer Matrix Treatment of Aromatic Molecule Adsorption on Graphene

We have previously reviewed matrix methods for the statistical mechanical treatment of one-dimensional lattice fluids[12, 25] to which the Reader is referred.

The Constant pressure partition function equation (1) can be written as the sum of the products of n given by

$$\Xi = \sum_{\alpha=1}^{j} \sum_{\beta=1}^{j} \sum_{\gamma=1}^{j} ..... \sum_{\omega=1}^{j} A_{\alpha\beta} A_{\beta\gamma} A_{\gamma\delta} ..... A_{\omega\alpha} \qquad (6)$$

where the N summations run over the 3 possible conformers on the graphene surface. Cyclic boundary conditions have been assumed where the lattice is folded on to a ring. As is usual in the matrix method we define the terms $A_{\alpha\beta}$ in (6) as the product of internal partition functions f_{α} for species α and f_{β} for cluster β and an interspecies interaction term:

$$A_{\alpha\beta} = (f_{\alpha} f_{\beta})^{1/2} f_{\alpha\beta} \qquad (7)$$

where the subscripts α,β run over the species 1 to 3. The internal partition function f_{α} is given by

$f_{\alpha} = \exp(-(\delta\pi\upsilon_0 + u_{\alpha})/kT)$ where δ is the number of sites occupied by species α and u_{α} is the energy of adsorption from solution onto the graphene surface. The factor $f_{\alpha\beta}$ in the Constant pressure partition function must include terms for all separations on the lattice for each pair of nearest neighbour pairs of conformers α,β. $J_{\alpha\beta}$ is the interaction energy of nearest neighbour pairs of conformers α,β then there must be a factor $\exp(-\frac{J_{\alpha\beta}}{kT})$ in the Constant pressure partition function for

each neighbouring pair. This factor must be modified[23, 12] for any number of vacant sites between the conformers α,β. to give

$$f_{\alpha\beta} = \exp(-\frac{J_{\alpha\beta}}{kT}) + \exp(-\frac{\pi v_0}{kT}) + \exp(-\frac{2\pi v_0}{kT}) + \exp(-\frac{3\pi v_0}{kT})....$$

The second and subsequent terms form a geometric progression which is easily summed to give

$$f_{\alpha\beta} = \exp(-\frac{J_{\alpha\beta}}{kT}) + \exp(-\frac{\pi v_0}{kT}) / (1 - \exp(-\frac{\pi v_0}{kT}))$$

We have observed that the essential features of the MOF adsorption iostherms can be reproduced by introducing two limiting cases by setting selected values of $\varepsilon_{\alpha\beta}$ to either zero or infinitely repulsive as described for models A and B below.

Using the inner product rule $D_{ij} = \sum_k B_{ik} C_{kj}$ for matrix multiplication of a pair of conformable matrices $\mathbf{B}$ and $\mathbf{C}$ the Constant pressure Partition function given in equation (6) can be expressed as:

$$\Phi(\pi, T, \mu) = \sum_{\alpha=1}^{j} (\mathbf{A}^N)_{\alpha\alpha} = \mathrm{Tr}\,(\mathbf{A}^N) = \sum_{i=1}^{j} (\lambda_i)^N \tag{8}$$

where $\lambda_1, \lambda_2, \lambda_3, ... \lambda_j$ are the eigenvalues of the transfer matrix $\mathbf{A}$ which is given below as

$$\mathbf{A} = \begin{pmatrix} f_1 f_{11} & \cdots & (f_1 f_j)^{1/2} f_{1j} \\ \cdots & \cdots & \cdots \\ (f_j f_1)^{1/2} f_{j1} & \cdots & f_j f_{jj} \end{pmatrix} \tag{9}$$

As is usual in matrix evaluations of partition functions only the largest eigenvalue of $\mathbf{A}$ concerns us here since for large N equation (9) reduces to

$$\Xi(N, \pi, T) = (\lambda_{\max})^N \tag{10}$$

where $\lambda_{\max}$ is the largest eigenvalue of the matrix $\mathbf{A}$ found as discussed below in particular circumstances.

As is usual in statistical mechanical lattice models, the parameters describe a "coarse-grained" range of configurations of molecules interacting in with effective way. These parameters bring together the most probable interactions between aromatic molecules and graphene surface when "dressed" by the presence of solvent molecules. The problem is too complicated to distinguish the various contributions.

Eigenvalues of the Transfer Matrix

It is unusually possible to find all the eigenvalues of the transfer Matrix analytically for the special case where all $f_{ij} = 1$ by exploiting some properties of symmetrical matrices and this analysis can be used to obtain approximate adsorption isotherms.

As discussed in ref[13] we have studied the symmetrical matrix eigenvalue-eigenvector equation

$$\begin{pmatrix} f_1 & \cdots & (f_1 f_j)^{1/2} \\ \cdots & \cdots & \cdots \\ (f_j f_1)^{1/2} & \cdots & f_j \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_j \end{pmatrix}_k = \lambda_k \begin{pmatrix} c_1 \\ \vdots \\ c_j \end{pmatrix}_k \tag{14}$$

It it may be seen that one of its eigenvalues and associated eigenvector is

$$\begin{pmatrix} f_1 & \cdots & (f_1 f_j)^{1/2} \\ \cdots & \cdots & \cdots \\ (f_j f_1)^{1/2} & \cdots & f_j \end{pmatrix} \begin{pmatrix} f_1^{1/2} \\ \vdots \\ f_j^{1/2} \end{pmatrix} = (\sum_{i=1}^{j} f_i) \begin{pmatrix} f_1^{1/2} \\ \vdots \\ f_j^{1/2} \end{pmatrix} \tag{15}$$

The rules for the inner product of 2 conformable square matrices gives the maximum eigenvalue as $\lambda_{\max} = (\sum_{i=1}^{j} f_i)$. We have the relations

$$Tr \begin{pmatrix} f_1 & \cdots & (f_1 f_j)^{1/2} \\ \cdots & \cdots & \cdots \\ (f_j f_1)^{1/2} & \cdots & f_j \end{pmatrix}^2 = \sum_{m,n} f_m f_n = \sum_{k=1}^{j} (\lambda_k)^2 \tag{16}$$

Since

$$\sum_{k=1}^{j} (\lambda_k)^2 = \sum_{m,n} f_m f_n = (\lambda_{\max})^2 \tag{17}$$

and since all the eigenvalues of a symmetrical matrix are real then all the other eigenvalues of the transfer matrix in equation(14) are zero.

If analytical approaches are not acceptable the eigenvalues of the transfer matrix can be numerically calculated using mathematical software.

9

Adsorption Isotherms of aromatic Molecules on Graphene

The Gibbs' Free energy of the adsorbed phase is given by using eqn(10).

$$G(N,\pi,T) = -kT \ln(\Xi(N,\pi,T)) = -NkT \ln(\lambda_{\max})$$

The chemical potential μ of the adsorbed phase is given by (using eqn(4))

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,\pi} = -kT \ln(\lambda_{\max})$$

The equilibrium density ρ of the adsorbed phase at a pressure π is obtained (using eqn(4))
as follows

$$V = \left(\frac{\partial G}{\partial \pi}\right)_{T,N} = -NkT \frac{\partial \ln(\lambda_{\max})}{\partial \pi} = Mv_0$$

Hence

$$\rho = \frac{N}{M} = \frac{-v_0}{kT \frac{\partial \ln(\lambda_{\max})}{\partial \pi}}$$

The chemical potential of the solution and adsorbed phase must be equal. The adsorbed molecules occupying the cells are in equilibrium with those in solution at pressure P and temperature T. The mole fractions is denoted by X. The chemical potential[27] is given by $\mu = \mu^0 + kT \ln(X)$ where the standard chemical potential is μ^0. Hence if we treat the standard chemical potential as an adjustable parameter the required solute concentration can be calculated.

Phenyl hydroquinone adsorbed on Graphene Nanoplatelets

Fig. 3a shows an adsorption isotherm calculated for phenyl hydroquinone adsorbed on graphene. The model reproduces the experimentally observed 3 steps shown in Fig. 2b and thus confirms the physical picture proposed by Compton and co-workers in ref.[14]

As shown in Fig. 3a, at low solute mole fraction the density of the adsorbed phase peaks at 1/3, which reflects the presence of close packed trimers on the graphene surface. At higher mole fractions, a second plateau is revealed, corresponding to a close packed density of ½ reflecting dimer adsorption. Further increases solute concentration, cause a further plateau in the adsorption isotherm at a close packed density of unity corresponding to monomers covering the whole graphene surface.

It is of some importance to note that the flat regions in the isotherms should not be confused with phase transitions due to attractive intermolecular forces. Rather, the jumps between the flat regions in the isotherms are indicative of conformational transitions. Phenyl hydroquinone molecules arranged on a lattice in monomer, dimer and trimer states may each have three possible ground state arrangements.

These are:

a) All molecules in the monomer state (111…111)

b) All molecules in the dimer state (222…222) and

c) All molecules in the trimer state (333…333).

At the absolute zero temperature, the most stable ground state of the ensemble with an internal pressure π on the graphene surface is the one with the lowest configurational enthalpy given by

$$H_c = E_c + \pi \upsilon_0$$

For M monomers, $\qquad\qquad H_1 = M(u_1 + \pi \upsilon_0 + J_{11})$

for M dimers, $\qquad\qquad H_2 = M(u_2 + 2\pi \upsilon_0 + J_{22})$

for M trimers, $\qquad\qquad H_3 = M(u_3 + 3\pi \upsilon_0 + J_{33})$

It is energetic competition between these three possible ground states that produces the flat region in the isotherm shown in Fig. 3a. At more elevated temperatures, the entropic contributions become more significant causing more rounding of these transitions. Similar phenomena have been described by us for hard spheres where repulsive interactions give isotherms which have an almost flat region and may be confused with a phase transition[22].

The adsorption energy on graphene of gas phase aromatic hydrocarbons per carbon atom is approximately[28] -7 kJ mol^{-1}, which for phenyl hydroquinone is about -84 kJ mol^{-1}. The adsorption parameters in this model are those of adsorption from solution and are significantly smaller, around -15 kJ mol^{-1}. This may reflect the fact that the complex phenomenon of adsorption from a solution involves the energetically costly extraction of the solute from the liquid solution.

These calculations are based on semiempirical and Density Functional Theory results verified by experiments which give a good description of small aromatic molecule adsorption on graphene from the gas phase[26]. However, a direct comparison of these with the interaction parameters is not straightforward.
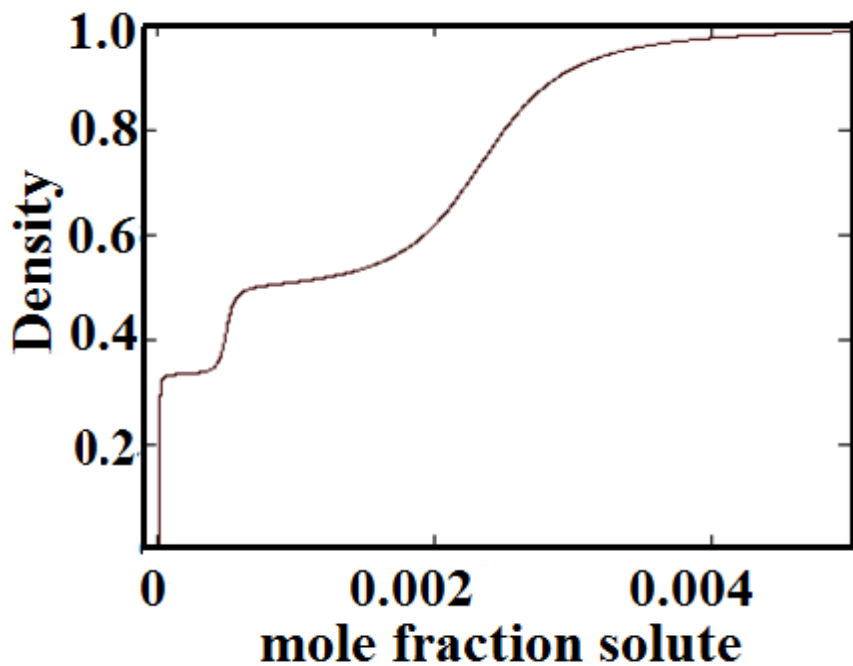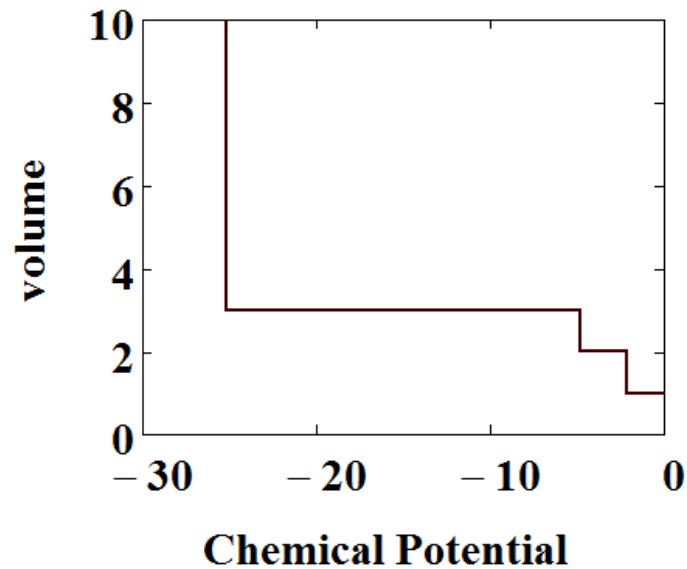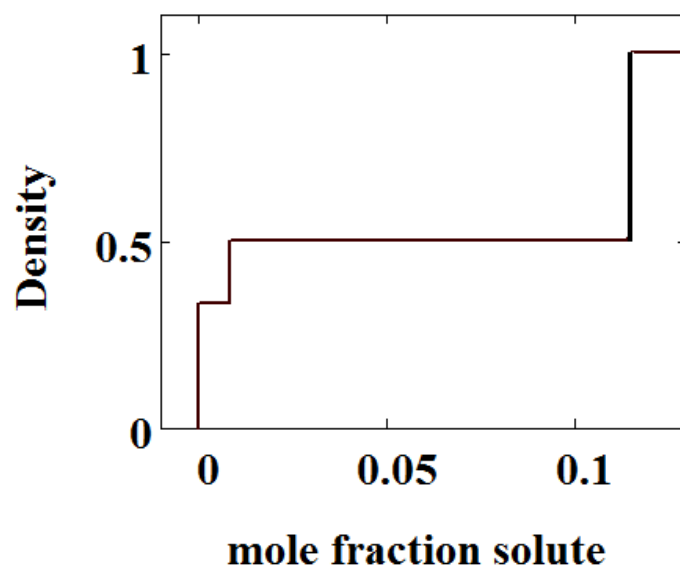
(a)
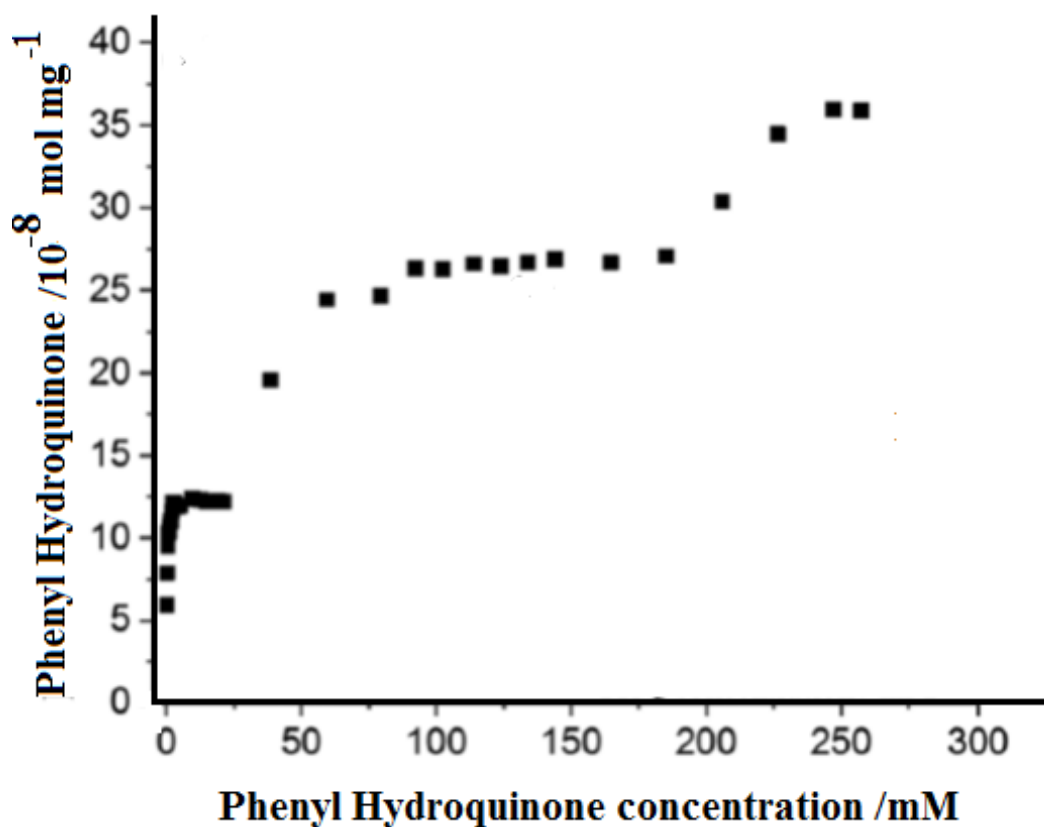
(b)

Fig. 3 (a) T=300 K, u_1= - 3.4 k T, u_2= - 5.5 k T, u_3= - 6.0 k T, J_{11}= -0.95 10^{-20} J J_{22}= -1.78 10^{-20} J J_{33}= -2.65 10^{-20} J, all other parameters are zero.

(b) Experimental results of Compton and co-workers in ref[14]. Modified from ref[14]. Reproduced from Ref. [14] with permission from the PCCP Owner Societies.

Fig.4a below is a plot of the adsorbed layer volume vs. chemical potential at low temperatures and shows 2 quasi-first order transitions, from right to left, monomer to dimer and dimer to trimer. The same same quasi-first order transitions are shown in Fig. 4b which is a plot of adsorbed density vs. chemical potential, from left to right, monomer to dimer and dimer to trimer.

(a)

(b)

Fig. 4 (a) Plot of adsorbed layer volume vs. chemical potential **(b)** density vs. solute mole fraction at low temperatures showing 2 quasi- first order transitions, monomer to dimer and dimer to trimer. T= 100 K, u_1= - 3.4 k T, u_2= - 5.5 k T, u_3= - 6.0 k T, J_{11}== -0.95 10^{-20} J J_{22}= -1.78 10^{-20} J, J_{33}= -2.65 10^{-20} J, all other parameters are zero.

Catechol adsorbed on Graphene Nanoplatelets

By assigning a large repulsive parameter, the trimer state can be rendered statistically insignificant. With such a parameter choice the model reduces to a monomer – dimer model. Thus, a description can be obtained of catechol adsorbed on graphene nanoplatelets[15].

The computed adsorption isotherm is shown in Fig 5a with the experimental ones in Fig. 5b.

At low solute mole fraction the density of the adsorbed phase peaks at 1/2, which reflects the presence of close packed dimers on the graphene surface, while at higher mole fractions, a second plateau is reached with a close packed density of unity, corresponding to monomers occupying the entire graphene surface. As for phenyl hydroquinone, it is the energetic competition between two possible ground states that produces the flat region in the isotherm.

Plateaus in adsorption isotherms occur widely as discussed many years ago by Bell and Dunne[25]

(a)

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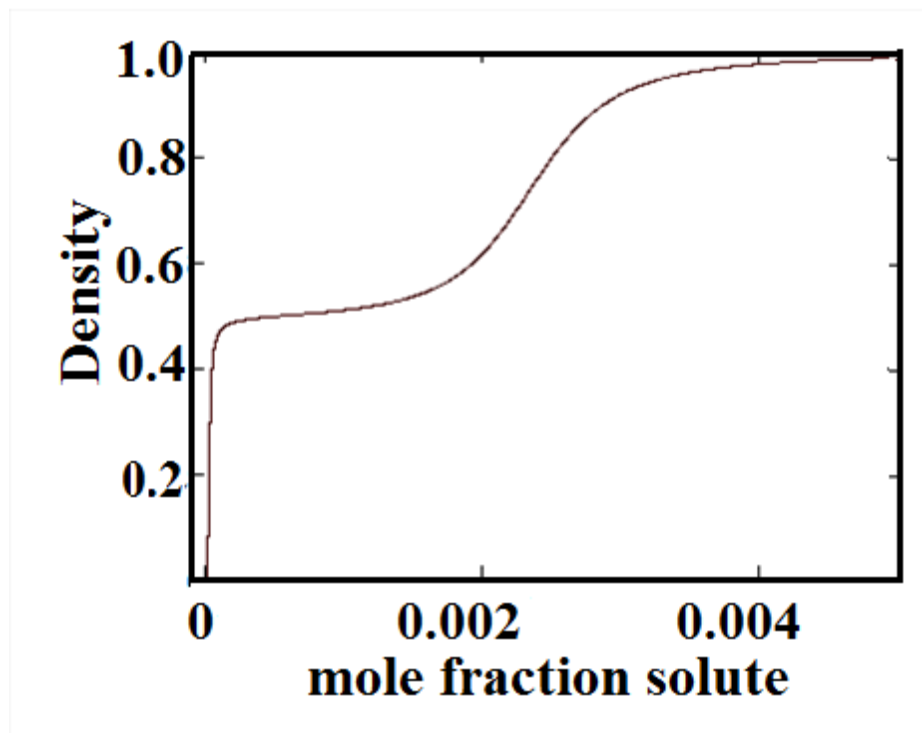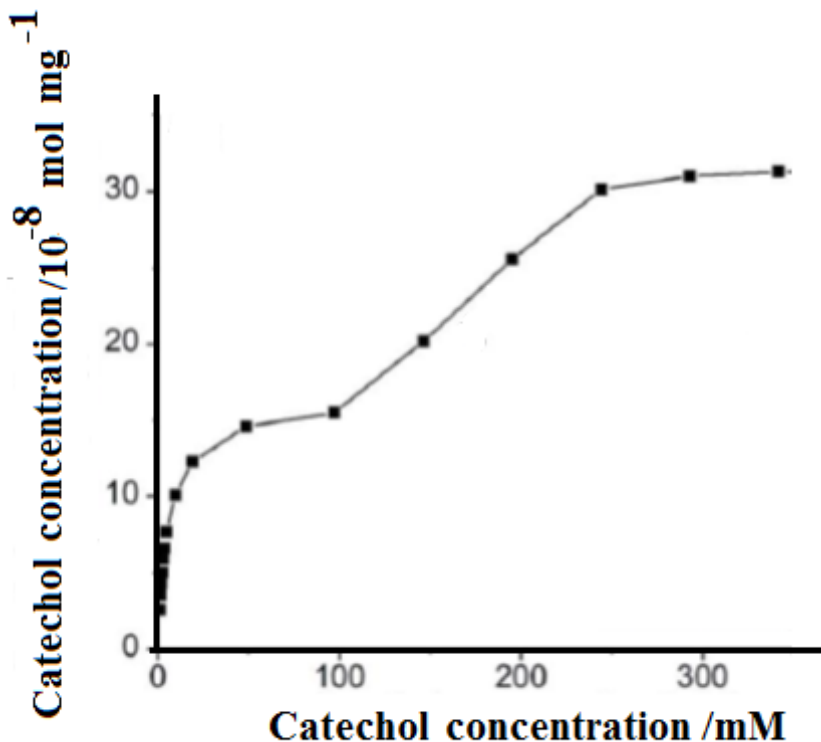
(b)

Fig. 5 (a) T=300 K, u_1= - 3.4 k T, u_2= - 5.5 k T, J_{32}= -1.78 10^{-20} J, J_{11}== -0.95 10^{-20} J, all other parameters are zero. (b) Experimental results of Compton and co-workers in ref[15]. Modified from ref[15]. Reproduced from Ref.[15] with permission from the PCCP Owner Societies.

It is appropriate to remark that both catechol and phenyl hydroquinone have approximately the same saturated density, 32 and 37.5 x 10^{-8} mol/mg respectively, possibly reflecting monomer packing in our model.

Approximate Solutions for Isotherms

It is of interest to note that approximate analytical expressions for the isotherms at low temperature can be obtained by taking the diagonal elements of matrix **A** (Eq. 9) as approximations to the eigenvalue obtained numerically above. The resulting approximate isotherms are compared with those calculated accurately in Fig. 6. Hence, a simple way to obtain these isotherms which avoids the calculation of eigenvalues has been obtained, reproducing the adsorption isotherm shape reasonably well at low temperature, albeit the approximate solution produces sharp conformational transitions.
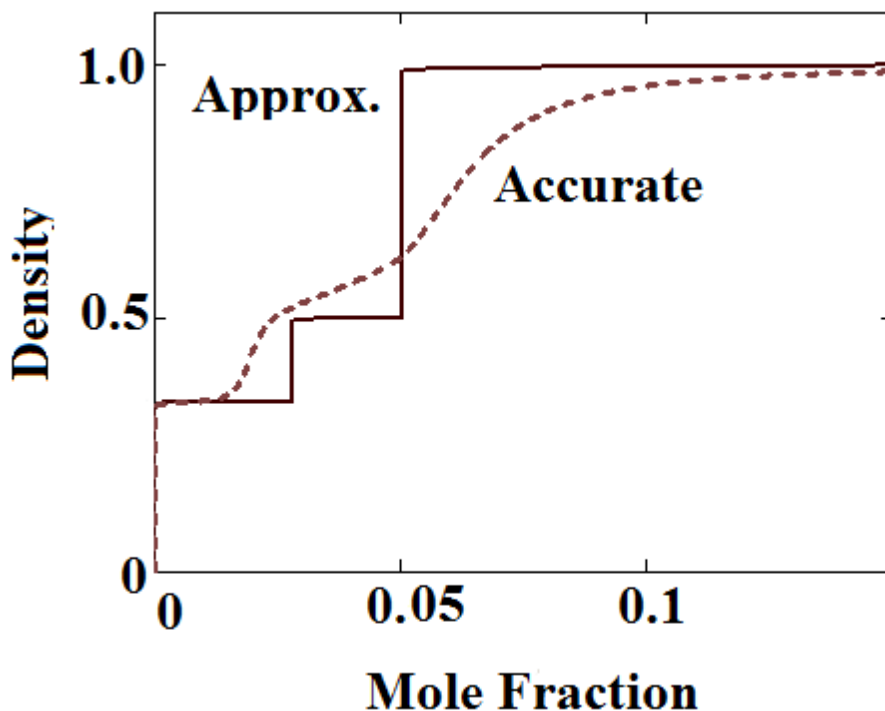
Fig. 6 Approximately vs. accurately obtained adsorption isotherms of phenyl hydroquinone on graphene nanoplatelets. T=300 K, u_1= - 3.4 k T, u_2= - 5.5 k T, u_3= - 6.0 k T, J_{11}== -0.95 10^{-20} J, J_{22}= -1.78 10^{-20} J, J_{33}= -2.65 10^{-20} J, all other parameters are zero.

Discussion and Conclusions

Our conclusions are that the adsorption isotherms for catechol and phenyl hydroquinone on graphene nanoplatlets can be modelled in a statistical mechanical theory which allows for adsorbed molecules to make transitions from lying-down to standing conformations.

The analysis presented allows the prediction of the shape of adsorption isotherms of large organic aromatic molecules adsorbed on graphene nanoplatlets.

With the increase of adsorbate concentrations, first a flat to edgewise then an edgewise to endwise phase change is predicted.

An approximate analysis allows the prediction of the adsorption isotherm shape in a form readily accessible to experimentalists.

Our method provides a powerful way to construct isotherms for adsorption from solution applicable over a wide concentration range. Since electrochemical electron transfer rates depend sensitively on molecular orientation when adsorbed on an electrode it should be possible to use our current approach to model the electrochemical kinetics of the aromatic molecule oxidation/reduction reactions when adsorbed on graphene electrodes.

It is pertinent to point out that solving one-dimensional models treated exactly in a statistical mechanical sense are usually the first line of attack when trying to obtain a theoretical description of a complicated problem. For example, one-dimensional models such as the Ising model have played a major role in the theory of condensed phases such as in magnetic systems. As is well known, these one-dimensional models are crude attempts to describe the physics of complicated materials. Their main virtue is that this allows the development of an exact nontrivial statistical mechanical treatment. The two-dimensional version of the Ising problem is the only example of a model with a phase transition that can be worked out exactly. It is a widely held view that no statistical mechanical model of molecules interacting in two or more dimensions has ever been solved exactly. The one-dimensional treatment usually indicates the incipient behaviour expected in an exact treatment in higher dimensions. In reference25 an exactly treated one-dimensional model with some features similar to the model presented here was investigated and which showed behaviour which parallels those discussed above for large aromatic molecules adsorbed on graphene. While we are aware of the limitations of the one-dimensional model, we may make some preliminary remarks which derive from a study of a diluted monomer-dimer model made by Bell and one of us some years ago[29]. There, a mean field theory using a Flory-Huggins statistical mechanical approximation was compared with modified accurate series expansions derived some years earlier by Gaunt[30] and Nagle[31]. This model is relevant to catechol adsorbed on graphene. Thus, although our model is quasi one dimensional we can be confident that in 2 dimensions these features will exhibit a comparable behaviour.

As is usual in statistical mechanics an accurate theory of aromatic molecule adsorption on graphene in 2 or 3 dimensions seems prohibitively difficult but work is underway to develop a tractable mean-field theory of this problem.

Conflicts of Interest

There are no conflicts to declare.

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